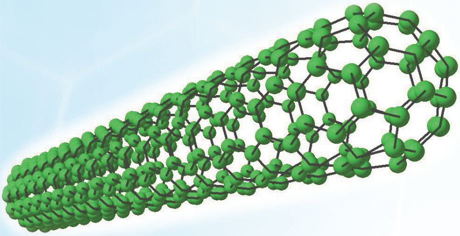
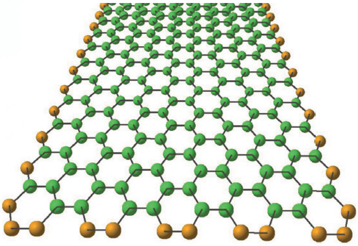
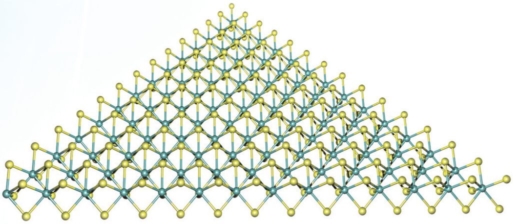
The Sixteenth International Conference on the Science and Application of Nanotubes







June 28(SUN) – July 3(FRI)
2015

Nagoya University, Nagoya, Japan

www.nt15.jp

FNTG
Research Society

SATL
Science of Atomic Layers

Welcome to NT15 in Nagoya !

On behalf of the NT15 National Organizing Committee and of the Chairmen, I am very delighted and honored to host the NT15 conference in Nagoya, Japan. Thanks to all of your strong cooperation, we are able to welcome more than 700 conference participants from all over the world here at the Nagoya University Campus, one of the largest NT conferences so far convened during the past 16 years.

Our main discussion topics, carbon nanotubes (CNTs), are increasingly important not only in basic materials science and the related research areas but in practical applications in various fields of industries. Because of this reason, we will have a “Special Panel Session for Applications of CNTs” in Thursday afternoon of July 2nd, where eight world-leading specialists on the applications / commercialization of CNTs will present talks and discuss in the panel. Graphene and other two-dimensional (2D) atomic layered materials are getting more and more important in NT conferences, and we place that 2D-materials are also the main discussion topics of the present NT15 conference. In fact, 230 poster presentations out of 550 total presentations are related to the 2D-materials.

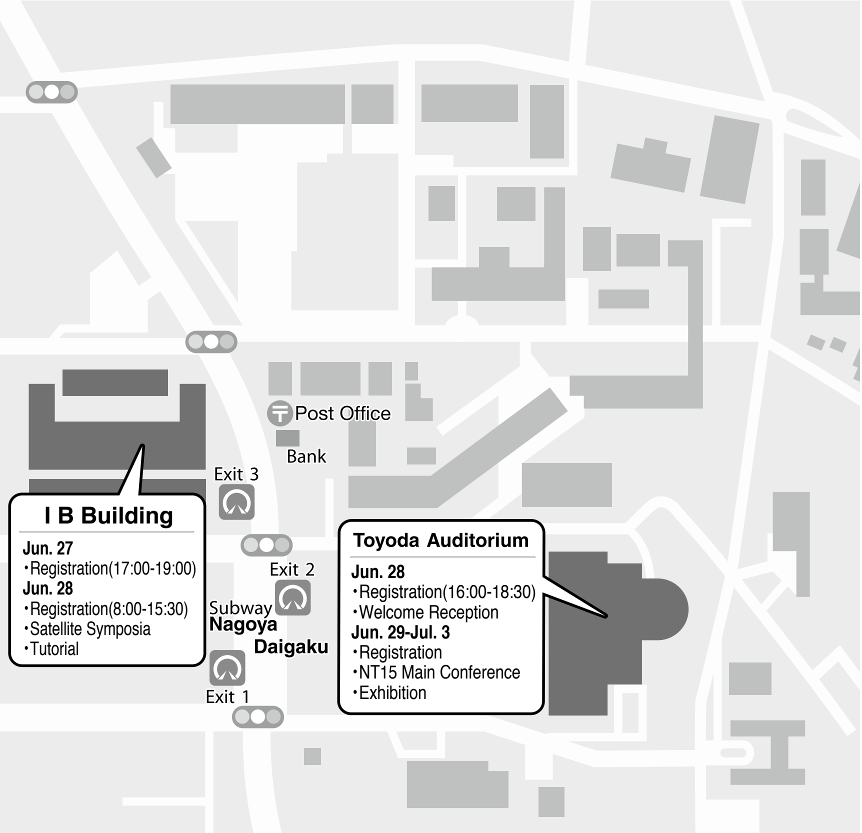
One of the crucial features of NT conference series is the presence of five satellite meetings, which deal with a diverse field of CNTs, graphene, 2D-materials and the related topics. This time, all the satellite meetings will be held on June 28th Sunday also in the University Campus, a day prior to the main conference.

Last but, of course, never least, I would like to thank all the NT15 company sponsors, the supporters of various research societies and the foundation-sponsors for making this great NT15 event possible. I must apologize for not mentioning them individually.

Nori Shinohara

Head Chair of NT15
Nagoya University

Campus Map



I B Building

Jun. 27
- Registration(17:00-19:00)

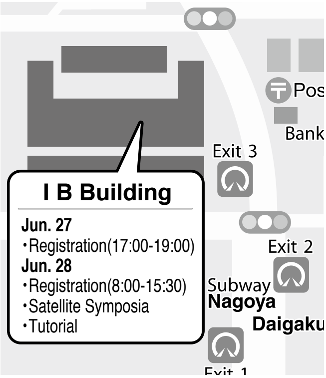
Jun. 28
- Registration(8:00-15:30)
- Satellite Symposia
- Tutorial

Toyoda Auditorium

Jun. 28
- Registration(16:00-18:30)
- Welcome Reception

Jun. 29-Jul. 3
- Registration
- NT15 Main Conference
- Exhibition

IB Building Floor Map



I B Building

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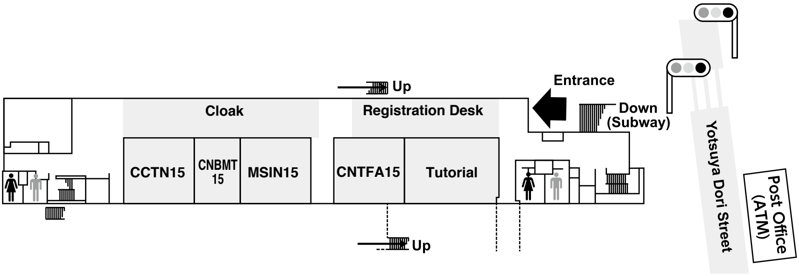
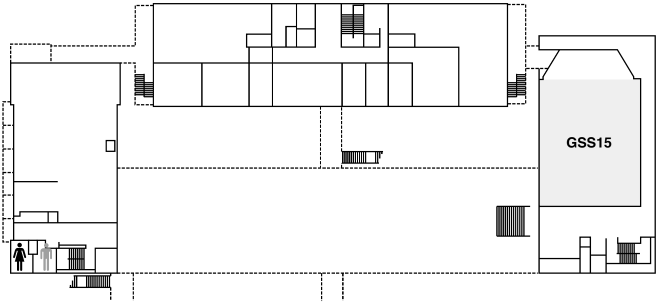
1F



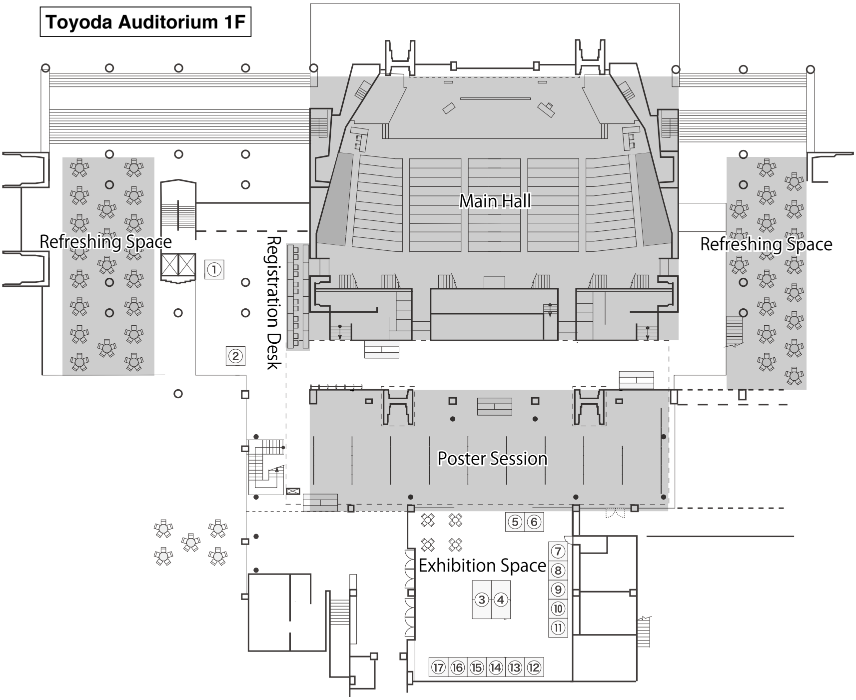
2F



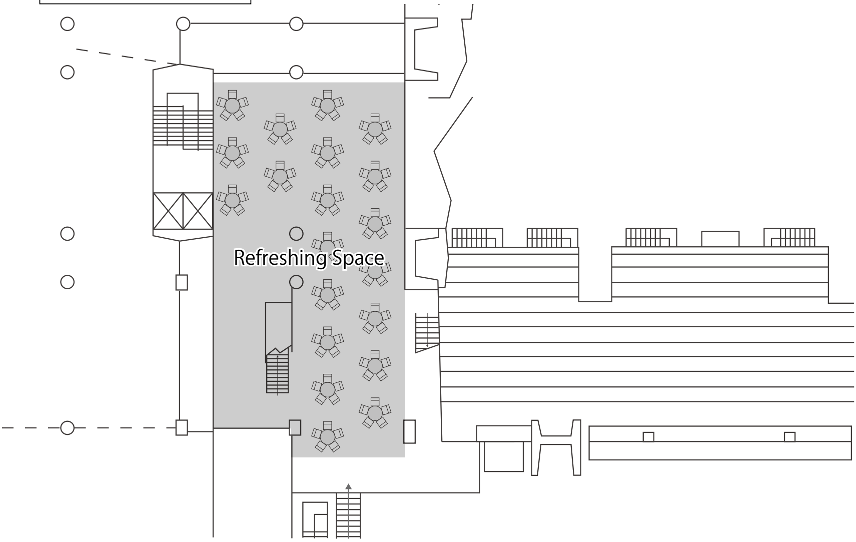
3F. 4F Satellite Poster Area

Toyoda Auditorium Floor Map

Toyoda Auditorium 1F



Toyoda Auditorium 2F



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ZEON

ZEON has developed mass production technology for single-walled carbon nanotubes using the innovative synthetic technology (Super-Growth Method), which has unique properties, including a high aspect ratio, high purity and highly specific surface area, and they hold promise for applications such as new specialty materials with non-conventional functionality and characteristics. ZEON will build a new plant of the new product in Japan and begin mass production in 2015.

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Based on its inorganic, metal and organic chemical technologies, the SDK Group provides individualized products in various areas including energy/environment, electronics, and basic materials for industrial use.

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Toyo Tanso was one of the first to eye the infinite potential of carbon. Based on the basic philosophy of manufacturing completely novel products and services, which we have held since our inception, we have taken on the challenge of pursuing unique and innovative carbon products for highly functional fields.

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MATERIALS
CAN CHANGE
OUR LIVES.

Charter of the Nanotube (NT) Conference Series

http://nanotube.msu.edu/nt/charter.html

1. Purpose.

The purpose of the NT conference series is to promote scientific progress, to stimulate free exchange of ideas, and to publicize progress in nanotube sciences.

2. Target attendance.

2.1 NT conferences are open to all persons interested and active in nanotube research.

2.2 The number of attendees or presentations per attendee may be limited to maintain the informal spirit of communication. Young researchers are treated with higher priority.

3. Format.

3.1 The organizers will assist in maximizing opportunities for sharing knowledge in an informal atmosphere.

3.2 NT conferences are held in one single plenary session. Parallel sessions are to be avoided.

3.3 Presentations of problems and needs is encouraged as much as presentation of solutions.

3.4 Contributions play a key role at NT conferences. At least half the conference time shall be devoted to contributed presentations.

4. Contributed presentations.

4.1 To provide maximum exposure to contributed results, contributors are invited to summarize their findings in a Poster format. The main purpose of Poster presentations is to facilitate asynchronous scientific discussions related to each specific contribution. It is desirable to have all posters on display during the entire conference.

4.2 The organizers secure adequate time and space for poster sessions. Creative ways to enhance communications, including refreshments, are encouraged.

4.3 Poster+ sessions, consisting of brief 2 minute/2 viewgraph summaries of contributions, may precede Poster sessions, to enhance the exchange of information in a balanced manner. All contributors are encouraged to expose their findings to everyone in this way if Poster+ sessions are offered.

4.4 At large conferences, Poster+ presentations may be substituted by a brief overview of the topic of a focussed poster session, presented by an expert in the field at the beginning of the session. Referring to specific contributions in the session, the Poster Chair should summarize the major progress, the major obstacles, and desirable future directions in the field. Ideally, this should occur in a democratic manner, representing all/most contributions. All contributors are encouraged to communicate their findings to their assigned Poster Chair for presentation well ahead of the conference.

5. Invited presentations.

5.1 Invited presentations are selected in a democratic way by members of the advisory board. Presentation of invited talks is reserved for leading, active researchers, not their substitutes. The selection of topics and speakers should reflect the most significant progress and cover the entire active nanotube field. The advisors will resist pressure to select invited talks on other grounds than scientific merit.

5.2 NT conference organizers should generally avoid inviting the same presenter at two consecutive conferences. To avoid conflicts of interest, the organizers should generally avoid inviting contributions of organizers and advisory board members.

6. Venue.

6.1 To pay respect to the international character of nanotube research, two consecutive meetings should not be held on the same continent.

6.2 The conference should preferentially be held a location associated with or close to an institution active in nanotube research.

6.3 Convenience of the conference facilities is preferred to luxury. Modest conference accommodations are to be preferred to reduce the conference expenses of participants and to encourage attendance.

7. Financial matters.

7.1 NT conferences are organized in a non-profit way. The organizers undertake any reasonable efforts to secure external sponsorship covering local and travel expenses of invited speakers, support student attendance, and reduce the conference fee. Any excess revenue is passed on to organizers of the sequel conference.

7.2 Financial liability for the NT conference rests with the organizers.

8. Satellite symposia.

8.1 Satellite symposia form an integral part of NT conferences.

8.2 Logistics of satellite symposia is taken care of by the NT conference, the scientific program is left to the satellite organizers.

8.3. At least one of the satellite symposium organizers is member of the national committee of the NT conference.

9. Miscellaneous.

9.1 NT organizers promote the spirit of informal communication also by providing name badges to participants. Both first and family names should be spelled out and printed in an easily legible, large font. Academic titles should be avoided.

10. Regulation.

All issues related to the organization of Nanotube Conferences are regulated by the Steering Committee of Nanotube Conferences (SCNC).

Session Chairs

Day	Time	Session	Chairman
Jun 28, Sun	15:00 - 16:00	Tutorial 1	Morinobu Endo
	16:00 - 17:00	Tutorial 2	Ming Zheng
	18:30 - 20:30	Welcome Reception	Hisanori Shinohara Ryo Kitaura
Jun 29, Mon	08:45 - 09:00	Opening	Hisanori Shinohara
	09:00 - 09:45	Keynote 1	Hisanori Shinohara
	09:45 - 10:15	Invite 1	Hisanori Shinohara
	10:15 - 10:45	Poster Talk 1	Hisanori Shinohara
	14:00 - 14:15	Oral 1	Alexander Högele
	14:15 - 14:30	Oral 2	Alexander Högele
	14:30 - 15:00	Invite 2	Alexander Högele
	15:00 - 15:15	Oral 3	Jin Zhang
	15:15 - 15:30	Oral 4	Jin Zhang
	15:30 - 15:45	Oral 5	Jin Zhang
	15:45 - 16:00	Oral 6	Jin Zhang
	16:00 - 16:30	Poster Talk 2	Jin Zhang
Jun 30, Tue	09:00 - 09:45	Keynote 2	Shigeo Maruyama
	09:45 - 10:15	Invite 3	Kaili Jiang
	10:15 - 10:45	Poster Talk 3	Kaili Jiang
	14:00 - 14:30	Invite 4	Christophe Bichara
	14:30 - 15:00	Invite 5	Christophe Bichara
	15:00 - 15:15	Oral 7	Hua Jiang
	15:15 - 15:30	Oral 8	Hua Jiang
	15:30 - 15:45	Oral 9	Hua Jiang
	15:45 - 16:00	Oral 10	Hua Jiang
	16:00 - 16:30	Poster Talk 4	Hua Jiang
July 1, Wed.	09:00 - 09:45	Keynote 3	Kazunari Matsuda
	09:45 - 10:15	Invite 6	Kazunari Matsuda
	10:15 - 10:45	Invite 7	Kazunari Matsuda
	11:15 - 11:45	Invite 8	Mauricio Terrones
	11:45 - 12:00	Oral 11	Mauricio Terrones
	12:00 - 12:15	Oral 12	Mauricio Terrones
	12:15 - 12:30	Oral 13	Mauricio Terrones
	12:30 - 12:45	Oral 14	Mauricio Terrones
	18:30 -	Banquet	Hisanori Shinohara Riichiro Saito

Day	Time	Session	Chairman
July 2, Thu	09:00 - 09:45	Keynote 4	Fei Wei
	09:45 - 10:15	Invite 9	Fei Wei
	10:15 - 10:45	Poster Talk 5	Fei Wei
	13:30 - 15:30	Special Panel	Young-Hee Lee
	15:30 - 15:45	Oral 15	Paola Ayala
	15:45 - 16:00	Oral 16	Paola Ayala
	16:00 - 16:30	Poster Talk 6	Paola Ayala
July 3, Fri	09:00 - 09:45	Keynote 5	Susumu Saito
	09:45 - 10:15	Invite 10	Susumu Saito
	10:45 - 11:15	Invite 11	Kazuhiro Yanagi
	11:15 - 11:45	Invite 12	Kazuhiro Yanagi
	11:45 - 12:00	Oral 17	Kazuhiro Yanagi
	12:00 - 12:30	Poster summary	Hisanori Shinohara
	12:30 - 13:00	Conf. summary	Hisanori Shinohara
	13:00 - 13:15	AD for NT16	Hisanori Shinohara
	13:15 - 13:30	Closing	Hisanori Shinohara

Sunday, June 28

15:00 – 16:00 **T1**

Introduction to carbon nanotubes, graphene, and beyond grapheme

16:00 – 17:00 **T2**

Structure sorting of single-wall carbon nanotubes

18:30 - 20:30 **Welcome Reception**

Monday, June 29

8:45 - 9:00 **Opening**

9:00 - 9:45
K1 **The background of the discovery of carbon nanotubes** (S. Iijima) ··· 54

9:45 - 10:15
I1 **Two-dimensional materials, heterostructures, and devices**
(Xiangfeng Duan) ··· 55

10:15 - 10:45 **Poster Talk 1**: (Susumu Okada)

10:45 - 12:45 **Poster Session 1, Coffee Break**

12:45 - 14:00 **Lunch**

14:00 - 14:15
C1 **Cooperativity, critical length scales and selectivity of adsorbate-carbon nanotube interactions** (Tobias Hertel) ··· 56

14:15 - 14:30
C2 **Aqueous two-phase bench top separation of carbon nanotubes beyond single chirality separations** (Navaneetha Krishnan Subbaiyan) ··· 56

14:30 - 15:00
I2 **Materials, physics, and functionalities of 2D crystals**
(Yoshihiro Iwasa) ··· 55

15:00 - 15:15
C3 **Optical properties of van der waals hetero structures composed of transition metel dichalcogenides** (Shinichiro Mouri) ··· 57

15:15 - 15:30
C4 **Observation of in plane step-edge growth of graphene in a STEM**
(Zheng Liu) ··· 57

15:30 - 15:45
C5 **Selective formation of zigzag edges in graphene cracks**
(Miho Fujihara) ··· 58

15:45 - 16:00
C6 **Integrating nano-carbons with plasmonic and photonic systems**
(Aravind Vijayaraghavan) ··· 58

16:00 - 16:30 **Poster Talk 2**: (Yan Li)
16:30 - 18:30 **Poster Session 2, Coffee Break**

Posters 1

Posters 2

Tuesday, June 30

9:00 - 9:45

K2 **Overcoming historical challenges in carbon nanotubes and nanoribbons to enable their application in transistors and photovoltaics** (Michael S. Arnold) ········ 150

9:45 - 10:15

I3 **Beyond carbon nanotube thin-film transistors: Logic circuits, memory, and heterostructures** (Mark C. Hersam) ········ 151

10:15 - 10:45 **Poster Talk 3**: (Ado Jorio de Vasconcelos)

10:45 - 12:45 **Poster Session 3, Coffee Break**

12:45 - 14:00 **Lunch**

14:00 - 14:30

I4 **Recent advances in understanding carbon nanotube growth through atomic scale simulations** (Erik C. Neyts) ········ 151

14:30 - 15:00

I5 **Computational Approach to Electrical Contacts in Carbon Nanotube Transistors** (Vasili Perebeinos) ········ 152

15:00 - 15:15

C7 **Structure of double wall carbon nanotubes by combining a robust HRTEM approach and tight binding calculations**
(Annick Loiseau) ········ 153

15:15 - 15:30

C8 **Growth of high-density horizontally aligned SWNT arrays using trojan catalysts** (Jin Zhang) ········ 153

15:30 - 15:45

C9 **Selective cloning of (9, 4) carbon nanotubes by chemical vapor deposition** (Yoshikazu Homma) ········ 154

15:45 - 16:00

C10 **Origination of chirality selectivity in single-walled carbon nanotube growth catalyzed by tungsten-based intermetallic compounds: a theoretical study** (Xiao Wang) ········ 154

16:00 - 16:30 **Poster Talk 4**: (Sofie Cambré)

16:30 - 18:30 **Poster Session 4, Coffee Break**

Posters 3

Posters 4

Wednesday, July 1

9:00 - 9:45

K3 **Bottom-up fabrication of graphene-related materials: From molecules to nanoribbons and nanotubes** (Roman Fasel) ··· 244

9:45 - 10:15

I6 **Important factors in chirality-specific growth of single-walled carbon nanotubes** (Yan Li) ··· 245

10:15 - 10:45

I7 **Harvesting energy with semiconducting single-walled carbon nanotubes** (Jeffrey Blackburn) ··· 246

10:45 - 11:15 **Coffee Break**

11:15 - 11:45

I8 **Carbon nanotube transistors: toward fundamental limits** (Lian-Mao Peng) ··· 246

11:45 - 12:00

C11 **Thermoelectric flexible film based on cobaltocene-encapsulated carbon nanotubes** (Tsuyohiko Fujigaya) ··· 247

12:00 - 12:15

C12 **Tuning of thermoelectric properties of single wall carbon nanotubes by electric doulbe layer carrier injections** (Kazuhiro Yanagi) ··· 247

12:15 - 12:30

C13 **Ice-assisted transfer of carbon nanotube arrays** (Yang Wei) ··· 248

12:30 - 12:45

C14 **Waveguide-integrated light-emitting carbon nanotubes** (Felix Pyatkov) ··· 248

12:45 - 14:00 **Lunch**

14:00 - **Excursion, Banquet**

Thursday, July 2

9:00 - 9:45

K4 **Carbon nanotube thin films** (Esko I. Kauppinen) ········ 250

9:45 - 10:15

I9 **Soft conductors from nanoscale carbon** (Matteo Pasquali) ········ 251

10:15 - 10:45 **Poster Talk 5**: (Annick Loiseau)

10:45 - 12:45 **Poster Session 5, Coffee Break**

12:45 - 13:30 **Lunch**

13:30 - 15:30 **Special Panel "Application of CNT"**

SP1 **Resiponsible Production and Applications of Carbon Nanotubes ~Promis for the future~** (Morinobu Endo) ········ 252

SP2 **A road to carbon nanotube application and commercialization** (Shoushan Fan) ········ 252

SP3 **SWNT thin films for high optical quality flexible touch panels** (Esko I. Kauppinen) ········ 253

SP4 **Carbon nanotube x-ray: from scientific curiosity to patient imaging and commercial production** (Otto Zhou) ········ 253

SP5 **Putting the carbon nanotubes to use as the industrial materials** (Motoo Yumura) ········ 254

SP6 **Nano-carbon application activities in Korea** (Seunghyun Baik) ········ 255

15:30 - 15:45

C15 **Hierarchically structured carbon nanotube-graphene fibers for micro-supercapacitors** (Yuan Chen) ········ 256

15:45 - 16:00

C16 **CNTs; Devils or Angeles?** (Susumu Katagiri) ········ 256

16:00 - 16:30 **Poster Talk 6**: (Seunghyum Baik)

16:30 - 18:30 **Poster Session 6, Coffee Break**

Posters 5

Posters 6

Friday, July 3

9:00 - 9:45

K5 **When nanotube dreams come true** (David Tománek) ·························· 348

9:45 - 10:15

I10 **Near-field and ultrafast optical microscopy of carbon nanotubes and graphene** (Achim Hartschuh) ·························· 349

10:15 - 10:45 **Coffee Break**

10:45 - 11:15

I11 **Variance Spectroscopy Studies of Single-Walled Carbon Nanotubes** (R. Bruce Weisman) ·························· 349

11:15 - 11:45

I12 **Comparing advanced functionalization routes to tailor 1D and 2D nanocarbons** (Thomas Pichler) ·························· 350

11:45 - 12:00

C17 **Ultra-long carbyne inside double-walled carbon nanotubes** (Lei Shi) ·························· 351

12:00 - 12:30 **Poster Summary and Award**: (Younghee Lee)

12:30 - 13:00 **Conference Summary**: (Mildred S. Dresselhaus)

13:00 - 13:15 **AD for NT16**: (Paola Ayala)

13:15 - 13:30 **Closing**

Sunday

T1

Introduction to carbon nanotubes, graphene, and beyond graphene

Mildred S. Dresselhaus

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NT15, held in Nagoya, Japan, in 2015, is the next NTXX conference in the series of annual conferences held alternately in Asia, Europe, and North/South America since 1999. The first conference in 1999 was devoted to nanotubes emphasizing the science and potential applications of cylindrical structures of about a nanometer in thickness made of a single layer of carbon atoms. A tutorial introduction to the structure, properties, and applications of carbon nanotubes will be presented. After several years, the NTXX conference series expanded to include graphene and graphene/ nanotube.related studies, and this tutorial will also provide some tutorial background for understanding the structure and properties of graphene. More recently, the NTXX conference has expanded to include composites of nanotubes with few-layer transition metal dichalcogenides, which will therefore also be reviewed in this tutorial, along with the newest few-layered material, phosphorene, consisting of a few layers of the phosphorus allotrope black phosphorus, which was discovered in bulk form in 1914 and in few-layer form in 2014. The aim of his tutorial will be to welcome newcomers to this conference and to help them benefit from the presentations made by the international speakers.

T2

Structure sorting of single-wall carbon nanotubes

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Single-wall carbon nanotube (SWCNT) is constructed from flexible sp^2 network which allows variety of chiral structures. This leads to variety of physical properties using only one element. This structural flexibility can be said to be one of the most interesting properties of SWCNT. On the other hand, high-quality sample is always required for both scientific research and application development. In this case, the structural flexibility is a big problem to get high-quality sample. Most of synthesis methods failed to produce single-chirality SWCNTs. Very recently, some successful methods can produce nearly single-chirality, but the production amount is still tiny. Therefore structure sorting technique is still very important in the field of SWCNT research. In this tutorial, I would like to discuss some typical methods of structure sorting from a historical viewing point. The mechanisms of the sorting will be also discussed focusing on the surfactant molecules that act very important role in the sorting procedure. Importantly, the surfactants have to be removed before being applied to electronic devices. This is the present target of research. I would like to introduce our latest results about large scale structure sorting and try to give a future perspective.

Monday

K1

The background of the discovery of carbon nanotubes

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Any discovery in science has not been made without a certain background closely related to the discovery. The case of carbon nanotubes is not an exception. I would like to speak how the nanotube was discovered after my long research carrier. The carbon nanotubes were reported in 1991 for the first time but the most of people did not know what I have been doing before the discovery. I would like to emphasize the importance of my experiences with various nanostructured materials including carbon. Interestingly all of these materials are related to the carbon nanotubes in various aspects. Another primary factor of the discovery is an atomic structure characterization of the nanomaterials, which is performed by a high resolution electron microscope. Without this instrument there will be no chance for us to find carbon nanotubes. In this connection I was lucky to have had ample experiences with this instrument. I would like to present my experiences with mostly carbon materials in chronological order in my own research carrier, so that it will be understood that accumulation of these experiences leads to the discovery of the carbon nanotubes [1-4]

1) "High resolution electron microscopy of crystal lattice of titanium-niobium oxide", S. Iijima, *J. Appl. Phys.*, **42**, 5891-5893 (1971).
2) "High resolution electron microscopy of phase objects: Observation of small holes and steps on graphite crystals", Sumio Iijima, *Optik*, **47**, 437-452 (1977).
3) "Direct observation of the tetrahedral bonding in graphitized carbon black by high resolution electron microscopy", S. Iijima, *J. Crystal Growth*, **50**, 675-683(1980). "Helical micro-tubules of graphitic carbon", S. Iijima, *Nature*, **345**, 56-58(1991).

I1

Two-dimensional materials, heterostructures, and devices

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Abstract

Two-dimensional layered materials (2DLMs), such as graphene or molybdenum disulfide, represent ideal 2D materials systems for exploring fundamental chemistry and physics at the limit of single atomic thickness. With *van der Waals* interactions between neighboring layers, different 2DLMs can be flexibly integrated without the limitation of lattice mismatches. This approach therefore opens up vast possibilities to combine materials nearly arbitrarily and to control distinct properties at the atomic scale, enabling entirely new opportunities beyond the reach of existing materials. I first give a brief overview of our research efforts in rational design and synthesis of a wide range of 2D materials and heterostructures with exquisite control of chemical composition, physical dimension, heterostructured interfaces, and electronic/optic properties. I then discuss exploring these 2D materials and their heterostructures as new platforms for diverse areas of application, including electronics, biomedical sensing, and energy technologies. Examples discussed include: ultra-high speed transistors; a new design of vertical transistors for ultra-flexible electronics; new types of tunable photonic devices; and graphene-molecule conjugates for band-gap engineering, molecular sensing, catalysis, and energy storage.

I2

Materials, physics, and functionalities of 2d crystals

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Two-dimensional (2D) crystal of transition metal dichalcogenide (TMD) is attracting a significant interest as a beyond graphene material with a valley degree of freedom and spin-orbit interaction. First, we report an experimental observation of the valley dependent Zeeman-type out-of-plane spin polarization using spin- and angle resolved-photoemission spectroscopy in MoS_2 [1], which is fully consistent with a theoretical prediction [2]. This became possible by choosing noncentrosymmetric bulk crystals, so called 3R polytype. Photoluminescence circular dichroism proved that the noncentrosymmetric stacking effectively preserves the information of valley polarization even in multilayers.

We also demonstrate FET related new functionalities, including gate-controlled Zeeman-type spin splitting [3], an ambipolar FET [4], and electric field induced superconductivity [5]. Finally, we demonstrate the electrically switchable chiral light source, an electro-optical conversion device [6].

[1] R. Suzuki et al, *Nat. Nano.* 9, 611 (2014).
[2] D. Xiao et al., *Phys. Rev. Lett.* 108, 196802 (2012).
[3] H. T. Yuan et al., *Nat. Phys.* 9, 563 (2013).
[4] Y. J. Zhang et al., *Nano Lett.* 12, 1136 (2012), ibid. 13, 3023 (2013).
[5] J. T. Ye et al., *Science* 338, 1193 (2012).
[6] Y. J. Zhang et al., *Science* 344, 725 (2014).

C1

Cooperativity, critical length scales and selectivity of adsorbate-carbon nanotube interactions

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The dispersionof carbon nanotubesinsolventsplaysakeyrolefor their application in thin film-, coating- and device-technologies as well as for their fundamental spectroscopic investigation. The thermodynamics and kinetics of solvent or surfactant interactions with nanotube surfaces however are rarely studied and difficult to come by. Here we report on investigations of the interaction of amphiphilic molecules and oligomers with carbon nanotube (CNT) surfaces in aqueous and organic environment and on the effect of such interactions for the photophysical properties of CNTs. To do so we use a combination of fluorescence-, absorption-, femtosecond time-resolved- and spectroelectrochemical studies.
The experiments reveal the importance of SWNT interactions with the solvent as well as of solvent interactions with the dispersion additive. Among the phenomena that are expected to be of broader significance than just for the dispersion of carbon nanotubes are i) the discovery of nanoparticle mediated cooperativity for dispersion with classical amphiphilic surfactants, iii) entropy-enthalpy compensation and iii) the importance of polymer Kuhn lengthsif nanoparticles are dispersed with extended molecular structures.

C2

Aqueous two-phase bench top separation of carbon nanotubes beyond single chirality separations

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Recently aqueoustwo-phase(ATP) separationhas beenshown promisingasanew scalable, low cost method to separate single-wall carbon nanotubes (SWCNTs) by diameter1. TheATP separation mechanismis dictatedby thehydrophobicityof the surfactant-SWCNT system, which we found to be strongly dependent on the combination of surfactants used, and on various other parameters that influence the specific surfactant stacking on the SWCNT walls[2]. In this presentation, we will demonstrate ATP as a method to characterize and understand the surfactant structure around the SWCNTs and the importance of surfactant structure in determining the nanotubes partition in ATP using a combinationofvarious spectroscopicand microscopic techniques. We will discuss both single chirality isolation and multi-chirality extraction of highly pure, full-length SWCNTs[3] using inexpensive benchtop centrifuges without any pre-ultracentrifugation and even without sonication, thus simplifying the SWCNT separation.

[1] Khripin et al, JACS, 135 (2013) p6822
[2] Subbaiyan, et al, ACS Nano8(2014) p1619.
[3] Subbaiyan, et al, NanoRes. DOI 10.1007/s12274-014-0680-z

C3

Optical properties of van der waals hetero structures composed of transition metel dichalcogenides

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Transition metal dichalcogenides (TMDs) have attracted much attention as a novel two-dimensional semiconductor [1,2]. Van der Waals hetero-structures composed of TMDs are suitable platform to realize functional semiconductor devices [3]. In addition, rapid carrier separation could cause unusual exciton (bound electron-hole pair) effects including formation of inter-layer excitons [4]. We studied optical properties in van der Waals hetero-structures building from monolayers (1L)-MoS2 and MoSe2.

1L-MoS2/1L-MoSe2 hetero-structure was fabricated using transfer method by PDMS. We measured photoluminescence (PL) spectra under variable temperature. PL from 1L-MoS2 (~1.87 eV) and 1L-MoSe2 (~1.6 eV) in the hetero structure was quenched and their peak energies were red-shifted as compared with that in isolated monolayers. We found that broad PL peak (~1.45 eV) appears below 160 K and its intensity increases with decreasing temperature. This behavior is attributable to the formation of inter-layer excitons and their thermal dissociation due to small conduction band offset (~0.07 eV). Detailed exciton dynamics will be discussed in the presentation.

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[3] A. K. Geim et al., Nature 499, 419 (2013).
[4] P. Rivera et al., Nat. Commun. 10.1038/ncomms7242 (2015).

C4

Observation of in plane step-edge growth of graphene in a STEM

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In order to realize graphene devices, it is essential to establish a structural analysis technology for identifying and detecting the lattice defects and edge structures of graphene at an atomic level.For development of graphene materials with controlled defects and edge structures, it is also very important to perform analyses such as their thermal stability and electronic states. Because it is not easy to control the growth direction of the graphene, in order to achieve a more controlled graphene nano-devices, it is necessary to identify the orientation relationships between the seed crystal and the growth layer and clarify the effect of catalyst atoms in growth processes.To understand such a growth mechanism at an atomic level, direct visualization of graphene network growth is very useful. We report here a direct observation of graphene growth and domain boundary formation inside a scanning transmission electron microscope (STEM), by using residual hydrocarbon in the microscope chamber as a carbon source for in-plane graphene growth from the step-edge of a bilayer graphene on the terrace of the first layer graphene. The graphene growth mechanism was analyzed at an atomic level. Single Si atoms may act as catalytic active sites for the step-edge growth.

C5

Selective formation of zigzag edges in graphene cracks

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Graphene edges have attracted much attention due to their unique electrical and magnetic properties. To understand these properties, it is highly desired to prepare clean, smooth, and structure-controlled edges. However,structure selectivepreparation of zigzag or armchair edges has not been achieved yet.

Here, we report the selective formation of the zigzag edges by cleavage with thermally-assisted tensile stress. Graphene grains were grown from methane on copper foil by using chemical vapor depositionat 1075 ℃. After coolingto room temperature, we occasionally observe the cracks which propagate along the zigzag edge direction. Statistical analyses of the crack direction suggest that uniaxial tensile stress is applied to the notches of graphene grains around Cu grain boundary. This is consistent with the molecular dynamics simulation under a similar condition, which indicates the preferential formation of the zigzag edges. The origin of stress is probably due to the non-uniform thermal shrinking of Cu substrates. Furthermore, we demonstrate the carrier tuning around graphene edges by applying the electric field to the cracks. Our findings pave the way for the fabrication and applications of smooth, long zigzag edges of graphene and other two dimensional materials.

C6

Integrating nano-carbons with plasmonic and photonic systems

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I will summarise our recent efforts in integrating nano-carbon systems such as graphene and carbon nanotubes (CNTs) with a variety of plasmonic and photonic systems.

First, we consider plasmonic antennae, in particular, gold nano-dot dimers. I will discuss how a layer of graphene wrapped over dimers can be used to evaluate their efficiency by observing the enhancement in Raman spectroscopy signal. 1,2 In addition, the enhancement in Raman signal can itself be used to shed light on the optoelectronics of the light-scattering processes involved. Similarly, we can also integrate single-wall carbon nanotubes in between these antennae dimers using bottom-up dielectrophoretic assembly and observe Raman enhancement.[3]

Graphene can alsobe wrapped around silicon waveguides. The evanescent field of these waveguides can be used for chemical sensing and photodetector applications, and a coating of graphene can be used to enhance sensitivity and selectivity in these applications. However, the absorption properties of graphene could hinder its effectiveness. We propose ideal scenarios for the application of graphene coated waveguides.[4]

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[2] PSS (RRL), 2013, 7, 1067-1070.
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[4] Optics Express, 2014, 22, 18625-18632.

P1

Biocompatibility evaluation of boron nitride nanotubes on freshwater planarians

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Boron nitride nanotubes (BNNTs), structural analogs of more famous carbon nanotubes, represent an innovative and extremely interestingclassof nanomaterials because of their peculiar chemical and physical properties. Apart of their exploitation in nanotechnology and engineering, recent findings have suggested a number of applications in the biomedical field, including drug delivery, tissue engineering, and biosensors. Envisioning medical applications, extensive biocompatibility investigations are mandatory before any further advancement toward pre-clinical testing. Here, we report on the effects of ultra-pure BNNTs on the freshwater planarians (Dugesia japonica), one of the best-characterized in vivo models for developmental biology and regeneration research, which is also currently being rediscovered as a useful animal model for pharmacology, nervous system development and regeneration, and nanotoxicology research.

Obtained results indicate that BNNTs are biocompatible in the investigated model, since they do not induce oxidative DNA damage and apoptosis, and do not show adverse effects on planarian stem cell biology and on de-novo tissue regeneration. Collected findings once more confirm biosafety of BNNTs, and represent another important step toward their realistic application in nanomedicine.

P2

Automated experimentation applied to carbon nanotube synthesis

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Carbon nanotubes have an exciting array of applications which span mechanical, electrical, thermal and chemical/sensing. However, full exploitation is slowed by a lack of control over synthesis. Despite the two decades since the explosion of work in the area, progress in controlled production of nanotubes is impeded by our lack of understanding of the fundamental mechanisms of nucleation and growth.

To this end, we have developed a method, Automated Rapid Experimentation and in-situ Spectroscopy (ARES) which speeds the rate of experimentation by 100 times. We are also exploring experimental parameter space autonomously, using the same AI and machine learning approaches used in advanced robotics. Our intent is to integrate computation and simulation explicitly into our closed-loop experimentation system to direct the path of exploration, yielding faster results with better fidelity than conventional approaches. We use this to determine the conditions which discriminate between single wall and multiwall carbon nanotube synthesis.

P3

Physical property of graphite-like compound fabricated by pulsed light irradiation

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Application of new carbon materials such as fullerene, graphene, carbon nanotube, carbon nanohorn, and cluster diamond have been studied in electronics, information processing, nanotechnology, energy, and biotechnology. Recently, we have reported promising results for formation of siloxene-like multilayer by heat treatment of solution-processed thin films using linear and network polysilanes containing anthryl groups as a precursor. In this study, we report the effect of pulsed xenon light irradiation on thin films of network polysilanes with various substitutents.We observe the shift to a longer wavelength of the absorption edge in UV-visible absorption spectra of the thin films of network polysilane containing anthryl groups, when the thin films were irradiated at energy density above a critical value. This behavior is interpreted in terms of the formationof electronically conductive films by the dissociation of anthryl groups from silicon structures and the accompanying reconstruction of anthryl groups into carbon nanohorn structures with elimination of silicon structures. The structural changes accompanying pulsed light irradiation were analyzed with Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

P4

Morphology-controlled fabrication and advanced properties of carbon nanotube fibers, thin films and aerogels from aerogel technique

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Carbon nanotube (CNT) manufacturing system producing km-long CNT fibers, aligned CNT thin films and fiexible large-scale CNT aerogels using the CNT aerogel technique has recently developed successfully. The CNT aerogel technique is more advanced than the spinning and wet techniques reported by other studies in terms of: (i) high reproducibility of the CNT fibers, (ii) high manufacturing capacity of the CNT fibers (up to a kilometer of CNT fibers per hour), (iii) less man power requirement, (iv) low-cost manufacturing method, (iv) fairly well-controlled system through the computer software, (v) various products possible (CNT fibers, thin films and aerogels), (vi) well morphology controlling of the CNT fibers (types and diameters) having advanced multi-properties. Morphology control and multi-properties of these CNT-based products are also quantied comprehensively. The CNT manufacturing system is ready for the industrial scale-up not only for the defense applications, but also for others as in medicine, composites, microelectronics, solar cells, energy storage and electronic components.

P5

Sulfur-induced chirality changes in single-walled carbon nanotube synthesis on Co/SiO2 catalyst

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Selective synthesis of single-walled carbon nanotubes (SWCNTs) with different chiral structures is desirable for their potential applications. We show that introducing sulfur-containing compounds into carbon feedstock may efficiently alter the chiral selectivity of a Co/SiO2 catalyst toward different chiral species. When carbon disulfide (0.0001 wt%) was added to ethanol, the carbon yield increased significantly from 4.8 to 14 wt% without chirality changes. The changes in chiral selectivity are correlated with the significant changes in the carbon yield. With further increase of carbon disulfide concentration, the chirality distribution shifted from smaller diameter chiral nanotubes, such as (7,6) at 0.9 nm, toward larger diameter chiral ones, such as (8,7) at 1 nm and (9,8) at 1.2 nm, in addition to a sharp decrease in the carbon yield. Further, when a different sulfur-containing compound was used, the chiral selectivity changed differently. Thiophene (0.1 wt%) in ethanol led to a good chiral selectivity toward (9,8) nanotubes with a relative abundance of 43.1% among all semiconducting nanotubes.We propose that sulfur may selectively block active sites on Co particles through dynamic interactions among sulfur, hydrogen, carbon and Co metal particles. Sulfur-containing compounds may be used as an efficient additive to tune the chirality of SWCNTs.

P6

Synthesis and properties of nitrogen-embedded porphyrins

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Enormous interest exists in the development of organic conjugated materials due to their intriguing electronic and optoelectronic properties. The introduction of amine-type nitrogen into the conjugation largely enhances the electron-donor ability and significantly alters their properties. However, few examples of such amine-type nitrogen-embedded compounds have been reported due to their synthetic difficulty. Therefore, a new class of amine-type nitrogen-embedded compounds is required.

Recently, we achieved the synthesis of amine-type nitrogen-embedded porphyrins. They showed interesting properties caused by the effective interaction between the porphyrin conjugation circuits and peripherally embedded nitrogen atoms. For example, the perturbation of the nitrogen lone pair to the porphyrin conjugation system raised the HOMO to decrease the HOMO-LUMO gap. In addition, the large porphyrin conjugation system enhanced the electron-donor ability to stabilize the radical cation. The synthesis and photophysical properties of these nitrogen-embedded porphyrins will be disclosed in the presentation.

P7

Palladium islands in palladiumtungsten nanoparticles form catalytic hotspots for oxygen reduction

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The oxygen reduction reaction kinetics at the cathode side, in proton exchange membrane fuel cells, is the limiting factor for realizing sustainable solutions for the transportation sector. Thus finding efficient and inexpensive electrocatalysts is the major technical challenge. Here, we demonstrated the synthesis of palladiumtungsten bimetallic nanoparticles supported on ordered mesoporous carbon. This new hybrid catalyst material exhibit a very low percentage of noble metal (palladium:tungsten=1:8), although, its catalytic performance for ORR is equal to commercial 60% platinum/Vulcan. The high catalytic efficiency is explained by the formation of small palladium islands at the surface of palladiumtungsten nanoparticles. The palladium islands are 1 nm in diameter and might contain between 10 to 20 Pd atoms. Our results may provide insight into the formation, stabilization and performance of bimetallic nanoparticles for catalytic reactions.

P8

Fullerenes C60-collapsed carbon nanotube hybrids

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We create a variant of carbon nanotube peapods by packing fullerenes C60 molecules inside the open edge ducts of previously collapsed carbon nanotubes. The C60 insertion is accomplished through a facile single-step solution-based process. The overfilling of the collapsed nanotubes leads to a partial or complete reinflation, where C60 molecules occupy the full cross-section of the tubes, resulting in few-wall, large diameter cylindrical nanotubes packed with crystalline C60 solid cores. Finally, theoretical modeling is used to evaluate favorable low-energy structural configurations.

P9

Metal-carbon composites for producing single-walled carbon nanotubes in high yield

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High crystallinity SWNTs are synthesized by arc discharge evaporation of carbon electrode. The transition metals such as Fe, Co, Ni are known as an effective catalyst for fabricating SWNTs, so that a cored graphite rod with packed with the mixed powder of desired metal and carbon is used as the electrode. However, the yield is low due to the weak bonding between metal catalyst and carbon powder. In this point of view, a solid metal-carbon composite is an ideal electrode. Our company has been developed metal-carbon composites containing fine metal particles (KLASTA MATE).

KLASTA MATE can produce SWNTs in high yield and has been supplied wide range of customers from research application to industrial productions. Nowadays, a pitch impregnated KLASTA MATE is newly developed to enhanced the yield. It is well known that metals are more easily evaporate than carbon, so that the concentration of metal catalyst in electrode decreases during the arcing. The pitch impregnation prevents this phenomenon, owing to fixing the metal catalyst inside the carbon electrode. This newly developed KLASTA MATE can produce SWNTs more than previous one.

P10

Purification of single-walled carbon nanotubes using halogen gas treatment combined with freeze drying process

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Halogen gas treatment is known as purification method of graphite which contains ash constituents (such as metals and Si), and has already been commercialized by graphite manufacturing companies. We have applied halogen treatment to purification of as-grown SWNTs. However, cotton-like morphology of as-grown SWNTs limits the filling efficiency in reaction chamber. It is necessary to change the form and to increase the bulk density of SWNTs for industrial application of halogen treatment.

Here we employ freeze drying to obtain SWNTs materials with appropriate bulk density. In this case, each SWNT are dispersed in frozen water, and then which is sublimed. The resulting SWNTs powder exhibit porous and powder-like form. On the other hand, conventional thermal drying SWNTs produce dense and hard materials because evaporation of liquid solvents generates capillary force among each SWNT and strongly packs them.

We compare the freeze dried and the conventional thermal dried SWNTs by means of halogen treatment. Metal content of freeze dried SWNTs is much lower compared to the conventional dried one, in addition, can be easily dispersed in solvents with no aggregations.

P11

One-dimensional conducting sulfur inside carbon nanotubes

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We repot herein the experimental identification of a conducting character of monatomic sulfur chains inside single-wall and double-wall carbon nanotubes (SWCNTs and DWCNTs, respectively) [1]. Our high-resolution transmission microscopy and synchrotron X-ray diffraction reveal that this one-dimensional (1D) phase of sulfur consists of *planar* linear or zigzag conformations. As predicted previously, those 1D planar geometries are essential for sulfur to become metallic [2]. Most importantly, the presence of 1D sulfur can enhance the electric conductivity of pristine CNTs, implying that filling villain sulfur is a plausible way for improving electric transport properties of CNT-based devices (*e.g.*, transparent conductive films).

To further investigate electronic properties of the hybrid 1D electron systems, we performed resonant Raman spectroscopy using metallic-/semiconducting-sorted SWCNTs. We will demonstrate that 1D sulfur chains encapsulated inside metallic-SWCNTs (S@Met-SWCNTs) exhibit two additional Raman bands only with 532 nm excitation, which we assign to charge density waves within 1D sulfur chains. Those Raman bands are obscured in 1D sulfur inside semiconducting-SWCNT, indicating that the 1D sulfur chains are imposed upon a collective electron state by interacting with Met-SWCNTs.

[1] T. Fujimori *et al., Nat. Commun.* 4(2013) 2162.
[2] M. Springborg & R.O. Jones, *Phys. Rev. Lett.* 57 (1986) 1145-1148.

P12

Towards green, sustainable, and self-loop production of single-walled carbon nanotubes: the recycling and regeneration of Fe/MgO catalysts

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Single-walled carbon nanotubes (SWCNTs) are being highly concerned due to their excellent intrinsic properties and potential applicationsin the area of energy conversion and storage. How to produce SWCNTs in a sustainable way is the first step for their low-cost production and bulk applications. In this contribution, raw SWCNTs with a purity of 5% were synthesized by chemical vapor deposition (CVD) on Fe/MgO catalysts in a fluidized-bed reactor at a scale of about 1kg h^{-1}. High-purity SWCNTs were available via facile acid treatment and the waste Mg^{2+}/Fe^{3+} solution was used as a resource for Fe/MgO catalyst generation. An EDTA-2Na/Na_2CO_3-assistant one-step precipitation method was explored to recover most of magnesium as basic magnesium carbonates without carrying impurities of iron. The Fe/MgO catalysts were then regenerated from these basic magnesium carbonates through facile metal particle loading and calcination. High-quality SWCNTs with a yield of 5.2% can be available based from these regenerated catalysts, and a specific surface area larger than $1000 m^2 g^{-1}$ was achieved. This work developed a sustainable process for the recycling and regeneration of Fe/MgO catalysts, achieving the goal of circular utilization of magnesium resources and also decreasing the potential contamination to the surrounding environment.

P13

SWCNT growth from chiral and achiral carbon nanorings: prediction of chirality and diameter influence on local growth rates

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Catalyst-free, chirality-controlled growth of single-walled carbon nanotubes (SW-CNTs) from organic precursors is demonstrated using quantum chemical simulations [1]. Growth of (4,3), (6,5), (6,1), (10,1), (6,6) and (8,0) SWCNTs was induced by ethynyl radical (C2H) addition to organic precursors. The role of C2H is twofold: The radicals directly attach to the growing rim, and also abstract hydrogens from it, allowing less reactive hydrocarbon species such as acetylene to contribute to growth.
The simulations show a strong dependence of the SWCNT growth rate on the chiral angle, θ. The SWCNT diameter however does not influence the SWCNT growth rate under these conditions. This indicates that the SWCNT growth rate is an intrinsic property of the SWCNT edge itself. Conversely, we predict that the rate of local SWCNT growth via Diels-Alder cycloaddition of C2H2 is strongly influenced by the diameter of the SWCNT. Consequently, a maximum local growth rate may exist for an optimal diameter/chirality combination at a given C2H/C2H2 ratio. We also find that the ability of a SWCNT to avoid defect formation during growth is an intrinsic quality of the SWCNT edge.

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P14

Optical band-gap narrowing of iron oxide nanotubes by temperature annealing and zinc doping

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Regarding renewable energy technology for the sunlight, it is important to develop materials having optical band-gap smaller than 2.5 eV(~500 nm) where the spectral irradiance of sunlight indicates maximum. In addition, tubular structure is one of efficient structure due to it large surface area. We focused iron oxides as the sunlight harvesting material and synthesized iron oxide nanotubes.
Preparation is based on the sol-gel technic. Structural properties of obtained iron oxide nanotubes were characterized by TEM and XRD, and it was found thatthe tubes have outer (inner) diameter of ~10-15 nm (~5-10 nm) with the length of ~100 nm. Crystal structureis representedbythe magnetite structure. Optical bandgapis estimated by Tauc plots of UV-V is absorption data, indicating band gap narrowing from ~2.7 (~460) to ~2.3 eV (~540 nm) by annealing the sample.
Partial substitution of Fe^{2+} to Zn^{2+} was also carried out by the same sol-gel technic. Structural features were characterizedby TEM and XRD. By these analyses and XPS, it was found that the composition of nanotubes is represented by $Zn_xFe_{3-x}O_4$, where x is adjustable in the range between 0 and 0.66. Optical band-gap was lowered to ~2.0 eV (~620 nm) when $x = 0.27$.

P15

Transistors without semiconductors by functionalized boron nitride nanotubes

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Nanotube-based electronics are still hindered by effective synthesis of semiconducting carbon nanotubes. On the other hand, boron nitride nanotubes (BNNTs) are insulators and not applicable for electronic devices [1]. Here we demonstrated that BNNTs functionalized with gold quantum dots (QDs) can form field effect transistors (FETs) without involving semiconducting properties.

High-quality BNNTs are first deposited with crystalline gold QDs. Four-probe scanning electron microscopy (4-probe STM) [2] suggests that QDs-BNNTs are insulating at low bias voltages and switch to a conducting state at higher biasing with a switching ratio of 10^4.The turn-on voltages are foundto decrease withthe decreaseof nanotube length, and can also be modified by gate voltages. In addition, in-situ STM was performed inside transmission electron microscopy (STM-TEM) while bending the QDs-BNNTs. Result indicates that the transport properties are invariant when a QDs-BNNT are bent from zero to 75^{o}. Detail experimental results and theoretical simulation will be discussed in the meeting.

Acknowledgement: This work is supported by the U. S. Departmentof Energy, Basic Energy Sciences, Materials Sciences and Engineering Division (DE-SC0012762) and the Center for Nanophase Materials Sciences (Project CNMS2012-083). [1]. (Review)J.Wanget.al, Nanoscale 2, 2028 (2010). [2]. C. H. Lee, et. al, Advanced Materials 25, 2544 (2013)

P16

Low temperature growth of ultra-high mass density carbon nanotube forests on conductive supports

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Growth of dense CNT forest on conductive supports by CVD is of great importance for variety of industrial applications such as interconnects in LSI and heat dissipation devices. The growth on conductive supports is generally more challenging than that on insulating supports. This mainly comes from the diffculties of the catalyst nanoparticle formation, so we need to engineer the catalyst/underlayer systems. On the other hand, lowering process temperature during CVD is another key issue since versatile supports and substrates are available. Recently, using Co-Mo catalyst, we have achieved the growth of CNT forests on conductive Ti-coated Cu supports at 450℃ with a record high mass density of 1.6 $\mathrm{g\ cm^{-3}}$ [1, 2]. This time, using Co/Al/Mo multilayer catalyst system, we grow a dense CNT forest with an extremely narrow inner spacing of each tube. The forest shows the thermal effusivity of 1840 $\mathrm{J\ m^{-2}\ s^{-0.5}\ K^{-1}}$ and the thermal conductivity of 4.0 $\mathrm{J\ s^{-1}\ m^{-1}\ K^{-1}}$, suggesting the forest is potentially useful for the heat dissipation devices. The growth mechanism and the kinetics of dense CNT forests will be discussed.

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P17

The role of surfactants in aqueous two-phase and density gradient ultracentrifugal separations

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Solubilization of single-wall carbon nanotubes (SWCNTs) with bile salt surfactants[1] has enabled major advances in their processing, purification and spectroscopic characterization. These surfactants enable the structure sorting of SWCNTs by density gradient ultracentrifugation (DGU)[2] and aqueous two-phase (ATP) extraction[3], as theydetermine both the relative density[4] and hydrophobicity for different chiralities.[5,6] We present wavelength-dependent fluorescence-excitation and Raman spectra measured directly after DGU, in situ, as a function of height in the centrifuge tube. These in situ DGU experiments provide an easily interpretable observable, i.e. buoyant density asa functionof chiral structure. We combine thisin situ characterization with concentration-dependent ATP separations for different surfactants and, as such, obtain a more detailed understanding of and control over both separation mechanisms.

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P18

Improvement of the purity of separated semiconducting single-wall carbon nanotubes using a polymeric surfactant

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Single-wall carbon nanotubes (SWCNTs) are promising material for various applications such as flexible electronic devices. Forthe electrical application, metallic (M) and semiconducting (S) SWCNTs have to be separated after the synthesis because of the difficulty in controlled growth. We have developed the efficient separation method of M-and S-SWCNTs using gel column chromatography.

In the presence of sodium dodecyl sulfate (SDS), although M-SWCNTs are recovered without adsorbed to the agarose-based gel column, S-SWCNTs are adsorbed and eluted by deoxycholate (DOC). However, these anionic surfactants shouldbe removed for better performance of the electronic device applications. We searched alternative surfactant instead of DOC and newly found a non-ionic polymeric surfactant that elutes S-SWCNTs from the gel with extremely low concentration. By using this surfactant, the novel agarose-based gel that was not able to release S-SWCNTs by DOC solution could be used for the gel-column separation. The purity of S-SWCNT was highly improved by combining conventional gel and the new gel.

This presentation is based on results obtained from a project commissioned by the New Energy and Industrial technology Development Organization (NEDO).

P19

Carbon nanocrosses: Synthesis, characterization and growth mechanism of a novel carbon nano-structure

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Nanoscience promises a future of novel devices and technologies that harness the atomic or molecular structure of matter. An intriguing manifestation of this paradigm is in the exploiting novel properties of carbon at the nanoscale with many interesting amorphous and crystalline phases, which each shows a variety of one-, two-, and three-dimensional morphologies of branch, star, helix, pipette, cone, bead, bud, and pearl etc.. We report the growth and detailed structural investigation of a novel morphological manifestation of carbon-based nanostructures in the form of crosses with hollow interiors. The center of the crosses is a whole of carbon in the scale from about 160 nm to about 180 nm. The four branches of the cross junction are tapered uniformly to form pointed tips respectively where the tips are single-walled carbon nanotubes (SWNTs) or twin SWNTs. These conical branches of the nanocrosses are composed of coaxial cylindrical graphene sheets, a continuous shortening of the graphene layers in the outer surface along the axial direction. We propose that the carbon nanocrosses grow by the liquid droplet theory, in which the hydrocarbon liquid droplet spread out by making menisci as a result of Rayleigh instability when it deposit on the crossed nanotubes.

P20

Single-walled carbon nanotube growth on Al_2O_x/Pd/Al_2O_x multilayer catalyst using alcohol gas source method

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Single-walled carbon nanotubes (SWNTs) are anticipated to be applied to the field of electronics. For application to LSI device process, it is necessary to grow SWNTs at low temperature and under high vacuum. So far, we reported SWNT growth in a high vacuum using Pt catalysts, however, the yield below 700℃ was not high. In this study, we used Pd as a catalyst for low temperature growth.

Using rf-sputtering and electron beam evaporator, Al_2O_x/Pd(0.1 nm)/Al_2O_x structures were formed on SiO_2(100nm)/Si substrates. SWNT growth was carried out on them using the alcohol gas source method.

When the ethanol pressures were 1×10^{-4}～1×10^{-3} Pa, both G band and RBM peaks were observed in Raman spectra of the samples grown at 500 and 600℃, indicating that SWNTs grew even at low temperature. SEM observation showed SWNTs grew on all over the substrate surfaces. From the wavenumbers of RBM peaks, SWNT diameters were estimated to be distributed between 1.2 and 1.8 nm. Our results showed that Pd catalysts are suitable for SWNT growth at low temperature under a high vacuum.

P21

Single-wall carbon nanotube films with optical and electrophysical properties tunable via time-depended filling of nanotube internal channel with acceptor molecules

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Nowadays films of single-wall carbon nanotubes (SWCNTs) are very promising for application in fiexible highly conductive and transparent electronics, light sensitive electronics and nonlinear optics. One of the most important problems is providing a variation of optical, mechanical, electrophysical and chemical properties of this unique material. These properties should be changed in a controllable way.

Here we present a new approach to tune the optical and electrophysical properties of transparent conductive films formed from SWCNTs. A net of SWCNTs grown by an aerosol chemical vapor deposition techniqueis used asa ground for a gas-phase filling the NT internal channels with strong electron acceptors (iodine or copper chloride). This leads to a remarkable charge transfer from nanotubes to species formed inside them. The approach allows to change step-by-step the Fermi level position, optical transmittance and conductivity of SWNTs. The filling degree is determined by the treatment duration. Thus, this approach provides a p-doping degree variation and the Fermi level shift determined by the treatment time. The effect leads to a smooth changing the optical transmittance and electrical conductivity of SWCNT films. These results are very promising for applications in light-sensitive electronics and nonlinear optics.

P22

Finite carbyne chains synthesized in liquids by femtosecond laser pulses

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The linear 1D carbon chains (LCC) with polyynic sp bonds were synthesized by femtosecond laser ablation of graphite particles, suspended in liquids. The absorption spectra of the suspensions in different media (hexane and water) and at various temperatures were measured after the laser irradiation. The narrow absorption lines at 189, 199, 215, 225, 262, 276, 296, 325, 340 and 369 nm were clearly seen; they corresponded to the absorption of the finite carbyne chains CnH2, where n=218. Thus, the maximum detected length of LCC was 22A. The thresholds of laser intensity for the formation of LCCs in water and hexane were estimated. After laser synthesis the absorption spectra of LCC demonstrated gradual degradation. The decay of LCC was caused by the oxidation of the carbyne chains and formation of cross-links. Based on the intensity of the absorption lines, the lifetime of LCC in hexane and water at room temperature was estimated to be 40 days and 1 day, respectively. At the elevated temperature the lifetime of LCC in hexane decreased.

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P23

Wearable pulse active sensor based on tellurium dioxide microwires

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The wrist-worn device, along with health-care management, is rapidly growing in importance today. We have demonstrated the wearable health monitoring active sensors that was first made using tellurium dioxide triangular microwires. In this work, the α-TeO2 triangular microwires were synthesized on a silicon substrate by a vapor transfer process at 500℃. Unlike wurtize structures, which exhibited a commonly spontaneous polarization along with the [0001] axis, the non-centrosymmetric α-TeO2 has a unique growth direction along with the [110] axis. The PDMS-triangular microwires composite underwent a natural gravity-driven settling process during the solidification process, leading to the triangular microwires being randomly distributed on the substrates surface with a horizontal orientation. The triangular microwires were then capsulated by the polydimethylsiloxane (PDMS) to fabricate the wearable and skin-attachable devices, which successfully analyzed the tiny physical motions, for instance, a pulse driven sensor and a touchless control of smart devices.

P24

Stability and electronic structure characteristics of charged and passivated TiO2 nanotube

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Titanium dioxide nanotube shows great potential in applications on biomedical, photocatalysis, and dye-sensitized solar cells. The stability and electronic properties of TiO2 nanotube have been attracted much attention. In the present study, the influence of charge defect and passivation (with H and OH) on the stability and electronic properties of anatase TiO2 nanotube was investigated by first principles calculations. The adsorption sites of H and OH group on the surface of TiO2 nanotube are optimized. Calculations indicate that the stability of TiO2 nanotube is reciprocally relates to the charged states. Both the positive charge and the passivation of H and OH enlarge the diameter of the TiO2 nanotube. The electronic structures are analyzed to clarify mechanisms of the influence of charge and passivation on the stability of the TiO2 nanotube.

P25

Separation of large diameter single-wall semiconducting carbon nanotubes by gel filtration

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Carbon nanotubes (CNTs) have caught world-wide attention as potential replacement for novel semi-metal and transition metal-based materials in mechanics and electronics application. However, wide structural diversities of CNTs may provide drawbacks to the electronic application through altering the electronic properties of CNTs as either metallic or semiconducting. Therefore, sorting CNTs based on their electronic properties has become more and more essential for the electronics application of CNTs.

Although a number of groups have reported on the separation of metal-semiconductor CNTs, the small diameter CNTs of less than 1.4 nm across have been largely reported. In contrast, separation of larger, 1.7 –2 nm diameter of semiconducting CNTs have not been reported in spite of their interesting properties of small electronic band-gaps which hold high carrier mobility potential.

Here, we demonstrate separation of large diameter semiconducting CNTs from pyrolytic-method (eDIPS) grown CNTs by a simple gel filtration method. As large as 1.7 nm diameter CNTs have been successfully separated from the as-grown sample. In addition, due to the characteristic broad large diameter distribution of the CNTs, diameter-dependence elution is also obtained without any complicated treatment.

P26

One-pot chirality selective sorting of single-walled carbon nanotubes using strategically-designed fluorene copolymers

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Single-walled carbon nanotubes (SWNTs) are produced as mixtures of numerous chiralities including semiconducting-and metallic-tubes, which should be separated to educe their intrinsic superior properties. Among various techniques for the chirality-separation, synthetic polymers have advantages, such as high and designable chirality-selectivity, right- or left-handed tube separation and simple one-pot procedure. [1-6]
We have developed a precise design and synthesis of highly functional fluorene-based copolymers, which recognize specific chiralities of semiconducting-SWNTs. The introduction of bipyridine into polyfluorene leads to 97% selective extraction of (6,5) SWNT, and BINAP moieties in the fluorene copolymers recognized handedness of SWNTs. Recently, we have succeeded extraction of the semiconducting-SWNTs, then removal of the wrapping polymers from the SWNT surfaces based on polymerization/depolymerization through metal-ligand coordination and hydrogen bonding. The purity of the obtained semi-conducting-SWNTs without any surfactants reached ～99%.

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P27

Direct synthesis of graphdiyne nanowalls on arbitrary substrates

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Graphdiyne, a novel two-dimensional (2D) carbon allotrope composed of sp-sp^2 carbon atoms, is predicted to exhibit extraordinary properties[1]. However, due to its instability and complex structure, the synthesis remains to be a formidable task. Recently, Li et al. first prepared 2D graphdiyne film (about 1 micrometer thick) by conducting cross-coupling reaction with copper foil as both catalysts and supporting substrate[2]. However, for practical applications and better characterizations, it will be desirable to synthesize graphdiyne on different substrates. Herein, we developed a new route to directly synthesize graphdiyne nanowalls on arbitrary substrates by using copper envelop catalysis. In alkaline solution, copper transforms to copper-pyridine complex, which acts as a running catalyst for acetylenic coupling reaction. The running catalyst can diffuse from copper envelop to target substrates by concentration gradient. Through this method, graphdiyne nanowalls are synthesized on both conducting (Au, Ni, W foils) and insulating (SiO_2) substrates, even on stainless steel meshes etc. Consequently, our methodology not only realizes direct synthesis of graphdiyne nanowalls on arbitrary substrates, but also paves the way forward to the realization of graphdiyne applications in electronics and energy storage.

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P28

Growth of single-walled carbon nanotubes with narrow chirality distributions from Rh catalysts by alcohol gas source method in high vacuum

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Single-walled carbon nanotubes (SWNTs) have been anticipated for application in a lot of future nanodevices. To fabricate SWNT devices, it is important to grow SWNTs with uniform chirality and diameter. So far, we have reported SWNT growth using Pt catalysts and succeeded in obtaining SWNTs with small diameters below 1.2 nm [1]. This suggests that metal catalysts with high-melting points are effective to grow SWNTs with small and uniform diameters. In this study, we attempted to grow SWNTs using Rh catalysts whose melting point is 1966℃ and much higher than Pt.

Using Rh catalysts, SWNTs were grown on SiO2/Si substrates by the alcohol gas source method in the UHV chamber. The growth temperature was set between 500 and 800℃ and the ethanol pressure was varied between 1×10^{-4} and 1×10^{-2} Pa.

Raman and TEM results showed that SWNTs grew at 500～800℃ from Rh catalysts. When the growth temperature was below 600℃, the diameters of most SWNTs were reduced and distributed between 1.0 and 1.4 nm. Our results showed that Rh is a useful catalyst to grow SWNTs with narrow diameter distributions. We also discuss the difference between Rh and Pt catalysts in the SWNT growth.

P29

Chain length dependence of oligofluorenes for selective sorting of semiconducting single-walled carbon nanotubes

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Polyfluorenes have been remarked asfascinating dispersants that solubilize only semiconducting single-walled carbon nanotubes (sem-SWNTs)[1]. The selective extraction mechanism, however, has not revealed yet. Here, we synthesized oligofluorenes with different main chain lengths (FOn, n: the number of fluorene repeating unit) and examined their solubilization abilities for pristine-SWNTs.

The chain length controlled FOn, n = 9, 12, 15, 18, 21, 24, 27 were synthesized through Yamamoto coupling followed by recycling gel permeation chromatography purification. Sonication of SWNTs with FOn provided SWNT dispersions when the chain length was longer than n=12. Interestingly, the selective sem-SWNT extraction was observed when longer FOn (n > 15) were used. The selectivity was further investigated by vis/NIR absorption and photoluminescence (2D mapping) spectroscopies, which revealed that the chiralites of the extracted SWNTs were different by comparing poly (9,9-di-n-octylfluorene) and the longer FOn; thatis, (9,7) SWNT was extracted together with (7, 5), (7, 6), (8, 6), and (8, 7) SWNTs by PFO, although the SWNT dispersions using FOn did not contain (9, 7) SWNT. The present study indicates importance of the main-chain length of oligofluorenes on the sem-SWNT selectivity.

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P30

Single-walled carbon nanotube growth on graphene oxide using Pt catalysts by alcohol gas source method

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Recently, hybrid structures composed of carbon nanotubes (CNTs) and graphene have attracted much attention because they have high electrical conductivity and large surface areas, therefore, they are anticipated for application to electrodes of large-capacity storage batteries such as super capacitors. However, it is difficult to grow single-walled CNTs (SWNTs) directly on graphene layers. In this study, we attempted to direct growth of SWNTs on graphene oxides (GO) using Pt catalysts.

GO layers were stacked on SiO2/Si substrates by layer-by-layer (LBL) process using GO nanosheet sol solutions, the thickness of which were controlled by the sol concentration. After Pt catalysts (nominal thickness ~0.2 nm) were deposited on them, SWNT growth was carried out at 700℃ using the alcohol gas source method.

XPS results confirmed that GO layers were stacked on SiO_2/Si substrates, whose thickness was controlled by the number of the repetitions of the LBL process. Raman measurements showed that both G band and RBM peaks appeared after the growth procedure, indicating that SWNTs grew on the GO layers. SEM observations showed that the SWNT yield is dependent on the thickness of GO layers, and that the yield seems to increase as the thickness was reduced.

P31

High efficiency production of single-walled carbon nanotubes by the bipolar pulsed arc discharge and centrifugal purification

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Large scale production and purification of single-walled carbon nanotubes (SW-NTs) are still big challenge for their usage in commercial applications. Efficient production of SWNTs has been examined by using newly developed bipolar pulsed arc discharge with constant current and constant pulse duration. The advantage of the bipolar pulsed arc discharge is that both electrodes sublimate alternately at almost the same rate and there are no carbon deposits on the both electrodes, which means that all the sublimated carbon becomes soot containing single-walled nanotubes. The nanostructures of the synthesized SWNTs are characterized by a TEM and Raman spectroscopy.

The purification procedure involves a combination of dispersion and centrifugation, in which gelatin; an environmentally friendly material is used as a dispersing agent. Stable gelatin-SWNT dispersion is used in the centrifugation procedure for the better separation of pure SWNTs and impurities such as metal particles and amorphous carbons. Centrifugation easily removes impurity and leaves long undamaged SWNTs in solution by using effective centrifugal force and centrifugation time. The centrifugation is carried out for several times to completely remove impurity. Finally, the SWNTs are separated from the gelatin by heating and filtering. Each step of centrifugation, the solution is characterized by a transmission electron microscope, thermo-gravimetric analysis and Raman spectroscopy.

P32

Control of interactions between single-wall carbon nanotubes and hydrogels using redox reagents

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Single-wall carbon nanotubes (SWCNTs) dispersed with sodium dodecyl sulfate (SDS) are separated into metallic and semiconducting species using hydrogel columns. In the separation, metallic SWCNTs are flowed through the columns, whereas semiconducting species are adsorbed on the hydrogels in the columns. We have recently suggested that the separations are accounted for by the oxidation of the SWCNTs. In order to demonstrate the suggestion, adsorbability of the SWCNTs on to the hydrogels was investigated in the presence of various oxidants such as K_2IrCl_6 and NaClO. The semiconducting SWCNTs were found to be eluted from the columns by the oxidant solutions. The elution effect of K_2IrCl_6 was more pronounced than that of NaClO, which is consistent with their oxidation effect on the SWCNTs. In addition, molecular dynamics simulation showed that positively charged SWCNTs have more SDS molecules on their surfaces than uncharged SWCNTs. These results suggest that the oxidized SWCNTs by the oxidants are well wrapped by SDS molecules, leading to their desorption from the hydrogel and hence their elution from the columns.

P33

Bucky papers of (6,5) enantiomer SWCNTs

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Single-wall carbon nanotubes (SWCNTs) are produced as a mixture of various structures, and the inhomogeneity hinders their basic research and applications. We have reported (*n*, *m*) and enantiomer separation of SWCNTs by overloading or temperature-control gel column chromatography (1). Recently we have developed another separation method for (*n*, *m*) enantiomers of SWCNTs at very high purities using a mixed surfactant system (2). In this presentation, we show large-scale (6, 5) enantiomer separation of SWCNTs using the system. CoMoCAT SWCNTs (SG65) dispersion in sodium dodecyl sulfate (SDS) and sodium cholate (SC) was prepared by sonication and ultracentrifugation and was separated by using a chromatography system equipped with 430 ml column. Adsorbed SWCNTs to the column were eluted by stepwise increasing concentration of sodium deoxycholate in SDS/SC. After a few separation cycles, we could obtain milligrams of (6, 5) enantiomers of SWCNTs. Bucky papers of (6, 5) enantiomers were prepared from the separated solutions. This work was supported by KAKENHI No. 25220602

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P34

Growth of chirality enriched single-walled carbon nanotube horizontal arrays via temperature perturbation chemical vapor deposition method

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Chirality enrichment with direct growth is one of the biggest challenge in carbon nanotube synthesis since its discovery, and remarkable progress have been made in the past years. Most of these works are focused on the catalysts with specific structure, especially high melting point catalysts, but relatively lower efficiency. Otherwise, chirality enrichment using metal catalyst with high efficiency remains difficult, because of the amorphous morphology in growth condition. Theoretical calculations had proved that the difference of interaction energy between tubes and catalyst nanoparticles is much significant. Since the structure of carbon nanotube can be changed during growth process with a temperature-mediation[1], it is possible for us to use this energy differential. In this work, we first proposed to realize chirality enrichment by using temperature perturbation chemicalvapor deposition (TPCVD). This method could enrich SWNTs with small helix angle, which have lower interaction energy with liquid catalyst. SWNTs with helix angles under 10^o can be enriched upon 59%. Furthermore, SWNTs with suitable diameter can be enriched as well. For example, the contentof (15, 2) tubes by TPCVD process with can be enriched 8 times compared with a normal chemical vapor deposition process.

[1] Yagang Yao, et al., *Nat. Mat.*, **2007**, 6, 283.

P35

Synthesis of kilometres of continuous macroscopic fibres with controlled type of carbon nanotubes and bundle orientation

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CNT fibres have been synthesized by floating catalyst CVD [1]. Controlling synthesis parameters lead to the control of CNT type and CNT bundle orientation. Increasing sulphur precursor from 0.1% to 1.5% makes catalyst particles larger, increases inner diameter and number of layers of CNTs. Reactant feed rate, carrier gas and drawing winding rate determine the final fibre structure by fixing CNT orientation and therefore packing and properties.

The progressive transition from single-walled through collapsed double-walled to multi-walled is clearly seen by an upshift in the 2D (G′) band and by other Rama n spectra features. The increase in number of CNT layers and inner diameter results in a higher fibre macroscopic linear density and greater reaction yield (up to 9%). We establish the composition of the catalyst particles and position in the isothermal section of the C/Fe/S ternary diagramat 1400℃[2]. This helps explain the unusually low proportion of active catalyst particles in the direct spinning process (<0.1%) and the role of S in limiting C diffusion. A final critical observation is that varying the carbon source in the feedstock does not affect previous discussion. By doing mechanical test we obtain values of tensile strength as high as 2N/TEX.

P36

Exploring electrical conductivity of multi-walled carbon nanotubes containing long linear carbon chains

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Linear carbon chain (LCC) consisting of sp-hybridized carbon atoms is predicted to have interesting physical and chemical properties due to its ideal atomic 1D nature. Theoretically, LCC has been actively investigated as novel low-dimensional materials. Experimentally, due to its low stability, freestanding LCC was not produced. To overcome such problem, we focused on the nano-space in the hollow core of carbon nanotubes. Recently, long LCC within the hollow core of multi-walled carbon nanotubes (MWCNTs), synthesized by atmospheric arc discharge method, was analyzed using Raman and TEM in detail. In this study, we evaluated electrical resistivity of MWCNTs containing LCC in the temperature range from 5K to room temperature. We observed the large change in the electrical conductivity of MWCNTs before and after the disappearance of LCC.

P37

Conjugated microporous polymer aerogel: a new kind of carbon-based material for gas sorption and oil clean-up

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Recently, conjugated microporous polymers (CMPs) has received wide attentions because of their attractive features (e.g., microporosity, electronic properties) and broad applications. However, most CMPs showed a relative lower BET area (<1000 m^{2}g^{-1}), which is detrimental to many applications. Additionally, predominant micro-porosities in CMPs also deteriorate oil uptake performance.

To solve above problems, CMPs (poly(1,3,5-triethylnylbenzene)) aerogels have been prepared by Glaser coupling reaction with CuCl as catalysts.[1] The much improved BET area (up to ～1700 m^{2}g^{-1}) and hierarchical pores enabled materials with extraordinary performance in gas sorption (～3.47 mmol g−1 for CO2 at 273 K,1 bar) and oil uptake (13～53 times weight gain). To modulate pore structure, wettability, and homogeneity, a fluorosurfactant-assisted Glaser coupling method has also been developed.[2]

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2. R. Du, Z. Zheng, N. Mao, N. Zhang,W. Hu, J. Zhang, *Adv. Sci.* **2014**, DOI: 10.1002/advs.201400006.

P38

Autonomous experimentation applied to carbon nanotube synthesis

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Carbon nanotubes have an exciting array of applications which span mechanical, electrical, thermal and chemical/sensing. However, full exploitation is slowed by alack of understanding of the nucleation and growth mechanisms. Our group has endeavored to develop a method that addresses the critical bottlenecks impeding the speed of research by taking advantage of advances in robotics, artificial intelligence and in-situ/in-operando characterization. Our Autonomous Research System, ARES, designs, executes and evaluates its own CNT growth experiments. Artificial intelligence module (random tree/genetic algorithm) analyses experimentally obtained kinetic parameters and proposes new experiments to achieve user-defined objective. These are executed by ARES automatically, and fed back into the AI module to ensure machine learning.

Recent experiments utilized growth rate as an objective. The difference between experiment and objective behaves similar to what is typically seen in the control systems, with experimentally observed rate oscillating around the target. The cumulative root mean square (RMS) of the rate difference initially increases, followed by consistent decrease after ~50 experiments, indicating convergence. That is, after some unsuccessful experimentation, ARES was better able to achieve the objective growth rate. This is a clear demonstration of AI learning: convergence on the objective via closed-loop iterative experimentation without human intervention.

P39

Alcohol catalytic CVD synthesis of small-diameter single-walled carbon nanotubes from Pt catalysts

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Single-walled carbon nanotubes (SWNTs) have unique properties and are anticipated for application to nanoelectronics in future. Sofar, we have reported that SWNT growth using Pt catalysts by a gas source method in a high vacuum. However, the diameter and chirality distributions of SWNTs from Pt catalysts have never been clarified sufficiently. In this study, we carried out SWNT growth from Pt catalysts using a cold-wall CVD system in which ethanol gas could be flown uniformly inside the chamber and estimated the diameter and chirality distributions of grown SWNTs.

Pt catalysts deposited on SiO_2/Si substrates were used for SWNT growth and the grown SWNTs were characterized by SEM, TEM, Raman, photoabsorption and photoluminescence/excitation (PLE) spectroscopies. When the growth temperature was 700℃, web-like SWNTs were grown uniformly on the substrates at an ethanol pressure of 1 Pa. Raman and photoabsorption results showed that the diameters of most SWNTs were below 1 nm and (7,6) and (8,4) SWNTs were dominant in the PL mapping. In addition, as the growth temperature was reduced, the optimal ethanol pressure decreased and the SWNT diameters became smaller. Our results showed that Pt catalysts are suitable for growth of SWNTs with small diameters.

P40

Selective scission of C-O and C-C bonds in ethanol using bimetal catalysts for the preferential growth of semiconducting SWNTs arrays

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Single-walled carbon nanotubes (SWNTs) have been regarded as one of the most attractive candidates to be used as building blocks in the next generation electronics. For the fabrication of highly integrated circuits, SWNT arrays with semiconducting selectivity are highly desired. We herein developed a method combined with bimetal catalysts to preferential growth of semiconducting SWNTs using the different ways to decompose ethanol for different metals, such as, a reforming reaction occurs on Cu to produce C_{ads} and CO, while a deoxygenating reaction occurs on Ru to produce O_{ads} and C_2H_4. When the bimetal catalysts with an appropriate ratio were used, the produced C_{ads} and C_2H_4 can be used as carbon source for SWNTs growth and O_{ads} promotes a suitable and durable oxidative environment to inhibit the formation of metallic SWNTs (m-SWNTs). Different bimetal catalysts were developed, such as such as Cu/Ru, Cu/Pd and Au/Pd. Finally, we successfully obtained horizontally aligned SWNTs on a ST-cut quartz surface with a density of 4-8 tubes per mircometer and an s-SWNT ratio of about 93% using an Au/Pd (3:1) catalyst. The synergistic effects in bimetallic catalysts provide a new mechanism to control the growth of s-SWNTs.

P41

Bridging growth of carbon nanofibers by cleaving under carburizing heat treatment for oxidized iron foils

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We developed the bridge grown carbon nanofibers (BG-CNFs) with length of 100-200 μm such as carbon nanotubes (CNTs) and multi-layered graphene fibers (MGFs) by the unique cleaving process in carburizing heat treatment for the iron oxide foils in acethylene gas flow. The iron oxide foils were fabricated by oxidization of pure iron with high purity of 4 to 5 N. We clarified that the BG-CNFs were grown linearly between divided crack walls according to the cleaving motion under local carburizing heat treatment by using a laser beam and the microscope observation. The BG-CNFs with multi-graphene layer structure were observed by TEM, electron diffraction and Raman spectroscopy. The contact point of a BG-CNF on a prominent structure of the divided iron wall was observed by FIB (Focused Iron Beam) and SIM (Scanning Ion Microscopy). Observation of the cross section structure of the reacted iron specimens indicated that the oversaturated carbon was decomposed between the divided iron specimens in the carburizing process. We present a model that the BG-CNFs are grown by tension through cleaving of the peculiar iron phase including a large amount of carbon in the reduction and carburizing process for the iron oxide.

P42

Single-chirality separation of ultra-thin single-walled carbon nanotubes prepared by arc discharge

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Ultra-thin single-walled carbon nanotubes (SWCNTs) witha narrow diameter distribution are prepared by DC arc discharge evaporation of a Fe catalyst under an optimized H2/He atmosphere. These high-crystalline SWCNTs with selective small diameters were enriched with a pHtemperature controlled gel chromatography single-chirality separation process. Due to the clean surface and few defects, arc-discharge SWCNTs are more difficult to be wrapped by sodium dodecyl sulfate (SDS). These differences result in a stronger interaction between the SWCNTs with the gel beads, and the adsorbed SWCNTs cannot be eluted with high concentration SDS. Tuning the interaction through varying the pH and temperature enables the separation of five species from the SDS wrapped SWCNTs in aqueous solution, namely (7,5), (9,4), (7,6), (8,6), and (8,7), as evidenced by several optical spectroscopy techniques. The single-chirality separation of ultra-thin and high-crystalline SWCNTs could be used as a nanocontainer for preparing the novel 1D material.

P43

A sweet spot for highly efficient growth of vertically aligned single-walled carbon nanotube forests enabling their unique structures and properties

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We investigated the correlation of growth efficiency and structural parameters of single wall carbon nanotube (SWCNT) forests and report the existence of a SWCNT sweet spot in the carbon nanotube (CNT) diameter and spacing domain for highly efficient synthesis. Only within this region could SWCNTs be grown efficiently. Through the investigation of the growth rates for ~340 CNT forests spanning diameters from 1.2 to 8.0 nm and average spacing from 5 to 80 nm, this sweet spot was found to exist because it was constrained by several mechanistic boundaries that either hindered the formation or reduced the growth rate of SWCNT forests. Specifically, with increased diameter SWCNTs transitioned to multiwall carbon nanotubes (multiwall border), small diameter SWCNTs could only be grown at low growth rates (low efficiency border), sparse SWCNTs lacked the requirements to vertically align (lateral growth border), and high density could not be prepared (high catalyst density border). As a result, the SWCNTs synthesized within this sweet spot possessed a unique set of characteristics vital for the development applications, such as large diameter, long, aligned, defective, and high specific surface area. This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P44

Ethanol tuning the interaction of carbon nanotubes with gel for their chirality separation

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Surfactants or polymers are usually used for the liquid processing of single-wall carbon nanotubes (SWCNTs) for their structure separation. However, they are difficultly removed after separation and remain as impurities in the separated species, which alter the intrinsic properties of SWCNTs and affect their scientific research and technical applications. In this presentation, we report ethanol-assisted gel chromatography for the chirality separation of SWCNTs, in which ethanol is employed to tune the interaction between SWCNTs and an allyl dextran-based gel, achieving the single-chirality separation of SWCNTs. With this technique, sodium dodecyl sulfate (SDS) witha maximum concentration of 2 wt% was used in the whole separation process including desorption of SWCNTs from the gel, which is much lower than previously reported [Nat. Commun. 2 (2011) 309]. Clearly, the use of ethanol enables the working concentration of SDS to be dramatically reduced, and cut down the separation cost. More importantly, ethanol is easily to be eliminated because its volatility, which decreases impurities in the separated nanotubes. The ability of ethanol to tune the interaction of SWCNTs with gel also gives deeper insights into the separation mechanism of SWCNTs by the gel chromatography technique.

P45

Single-walled carbon nanotubes grown from nano carbon seeds

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Carbon seeds like nano-diamond, fullerene fragments and nanotube segments have been used to synthesize carbon nanotubes (CNTs). This new route may produce high purity nanotubes free from metal impurities, which will promote the application of nanotubes and contribute to understanding on the growth mechanisms of CNT. We comprehensively studied the growth of single-walled carbon nanotubes (SWCNTs) from nano-carbon seeds include fullerene and short nanotubes. Various parameters such as the pretreatment condition, substrates and carbon sources are investigated and their influences on the re-growth of SWCNT were thoroughly evaluated. By varying these parameters, the pretreatment as well as the growth conditions suitable for hot-wall and cold-wall chemical vapor deposition were established, and the re-growth of nanotubes from seeds was realized in these two systems. According to our experimental observation, the pretreatment is proved to be an indispensable process used to active the nano-carbon seed. The growth window is narrow, and the efficiency of re-growth is largely determined by various conditions. On the basis of those experimental results, the process and mechanism of SWCNT re-growth are discussed.

P46

Disorder effects on magneto-transport on the surface of a topological insulator

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A three-dimensional (3D) topological insulator supports novel topologically protected 2D Dirac fermions on its surface. It has been clarified that 2D massless Dirac fermions are not localized and remain conducting in disordered systems with time-reversal symmetry. Numerical calculations of conductance show that the conductance increases with increasing system size. On the other hand, in the interface of a ferro-magnetic insulator and a topological insulator, a variety of unique magneto-transport phenomena have been proposed. When the magnetization changes spatially, the conductance of surface Dirac electron changes. In this work, we study the disorder effects in the magneto-transport regime on the surface of a topological insulator interacting with magnetic moments. Since, on the surface of a topological insulator, out-of-plane magnetization inducesa mass gap, while in-plane magnetization hasa roleof an effective vector potential, the effects of disorder on the magnetoconductance might be qualitatively different. Our numerical calculation shows the magnetoconductance with in-plane magnetization field is robust against disorder compare to that with out-of-plane magnetization field.

P47

Spectral sensitivity of pristine and zinc doped iron-oxide nanotube based solar cell

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Organometal halide perovskite on titanium-oxide is a pioneering material and is widely used for sensitized perovskite solar cell, where the perovskite mainly works as the light absorber and the photoelectrons generated are transferred to mesoporous scaffold of titanium-oxide. Since the optical band-gap of titanium-oxide is in the ultra-violet range, it is not efficient to absorb the sunlight. Optical band-gap of iron oxide is much narrower than that of titanium-oxide and hence we focused this material for the mesoporous scaffold of sensitized perovskite solar cell.

Pristine iron-oxide (Fe_3O_4) and their zinc doped ($Zn_xFe_{1-x}O_4$) nanotubes (Fe-ox-NT or ZnFe-ox-NT) were used as the electron transporting layer of the solar cell, which is composed of, from the negative electrode, FTO/dense-Fe-ox/Fe-ox-NT (or ZnFe-ox-NT)/$CH_3NH_3PbI_3$/Au. Magnitude of spectral sensitivity in the range of the wavelength longer than ～450 nm indicated greater values than that based on Fe-ox nanoparticles, which is explainable by narrowing the optical band gap. Although it was found that IPCE of the cell was improved when P3HT was spin-coated on the PbI3 layer, zinc doping to Fe-ox-NTs worsened the characteristic.

P48

Single-structure separation of carbon nanotubes by gel chromatography

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Each chiral single-wall carbon nanotube (SWCNT) has a pair of optical isomers (i.e., left-and right-handed structures), which exhibit different optical activities and have potential applications in optical components, biological sensors, production of chiral light, and asymmetric autocatalysis. Production of single-isomer species is the ultimate step for obtaining true single-structure SWCNTs and, thus, is critical to truly unlock their intrinsic properties and advance their applications. In this presentation, we report the optical isomer separation of single-chirality SWCNTs by gel chromatography, which we recently developed for the chirality separation of SWCNTs. This method uses the difference in the interactions of the two isomers of a chiral SWCNT with an allyl dextran-based gel, which result from the selective interaction of the chiral moieties of the gel with the isomers. Using this technique, we sorted optical isomers of nine distinct (n, m) single-chirality species from HiPco-SWCNTs, which is the maximum number of isolable species of SWCNTs reported to date. Because of its advantages of technical simplicity, low cost, and high efficiency, gel chromatography allows researchers to prepare macroscopic ensembles of single-structure SWCNTs and enables the complete discovery of intrinsic properties of SWCNTs and broadens their applications.

P49

Synthesis and catalytic activity of single-shell carbon-encapsulated iron nanoparticles decorated on single-walled carbon nanotubes

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Efficient hydrogen evolution reaction (HER) through effective and inexpensive electrocatalysts is a valuable approach for clean and renewable energy systems. A highly active and durable non-noble metal catalyst for the HER is reported here by decorating single-shell carbon-encapsulated iron nanoparticles (SCEINs) on single-walled carbon nanotubes (SWNTs). The catalyst exhibits catalytic properties comparable to those of platinum. The high catalytic activity of SCEINs is attributed to a considerable charge transfer from the iron nanopaticle to the carbon cage. The SCEIN/SWNT is synthesized by a novel fast and low-cost aerosol chemical vapor deposition method in a one-step synthesis. In SCEINs the single carbon layer does not prevent desired access of the reactants to the vicinity of the iron nanoparticle but protects the active metallic core from oxidation. In our experiments for synthesis of CNTs, iron nanoparticles with an average size of 2.6 nm are mostly inactive for the growth of CNTs and they are preferentially encapsulated with a layer of carbon, instead of growing CNTs. On the contrary, the larger particles may catalyze the growth of carbon nanotubes. This finding opens new avenues for the growth of metal nanoparticles encapsulated with a fullerene-like carbon cage which can be used in various applications.

P50

Formation of carbon nanotubes filled with Cu-binary alloys and elution of encapsulated metals at low temperature

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It is well-known that carbon nanotubes (CNTs) have one-dimensional nanospace and some metals and metal compounds can be encapsulated in the nanospace of CNTs. In our previous studies, we had succeeded in fabricating CNTs filled with copper (Cu@CNTs) in large quantities by arc discharge with hydrogen gas. Furthermore, we had found that the Cu@CNTs have some fruitful properties such as elution of encapsulated copper at about 400℃. In this study, we succeeded in formation of CNTs filled with Cu-Ge and Cu-Ti alloys (Cu-Ge@CNTs and Cu-Ti@CNTs, respectively) by the arc-discharge method. Analyses of transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) clarified that CNTs perfectly filled with Cu-Ge and Cu-Ti binary alloys. The Cu-Ge@CNTs and Cu-Ti@CNTs were heated at 150-1100℃ under a high vacuum. Results of TEM indicated that encapsulated Cu-binary alloys eluted from CNTs at about 200℃ lower than elution temperature of Cu@CNTs. Analyses of XRD clarified that Cu-Ge and Cu-Ti alloys in CNTs were encapsulated in crystalline Cu_3Ge and amorphous Cu-Ti, respectively. However, Cu-Ti alloy eluted from CNTs changed amorphous to particles of Cu_3 Ti crystalline after heating. Moreover, results of XPS showed that TiO_2 layers were formed on surfaces of the Cu_3Ti alloy particles.

P51

How evolve the diameter and chirality distribution of single-walled carbon nanotubes with the synthesis time in CCVD

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Controlling the diameter and chirality distribution of single-walled carbon nanotubes (SWCNT) is crucial for their large-scale application. Although Catalytic Chemical Vapour Deposition (CCVD) is the most popular method for synthesizing SWCNTs, CCVD-grown SWCNTs usually present a large distribution of diameters and chiral angles. Several works have been devoted to understand and control the processes at the origin of this distribution. We previously evidenced several processes hindering the growth of small-diameter SWCNTs: catalyst coarsening, absence of nucleation, catalyst poisoning.1,2

Here, we report on the evolution of the diameter and chirality distribution of SW-CNTs with the synthesis time using two different approaches: in situ Raman monitoring and ex situ Raman characterization of samples frozen at different times. In most cases, the diameter distribution of SWCNTs is observed to significantly evolve with time. The type of evolution (e.g. toward smaller or larger diameters) strongly depends on the growth conditions. Post-growth analyses by HRTEM were performed to determine the underlying processes. Beside the evolution of diameter, we will also discuss how the evolution of the RBM inform on the evolution of the chirality distribution during CCVD.

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P52

Structural analysis of electrochemically synthesized TiO_2 nanotubes

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The as-grown structure of electrochemically synthesized titania nanotubes is investigated by scanning electron microscope (SEM), as well as combination of cross-sectional and high-resolution transmission electron microscope (TEM). The study reveals that all of the tubes are closed at both ends with caps which contain pentagonal carbon rings. It also reveals a preferred growth direction of the nanotubes relative to the substrate surface and the thickness of a thin barrier layer that exist between the metal surface and the nanotubes. Additionally, a new growth, layered model of the anodic TiO2 nanotubes is presented to obtain further understanding of the growth mechanism.

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P53

Molecular dynamics growth of defect-rree single-walled carbon nanotubes

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Molecular dynamics (MD) simulations are useful to analyze the growth mechanism of single-walled carbon nanotubes (SWNTs) on atomic scale, which is difficult to observe experimentally. However, SWNTs grown in MD simulations have been defective and it was difficult to analyze the detail of the growth mechanism and their chirality. We performed classical MD simulations to reproduce SWNT growth using Brenner-Tersoff. potential as the potential among chemically-bound carbon atoms, Tersoff type potential [1] among metal atoms and carbon atoms, Lennard-Jones potential among free carbon atoms. A metal cluster catalyst, iron or cobalt is arranged at the center of a 10 nm cube cell under periodic boundary conditions along the three axes and free carbon atoms are supplied into the cell keeping the number of free carbon atoms. The temperature of the metal atoms are controlled by Nose-Hoover thermostat. We tuned the temperature and free carbon density, and succeeded in the growth of defect-free SWNTs under lower free carbon density. Their chiralities were clearly assigned as (14, 1), (15, 2) and (9, 0). The growth simulation results showed that the wall parts of the SWNTs grew with the kink running along the zigzag edge. In addition, growth of SWNTs from tungsten-cobalt catalysts will be discussed.

[1] T. Matsuo, to be submitted.

P54

An advanced lithium ion battery based on a sulfur-doped porous carbon anode and a lithium iron phosphate cathode

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Here the S/N doped porous carbon (SPC or NPC) was successfully synthysized from pitch using the porous magnesium oxide (MgO) as templates, which exhibited excellent cycling stabilities and high specific capacities for Li storage because of excellent conductivity and unique pore-size distribution. As an anode material for Li ion batterie (LIB), SPC presents higher Li storage capacity (1380 mAh/g at the current density of 50 mA/g), superior rate capability (493 mAh/g at 1000 mA/g) and excellent cycling stability (remaining a reversible capacity of 788 mAh/g at 150 mA/g after 100 cycles) in comparison with NPC and PC. The full LIB with SPC as anode and LiFe-PO4 (LFP) as cathode (LFP/SPC) can afford a higher reversible capability (152 mAh/g at 0.2 C and 131 mAh/g at 1 C) than that of the full cell fabricated by the graphite (118 mAh/g at 0.2 C and 101 mAh/g at 1 C). Hence, we believe that these unique features of SPC exhibit a practical substitution for the graphite in LIBs and broaden roads to hybrid devices with high energy density and power density.

P55

Ambushed catalysts for reduplicated growth of horizontally aligned carbon nanotube arrays

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Carbon nanotubes (CNTs) have captured tremendous research and business interests due to their predominant properties. Among these, Aligned CNTs grown on surfaces by catalytic chemical vapor deposition, with their macroscale length, low defects and parallel alignment, are ideal candidates for fundamental materials in nanoscale science & technology research and building blocks in next-generation electronics. However, there are still big challenges to promote the development of innovative synthetic techniques. Meanwhile, researchers are still making sustaining efforts towards chirality-selected growth and mass production. In this work, we report a facile in-situ catalyst loading process for the high efficiency and reliable growth of horizontally aligned CNTs on surfaces. Catalysts ambushed in the reactor would migrate to the targeted substrate and induce the growth of aligned CNTs. This in-situ catalyst loading strategy for the growth of aligned CNTs on surfaces avoided the deposition of catalysts before each round of growth and the related randomicity, and thus the growth of CNTs on bare surfaces could be repeated up to 50 times with one-time catalysts ambushing process. Moreover, the mass production of aligned CNT arrays on surfaces can be realized with a rational process.

P56

A new one-step CCVD technique for the production of MWCNT aerogels

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MWCNT aerogels combine unique properties of their basic building element with related characteristics of aerogel structure.

Here we report a new one-step approach for MWCNT aerogel production via CCVD technique by using a preformed catalyst. It based on multi-centered growth of MWCNTs provided by formation of multiple nanosized catalytic centers on the surface of the support particle. Tangling of the MWCNTs during the following growth provides formation sponge-like structure of aerogel. Due to intensive nanotube growth, a volume of resulting material increases a hundred times in comparison with a volume of preformed catalysts. This results in the formation of aerogels with density of 0.03-0.08 g/cm3.

Any shape of aerogels is possible to obtain by using different geometry of preformed catalysts (balls, cylinders etc.). In situ produced MWCNT aerogels demonstrate high electrical conductivity (several S/cm), remain stable in different solvents and hold more than 2000 their wieght. Pores of size >120 nm occupy >95% of aerogel volume whereas smaller pores take up <2%. MWCNT aerogels show electric polarizability values close to metals while having a substantially lower weight (8-12 GHz).

Due to rigid, tunable shape and pore structure, MWCNT aerogels are promising for such applications as EMI and acoustic shielding materials, gas sensors and substrates for biological objects.

P57

Diameter selective dispersion of carbon nanotubes via polymers: a competition between adsorption and bundling

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For most microelectronic and optoelectronic applications of single-walled carbon nanotubes (CNTs) purification or selection of certain species is a challenging first step. Here, we study the mechanism of the selective dispersion of single-walled CNTs by aromatic polymers. Using extensive molecular dynamics simulations we demonstrate that the diameter selectivity is the result of a competition between bundling of CNTs and adsorption of polymers on CNT surfaces. The preference of certain diameters corresponds to local minima of the binding energy difference between these two processes. Such minima occur due to abrupt changes of the CNT's coverage with polymers. For the tested polymers (PFO, PFH, PFH-A and PFD-Py) our simulation results can explain the reported experimental findings on a quantitative level. Our study resolves a controversy regarding the understanding of CNT selection methods and defines a theoretical framework for the further understanding and improvement of dispersion/extraction processes.

In experiment, we have achieved an efficient extraction of semiconducting CNTs with both PFO and PFH-A. The characterization with adsorption, PL and Raman spectroscopy confirmed the absence of metallic CNTs and presence of semiconducting CNTs of particular diameters. The field-effect transistors built with theextracted CNTs show perfect transfer characteristics with the ON/OFF ratio of 10^6.

P58

Nitrogen-doped carbon sponges

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In the present work, nitrogen-doped carbon sponges are synthesized by pyrolyzing a mixture of benzylamine and ethanol solutions containing ferrocene and thiophene at 960 and 1020℃. The spray contained in the nebulizer is transported by an argon-hydrogen flow of 0.8 l/min through the reaction chamber during 120 min. The resulting material is collected by scraping inside of the quartz tube. Several samples were obtained depending on the region of the tubular furnace. The samples were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. It was found that the temperature profile inside the tubular furnace plays a crucial role in the produced samples. A system of curved carbon nanotubes and junctions interlaced with graphitic nanoribbons was found near to the central region of the furnace. In the furnace ends, the produced samples consist of carbon nanotubes covered by small nanoparticles. The produced sponges are highly hydrophobic, with oil absorber properties. It is also extremely easy to functionalize them when acids. Finally the formation mechanism of our sponges is discussed.

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P59

Nitrogen-doped multiwalled carbon nanotubes fabricated by chemical vapor deposition method: A study across the reactor

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Since the discovery of the carbon nanotubes, the chemical vapor deposition (CVD) method for the carbon nanotube production has been reported by varying temperature, time of synthesis, precursors, among other parameters. However, few efforts regarding the sample quality grown through the synthesis reactor have been addressed [1,2]. In the present investigation, nitrogen-doped multiwall carbon nanotubes (N-MWCNTs) were produced by ultrasonic spray CVD method using a two furnaces configuration. The N-MWCNTs were collected by scraping inside the quartz tube, which was used as the reactor. More than 50 samples corresponding to different regions (1 cm long) were classified and exhaustively characterized by scanning electron microscopy, X-ray diffraction (XRD), and Raman spectroscopy. TEM characterization reveals that the N-MWCNTs and encapsulated nanoparticles exhibit different morphologies that strongly depend on the position in which they were obtained. For example, gamma-Fe was found in the 27th and 51th centimeters and it was not observed in other furnace regions. These results are concomitant with the XRD data, which showed that this phase exist in such centimeters. Raman spectroscopy results revealed an interesting nitrogen-concentration profile with the sample location.

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P60

Synthesis of graphdiyne nanowalls using acetylenic coupling reaction

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Graphyne refers to a family of carbon allotropes composed of sp and sp2 hybridized carbon atoms in two-dimensional plane. Some structures are envisioned to have novel electronic band structure and expected as competitors for graphene. Among these structures, graphdiyne is a certain framework containing hexagonal benzene rings connected by diacetylenic linkages. It is predicted to be promising in applications in semiconductor devices, optical absorption, gas separation, catalysis, energy storage and so on.

Graphdiyne film was successfully fabricated on the surfaceof copper foil via an in situ Glaser coupling reaction in 2010. Since then, graphdiyne nanotubes and graph-diyne nanowires were obtained with a template-assisted method and a VLS growth process, respectively.

Synthesizing graphdiyne with a well-defined structure is of great challenge. Here we utilize a modified reaction Glaser-Hay coupling to regulate the initial concentration of catalytic reaction sites, and successfully obtained graphdiyne nanowalls. Raman spectra, UV-Vis spectra and HRTEM results confirmed the features of graphdiyne. Through mechanical exfoliation, we obtained graphdiyne nanosheets with thickness ranging from several to tens of nanometers. Due to highly conjugated structure and uniformly distributed sharp walls, graphdiyne nanowalls exhibited excellent and stable field emission properties.

P61

Low temperature CVD growth of graphdiyne films on silver foil

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Graphdiyne, a new form of two-dimensional carbon materials containing *sp*-and sp^2-hybridized carbon atoms, is expected to have fascinating electronic properties. These properties and potential applications in nanoelectronics, hydrogen storage and gas separation have attracted wide-spread attention. Graphdiyne was first synthesized on copper in solution by Y. L. Li et al. Nevertheless, solution method is limited to the lack of controllability on thickness, morphology and structure. We demonstrate herein the controlled growth of graphdiyne film by using low temperature chemical vapour deposition (CVD) technique. We choose 1, 3, 5-triethynylbenzene and hexaethynylbenzene, respectively as precursor molecules and silver as catalytic substrate to synthesize graphdiyne via an alkyne homo-coupling reaction. Silver was reported to be the best catalyst for on-surface homo-coupling of alkynylated arenes. During the deposition process, C-C covalent bond between two precursor molecules was formed with the breaking of C_{sp}-H bond on thermal activation. Uniform carbon films were obtained in such a way, which were characterized by Raman, UV-Vis and XPS measurements. The transport measurements showed a resistance of ca. 10^5 ohm.

P62

Assembly of phosphorus nanowires inside carbon nanotubes

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Unique diamond nanowires have been synthesized by fusing small diamondoid molecules contained inside a carbon nanotube (CNT) [1]. In a similar way, we propose that phosphorus nanowires may be formed by fusing P_4 molecules of white phosphorus inside a carbon nanotube. Low-dimensional phosphorus nanostructures, including 2D phosphorene [2], are rapidly gaining attention due to their favorable electronic properties. Firs results on 1D phosphorene nanotubes [3] indicate promising electronic properties similar to those of semiconducting 2D phosphorene. I will present results based on *ab initio* density functional theory indicating that P_4 molecules are pulled inside a CNT by a capillary force. Activated transformation of the 1D molecular solid to a nanowire is favored in an effective high-pressure environment within the nanometer-diameter cylindrical cavity and should occur at elevated temperatures.

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P63

Microwave-assisted synthesis of graphene oxide nanoribbons and their applications

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We demonstrated the microwave-assisted synthesis of graphene oxide nanoribbons (GONRs) from the unzipping of multiwalled carbon nanotubes (MWCNTs) and their applications since 2011. [1-5] A core-shell MWCNT/GONR-modified glassy carbon electrode was used to electrochemically detect ascorbic acid, dopamine, and uric acid. [1, 5] The specific capacitance is 252.4 Fg^{-1} for the supercapacitor electrode with the MWCNT@GONR. [2] We also modified GONRs with phospholipid-polyethylene glycol (PL-PEG) to prepare PEGylated GONRs for biodistribution and drug delivery studies. [3] The reduced GONR was further used as the catalytic film of the counter electrode of a dye-sensitized solar cell (DSSC) with an efficiency of 6.91 %. The details of our papers and patent applications since 2011 will be discussed and presented in this conference.

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P64

Quantum chemical study on the optical response properties of pi-stack aggregates of open-shell polycyclic aromatic hydrocarbons

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Geometric features and physical properties of the pi-stack type one-dimensional aggregates of polycyclic aromatic hydrocarbons (PAHs) incorporated in carbon nanotubes have been investigated intensely as novel multi-functional materials. On the other hand, several PAHs and their related molecules having unpaired electron(s), i.e., open-shell PAHs, have attracted much attention since they are expected to show unique covalent-like interactions between the monomers in solution and/or in crystal phase. In this study, we investigate the relationship between the structures and electronic excitation properties of molecular aggregates composed of open-shell PAHs, and then discuss the open-shell character dependence of their static and dynamic optical response properties. We here employ several PAHs, such as a phenalenyl, as the monomer unit, and then we evaluate the excitation properties of several pi-dimers and -tetramers with different inter-monomer distances and orientations by using the quantum chemical calculations. The linear and third-order nonlinear optical response properties of these systems are evaluated by the sum-over-states method, and then we discuss the structural dependences of open-shell characters and optical response properties of molecular aggregates composed of open-shell PAHs.

P65

Semiconducting SWNTs on demand by polymer wrapping: towards a very high performance (ambipolar) field effect transistors

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Owing to their 1-D structure and true bandgap, single-walled carbon nanotubes (SWNTs) is still the leading candidate to replace silicon for high-speed and low-voltage electronics. Moreover, they are intrinsic semiconductors, allowing the transistors (FETs) can change polarity by gate voltage (ambipolar), beneficial to miniaturize CMOS-like architecture. Nevertheless, the ambipolar FET utilization for CMOS requires high current modulation (on/off ratio) values. Achieving this together with high mobility are still a great challenge for SWNT network device.

Here we report FETs utilizing polymer-wrapped semiconducting SWNT showing on/off-ratio up to 10^8, fulfilling the industrial requirement for CMOS application, with mobility up to 3.7cm^2/V.s. Semi-aligned SWNT networkis obtained by employing blade coating, an effectiveand scalable process. The semiconducting SWNTs are selected by wrapping them using polyfluorene (e. g. PF8～PF12) and polythiophene derivatives (i. e. P3DDT). We discuss the influence of the side-chain length towards selection of the nanotubes and the effect of polymer backbones to the FET performance: (i) Large diameter SWNT provide higher FET mobility (～16cm^2/V.s); (ii) utilization of some polymers provide much symmetrical ambipolar transport than the others. These strategies will highly influence the SWNT-network FET usage in practical electronic applications.

P66

Magnetic and optical properties of g-C_4N_3 nanotubes: A first-principles study

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Magnetism arising from system constructed with carbon and nitrogen has drawn considerable attention. Recently, the half-metallic g-C_4N_3 possesses ferromagnetic ground state that has been revealed theoretically. [1,2] Its planar structure is similar to graphene if we ignore its periodic vacancy, which rises our interests on its nanotubular structure. Indeed, C_3N_4 nanotube was synthesized successfully. It is worthwhile exploring g-C_4N_3 nanotubes for fundamental physics aspect. And from perspective of materials science, the magnetic g-C_4N_3 sheet with half-metallicity may form one type of extraordinary one dimensional materials.

Thus, in this study, a newly designed 1D nanotube based on g-C_4N_3 is predicted theoretically. [3] The thermal stability at room temperature of this tube structure is proved by ab initio molecular dynamics. The armchair tubes exhibit ferromagnetic ground state and half-metallicity, while the zigzag tubes properties are dependent on the size of tubes, thereupon, a hypothetical rule for chirality-dependent magnetism is proposed. Additionally, optical property is investigated by presenting the frequency dependent dielectric functions and absorption coe.cients. Our works introduce a uni.que member with interesting properties to the nanotube family.

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P67

Milligram-scale separation of high-purity single-chirality SWCNTs

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Chirality separation technique is highly desired for bringing out high electronic performance of single-wall carbon nanotubes (SWCNTs) that are normally produced as mixture of variety of chiral structures. However, existing methods still have difficulties to obtain high-purity single-chirality SWCNTs with high throughput. Previously, we reported an overloading gel chromatography method for single-chirality separation where we used only selective adsorption of SWCNTs to the gel [1]. In this work, we have improved the throughput by combining selective adsorption and selective desorption without degrading the purity and have demonstrated 1 mg/day separation.

We used high-performance liquid chromatography system with 400ml gel column. Selective adsorption was controlled by mixing sodium dodecyl sulfate (SDS) in sodium cholate (SC) solution with an appropriate ratio. Selective desorption was performed by stepwise increase of sodium deoxycholate to the SDS/SC mixture solution. This method realized high-purity (>90 %) separation of single-chirality (9,4) and (10,3) SWCNTs in a cycle with high throughput (>1 mg/day). We would like to emphasize this novel method is superior to low cost, high purity, high yield, and high throughput.

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P68

Preparation of platinum nanowires inside carbon nanotube

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Carbon nanotubes have extremely small confined nanospaces exhibiting less than a few nanometer width and micrometers length. By using the interiar spaces, novel one-dimensional nanowires and arrays including metal, metallic oxides, and various molecules, have been prepared. In this study, we demonstrate the preparation and structural analysis of platinum nanowires inside single walled carbon nanotubes (SWCNTs). Our detail TEM observation clearly suggests the growth of platinum nanowires within SW-CNTs.

P69

High-resolution electron microscopy of graphene nanoribbons formed by coronene filling of single-wall carbon nanotubes

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Graphene nanoribbons have attracted a great interest being one-dimentional objects with a band gap inversely proportional to the ribbon width. One of the most reliable techniques to form nanoribbons is to fill the nanotubes with coronene molecules [1, 2].

According to the data of optical spectroscopy and theoretical modeling, the process carbon nanotubes filling with coronene molecules presumably occurs in two steps: the SWNT samples are first filled with coronene molecules, which form stacks in the channels of the nanotubes; annealing at 480℃ in Ar resulted in transformation of stacks into nanoribbons [1].

Here we present HRTEM measurements clearly showing this transformation. After the first stage of the filling process, coronene stacks are clearly seen. The second stage is a transformation of coronene stack into nanoribbon. The nanoribbons are clearly seen due to their movement inside the nanotubes. There is a change of contrast depending on their orientation relative to the electron beam.

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P70

Deposition of cadmium sulfide nanoparticles on fluorinated carbon nanotubes

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Fluorinated multi-walled carbon nanotube/cadmium sulfide (F-MWCNT/CdS) hybrid materials have been first time synthesized. Carbon nanotubes produced by CVD method were fluorinated using gaseous trifluoride bromine. Cadmium sulfide nano-particles was deposited on the surface of fluorinated multi-walled carbon nanotubes paper using aqueous chemical bath containing thiourea, cadmium chloride, and ammonia for different period of time. Morphology, structure and composition of the FMWCNT/CdS hybrid materials were studied by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. Electric field and light induced luminescence properties of CdS particles located on initial and fluorinated carbon nanotubes was studied.

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P71

Synthesis of electrical characterization of coffee ground-derived graphene-sheet fibers by microwave plasma irradiation

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Graphitic carbon, from common graphite, fullerene and carbon nanotubes to filamentous graphite and carbon nanowalls, which are regarded to be formed by the assembly of hexagonally atomic graphene under the conditions of defects, rolled or paralleled each other, has led to much speculation of carbon materials in theory and applications. Here we report that a novel form of graphitic carbon, graphene-sheet fiber, produced by microwave plasma irradiation of waste coffee grounds without any special treatment or the use of additional reagent. The fiber-like structures are composed of few-layer graphene which grow coaxially. Transmission electron microscopy reveals that no cylindrically hollow structure exists inside graphene-sheet fibers, suggesting that the new form is not graphene-decorated carbon nanotubes (graphenated carbon nanotubes). The resulting fibers possess a large amount of graphene edges and high conductivity, Due to these advantages, graphene-sheet fibers can be used as electrodes for electrochemical energy conversion and storage. The detailed results will be presented in the coming conference.

P72

Geometric and electronic structures of two-dimensional networks of fused C_{36} fullerenes

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Electronic structures of nanocarbon materials with nanometer thickness decisively depend on the external environment conditions, such as substrates, adsorbates, and external fields. Indeed, it has been demonstrated that the bilayer graphene undergoes phase transition from metallic to semiconducting phases under the perpendicular electric field. Then, further increasing electric field, the bilayer graphene is again a metal in which the carriers exist in pi and nearly free electron states. Inthe present work, based on the density functional theory with the local spin density approximation an the effective screening medium method, we theoretically design the two-dimensional C allotropes consisting of fused polyhedra of C_{36} fullerene, which is expected to exhibit unusual physical properties under the electric field. We find three metastable structures of 2D sheets of fused C_{36} polyhedra: Two of three are semiconductors with flat dispersion band in the highest branch of the valence band due to the localized nature of the state. According to the flat band states, under the electric field, these two C_{36} sheets exhibit magnetic spin ordering on surface atomic layers facing to the counter electrodes with the magnetic momentof about 2 μ_B/nm^2.

P73

On the purification of boron doped single-walled carbon nanotubes by density gradient ultracentrifugation

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Changes in the intrinsic properties of a single-walled carbon nanotube (SWCNT) can be expected according to the bonding configuration that heteroatoms induce when incorporated in their graphitic lattice. In the case of the B-doped SWCNTs, understanding the atomic bonding environment and doping levels is particularly important to achieve their potential applications hinderedby the tubes´ heterogeneity, bundling, and presence of catalytic by-products. We have mastered the production of B-doped SWCNTs using high-vacuum assisted chemical vapor deposition and here we show our progress towards their purification. The density gradient ultracentrifugation method has been investigated as an alternative to the chemical purification treatment, as this last procedure using mild acids is potentially more reactive with the B atoms incorporated in the lattice. In order to characterize this material, multifrequency Raman spectroscopy was performed followed by optical absorption studies before and after the puri.cation treatments, which has allowed us understanding the changes in the tubes morphology and optical properties. Especially variations in the diameter, defect concentration and chiralities. To the best of our knowledge, this study provides the first relevant results regarding the scalability of this purification process as a significant step toward the application stage of B-doped SWCNTs.

P74

Sorting of double walled carbon nanotubes according to their outer wall electronic type via a gel permeation method

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We demonstrate the application of the gel permeation technique to the sorting of double-walled carbon nanotubes (DWCNTs) according to their outer wall electronic type. Our method uses the Sephacryl S-200 gel and yields sorted fractions of DW-CNTs with impurities removed and highly enriched in nanotubes with either metallic (M) or semiconducting (S) outer walls. The prepared fractions are fully characterized using optical absorption spectroscopy, transmission electron microscopy and atomic force microscopy, and the entire procedure is monitored in real time using process Raman analysis. The sorted DWCNTs are then integrated into single nanotube field effect transistors, allowing detailed electronic measurement of the transconductance properties of the four unique inner@outer wall combinations of S@S, S@M, M@S and M@M.

P75

Morphology-manipulation and surface-functionalization of boron nitride nanostructures toward controllable wettability

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Continuous progress in nanomaterial syntheses and extensive research on interfacial phenomena of low-dimensional materials have brought the advent of a new area of nanoscale interface engineering which aims at employing nanoscale interfacial features to obtain materials with modi.ed or totally new properties. An example of interface-related properties is wettability of materials, where the interfacial interactions determine the wetting degree.

Here we report the results of a systematic 5-year research work on development of a CVD method to synthesize hierarchical boron nitride (BN) nanostructure films consisting of vertically aligned and randomly distributed nanotubes, nanosheets, and nanocones, followed by the application of a facile one-step plasma method to achieve covalent chemical functionalization on the surface of these chemically inert nanostructures.

As a result, an unusual rise to the intrinsic water-repellencyof the BN films was observed due to nanoscale topography, and by controlling the surface morphology, a wide range of water contact angles (CAs) between ～50° to ～160° was achieved. Moreover, by tailoring the concentration of the grafted functional groups, superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic patterns could be created on the BN nanostructure films. Also, by introducing a gradient of the functional groups, directional liquid spreading was achieved on the film surfaces.

P76

Simultaneous discrimination of diameter, handedness, and metallicity of carbon nanotubes by caliper-shaped host molecules through complexation

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We have been developing methodology to discriminate the handedness and diameter of SWNTs through molecular recognition using tweezer-shaped chiral molecules, namely nanotweezers. Although relatively small diameters of SWNTs (less than 1.0 nm) were discriminated well by nanotweezers, theywere not able to form stable complexes with SWNTs having diameters larger than 1.0 nm. In this context, we designed caliper-shaped chiral molecules, namely nanocalipers, for the structural discrimination of SWNTs with larger diameter and even DWNTs.

As expected, we obtained optically active SWNTs with diameters larger than 1.0 nm and, unexpectedly, enriched metallic SWNTs over semiconducting ones. The optically active metallic SWNTs are identified for the first time, in addition to the optically active semiconducting SWNTs with such large diameters. On the other hand, optically active DWNTs and metallic SWNTs with narrow diameter distribution were also obtained through the extraction using chiral nanocalipers with larger cavity and achiral ones, respectively.

P77

Fabrication and compressive property of aerographite spiky-shell particles

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Aerographite is fabricated by deposition of carbon on tetrapod ZnO template with subsequent etching of ZnO[1]. Thereby, aerographite has hollow structure with super-low density and unique morphology transferred from template. Recently, urchin-like ZnO particles with micrometer-order diameters named nanorod-microsphere were fabricated[2]. In this study, spiky-shell particles of aerographite were fabricated with this microsphere as the template. The spiky-shell consists of numerous hollow nanorods with 100nm diameters and 10 nm thick-nesses. This morphology makes aerographite interesting material; it must be the lightest microparticles, and the spiky structure may ensure mechanical strengths. Compression tests were performed on individual aerographite particles in a scanning electron microscope. Uniaxial compressed force applied toa particle by parallel planes of two cantilevers, and the deformation was monitored in real-time. Compressive force was estimated from the deflection of cantilevers. As the result, some particles recovered shapes after 50% compression. Stress-strain curve suggested compressive bending of surrounding nanorods absorbed the force applied to the particles under strain less than 20%. The curve often showed large hysteresis by advancing cracks under strain above 25%. Fracture stress ranged in 13-36MPa.

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P78

Development of a novel pot-shaped carbon nanomaterial

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We have developed a novel carbon nanomaterial, named *carbon nanopot*, using the submarine-style CVD technique. Detailed TEM observations have revealed that each carbon nanopot is composed of multi-layered graphene sheets, has an open end, a closed end and a hollow inner space. The material is produced in series to form fibers with the length of several tens micrometers, and is separable to individual carbon nanopots. The typical size of the individual carbon nanopot is 20-40 nm in diameter, and 100-200 nm in length. The aspect ratio is much larger than that of conventional nanobell, which suggests higher potential of this material for the application to drug delivery vehicles. In the synthesis, graphene oxide was applied to support iron catalyst. We have found that UV-irradiation of the GO-supported catalyst is very effective to enhance the growth of carbon nanopot and suppress the growth of bamboo-type carbon nanotube. We propose a growth model of carbon nanopot, taking the above results into consideration, in which particles of metal catalyst move between the inner space of carbon nanopot and the surface of GO repeatedly. This material could be a unique nanomaterial applicable widely as nano-containers, components for nanofabrication, or functional fibers for composite material.

P79

Lattice vibration in diamond isotopic layered superlattice

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Diamond isotopic superlattice consisting of ^{12}C and ^{13}C diamond layers was created and the confinement of carriers to ^{12}C diamond layers was demonstrated by cathodoluminescence experiments [1]. It is expected that this phenomenon is caused by electron-phonon interaction. However, details of lattice vibration and its effect on electronic states in diamond isotopic superlattice have not been reported theoretically so far.

In this study, we compute lattice vibration in diamond superlattice using Density Functional Perturbation Theory [2] with a special combination of Fourier and inverse Fourier transformations for isotopic superlattice. As a result, the density of states of Lattice Vibration (LV-DOS) of the superlattice having alternately stacked 36 ^{12}C layers and 36 ^{13}C layers ((36, 36) superlattice) is found to be nearly equal to the arithmetic mean of LV-DOS of the ^{12}C diamond and that of the ^{13}C diamond. On the other hand, LV-DOS of the (4, 4) superlattice is nearly equal to LV-DOS of virtual $^{12.5}$C diamond. In addition, we will also discuss the application of the present method to the ^{12}C/^{13}C nanotube superlattice.

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P80

Metallic/semiconducting separation by electric-field-induced layer formation method applied to purified SWCNTs

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Separation of metallic and semiconducting single-walled carbon nanotubes (SW-CNTs) has been intensively investigated. Recently, we had proposed a method to separate metallic and semiconducting SWCNT solution by Electric-Field-induced Layer formation (ELF) method [1] which utilizes free flow electrophoresis of SWCNTs dispersed in nonionic surfactant solution. In this presentation, we report the results of ELF separation applied to SWCNTs purified for the removal of metal catalysts.

SWCNTs synthesized by using eDIPS method [2] were purified by the procedure that consists of low temperature oxidation, soaking in HCl solution, and vacuum annealing. The purified SWCNTs were dispersed in aqueous solution of polyoxyethylene (100) stearyl ether by sonication and ultracentrifugation. After the treatment, metallic and semiconducting SWCNTs were separated by ELF method. The optical-absorbance spectra of separated fractions showed the enrichment of metallic/semiconducting peaks. Raman spectra suggested that 98% semiconducting SWCNTs were obtained. We found that vacuum annealing plays an important role to achieve successful separation with this method applied to the purified SWCNTs.

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P81

A rosette cooling cell: more effective container for solubilization of single-walled carbon nanotubes under probe-type ultrasonic irradiation

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Probe-type ultrasonication has been employed for surfactant-aided solubilization, or individualization, of single-walled carbon nanotubes (SWNTs). The resulting solution can be used not only for spectroscopic analyses such as absorption, photoluminescence and circular dichroism, but also for separation by density gradient ultracentrifugation, dielectrophoresis, chromatography, and polymer wrapping. In spite of its importance, the sonochemical processing of SWNTs has not been considered seriously. Herein, we report on a more efficient cooling cell for probe-type ultrasonication. As compared with a conventional cylindrical cell, the concentration of the SWNTs solubilized in water was found to be almost double in a rosette cooling cell after ultra-centrifugation. The efficiency of a rosette cell can be attributed to the higher efficiency in circulation and cooling of the SWNT dispersion as well as enhancement of the cavitation process.

P82

Annealed N-doped porous carbon with enhanced supercapacitor performance

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Doping by heteroatoms is effective route of improving electrochemical properties of carbon. A series of porous carbon with different nitrogen contents was prepared using acetonitrile as nitrogen source and CaO nanoparticles as a template, which is a reaction products of calcium tartrate decomposition at 700, 800 and 900°C. The obtained carbon has a high surface area with predominant pores content in mesoporous range. The Fourier transform Infrared, X-ray photoelectron and near-edge X-ray absorption fine structure spectroscopy revealed a rich functional composition of the materials. The nitrogen content (3.9-5.1 at.%) and Brunauer-Emmett-Teller surface areas (436-670 m2/g) of N-doped porous carbons showed specific capacitive performance up to 130F/g. TGA and mass-spectroscopy analysis showed that nitrogen-containing species stay in samples up to 400°C. The specific capacitance of annealed N-doped carbon material exhibited improved specific capacitance (200F/g) due to enhanced electrolyte-electrode interaction and additional pseudocapacitance. The work was financially supported by the Russian Foundation for Basic Research (grant 13-03-00884-a).

P83

Purify and release of semiconducting-single-walled carbon nanotubes using dynamic formation of hydrogen-bond polymers

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It is great challenge to develop an efficient technique to separate the semiconducting-tubes (SWNTs) from their metallic-isomers with preserving their structural and electrical identities. Synthetic and natural polymers such as polyfluorenes and DNAs are ideal solution to extract semiconducting-SWNTs, although their wrapping is too tight to remove from SWNTs without damages to the surface. We previously reported strategical method to purify semiconducting-SWNTs using dynamic supramolecular chemistry of coordination polymers, in which polymers can be removed from SWNTs in mild conditions. In an research for more facile separation method, here we report novel synthetic polymer based on hydrogen-bond. The obtained purified semiconducting-SWNTs were found to keep their original length by atomic force microscopy and their D-band was much smaller than other separation technics.

P84

Energetics and electronic structures of nano-Saturn: Novel inclusion compounds consisting of C_{60} and cyclohexabiphenylene

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Recently, novel inclusion compounds can be synthesized by inserting fullerene molecules into the internal spaces of hoop-shaped oligoarene molecules. The hybrid networks of hoop and hollow-cage molecules are expected to have peculiar mechanical and electronic properties that may be suitable for the constituent units of future molecular devices.
In the present work, we aim to theoretically design a nanoscale model of Saturn by assembling C_{60} and cyclohexabiphenylene (CBP), which possesses a ring structure of hexagonally connected six biphenyl groups, based on energetics using density functional theory. Our calculations showed that the nano-Saturn is energetically stable compared with the other known inclusion compounds consisting of C_{60} and cycloparaphenylene (CPP). Furthermore, the inclusion reaction of C_{60} is exothermic without any energy barriers during the reaction, indicating that C_{60} will be spontaneously included inside CBP if CBP is successfully synthesized.

P85

Topological phases in multi-orbital honeycomb lattice

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Silicene, Germanene and Stanene, the counterpart of graphene for silicon, germanium and tin, with low buckled honeycomb geometry, have specific electronic nature. Due to their large spin-orbit coupling, quantum spin hall effect can be observed in an experimentally possible temperature regime, so that they are expected as candidates of two-dimensional topological insulators. In our studies, we consider their edge statesby using the multi-orbital Hamiltonian, in comparison with those for the single-orbital Hamiltonian. We show the importance of multi-orbital degrees of freedom for the edge state. We also investigate hydrogen termination electronic states in the novel two-dimensional materials.

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P86

Quenching effect of carbon nanomaterials on the fluorescence of aromatic compounds

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The fluorescence of polycyclic aromatic hydrocarbons (PAHs) and water-soluble vitamins in dispersions of carbon nanomaterials in aqueous solutions of surfactants of different nature (i.e. anionic SDS, cationic CTAC, non-ionic Brij 35) and/or hydrophilic polymers (i. e. PEG) has been thoroughly investigated. Further, the state of nanomaterial dispersion has been investigated by SEM, and the carbon nanomaterial-aromatic compound interfacial interactions by Raman spectroscopy. A quenching phenomenon of the fluorescence of several vitamins has been found in the presence of single-walled carbon nanotubes (SWCNTs), graphene (G) and graphene oxide (GO), the effect being stronger for GO dispersions. Astrong quenching of PAH fluorescence has also been observed for SWCNT dispersions in CTAC, related to the improved dispersion capability of this surfactant and its stronger adsorption onto the SWCNT surfaces. The fluorescence intensity ratio calculated in the absence and in the presence of carbon nanomaterial follows the Stern-Volmer equation. The developed nanocomposites could have potential applications in the field of optical sensors or for the fabrication of selective preconcentration/extraction systems for the aromatic compounds. (Financial support from MINECO (National project MAT2013-47898-C2-2-R.) and AMDP for a Ramón y Cajal Senior Research Fellowship are gratefully acknowledged).

P87

Calculating core level binding energies for graphene and azafullerenes

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X-ray photoelectron spectroscopy (XPS) combined with first principles modeling is a powerful tool for determining the chemical composition of novel materials, such as graphene and carbon nanotubes doped with heteroatoms [1].

As a model system, we calculated the C1s binding energy of graphene using two methods based on density functional theory total energy differences: a calculation with anexplicit core-hole [2], and an all-electron extension of the delta self-consistent field method [3], with the latter giving absolute energies close to graphite measurements.

Furthermore, we analyzed spectra of C_{60} and $C_{59}N$ fullerene powders [4], elucidating the identity of the oxygen signal. The calculations also allow us to quantify the effect of $C_{59}N$ dimerization on its N1s core-level shift (0.4 eV), with implications for interpreting other nitrogen-doped systems.

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P88

Carbon nanotubes capped by magnetic nanoparticles. Molecular dynamics prediction of potential application as a drug delivery system

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The properties of single and triple walled carbon nanotubes functionalized by magnetic nanoparticles through triethylene glycol chains were studied using molecular dynamics simulations. Such molecular architecture can form a kind of molecular nanocontiner provided that its parameters are suitably chosen. We found that the most important parameters controlling the behaviour of the discussed system concern the dispersion interactions and magnetic interactions particularly magnetic anisotropy constant of the nanoparticles. By testing various sets of those parameters and keeping their values in experimentally reasonable ranges we found the optimal architecture of the nanocontiner. That architecture reveals the following properties; At ambient conditions the magnetic nanoparticles adhere to the nanotubes tips due to dispersion forces. That state is thermodynamically stable and spontaneous detaching of the nanoparticles does not occur. When the system is exposed to an external magnetic field the magnetization reversal proceeds and, due to the coupling between Neel and Brown rotations the nanoparticles detach from the nanotube tips. As a result the inner cavity of the nanotube becomes available for other molecules diffusing in and out of the nanotube. Thus, the discussed system can be utilized in the area of nanomedicine as a magnetically controlled drug delivery vehicle.

P89

Sidewall functionalization of carbon nanotubes as a method of controlling structural transformations of the magnetically triggered nanocontiner. a molecular dynamics study

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The magnetically triggered nanocontiner, that is magnetic nanoparticles covalently linked to carbon nanotube tips, is able to make reversible cycles of capping and uncapping the nanotube inner cavity. The capped form is when the magnetic nanoparticles adhere to the nanotube tips whereas the uncapped one forms when the magnetic nanoparticle shifts to the nanotube sidewall. The feasibility and likelihood of these two structural forms of the nanocontiner depend on the energetic profile associated with the transitions between them. This work discusses two approaches for controlling that balance that is covalent functionalization of the nanotubes sidewalls by incorporation of polar amide groups and noncovalent functionalization based on adsorption of charged fine colloid nanoparticles. Single and triple walled carbon nanotubes were analysed as well as the presence of cisplatin molecules encapsulated in the nanotubes inner cavities. Both approaches might result in obtaining the preferred energetic balance that is less stable uncapped state and relatively low activation barrier for spontaneous transition from the uncapped to the capped state. However, adsorption of fine colloids turned out to be too weak to provide long-term stability of the system. Amide functionalization provides the best results in terms of the energetic profile, stability and other systems parameters.

P90

Molecular dynamics study of Congo red interaction with carbon nanotubes

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This work deals with molecular dynamics simulations of Congo red (CR) interaction with carbon nanotubes (CNT). We studied several combinationsof systems para.meters in order to assess how the nanotube parameters and Congo red density affect the structure and stability of CNT-CR conjugates at variouspH conditions. We found that CR binds strongly to the CNT surfaces and the CNT-CR conjugates are thermo-dynamically stable according to the determined values of free energies. Adsorption on wider nanotubes is stronger than on the narrow ones and larger densities of CR on the CNT surfaces lead to weakening of biding energy per single CR molecule. Changes of pH, that is varying concentration of protonated and deprotonated forms of CR, lead to significant changes in binding energies as well as to qualitative changes of structure of the adsorbed CR. It was found that at pH > 5.5 the CR molecules readily occupy inner cavities of the nanotubes. Upon lowering pH the occupation of the inner space of CNTs is strongly reduced and the preferred configuration is formation of a densely packed CR layer on the sidewalls of the CNT. This effect can be utilized in pH controlled corking/uncorking of carbon nanotubes in water solutions.

P91

Graphene made by exfoliation of graphite intercalation compound

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We show that graphene can be obtained from mechanical exfoliation of graphite intercalation compound (GIC). We used SbCl5-GIC that is chemically stable in the atmospher. Mono to several layers graphene were obtained by choosing them with optical microscope. The flakes were not thin flake-GIC. Carrier due to dopant ($SbCl_5$) is extremely diminished and virtually negligible, which was verified by measuring electronic transport using the FET device of the flakes. Carrier mobility was not poor as compared with that for pure graphite. It was estimated to be about ~3000 cm^2/Vs. We found a possible relevance of the stage number to the frequency for layer number of exfoliated flakes. Electron probe microanalysis showed that atomic composition of C and Sb fluctuated locally forming a domain-like structures although X-ray diffraction showed clear peaks for stage structes in GIC. We conjectured that non-uniform intercalation created microscopic cracks in the GIC and they served as easily exfoliating spots.

P92

Aerographite a taylored 3D multiscale tubular network

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Aerographite (AG) is a novel hierarchical carbon nanomaterial formed by a 3D-network of directly interconnected thin-walled graphite layers. AG is synthesized using a single-step CVD process on ZnO templates, which enables deposition of graphite with simultaneous removal of the template. The highly porous structure with tailored elements of covalently bonded graphite in all three-room directions delivers pathways for electrical conduction and mechanical load transfer. The basic network topology is given by µm − sized tetrapod albuilding elements (typical dimension of tetrapod arms : l～10-20 µm, d～1-5 µm). The structure of the AG can be in fluenced by selective CVD parameter－sets which lead to completely different graphite wall sand macroscopic properties.

1) closed-shell (CSAG): Hollow and graphitic (wall thickness >10 nm, sp2 carbon)
2) hollow-framework (HF AG): Carbon ribbons on former surface of removed ZnO tetrapod arms. Resulting in a network of carbon ribbons, organized in a µm－sized tetrapod network.
3) closed-shell-.lled (CS-FAG): Like the CS AG but with additional graphitic filling.

All threevariantsexhibit completelydi.erent mechanical and electrical behaviour and had been introduced 2012. We discuss the basic mechanical characterizationof as produced AG with different densities and the benefit of using CS-AG as an electrically conductive 3D interpenetrating network.

P93

The improvement of thermal properties of nanocarbon doped-elastomer

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The stabilization effect of different type of nanocarbon additives (mix fullerene, fullerene soot, VGCF and various types of carbon black) on thermal behavior of elastomer was investigated. The nanocarbon doped-elastomer was fabricated using solution dispersion methods using ultrasonic and wet-jet mill method. Prior to mixing with elastomer, well-dispersed nanocarbon slurry in organic solvent was prepared using high rotation dispersion (IKA Magic Lab) and followed by high pressure wet-jet mill. Thermogravimetric analysis revealed that thermo-oxidative degradation temperature as well as thermal resistance of elastomer was strongly a.ected by concentration and chemical nature of carbon material. The presence of small amount of mix-fullerene (0.08%) within elastomer matrix improves thermal degradation by ～20^{0}C, which is almost equal to the effect of MT carbon (3%) and VGCF carbon (3%) within elastomer. Meanwhile, the presence of fullerene soot (3%) shifts the degradation temperature as high as ～80^{0}C, indicating potential antioxidant properties for elastomer. Further studies indicated that there was linear correlation between thermal stabilization properties of carbon material and the presence of 5-member rings carbon structure within carbon materials. On the basis of this result, we speculated that thermal stabilization of elastomer is mainly due to radical reaction between elastomer radical and pentagon structure of carbon materials.

P94

Rational recipe for bulk growth of graphene/CNT hybrids: New insight from the in-situ characterizaiton on working bifunctional catalysts

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The graphene/carbon nanotube (CNT) hybrids are considered one of the most advanced nanostructures with intrinsically self-dispersion properties for large-volume applications. However, owing to the limited understanding on the complex growth mechanism and non-linear kinetics, rational design of growth procedures and related multiphase reactors for the production of thehybrids remain great challenges. In this contribution, the in-situ monitoring of graphene/CNT hybrid synthesis on layered double oxide bifunctional catalystswas carriedoutinan online thermogravimetric reactor. The rapid growth of CNTs occurred at the initial 90 s and a slow deposition of graphene was the dominant reaction in the second stage. Based on this unique growth behavior, a coupled fluidized-bed reactor system was proposed to improve the quality of hybrid products. The deposition of amorphous carbon byproduct was significantly suppressed and the qualityof the hybrid products was greatly enhanced through the two-stage growth process.

P95

Multi-functionality of three-dimensional nanoporous graphene

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Here we would like to report a novel 3D nanoporous graphene sheet with preserved 2D electronic nature, tunable pore sizes and high electron mobility for electronic applications, successfully synthesized by using nanoporous metal based chemical vapor deposition (CVD) method. The complex 3D network comprised of interconnected graphene whose structure was exactly duplicated from the morphology of nanoporous metal having periodic structures confirmed with transmission electron microscope (TEM) tomography remains to be a 2D coherent electron system of the mass-less Dirac fermions investigated with angle-resolved photoemission spectroscopy (ARPES). The transport properties of the nanoporous graphene show a semiconductor-like behavior and strong pore size dependence together with unique angular independence. The 3D nanoporous graphene keeps high electron mobility of ca. 500 $cm^2/(Vs)^{-1}$, which can be applicable for 3D graphene transistor. Furthermore, the chemical properties of 3D nanoporous graphene was investigated for metal-free graphene catalysts by synthesizing chemically doped graphene. The chemically doped graphene have greatly promoted chemical activities towards both oxygen reduction reaction and hydrogen evolution reaction. The free-standing, large-scale nanoporous graphene and chemically doped graphene with well-preserved 2D electronic properties and high electron mobility holds great promise for practical applications in 3D electronic devices such as 3D graphene transistors.

P96

Light-assisted in-situ polymer formation on carbon nanohorns

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Carbon nanomaterials absorb light in a wide range from UV to IR and convert the light energy to thermal energy. The photothermal conversion has been shown to be useful for photothermal tumor therapy by animal tests. Here we report a method for in-situ polymer formation by using carbon nanohorns (CNHs) under light irradiation. In this method, CNHs absorbs light and work as molecular heater to raise the local temperature, which helped selectively forming the polymers on and inside CNHs. This method is quite useful for synthesis of nanocarbon-polymer composites and surface functionalization of carbon nanomaterials.

Polycaprolactone (PCL) is aliphatic polyester composed of hexanoate repeat units. Irradiating near infrared light (808nm) for 1 hour, the local temperature around CNH increased and the ring of cyclic monomer caprolactone was opened, leading to the polycaprolactone (PCL) formation on and inside the CNHs. The number average molecular weight (Mn) of the obtained PCL was 6982. In a control experiments without CNHs, Mn of PCL was only 555.

P97

Eliminating indoor ozone by titanian nanotubular photocatalysts

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In this study, ozone removal efficiency by three visible-light driven photocatalysts including nitrogen-doped TiO2 nanotubes (TiO2-N), TiO2 nanotubes hydrogenated at 300℃ and 350℃ (TiO2-H300 & TiO2-H350) was evaluated. Two commercial photocatalysts, P25 and Merck, were used for comparison. The effects of ozone concentration (50-250 ppb), relative humidity (RH35-80%), and mass transfer on the ozone removal efficiency were investigated. Alkaline hydrothermal method was exploited in preparing TiO2 nanotubes from Merck TiO2. To produce nitrogen-doped TiO2 nano.tubes, TiO2 nanotubes were annealed at 400℃ for 3 hours in NH3(g) atmosphere. The hydrogenation was processed at 300℃ and 350℃ in 20.0 bar H2(g) for 5 days in non-stirred pressure vessel. All samples were analyzed by HRTEM, SEM, powder XRD, and XPS. The ozone removal efficiency of TiO2-N, TiO2-H300 and TiO2-H350 is 3-4 times higher than that of the Merck TiO2. Among all tested photocatalysts, P25 has the highest efficiency on ozone removal. The experimental results of various ozone concentrations indicate the kinetic fits the Langmuir-Hinshelwood model. The ozone removal efficiency of TiO2-H300 and TiO2-H350 decreased with the increase of RH. It may be due to that H2O increased electron-hole recombination through inducing structural bendingin the surface of TiO2.

P98

Computational brightness evaluation of carbon nano field emitter grown by field emission induced growth

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We have studied carbon nano field emitters grown by field emission induced growth (FEIG) for high brightness electron source of electron microscopy. It has been already reported that the FEIG nano emitters were easy for gun alignment and obtained better SEM images than carbon nanotube (CNT) emitters. However its brightness value has not been evaluated because it requires virtual source size which could not be measured experimentally. Therefore, in this study, brightness of FEIG nano emitters were evaluated by means of computer simulations. In the simulation, commercially available softwares ELF/ELFIN and ELF/BEAM were used for electric field and electron trajectory calculations, respectively.

As the simulation results, it was revealed that FEIG nano emitters have 1 to 3 orders higher brightness than normal tungsten emitters. It was also revealed that optimum radius range of the nano emitter was 1 to 10 nm.

Emission current vs voltage (I-V) characteristics obtained during a FEIG experiment were also analyzed by the simulation. It was confirmed that radius of the nano structure increased from 0.4 to 2 nm during the growth, which led brightness increase by about 100 times.

P99

Confinement into single-walled carbon nanotubes: supramolecular organization and physical interactions

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1D hybrid nano-systems are elaborated with photo-active -conjugated molecules encapsulated into the hollow core of single-wall carbon nanotubes. The physical properties can be tuned by modifying the structural properties, providing practical routes to fit different requirements for potential applications. In this study, we report results obtainedby endohedral functionalization of single wall carbon nanotubes with quathertiophene (4T) and phathlocyanine (MPc) molecules. The structural properties are investigated mainly by x-ray diffraction and/or Transmission Electron Microscopyand Raman spectroscopy. We evidence that the supramolecular organization of confined oligothiophenes (from 1 to 3 chains into a nanotube section) depend on the nanocontainer size 1. The physical interactions can switch from molecule-molecule to molecule-nanotube interactions depending on the tube diameter. They can give rise to permanent and photo-induced charge transfer. The supramolecular organization of MPc molecules is shown to be a 1D-phase for which the angle between the molecule ring and the nanotubes axis is close to 32°. Confined MPc molecules display Raman spectra hardly altered with respect to the bulk phase, suggesting a rather weak interaction with the tubes 2.

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P100

Polymorphism of two-dimensional $MoTe_2$: A density functional study

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Transition metal dichalcogenides (TMDs) have attracted much attention due to their distinctive properties and potential applications for low-dimensional nanoscale devices. In particular, polymorphism in TMDs leads to intriguing physical phenomena such as band gap opening, charge densitywaves, superconductivity, and spin-valley coupling. However, most researches have been focused on trigonal prismatic 2H and octahedral 1T phases, as they are the most common structures in TMDs.

Here, we investigate the structural and electronic properties of $MoTe_2$ in distorted octahedral phase (1T) through first-principles density functional calculations. In contrast to the 1T phase, which is metallic, we show that 1T-$MoTe_2$ exhibits a small band gap opening that originates from the strong spin-orbit coupling. We clarify that a structural distortion from 1T to 1T is driven by electron-phonon interactions. A nesting vector in the Fermi surface is responsible for the Peierls-like distortion which leads to the more stable 1T phase. Furthermore, this new class of semiconducting $MoTe_2$ unlocks the possibility of topological quantum devices based on nontrivial Z_2-band-topology quantum spin Hall insulators.

P101

Electronic properties of MoS2 on SiO2 altered by surface polarity and dangling bonds

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Following the discoveryof graphene, transition metal dichalcogenides MX2 (M= Mo,W, X = S, Se, Te) have attracted much attention because of their potential applications for low-dimensional electronic and optical devices. In particular, MoS2 has emerged as a promising material for field-effect transistors with high current on-off ratios at room temperature. When MoS2 is deposited on a SiO2 substrate, the electronic and transport properties are affected by interactions between MoS2 and SiO2. Therefore it is important to understand the nature of interlayer coupling and the electronic modification of MoS2 on the substrate.

In this work, we investigate the electronic properties of monolayer and bilayer MoS2 on SiO2 through first-principles density functional calculations. In monolayer MoS2, due to the interlayer coupling between MoS2 and SiO2, the valence band edge state at the center of the Brillouin zone tends to shift upward, reducing the indirect band gap, whereas the direct gap at the Kvalleys is less sensitive to substrate conditions. In bilayer MoS2, surface O-dangling bonds break the inversion symmetry by inducing dipole fields across the interface. Therefore, a strong coupling between the spin and valley degrees of freedom takes place, similar to that found in monolayer MoS2.

P102

Growth and characterization of 1T'-layered transition metal ditelluride single crystals

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Two-dimensional transition metal diclacogenides (MX_2s) are attracting much attention as promising materials for a new generation of optical and electronic devices. Some semiconducting MX_2s are complementary or competitive to graphene because of the existence of a native band gap. Among MX_2s, group-6 transition metal ditellurides having 1T'-layered structures (beta-$MoTe_2$ and WTe_2) are gathering further attention as stable candidates to realize the quantum spin Hall effect device. They are known to have a distorted CdI2-type unit layer structure with one-dimensional zigzag chains of metal atoms, which differs from the 2H-type trigonal prismatic unit layer structure of MoS_2, WS_2, $MoSe_2$, WSe_2 and alpha-$MoTe_2$. Recently, we have succeeded in growing single crystals of these two 1T'-ditellurides by the chemical vapor transport method using Br_2 as the transport agent. In the presentation, we will report the characterization of their structures and physical properties by the measurement of X-ray diffraction, Raman spectra, X-ray photoelectron spectra, Hall effects and electric conductivities. It has been observed that these ditellurides have higher electric conductivities than 2H-type semiconducting MX_2s, suggesting their semimetallic electronic properties.

P103

Growth, electronics and optoelectronics of graphene and graphene-like layered materials

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Two dimensional nanomaterials such as graphene and layered inorganic materials are promising for future nanoscale electronics and optics. We report a low-temperature method toward synthesis of large area heavily heteroatom doped graphene on copper foils via a free radical reaction using polyhalogenated aromatic compounds. This low temperature method allows the synthesis of single layer nitrogen doped graphene film with high nitrogen content, and the production of large area sulfur doped film for the first time. We also studied impactof dielectric layer and metal contacts on the performance of 2D layered materials based devices. And we discover that carrier scattering from chemical impurities of hydroxyl groups and absorbed water molecules at oxidized dielectric plays a central role in determining the mobilities of 2D layered semiconductors based FETs, and suppression of this carrier scatter can significantly enhance the performance of 2D layered semiconductor devices.

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P104

Butadiene-bridged pyrene dimers: model molecules of bilayer graphene

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Oriented AB stacked bilayer graphene has attracted significant attention as zero-bandgap semiconductors. Alternation of the stacking of bilayer graphene modifies its electronic and optical properties. Pyrene, a partial model molecule of graphene, has attracted much attention for luminescence and semiconductor materials. Pyrene derivatives frequently form face-to-face stacking in the solid state. Here, we report the synthesis of pyrene dimers bridged by a butadiene unit as model molecules of bilayer graphene. X-ray diffraction analysis revealed that the conformation of thebutadiene unit was dependent on its substituents. Inpyrene dimers with aryl substituents on the butadiene unit, two pyrenyl groups aligned in the same direction like bilayer graphene. These pyrene dimers exhibited photochromic behavior in solution upon irradiation of UV light. In addition, red-shifted and broadened emissionwas observed for some pyrene dimersin the solid state. The charge carrier mobility of pyrene dimers with alkyl substituents was higher than that of aryl counterpart.

P105

Low-cost and high yield method for synthesis of ultrasmall uniform graphene oxide nanosheets and its applications

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Graphene, one-atom thick two-dimensional nano carbon materials, has attracted more and more attention, due to its outstanding electrical, optical, mechanical, and thermal properties. Meanwhile, graphene oxide (GO), a soluble precursor for synthesizing graphene or reduced graphene oxide, has also been widely studied in various fields for its special chemical structure. Graphene oxide nanosheets (GONSs) with lateral size less than 100 nm have attracted more and more attention for its wide range of potential applications, from bionanotechnology and nanobiomedicine to surfactant. But at present GONSs are commonly prepared utilizing graphite nanofibers or graphite nanopowders which are bothexpensive. Herea timesaving,high yield, low-costand no strong acid method was proposed for preparing ultrasmall uniform GONSs with average lateral size of ～30 nm, utilizing common graphite powder as raw material. The obtained GONSs are able to disperse single walled carbon nanotubes (SWCNTs) effectively, and the created dispersion could withstand high-speed centrifugation. So GONSs could indeed be served as a superior surfactant for dispersion of SWCNTs, and the dispersion could be further applied into electronic applications, because GONSs could be further reduced to reduced GONSs or graphene nanosheets.

P106

The topological and electronic structure of starfish nanocarbon

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Purpose

We proposed new structures named starfish nanocarbon (SFNC) and analyzed the relationships between their structures and electronic states.

Definition

The structures of SFNCs are like roundabout made of N nanotubes. And they are defined by satisfying all following conditions. 1. They are composed of hexagons and heptagons. 2. Their central axis is composed of 2N heptagons and peripheral 4N hexagons. 3. They have N equal arms. The arms are zigzag-tube or armchair-tube.

Results & Discussion

The number of SFNCs that satisfy all the conditions was found to be 12. They have 4N heptagons aside from those in the axis. The structures of SFNCs, including the shape of the arm, are distinguished by the configuration of heptagons. As an application of SFNC, two or more different SFNCs are able to combine and make chimera. SFNC is therefore a potential junction that connects different types of NTs. By a topological consideration, the total number of heptagons was proved to be 6N for all SFNCs with N arms.

Twelve SFNCs are divided into 3 groups by the electronic states. We therefore found the structure and electronic states of SFNCs are corresponding and determined by the configuration of 4 heptagons per arm.

P107

The transport properties of WSe2 nanotube heterojunctions: A first-principles study

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Using the non-equilibrium Green's function method within the framework of density functional theory, we investigate the I-V characteristics and dynamical conductance, of Au, Na encapsulated WSe2 nanotube heterojunctions. First-principles transport calculations show that from I-V curves large rectification ratio is found for the (8, 0) WSe2 nanotubes. For dynamic conductance we find that the imaginary part of dynamic conductance exhibits a linear dependence on frequency with a negative slope showing capacitive-like behavior while the real part of dynamic conductance decreases quickly as frequency increases and changes slowly with frequency above 1 THz. We find that the spin-orbit interaction (SOI) is very important for WSe2 nanotubes. Due to the band splitting originated from SOI, the transmission gap is decreased by about 48% and 16% in the transmission spectrum of (5, 5) and (8, 0) heterojunctions, respectively. The current of (5, 5) heterojunction under small bias is almost doubled and the rectification ratio of (8, 0) heterojunction is enhanced by more than 120% due to SOI. Moreover, the dynamic conductance of (5, 5) heterojunctions with SOI is much smaller than that without SOI while the corresponding emittance is larger than that without SOI.

P108

CVD growth of monolayer $Mo_{1-x}W_xS_2$ alloy

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Monolayer transition metal dichalcogenides (TMDCs) have drawn great attention owing to their splendid catalytic, electronic, optoelectronic properties and the promise of application in valleytronics. In order to realize tuning of those properties and explore new phenomena, reports by other groups have shown successful synthesis of monolayer TMDC alloys with uniform substitution of chalcogen atoms such as $MoS_{2-x}Se_x$ by chemical vapor deposition (CVD) method. [1] On the other hand, in the CVD growth of monolayer $Mo_{1-x}W_xS_2$, an example of transitional metal substituted TMDC alloy, large difference in physical and chemical properties of different transitional metal-containing precursors makes the formation of MoS2/WS2 heterostructure more preferable than $Mo_{1-x}W_xS_2$ alloy. And, the reported synthesis of truly compositionally uniform monolayer $Mo_{1-x}W_xS_2$ alloy is limited to the chemical vapor transport and cleavage method and the co-thermolysis of $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ precursors. [2,3] Here, we report a 1-step CVD growth of monolayer $Mo_{1-x}W_xS_2$ alloy with uniform mixture of Mo and W atoms to the atomic scale by optimizing CVD conditions.

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P109

Growth and optical properties of high-quality monolayer WS_2 on graphite

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Atomic-layer transition metal dichalcogenides (TMDCs) have attracted appreciable interest due to their tunable bandgap, spin-valley physics, and potential device applications. However, the quality of TMDC samples available still poses serious problems, such as inhomogeneous lattice strain, charge doping, and structural defects. Here, we report on the growth of high-quality, monolayer WS_2 onto exfoliated graphite by high-temperature chemical vapor deposition (CVD). Monolayer WS_2 single crystals grown presents a uniform, single excitonic photoluminescence peak with a Lorentzian profile and a very small full-width at half maximum of 21 meV at room temperature and 8 meV at 79 K. Furthermore, in these samples, no additional peaks are observed for charged and/or bound excitons, even at low temperature. These optical responses are completely different from the results of previously reported TMDCs obtained by mechanical exfoliation and CVD. Our findings indicate that the combination of high-temperature CVD with cleaved graphite surface is an ideal condition for the growth of high-quality TMDCs, and such samples will be essential for revealing intrinsic physical properties and for future applications.

P110

Ambipolar insulator-to-metal transition and electric-field-control of thermoelectric properties in black phosphorus

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Black phosphorus is a van der Waals type semiconducting layered material with a puckered honeycomb structure where each phosphorus atom is covalently bonded with three adjacent phosphorus atoms and has a direct band gap of 0.3 (bulk) - 2 (monolayer) depending on the number of layers, which can be promising material for optoelectronics devices such as photodetector.

In this presentation, by using ionic liquidgating method, we report the field effect control of the ambipolar metal-insulator transition and thermoelectric properties in a black phosphorus thin flake. We observed a large modulation of the sheet resistance by more than 4 orders of magnitude in both electron channel and hole channel [1]. Moreover, we succeeded in controlling the thermoelectric properties in hole side for the first time. These results suggest black phosphorus will be a key material for not only understanding physics of the conduction channel produced by ionic gating underlying ambipolar metal-insulator transition, but also potential functions for fabricating formation of p-n junction and as a new thermoelectric material.

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P111

A new borate approach for the synthesis of BN-nanotubes with a high yield

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Extraordinary mechanical strength and chemical inertness of boron nitride nanotubes (BNNTs) make them an attractive material for reinforcement of advanced plastics, ceramics or metals for innovative applications in aerospace, automobile and other industries. Deterrent to a wide technological use of BNNTs is their poor availability on the market. Nowadays only a few laboratories around the world have reported on the synthesis of BNNTs with different qualities in tens of grams per hour yields. Lack of practical models for the BNNTs nucleation and growth is a bottleneck for their high yield synthesis. To sheda new light on these phenomena wehave studied an in.uence of alkaline and alkaline-earth oxides (MeOx) on reaction of boron oxide with ammonia. Reactions of oxide mixtures (MeO_x+mB_2O_3) for m=0,25-5 have been explored in a temperature range of 900-1250℃. It was found that various BN-nanostructures like nanoparticles, graphene-like flakes, nanotubes, and nanofibers had been grown dependently on borate composition and temperature. High quality straight and well-structured BNNTs with a diameter of 30-80 nm have been obtained in a certain range of temperatures and compositions. A model for BNNTs nucleation and growth using borates is proposed. The obtained results open prospects for a routine BNNTs growth at a high yield.

P112

Catalyst-free, self-assembly, and controllable synthesis of graphene flakecarbon nanotube composites for high-performance field emission

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Catalyst-free and self-assembled growth of graphene flakes (GFs) on carbon nanotube (CNT) arrays have been realized by using microwave plasma enhanced chemical vapor deposition. The shape of GFs was highly manipulated by adjusting the growth time, C concentration, and microwave power. We qualitatively discussed the nucleation and growth mechanism of GFs based on the growth parameter GF shape studies. The field emission (FE) properties of graphene flakecarbon nanotube (GFCNT) composites for different GF shapes were measured and found to be strongly influenced by the GF distribution. The opti-mal shape of GFs for FE had small scales, sharp edges, and sparse distribution on CNTs. The best FE properties with the optimal shape were observed with a low turn-on electric field of 0.73 V/lm and excellent stability, which are superior to those of the as-grown CNT arrays and GFCNT composites covered by densely distributed GFs. We consider that the large aspect ratio of CNTs and the unique FE stability of GFs play a synergetic effect on the improved FE properties.

P113

The theoretical prediction of raman in new carbon materials

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Graphynes, composed of sp-sp^2 carbon atoms, have attracted increasing interest of research due to particular optical, electrical and mechanical properties they might have. According to recent theoretical studies prediction, the systhesis of graphyne and graphdiyne are difficult but offer more possible compared to other graphynes, and they have been tried to form and got initial achievement[1]. For a new material, its widespread application is impossible without a convinient, fast, non-destructive characterization tool. Raman spectroscopy has performed remarkable ability for studing the properties of sp^2 and sp^3 carbon materials, such as diamond, graphite, carbon fibers and nanotubes. Naturally, we may expect it is also work in sp-sp^2 carbon materials[2]. By first-principles calculations, we investigated the Raman spectra of graphyne and graphdiyne, their peaks and corresponding lattice vibrational mode were considered. Finally, we showed frequencies of these vibrational modes according to the size of strain.

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P114

Size dependent carbon aggregation during CVD graphene growth: a theoretical study

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Graphene is a 2D allotrope of carbon consisting of atoms arranged in a hexagonal chicken wire pattern. A common method of graphene production is chemical vapour decomposition (CVD) on transition metal catalysts. A key intermediate structure in CVD graphene growth are coronene-sized islands [1], which act as templates for subsequent hexagon formation and extended graphene growth [2]. One potential mechanism by which this happens is Smoluchowski ripening, in which fragments coalesce on the catalyst surface, forming larger carbon fragments. For intermediate and large carbon fragments, this process is thermodynamically favourable [3]. What is currently unclear however, is whether Smoluchowski ripening describes the formation of small carbon fragments, which induce a greater deformation of the underlying catalyst surface [4]. Here we investigate this issue on Ni(111) and Cu(111) catalyst surfaces using density functional theory calculations.

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P115

Compressing interlayer distance of hBN without mechanical force: A new application of IR laser

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By performing the time-dependent density functional theory simulation, we propose an induction of optical phonon (A_{2u} mode) of hBN sheet with resonant IR that can contract the interlayer distance more than 10% of original distance. Induction of A_{2u} mode can alternatingly replace boron (B) and nitrogen (N) atoms oppositely in out-of-plane directions, and thus can induce dynamical dipole on each hBN layer in parallel. Then the parallel dynamical dipole drives attracting force to each hBN layer.

We used a plane-wave code for TDDFT-molecular dynamics (MD) within the Ehrenfest approximation under an alternating electric field (E-field) that mimics the IR laser. We found faster contraction under stronger intensity of the E-field while electronic excitation suppresses the contraction under too strong E-field. The electronic excitation canbe associated with energy-gap narrowing upon large amplitude of A_{2u} phonon or with multi-photon process in electronic excitation.

The current finding should be common in anylayered compounds which has out-of-plane optical phonon mode. We expect that the present results opened away to apply IR laser to induct a new chemical pathways in narrow space of 2D layered materials for formation of novel materials. This work has been published in PRL **114**, 116102 (2015)

P116

Fabrication of monolayer graphene on wide SiC terraces; an approach to produce pit-free and step-free graphene surfaces

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Monolayer graphene had been easily formed on SiC (0001) surfaces by suppressing the sublimation of Si atoms in an inert gas atmospheres or Si background during heat treatment. However, in the case of step-free or wide terrace surfaces, graphene nucleates both from step edges and on terraces by forming pits, leading to discontinuous growth of monolayer graphene.

In this report, by controlling the annealing processes, we succeed in growing monolayer graphene only from step edges on 4-micron-wide terraces extending over 100-micron-scale. Monolayer graphene grewacross the whole terrace without pit formation and covered above 90% areas of the surface, confirmed by scanning electron microscopy (SEM). Notably, no graphene boundary was detected by scanning tunneling microscopy (STM), showing that the monolayer graphene grown from step edges formed as one large domain of graphene.

P117

Formation of GNR from PTCDA

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Graphene nanoribbons (GNR) are narrowstrips of graphene, which shows metallic or semi-conducting properties depending on the width and edge structure. Therefore, application to various fields such as miniaturization of the circuit is expected. However, current technology for generating GNR is complicated and has a problem of high cost due to complicated processes. In this study, by using the PTCDA having a six-membered carbon ring structure as a starting material, we have tried to prepare GNR in a simple step.

P118

Controllable growth of graphene film and its application in solar cell

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In thiswork, we present that graphene films with different layers ranging from 1 to 7 can be controllably synthesized by a chemical vapor deposition (CVD) method. The layer numbers of graphene films are controlled precisely by regulating the flow ratio of CH_4 and H_2, reaction pressure, temperature and time. Furthermore,we have investigated the performance of Schottky junction solar cells based on silicon and graphene with different layers. The open-circuit voltage of solar cells shows an increase when increasing the number of graphene layers. However, the power conversion efficiency and short-circuit current density increase monotonically when the number of graphene layers is less than 4, and reduces as the number of graphene layers further increases. Our results demonstrate that the number of layers related to the work function and transmission of graphene plays a critical role in determining the performance of solar cells.

P119

Electrical and optoelectronic properties of MoS2/WSe2 heterostructrure

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Recently, graphene has attracted a great interestin material science due to its novel optical and electrical properties. Another class of two dimentional (2D) materials that is receiving an increasing amount of scientific attention is transition metal dichalcogenides (TMDs) such as MoS2, MoTe2, WS2, WSe2 While graphene lacks a bandgap, several 2D TMDs possess sizable bandgap around 1 2 eV which is promising for electronic and optoelectronic devices. Here, we investigate electrical and optoelectronic properties of a few layers MoS2/ few layers WSe2 heterostructure. MoS2 and WSe2 shown n-type and ambipolar behavior respectively. The heterostructure exhibited the p-n junction characteristics with open circuit voltage of around 0.3V and rectifying characteristic canbe modulatedby applying electric field. Photoluminescence intensity of both MoS2 and WSe2 was reduced significantly in the junction area by forming of depletion layer. This study demonstrates the exciting potential of MoS2/WSe2 heterostructure for the electrical and optoelectronic devices.

P120

Tunable surface oxidation of atomically thin WSe_2

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Controllable and uniform growth of oxide fi.lms on two-dimensional (2D) transition metal dichalcogenides is crucial for applications in electronics and optoelectronics. Here we demonstrate self-limiting oxidation of atomically thin WSe_2 via ozone (O_3) exposure at various temperatures. Below 100℃, the O_3 treatment resultsin the formation of oxides at the edges and dendritic oxide islands on the surface. With further exposure, the oxides grow laterally and coalesce to each other, ultimately forming a uniform film on top. However, oxidation does not progress to the underlying layers. At 200℃, the surface layers are oxidized in the layer-by-layer regime, up to trilayers. Using Raman and photoluminescence spectroscopy, we find that the underlying WSe_2 is mechanically decoupled from the top oxide. These observations have important implications for applications of layered transition metal dichalcogenides in 2D metal-oxide-semiconductor field effect transistors (MOSFETs), in analogy with the silicon-MOSFET.

P121

Bandgap-tunable lateral and vertical heterostructures based on monolayer $Mo_{1-x}W_xS_2$ alloys

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We report the single-step direct growth of lateral and vertical heterostructures based on bandgap-tunable atomic layer $Mo_{1-x}W_xS_2$ alloys by the sulfurization of patterned thin films of WO_3 and MoO_3. These patterned films are capable of generating a wide variety of concentration gradients due to the diffusion of transition metals during the crystal growth. Under high temperature condition, this leads to the formation of monolayer crystals of $Mo_{1-x}W_xS_2$ alloys with various compositions and bandgaps depending on the growth positions on the substrates. Heterostructures of these alloys are also obtained through the stepwise changes in W/Mo ratios withina single domain during low temperature growth. The stabilization of monolayer $Mo_{1-x}W_xS_2$ alloys, which often degrade even at room temperature, was accomplished by covering the alloys with other atomic layers. The present findings demonstrate an efficient means of both studying and optimizing the optical and electrical properties of TMDC-based heterostructures to allow their use in future device applications.

P122

Electrical conductivity of doped three-dimensional graphene

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Transparent conductive film (TCF) is used in various devices in our daily life such as transparent electrode of a solar cell and touch panels of smartphones. Indium tin oxide (ITO) is the most used materials for TCF, which is also suffering from the rise of cost due to the depletion of indium. Since carbon is much abundant compared to rare metals such as indium, there are lots of works reported for applying graphene to TCF. For the industrial application, we need to efficiently grow and transfer graphene from the substrate, which is pretty difficult. In this study, we have tried to improve the electrical property of three dimensional graphene by doping foreign atoms.

P123

Substrate effect on photoluminescence properties of tungsten disulfide atomic layers

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Transition metal dichalcogenides (TMDCs) have attracted a great deal of attention because of their unique properties: spin-valley-coupled electronic structure, valley pseudospin degree of freedom, intense photoluminescence and FET operation. The family of TMDCs atomic layers has provided a brand new and widespread platform to investigate physics in two-dimension, leading to the novel application called valleytronics in future. To explore the fascinating possibility of TMDCs, high-quality samples are indispensable. In this work, we have focused on substrates to realize high-quality samples.

WS_2 have been grown by the for the chemical vapor deposition method, where various substrates including SiO_2/Si, sapphire and hexagonal boron nitride (hBN) have been employed. Monolayer WS_2 crystals with triangular shape have successfully been grown onto all substrates used. We have found that intensity and FWHM of PL emission peak strongly depend on the substrates. Monolayer WS_2 on hBN exhibits, in particular, the most intense and sharpest PL emission (FWHMof 22.7 meV). Temperature dependence of PL spectra of WS_2 on hBN is signicantly different from WS_2 grown on other substrates, showing new feature at 2.016 eV. The observed unique PL properties of WS_2 on hBN clearly demonstrate the importance of substrate in investigations of physical properties of TMDCs.

P124

Two-dimensional metallic niobium disulfide (NbS_2): preparation, optical characterizations and transport properties

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Recent finding of high-temperature two dimensional (2D) superconductivity above 100 K opens up a fascinating new research direction towards pursuing high T_c super-conductors and understanding the underlying new physics. The extensive study of this new field strongly relies on the synthesis of 2D layered metallic systems. Preparation of 2D metallic systems, however, is not straight forward probably because of the stronger interlayer interaction, which is in stark contrast to the well advanced preparation technique of 2D layered semiconductors. We report here the first successful synthesis of a new 2D metallic transition metal dichalcogenides (TMDs), 3R-NbS_2, which exhibits superconductivity and charge-density-wave (CDW) phasesin bulk counterparts, down to the thinnest form (3 layers).

Our as-grown samples were directly synthesized on top of hBN substrates, showing fairly sharp triangular or hexagonal shapes. The Raman bands show systematic shifts depending on the layer numbers while the optical contrasts show strong layer number dependence both of which can be served as reliable signatures for layer number identification. Our transport data demonstrate that 3R-NbS_2 down to the thinnest form still preserve its metallic nature.

P125

Efficient growth of single-domain and millimeter-scale graphene by alcohol CVD method

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Graphene is attractive material due to its unique physical properties, and the growth of high-quality and large-size graphene is essential for industrial applications and for fundamental scientific research. We have studied CVD growth of single-domain graphene on oxidized copper foils using alcohol as the carbon source. The density control of graphene nucleation is important for synthesis of high-quality graphene, because the domain boundary degrades graphene properties and the maximum size of single-domain graphene is limited by the distance between adjacent nucleation points. We investigated the nucleation density of graphene by varying the ethanol pressure and reduction conditions of the oxidized copper foils with H_2. We found that the pre-reduction of the oxidized copper foils and low ethanol pressure condition result in the suppression of the nucleation density. Additionally by separating the nucleation stage of graphene on the oxidized copper foils from the following growth stage after reduction, large single-domain graphene was successfully grown with relatively short time.

P126

Direct synthesis of nitrogen-doped 3D graphene foam by inductively-coupled plasma-assisted chemical vapor deposition

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In this work, we present a new direct synthesis method for N-doped graphene based on thermal chemical vapor deposition with inductively-coupled plasma (ICP) using non-toxic pure nitrogen gas source. 3D N-doped graphene foam (GP foam) was fabricated on Ni foam using acetylene, hydrogen and nitrogen at 700-1000oC. The effects of various synthesis parameters including N2/C2H2/H2 flow ratio, ICP power, pressure, temperature and time on N-doped graphene structure have been systematically studied. Ni foam template was then etched in 3M HCl for subsequent characterizations. An optimal condition for high-quality N-doped graphene foam structure was found to be N2/C2H2/H2 of 7/4/84, ICP power of 200W, pressure of 0.7 Tor, temperature of 900oC and time of 1 minute. Rama spectra exhibited dominant 2D and G peaks with low D peak and notable D' peak at 1624 cm−1, indicating successful N-doping of few-layer graphene structure. The presence of N atoms in graphene was also confirmed by X-ray photoemission spectroscopy. Scanning/ transmission electron analyses confirm that the structures are nanometer-thick N-doped 3D graphene structure with high crystallinity. The CVD with ICP process allows the use of toxic gas source, produces high-quality N-doped graphene structure and thus is promising for commercial production.

P127

Effect of exfoliation processes on the flake size of graphene oxide

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One of the most popular and commercially viable routes to make graphene is by first oxidising graphite and exfoliating it to yield a water-stable dispersion of graphene oxide (GO). This can be subsequently reduced to graphene. While this process reliably produces high yield of monolayers, there is still a wide variation in the lateral size of these flakes. This would be critical depending on the application composites likely require larger flakes while drug-delivery would require much smaller sizes.

Here, we study the effect of two frequently used exfoliation methods, namely ultrasonication and shear exfoliation, on the lateral size of GO flakes. The GO starting material was produced without either of these processes and contains very large flakes in excess of 50 microns. We find that ultrasonication breaks down the flakes to smaller than 100nm, while shear exfoliation affects the flake size significantly less. We also demonstrate how the GO can be separated according to flake size into small (< 1 micron), medium (1 5 micron) and large (> 5 micron) flake size batches by ultracentrifugation. Taken together, these breaking and sorting techniques allow us to produce size-controlled GO flakes at high yield.

P128

Growth of large area graphene single crystal inside a restricted chamber by chemical vapor deposition

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Graphene single crystal without grain boundaries inner plane could enable scalable fabrication of graphene-based devices with high performance of electric transport. Graphene single crystal canbe easily obtainedby usinga backwardfaced quartz cuvette in a conventional tube furnace. The effect of the restricted chamber in controlling the graphene single crystal growth has been systematically studied by considering the influence of the flow rate and ratio of H2 and CH4 experimentally. Further numerical simulations and theoretical analysis were performed to uncover the underlying mechanism. The convection of CH4 was substantially suppressed inside the cuvette due to the nearly zero velocity of the local flow field, as a direct consequence of the blocking effect by the close-end geometry. The diffusivity of CH4 is much lower than that of H2, resulting in a slow transportation of CH4 as well. By using the specific experimental parameters, the mass ratio of H2 and CH4 increased about 3 times inside the cuvette, leading to preferential growth of graphene single crystals, as observed in our experiments. Based on these results, we believe that setup of our restricted chamber can provide another growth approach for scalable graphene single crystals and its analysis can help understand more growth dynamics of graphene single crystal.

P129

Interdependency of subsurface carbon distribution and graphene-catalyst interaction

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Growing graphene on a metal surface is one possible way to obtain high quality graphene, with a controllable number of layers. We investigate the synthesis of graphene on Ni that is of particular interest because the role of carbon solubility in subsurface layers is both difficult to investigate experimentally and important to understand how to produce high quality graphene.

To study the interaction of carbon with nickel at the atomic level, we have developed a tight binding model implemented in a Grand Canonical Monte Carlo code. With this method, we investigate the CVD synthesis of graphene on Ni (111) and correlate our results to experimental data [1]. We identify thermodynamic conditions (temperature and carbon chemical potential) to obtain a graphene monolayer. Moreover, depending on the growth conditions, we show that variable amounts of carbon atoms can be found in the subsurface layers, while the first subsurface layer shows a tendency for carbon depletion when graphene covers the Ni surface. With the support of in situ, time-and depth-resolved X-ray photoelectron spectroscopy (XPS), we discuss how this lower stability of carbon close to the surface can be used to control the number of layers [1].

[1] R. Weatherup et al., J. Am. Chem. Soc. 136, 13698 (2014)

P130

Fast characterization and rapid CVD synthesis of graphene for all-graphene field-effect devices

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Chemical vapour deposition (CVD) of graphene is the most promising method for large-area synthesis of monolayer graphene. For industrialization cost-effectiveness is as important as the high quality; this involves the minimization of time, energy and consumables. This work demonstrates extremely rapid synthesis as continuous mono-layer is achieved only in ~30s. uRaman mapping reveals high-quality fingerprint with high 2D/G and lowD/G ratios. Moreover, high mobility (~5000cm2/Vs) underlines the feasibility of the employed photo-thermal CVD (PTCVD) platform. Water cooled cold wall chamber and halogen lamps as heat source enable precise temperature control and fast ramp rates. Moreover, minimized deposition time limits the detrimental copper sublimation during deposition.

In addition to rapid synthesis, effective and rapid characterization is a vital prerequisite. Raman can be considered as superior method for analyzing carbon materials as it reveals many properties in detail, however, required time can be considered as a limitation. Here, multiphoton microscopy is shown to be a ultra-fast approach to characterize the number of layers as an area of 250x250um2 is scanned only in ~5s. Finally,the viability of PTCVD-grown grapheneis demonstrated using it as a channel, output branch and topgate electrode to realize all-grapheneT-branch devices, which display both rectifier and inverter characteristics.

P131

Band-like transport properties of reduced graphene oxide films

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Graphene oxide (GO) has attracted great interest in large area synthesis of graphene owing to cost-effective and mass production. Since GO includes rich oxygen-containing groups and defects, reduction and structural restoration of GO is an essential subject. The electrical transport properties of reduced GO (rGO) using conventional process such as thermal annealingin inert gas and hydrazine vapor are described by variable range hopping (VRH) model through localization states because of many defects still remaining in rGO, and is much different from intrinsic graphene properties. In this study, we found that high temperature treatment above 1100 ℃ in ethanol environment enables us to overcome this issue from analysis of carbon K-edge X-ray absorption fine structure (XAFS) spectra and conductivity of the rGO films. XAFS spectra indicate that the high temperature treatment leads to significant expansion of conjugated pi-electron system in the rGO films. The conductivity of the rGO films is described by the sum of VRH and thermal activation models. This means that the carrier transport shows band-like transport due to decreasing barrier height energy between localization states by expansion of conjugated pi-electron system.

P132

Practical chemical vapor deposition of graphene with sub-millimeter domain size at ～100% coverage in tens of minutes

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Chemical vapor deposition (CVD) with Cu foil catalyst is widely used to synthesize monolayer graphene and extensive efforts have been made to enhance the domain size and thus the properties of graphene. Millimeter-large domains were demonstrated, however as discontinuous films by CVD for tens of hours. For practical use of graphene, it is important to synthesize graphene at ～100% coverage in a reasonable time. We here report a two-step CVD process, in which nucleation and growth of graphene domains are separately controlled. To avoid undesirable graphene nucleation on defects, Cu foils were pretreated by electrochemical polishing and annealing under 760 Torr H2 at 1323 K. Then graphene was synthesized on the foils using CH_4 (8.3 mTorr)/H_2 (0-20Torr)/Ar at 76 Torr and 1273 K in two stages for 90 min in total. The first is nucleation stage; graphene "seeds" are nucleated at a moderate density $1/(0.1\ \mathrm{mm})^2$ at moderate H_2 pressures in 1 min. The second is growth stage; the graphene seeds are grown large to achieve ～100% coverage without additional nucleation at high H_2 pressures. Such graphene films, transferred to PET films by electrochemical delamination, showed a sheet resistance of 400-500 ohm/sq without doping.

P133

Synthesis of acene for graphene nanoribbon with different bandgap

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Graphene nanoribbons (GNRs) have drawn much attention as promising materials for nanoelectronic devices because the electronic properties of GNRs can be tuned widely as a function of the width and edge structure. Recently, Cai et al. have reported the excellent method to prepare atomically precise anthracene nanoribbons via a bottom-up approach based on the surface-assisted reaction of GNR precursors. This method can be used as a universal strategy to design band gap modulated GNRs with different width and edge structure. However, it is difficult to synthesize the corresponding acene because of the low solubility and stability. On the other hand, we have developed thermal and photochemical precursor methods to synthesize higher acenes. Briefly, bicyclo [2.2.2] octadiene (BCOD)-fused precursors can be converted to the corresponding acenes by the retro-Diels-Alder reaction, while α-diketon-type acene precursors can be converted to the corresponding one simply by photoirradiation. Importantly, these acene precursors are generally more soluble and stable than the corresponding acene. Here we report the synthesis of acene precursors for the bottom-up synthesis of GNRs with different width and edge structure by using thermal and photochemical precursor methods.

P134

Growth mechanism and controlled synthesis of single-crystal monolayer graphene on Germanium (110)

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Mechanically exfoliated graphene demonstrates extraordinary electrical and physical properties that could be harnessed to enable exceptional advances in technology. However, the initially reported micromechanical exfoliation of highly oriented pyrolytic graphite can only yield a minute amount of small single-crystal graphene, limiting the practicality of this method. Recently developed CVD methods could produce large-size and uniform polycrystalline graphene, but the electronic properties of CVD graphene are degraded by domain boundaries. Thus, the fabrication of large-size single-crystal graphene using CVD has attracted much interest among materials scientists.

In this research, we present the growth of single-crystal monolayer graphene on hydrogen-terminated germanium (Ge) surface. A single-crystal Ge substrate is a promising candidate for the growth of single-crystal graphene, because of its catalytic activity for the catalytic decomposition of the formation of graphitic carbon on the surface; the extremely low solubility of carbon in Ge even at its melting temperature, enabling growth of complete monolayer graphene. The structural features such as surface morphology crystallinity were investigated by SEM and AFM, TEM and resonant Raman spectroscopy. We believe that our approach for the synthesis of single-crystal monolayer graphene may be potentially useful for the development of many electronic devices.

P135

Precipitation of high-quality multilayer graphene using alumina barrier and Au capping layers

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Electrical wire is one the prospective applications of graphene, whose property is able to improve by the use of graphene. To realize superior graphene wire, the enlargement of the graphene grains and the increase of the number of the layer are important. In precipitation method, multilayer graphene is reproducibly produced by the annealing of a stacked structure consisted of metal catalysis and amorphous carbon. The use of alumina barrier and Au capping layers are helpful to improve the quality of multilayer graphene grown by precipitation method. In this paper, the growth conditions are optimized to obtain multilayer graphene with large grains and the effect of the barrier and the capping layers are independently investigated for clarifying the detailed mechanism of the precipitation. As a result, a multilayer graphene with more than 5-layers was successfully obtained, whose grain size was as large as 10 um. The Raman signal of the layers with an extremely low D peak was also acquired, which shows that the quality of the layers are excellent. The alumina barrier layer is found effective to suppress the nucleation of amorphous nuclei while the Au capping layer is useful to enlarge the grains during the precipitation.

P136

Nucleation control of multilayer graphene by precipitation method using diffusion barrier and two-step annealing

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Electrical wire is one the prospective applications of graphene. To realize superior graphene wire, both the enlargement of grains and the increase of the layer number of graphene are necessary. Precipitation method is useful to reproducibly grow multilayer graphene, where a stacked structure of metal catalysis and amorphous carbon is annealed in vacuum. In the paper, the nucleation control using diffusion barrier and two-step annealing is investigated to decrease the number of the nuclei and to produce multilayer graphene with large grains. The sample in the experiment has Ni/alumina/amorphous-carbon/sapphire structure. The temperature of two-step annealing was optimized to reduce the number of the graphene nuclei. Consequently, the density of nuclei was successfully decreased as low as $1.3 \times 10^5 \mathrm{cm}^{-2}$ using the two-step annealing. The resulted grain size of the multilayer graphene was found far larger than that of the sample precipitated by the conventional one-step annealing. The Raman signal with an extremely low D peak indicates the growth of a high quality multilayer graphene. The graphene nuclei is thought to only nucleate during the pre-annealing and to enlarge with consuming the precipitated carbons during the main-annealing.

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P137

First-principles molecular dynamics simulations for the initial stage of graphene growth on stepped SiC surface

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An epitaxial graphene sheet can be obtained by heat sublimation of Si atoms from the stepped SiC surface. However its atomic scale growth mechanism is yet not understood in detail.

In this study, the initial stage of the graphene growth processes on a stepped SiC(0001) surface are analyzedby first-principles molecular dynamics (FPMD) simulations. A first-principles calculation code PHASE whichis appropriate for efficient large scale parallel calculations is used. Our FPMD simulations proceed as follows. Before the start, some of the Si atoms on the top layer are intentionally removed from the initial SiC substrate to emulate the Si heat sublimation. MD is executed for 1 psec. under the condition of high temperature and then relaxed. Next, additional Si atoms are removed from the 2nd top layer, and then the same MD is repeated again. We tracked the behaver of the redundant C atoms during the series of these procedures. Where, when and how do those C atoms start to re-create the new C-C networks will be discussed in detail by comparing the results from several different patterns of the SiC substrates.

P138

CVD synthesis of high-quality graphene using liquid gallium catalyst at low temperature

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Chemical vapor deposition (CVD) is a promising method for industrial mass production of graphene films. However, the synthesis temperatures are still high (around 800℃ to 1100℃), which is not compatible with Si-based device processes. Therefore, reducing the synthesis temperature is crucial to realizing graphene-based electric applications.
Here, we report that a two-stage graphene growth method effectively reduced the synthesis temperature, where the graphene nuclei was grown in the 1st stage with high temperature (1050℃), followed by the 2nd stage of graphene growth at low temperature from 500℃ to 800℃. We used a c-faced sapphire substrate with a 0.2°offset angle and diluted methane gas as a source of carbon. The graphene seemed to grow from the initial nuclei and fully covered the surface after 10 minutes of 2nd-stage growth at 500℃. Raman mapping for 80 m square shows a uniform spectrum distribution with a large 2D/G ratio exceeding 2 as well asa large G/D ratio, suggesting our graphene is almost single-layer and has high crystallinity. We think the presence of graphene nuclei is the key to reducing the growth temperature.

P139

Molecular-orbital view of the whole band structure of silicene in an extended Weaire-Thorpe model

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Although silicene is considered as a silicon analog of graphene, there is an essential difference in that the sp3-type hybridization coming from the buckled structure is outside a single-band description unlikein graphene. In a context of three-dimensional silicon, the sp3 character was captured by Weaire and Thorpeina tight-binding model, and here we have extended the picture to silicene analytically [Y. Hatsugai, K. Shiraishi and H. Aoki, New J. Phys. 17, 025009 (2015)]. In this picture the entire energy bands consist of two types of singular dispersions — flat (or narrow) bands and (symmetry-protected) Dirac cones. Indeed, they have a one-to-one correspondence to the first-principles energy bands originally obtained by Takeda-Shiraishi [Phys. Rev. B50, 14916 (1994)]. Appearance of the flat bands is a characteristic feature of multi-orbital systems, where the itinerancy of electrons is due to the non-orthogonality of the hybridized (or "molecular") orbitals. An interesting observation is that the model contains a physical parameter that is tunable by how the silicene surfaceis terminated, which is predicted to substantially affect even the ordering of the flat and dispersive bands around the Fermi energy. Possible instabilities (structural and/or magnetic) are also discussed.

P140

Spin-filtering effect at the atomic boundary on transition-metal dichalcogenides

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We theoretically propose a novel spin-dependent electronic transmission at the atomic domain boundary in the transition-metal dichalcogenides (TMD), in which the spin-unpolarized electron beam is split into different directions depending on spins. We consider the monolayer and bilayer junction in hole-doped TMDs, and show that the up-spin and down-spin electrons transmit through the boundary with the different out-going angles. The spin-dependent transmission is attributed to the strong spin-orbit interaction and the different crystal symmetry between the monolayer and bilayer regions, and widely found in various TMDs MX$_2$ with M = Mo, W and X = Se, Te.

The spin-dependent transmission can be applied to spintronic devices. We propose the Y-junction where the spin-unpolarized electron beam coming from the bilayer channel split in two branches of the monolayer TMD depending on the spin. Since the separated up-spin and down-spin electric beams are well collimated, the Y-junction splits the electronic spins with high efficiency. The spin-filtering devices were also proposed for the conventional semiconductor with Rashba spin-orbit interaction, but the TMD junction has a big advantage over those systems in robustness of the spin-polarization. InTMD, the out-of-plane spin component is a good quantum number and this gives a very long spin lifetime.

P141

Electrical characteristics of MoS_2 flakes by catalytic etching via cobalt oxide

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MoS_2 is an attractivetwo-dimensional material for electrical applications due to its high-mobility and thickness-dependent bandgap. However, it is still challenging to etch MoS_2 flakes in modifying electrical characteristics of MoS_2 layers transferred on the source-drain electrodes of field effect transistor (FET). In this work, we report a change in the electrical characteristics of MoS_2 flakes by catalytic etching via cobalt oxide nanoparticle. The catalytic etching was performed by heating Co precursor-impregnated MoS_2 flakes on the FET with a back-gate structure in air. Before etching, the MoS_2 FET showed n-type behavior in transfer characteristic curve. However, ambipolar behavior was observed with high on/off ratio after heating Co precursor-impregnated MoS_2 layers in air. Atomic force microscope revealed that MoS_2 layers became thinned and defectiveby the catalytic etching process.

P142

Amorphous 2D carbon structures

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The recent appearance of 2D materials has for the first time allowed direct imaging of disordered atomic arrangements. So far, two amorphous 2D material shave been described: silica glass [1,2] and graphene amorphized during a transmission electron microscopy (TEM) experiment [3,4]. This controlled introduction of disorder has allowed us for the very first time to study the transformation of a crystal into an amorphous material. We have already shown [4] that the change from a crystal to a glass happens suddenly, and at a surprisingly early stage. Right after the transition, the disorder manifests as a vitreous network separating individual crystallites. After this, the vitreous areas grow until the structure turns into a random network.

More recently, we have extended the amorphization experiments to effectively amorphize large areas (several micrometers squared). The created structures are then imaged with the aberration-corrected Nion Ultra STEM 100. Additionally, we have created similarly amorphous 2D carbon membranes with an extremely simply setup using only a carbon evaporator and a NaCl target. In this way, structures with sizes of several centimeters squared can easily be created.

[1] Angew. Chem. 51, 4047 (2012)
[2] Nano Lett. 12, 10811086 (2012)
[3] Phys. Rev. Lett. 106, 105505 (2011)
[4] Sci. Rep. 4, 4060 (2014)

P143

2D Amino-based pi-conjugated nickel complex nanosheets

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Coordination compounds consist of metal ions or metal clusters in different coordination geometries, which are connected by a large number of bridging ligands via coordination bonds into multi-dimensional frameworks. The research on the chemistry of coordination compounds has been developing rapidly for the last twenty years, but the attention has been recently shifted onto the two-dimensional (2D) coordination compounds as graphene, the most widely studied nanosheet, has shown to possess a variety of interesting electronic, spintronic and photonic properties.

This work focuses on the study of two dimensional nickel complex nanosheets synthesized using the bottom up method with hexaaminotriphenylene ligand. This amino-based ligand is selected for this study because of its redox activity (ambipolar character) and structure. The resulting pi-conjugated structure accentuates its potential in electronic applications; similar to graphene but likely to be much complex due to additional interactions with the metallic ions. Furthermore, the amino-based nickel complex nanosheet is also likely to exhibit an ambipolar semiconducting character similar to that of mononuclear bis(diimine) nickel complexes previously reported.

P144

Semiconducting characteristics in self-ordered quasi-one dimensional graphene lateral superlattice

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Opening a band gap is indispensable to the development of high-performance graphene electronic devices. Formation of graphene nanoribbons (GNRs) is a promising approach to the band-gap opening in graphene, nevertheless GNR transistors are currently not in practical use, mainly because of the performance degradation due to uncontrollable structures. Here, we report a new approach to graphene band gap engineering, i.e. graphene lateral superlattices (LSLs), in which electronic states are modulated by periodic potentials, indicating ～ 0.1 eV band gap opening.
Graphene LSLs are found to be self-assembled on SiC(1-108) facets via surface decomposition of vicinal SiC(0001). SiC(1-108) facets consist of highly ordered pairs of a (0001) terrace and a (1-102) nanofacet with ～ 2.3 nm periodicity, on which monolayer graphene is corrugated. Combination of such morphological corrugation and one-dimensional potential modulation through the periodic SiC facet/terrace surface induces modification of electronic states in the monolayer graphene at K-points. In transport measurement, the graphene LSL exhibits semiconducting behavior with a band gap of ～ 0.1 eV, which agrees with the result of DFT calculations. In the presentation, we discuss the details of our results (STM, ARPES, LEED, transport, etc.) as well as the future prospect of our novel approach to graphene band-gap engineering.

P145

Graphyne derivatives: nanocarbon materials based on sp and sp^2 hybridization

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The density functional (DF) calculations have been carried out to investigate the stability, atomic and electronic structures of alpha-graphyne, beta-graphyne, and their derivatives (GYs) featuring extended carbon rings or chains. The analyses of structure and energy show that GYs with even-numbered hexagon edges have alternating single and triple C-C bonds (polyyne), energetically more stable than those with odd-numbered hexagon edges possessing continuous double C-C bonds (polycumulene). The calculated electronic structures indicate that GYs can be either metallic (odd N) or semiconductive (even N) depending on the parity of number of atoms on hexagon edges despite the edge length due to Jahn-Teller distortion. The semiconducting graphyne derivatives are found to possess Dirac cones (DC) with small direct band gaps <40 meV and large electron velocities ～ 0.3-0.7($\times 10^6$) m/s, 30-80% of that of graphene. Our DF studies suggest that introducing sp carbon atoms into the hexagon edges of graphene opens up an avenue to switch between metallic and DC electronic structures via tuning the parity of the number of hexagon edge atoms without doping. (Chen Sun, Yi Liu et al., Physica E 70, 190-197, 2015)

P146

Spectroscopic properties of BN layers

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In this talk, we examine the interplay between structure and spectroscopic properties of BN layers and how these properties can be further exploited in 2D layered heterostructures. We studied mechanically exfoliated crystallites by combining catho-doluminescence (CL) at 4K, HRTEM and Electron Energy Loss Spectroscopy (EELS) using a monochromated Libra 200 TEM-STEM at 80 kV.

BN displays original optical properties governed, in the energy range 5.5 6 eV, by strong excitonic effects [1]. From CL experiments, we will show that the excitonic emission consists of D and S lines. D lines are proved to be due to structural defects [1]. S lines are identified as the intrinsic luminescence of the material and their features are found to dramatically change when reducing the number of layers, providing with a signature of the 2D confinement [2].

Low-loss-EELS is an alternative approach to the nature of electronic excitations. One can indeed access to the onset of optical transitions and investigate their angular dependence. We will show that we can probe the whole Brillouin zone of BN layers and represent the plasmon dispersion as a function of the q momentum.

[1] A. Pierret et al, Phys. Rev. B, 89 (2014) 035414.
[2] L. Schué et al, in preparation

P147

Electronic structure of quasi-free-standing germanene on monolayer MX (M=Ga, In; X=S, Se, Te): density functional calculations

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Among the known Dirac materials family (graphene, silicene and germanene), germanene has the largest intrinsic carrier mobility (about twice as much as graphenes) and the largest spin-orbit coupling effect (10^4 larger than graphene). However, germanene, as well as silicene, can only be synthesized with high quality on metal substrates, and suffer from deformation on many common oxides. On the other hand, electronic devices require semiconducting or insulating substrates to reduce leakage currents. In this study, for the first time by using the ab initio density functional theory, the stability and electronic structure of germanene on semiconducting monolayer GaS, GaSe, GaTe and InSe are investigated. Our results suggest that these monolayers are promising as substrates for germanene devices. Germanene preserves its buckled-honeycomb structure on all studied substrates like the free-standing situation. Moreover, germanene keeps neutral and preserves its Dirac-cone-like band structure on monolayer GaTe and InSe. In these two cases, germanene has a bandgap of around 0.14 ～ 0.16 eV (estimated with the HSE functional) at the Dirac point, while the effective masses remain as small as 0.05 ～ 0.06 m_0. The estimated carrier mobility is up to 2.2×10^5 $\mathrm{cm^2V^{-1}s^{-1}}$.

P148

Hetero-structures in 2D systems: from doped monolayers to van der waals solids

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We will discuss the synthesis of large-area, high-quality monolayers of nitrogen-, silicon- and boron-doped graphene sheets on Cu foils using ambient-pressure chemical vapor deposition (AP-CVD). Scanning tunneling microscopy (STM) and spectroscopy (STS) reveal that the defects in the doped graphene samples arrange in different geo-metrical configurations exhibiting different electronic and magnetic properties. These doped layers could be used as efficient molecular sensors and electronic devices. In addition, the synthesis of hybrid carbon materials consisting of sandwich layers of graphene layers and carbon nanotubes by a self-assembly route will be discussed. These films are energetically stable and could find applications as field emission sources, catalytic supports, gas adsorption materials and super capacitors.

Beyond graphene, the synthesis of other 2-Dimensional materials will be described. In particular, we will discuss the synthesis of WS2 and MoS2 triangular monolayers, as well as large area films using a high temperature sulfurization of WOx clusters deposited on insulating substrates. We will show that depending on the substrate and the sizes of the oxide clusters, various morphologies of layered dichalcogenides could be obtained. In addition, photocurrent measurements on these materials will be presented. Our results indicate that the electrical response strongly depends on the laser photon energy.

P149

Growth and characterization of W-doped NbS_2 atomic layers

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Atomic-layer transition metal dichalcogenides (TMDCs) are attractive two dimensional materials because of their tunable electronic properties and unique spin-valley physics. To date, very few synthesis studies have been reported for metallic TMDCs such as NbS2 nanosheets. It is, therefore, still highly desired to prepare high quality, large area metallic TMDC atomic layers for unraveling their unique electronic phases in the two-dimensional limit.

We report the growth and characterization of W-doped NbS2 atomic layers. For the crystal growth, stacked WO3 and Nb films were prepared on various substrates including sapphire and graphite by electron beam deposition. These films were sulfurized by annealing under hydrogen/sulfur/argon atmosphere. We found that the addition of W atoms effectively prompts the growth of Nb-based TMDC crystals. The thickness of such crystals ranges from 4.2 to 70 nm. High-resolution AFM and FFT images reveal the honeycomb lattice of samples with lattice constant of 3.2 Å. These crystals have two characteristic Raman peaks at 360 cm^{-1} and 392 cm^{-1}, which can be assigned to WS2 E2g and NbS2 A1 modes, respectively. The resistivity of samples is around 10^{-5} ohm/m, which is comparable to that of bulk NbS2 (~10^{-6} ohm/m). These results strongly suggest that the present approach provides atomic layer W-doped NbS_2 crystals with metallic properties.

P150

Hexahydroxytriphenylene as a versatile and commercial exfoliant for 1D and 2D materials in aqueous and organic solvents through wet and dry processes

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Thin-layer 2D materials, such as graphene, hexagonal boron nitride (h-BN), and molybdenum disulfide (MoS_2), have attracted growing interest due to their unique physical and chemical properties. Since the layers are bound through van der Waals interaction, they have been directly exfoliated from the pristine bulk materials. The most typical way is the ultrasound irradiation in a liquid phase with or without additive.

In this paper, we will present a versatile exfoliant, hexahydroxytriphenylene, which exfoliated graphene in aqueous solution as well as a low boiling point organic solvent to give highly concentrated dispersions (as high as 0.19 and 0.13 mg mL^{-1}, respectively). The exfoliation was also successful in the dry process using ball-milling, leading to a few layer graphene with yield more than 80% from pristine graphite. In addition, h-BN, MoS_2 and SWNTs were also exfoliated in aqueous and organic solvents through ultrasound irradiation and ball-milling. Taking versatility, availability and removability into consideration, hexahydroxytriphenylene is considered to be superior to the exfoliants reported so far.

P151

The role of water molecules in graphene synthesis

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Graphene is a candidate for many electronic applications. The synthesis of graphene by chemical vapor deposition (CVD) is inevitably affected by various environmental factors such as moisture. Here we investigate the effect of adding a small amount of water on the graphene growth. Graphene was synthesized by low pressure CVD using Cu foils as catalyst. The foils were annealed at 500 ℃ in H2 atmosphere, followed by the graphene growth at 1000 ℃ in the flow of CH4, Ar, and H2. The water content in a chamber was controlled ranging from 10 ppm to 300 ppm.

X-ray photoelectron spectroscopy showed that adding water during annealing heavily oxidized the Cu surface, inducing tremendous surface roughness. This probably plays a role in the increase in the area of bilayer and multilayer graphene, confirmed by Raman spectroscopy. On the other hand, the addition of water during graphene growth exhibited strong etching effect on graphene, thereby resulting in the less nucleation and much slower growth rate of graphene, unlike the effect by surface oxygen [1]. These results suggest that the amount of water content must be carefully controlled for uniform, large-area graphene growth.

[1] Y. Hao et al., Science 342, 720 (2013).

P152

Probing edge-activated resonant Raman scattering from mechanically exfoliated 2D MoO_3 nanolayers

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We demonstrated spatially resolved vibrational analysis of mechanically exfoliated single-crystalline MoO_3 nanolayers. Raman scattering from MoO_3 was enhanced predominantly at the outside edges of the nanolayers. The enhanced Raman scattering at the edges was attributed primarily to the enhanced resonant Raman effect caused by a high density of oxygen vacancies localized at the edges. The localized vacancy sites corresponded to a non-stoichiometric phase of MoO_3, which would provide reactive sites with high catalytic activity.

P153

Electric double layer light-emitting diodes of monolayer WSe_2

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Because of the strong quantum confinement, optical properties of atomically-thin WSe_2 have been attracting interest [1]. Toward their optoelectronic applications, light-emitting devices are significantly important and, recently, light-emitting transistors of WSe_2 monolayers have been reported [2]. However, the remarkable physical pheno-mena of monolayer WSe_2, such as formation of charged exciton (trion) and large stark effect, have not yet been demonstrated by electrical excitation (electroluminescence, EL) due to lack of carrier density and/or electric field.

Here, we focus on electric double layers owing to their high specific capacitance and internal strong electric field. We propose novel light-emitting device, electric double layer light-emitting diodes fabricated with monolayer WSe_2 and ion gels. In this new device, p-i-n junction is self-assembly formed by applying voltage, leading to obvious EL emission at room temperature. In addition, both high carrier density ($\sim 10^{14}/cm^2$) and strong electric field (>100kV/cm) are realized during light emission, resulting in unique EL spectra which are different from normal photoluminescence spectra and similar to light emission from trions. We will discuss these interesting EL spectra from the aspect of trions and stark effect.

[1] X. Xu, et al., Nat. Phys. 10, 343 (2014).
[2] F. Xia, et al., Nat. Photon. 8, 899 (2014).

P154

Thermoelectric properties of CVD-grown transition metal dichalcogenide monolayers

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Monolayer transition metal dichalcogenides (TMDCs) have attracted a lot of research interests due to their two-dimensional layer structure. Recently, in single-crystal monolayer MoS_2, extremely high Seebeck coefficient (> 1 mV/K) was reported, suggesting high thermoelectric efficiency due to the low dimensional system [1, 2, 3]. As a next step, it is necessary to investigate thermoelectric properties of other TMDC monolayers to search better thermoelectric materials. Particularly, for future applications, the large-area polycrystalline samples should be tested. Moreover, because Seebeck coefficient correlates with carrier density strongly, we should control the carrier density of samples to maximize Seebeck coefficient. Therefore, in this research, we clarify the carrier density dependence of Seebeck effect in CVD-grown large-area WSe_2, WS_2 and MoS_2 monolayers. For carrier-density control, we fabricated electric double layer transistors (EDLTs) using ion gel, which is the mixture of ionic liquid and organic polymer. Finally, we successfully accumulated hole and/or electron carriers (> 10^{13} cm^{-2}) and obtained relatively high Seebeck coefficient (~ 0.1 mV/K) for all in monolayer TMDC films.

[1] M. Busceme *et al., Nano Lett.* 13, 358 (2013)
[2] J. Wu *et al., Nano Lett.* 14, 2730 (2014)
[3] L. D. Hicks, M. S. Dresselhaus, *Phys. Rev.* **B**, 47, 12727 (1993)

P155

Graphene oxide as a super material

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Graphene oxide (GO) and reduced graphene oxide (rGO) are nontoxic and inex-pensive two dimensional (2D) materials, which are stable at room temperature. Since the discovery of their electronic, optical, mechanical, thermal and chemical nature, GO and rGO have been adopted for numerous fascinating applications. In this time, we discuss the possibility of employing GO/rGO as solid electrolyte/proton conductors, ferromagnets, electrodes or electron mediators and as an ingredient of hybrid photocatalysts for water splitting. Nowadays, it is difficult to classify GO/rGO related researches separately. In most cases the functionality and application of rGO is necessarily associated with GO synthesis, its modification and subsequent reduction to rGO. However, the reduction of GO to rGO is the source of various defects, holes, imperfec- tions, semi hydrogenation state and band gap. All these influences affect most of the properties and utility of GO/rGO. Therefore, we will discuss functions with respect to both GO and rGO.

P156

Two-step growth and characterization of WS_2/MoS_2 heterostructures

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The heterostructures of two-dimensional semiconductors have attracted much attention for their potential applications in electronics and optoelectronic. Recently, several groups have reported the vapor-phase growth of lateral and stacked heterostructures based on semiconductor transition metal dichalcogenides (TMDCs) These studies basically use the continuous feeding of two precursors for the growth of two different TMDCs without changing reaction chambers. This process often leads to the alloying of heterojunction interfaces and/or secondary-grown materials because of the contamination of the remaining first precursors in the chambers. To avoid the contamination, it is desired to develop a two-step growth technique of the heterostructures with clean reaction chambers.
Here, we report the two-step growth of WS_2/MoS_2 heterostructures by using such clean environment. First, WS_2 monolayers were formed on a SiO_2/Si substrate by the sulfurization of WO_3 thin films. Then, the samples were put on another quartz tube to avoid the contamination of WO_3 during MoS_2 growth. The MoS_2 atomic layers were grown from sulfur and MoO_3 by chemical vapor deposition. This process leads to the formation of triangle-shaped MoS_2 grains on the WS_2 as shown in the AFM image and Raman spectra. In the poster, the details of sample preparation and characterization will be presented.

P157

Photoluminescence study for highly-localized impurity state in monolayer tungsten disulfide

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A novel photoluminescence (PL) peak has been observed from a monolayer of transition metal dichalcogenide (TMD), which is known to be an ideal 2D semiconductor. The PL peak appears near the low-energy side of neutral free excitons with very sharp peak width (10 meV) at low temperature (83 K). Systematic temperature-dependent PL measurements reveal that the peak can be explained by bound excitons being trapped by the surface impurities, which results in a highly localized state for the excitons. Since the optically detectable, highly localized impurity state promises to have extensive practical applications for quantum optics, our finding represents an important step in the study of 2D materials for use in quantum computation and information [1].

[1] T. Kato and T. Kaneko, ACS Nano 8, 12777 (2014).

P158

Efficient restoration of highly crystalline graphene from graphene oxide by ultrahigh temperature process under reactive environment

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We applied a solar furnace for the first time to restore crystalline graphene from defective graphene oxide (GO) by processes at ultrahigh temperatures in reactive en- vironment with ethanol. Crystallinity of graphene restored from defective GO should be improved by addition of ethanol into conventional processes under vacuum or inert environment at ultrahigh temperature. Solar furnaces are suitable for this purpose since they heat only samples at around 2000 ℃, and hence can be applied to reactive environments. The GO processed in ethanol at 1800 ℃ exhibits much better features of D- and 2D-bands in Raman spectra than those of GO processed at 1000 ℃ in ethanol and processed at 1700 ℃ in inert environment, and its crystallinity is comparable to CVD-grown graphene. 2D-band shape analysis indicates that processed GO does not have 3-dimensional AB stacking but has the turbostratic structure which maintains 2-dimensional physical properties of single-layer graphene. A trace amount of impurities in environment plays a significant role in defect formation, which reaches equilibrium with defect healing in ethanol environment. These results indicate that the ultrahigh temperature process under reactive environments is very effective for formation of highly crystalline graphene with turbostratic stacking towards single-layer electronics applications.

P159

Optical properties of CVD grown large-area WSe_2 monolayer under high-density electrochemical carrier doping

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Monolayer transition metal dichalcogenides (TMDCs) are attracting interest due to their direct band gap and strong two-dimensional quantum confinement. Particularly, observation of charged exciton at room temperature in mechanically exfoliated single-crystal samples is one of the solid evidences of confinement effect in TMDC monolayers and opens a new route to functional devices [1]. For future applications, we need to shift samples from micrometers-scale single crystals to centimeters-scale polycrystalline films [2]. In this research, we investigated quantum confinement effect and formation of charged exciton in CVD-grown large-area WSe_2 monolayers under high-density carrier doping.

Here, we fabricated electric double layer transistors (EDLTs) using the ion gel, which is the mixture of ionic liquid and organic polymer. We successfully accumulated both hole and electron carriers, resulting in highest carrier density of $2 \times 10^{20}/cm^3$. Finally, we measured the carrier density dependence of photoluminescence (PL) spectra. Interestingly, compared to single-crystal samples, it is not simply explained by exciton and charged exciton. However, PL spectra at highest carrier density suggest the formation of charged exciton in large-area samples, indicating strong quantum confinement effect.

[1] S. Mouri, K.Matsuda et al., Nano Lett, 13, 5944(2013)

[2] J. K. Huang, T. Takenobu et al., ACS Nano. 8, 923(2014)

P160

Direct growth of large-area graphene on insulator substrate by chemical vapor deposition using gallium vapor catalysts

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A single layer of graphene with dimensions of 20 mm x 20 mm was synthesized directly on an insulating substrate by gallium-vaporassisted chemical vapor deposition. Using Raman spectroscopy, the crystal quality of the graphene was found to improve with increasing Ga vapor density on the reaction area. In addition, two-dimensional Raman mapping showed that the graphene layer had a highly homogeneous crystal quality over a large area on the insulating substrate. From an analysis of the high-resolution TEM observations, we found that the synthesized graphene is mostly single-layer with a perfect atomic-scale crystal structure within its grains, which ranged in size from 50 nm to 200 nm. The electrical properties of graphene were evaluated by the curve of conductivity vs. back-gate voltage for the graphene FET configurations. The Dirac point of the FET showed a positive shift to around 40 V, which indicates that the synthesized graphene shows *p*-type characteristics. The hole mobility was determined to be 3.8 cm2/Vs. This small hole mobility is due to the electron scattering caused by the small multi-grains of the graphene channel.

P161

Electrochemical performance of MoS_2 decorated CNT arrays

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Combination of well-known materials into hybrids could lead to enhancing the properties of the components and overcoming the limitations of initials. Thus, MoS_2 is known to have low conductivity, which limits its use energy storage devices. Combining it with highly conductive CNT, one could get round the problems and prepare new materials.

We prepared MoS_2 decorated CNT arrays using hydrothermal technique. Initial CNT arrays were prepared using aerosol CVD. In the material obtained MoS_2 forms bead-like structures, composing of few layer sheets, on CNT walls. Varying amount of reagents used for synthesis, we can vary the resulting samples composition and permeability of MoS_2 surface layer. The samples obtained have specific capacity as supercapacitor electrodes as large as 180 F/g and high Li intercalation capacity. Obtained materials were fully characterized using different spectroscopic and microscopic techniques.

P162

Significant enhancement of the thermoelectric performance of phosphorene through the application of tensile strain

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We study the thermoelectric performance of strained phosphorene using ab initio calculations based on density functional theory combined with Boltzmann transport theory. We find that the thermoelectric power factor of phosphorene can be extensively modulated by applying tensile strain. Phosphorene is shown to exhibit a very large power factor exceeding 10 mW/m K under a 10 % strain, a value almost 100 times greater than the power factors of conventional flexible thermoelectric materials such as PEDOT: PSS and carbon nanotubes. In addition, the optimal chemical potential corresponding to the optimal doping amount is found to decrease with increasing strain, a phenomenon that is beneficial with regard to applications in thermoelectric devices employing a field effect transistor geometry. We clarify the underlying mechanism of the strain effect on the power factor by proposing the new concept of strain modulation of an energy valley. This new concept should allow for the development of new high-performance thermoelectric materials. Furthermore, based on these results, we propose that strain engineering may be employed to allow phosphorene to function as an environmentally friendly, flexible, high-performance thermoelectric material.

P163

Electronic structure of phosphorene under electric and magnetic fields

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We have qualitatively investigated the bulk and edge electronic structure of phosphorene systems under vertical electric fields and parallel magnetic fields by employing the Slater-Koster tight-binding model. Although there exist many first-principle calculations on the electronic structure of phosphorene, the tight-binding approach is an easier way to extract the physical meaning of the results. The crystal structure of monolayer phosphorene is a puckered honeycomb lattice where phosphorus atoms exist on two parallel planes. So, the external vertical electric field can modify the electronic structure by introducing the potential difference between the two planes. The vertical electric field decreases the energy gap due to the increase of the valence and conduction band width. The isolated midgap edge state at the zigzag edge splits into two subband corresponding to the two phosphorus planes. The parallel magnetic field can affect the electronic structure since the puckered lattice of phosphorene has finite thickness. It introduces the alternative magnetic flux into each hexagonal plaquette. The parallel magnetic fields break the degeneracy in the bulk and edge spectrum. The energy spectrum periodically changes against the flux quantum number passing through a single plaquette.

P164

Temperature dependent photoluminescence properties of monolayer molybdenum ditelluride

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Transition-metal dichalcogenides (TMDs) show emerging research interest as beyond graphene materials due to its novel properties and potential application in various fields i.e., fundamental research, photonic and device fabrication. TMDs have novel physical properties of tunable electronic structures and spin-valley coupling nature. Molybdenum ditelluride ($MoTe_2$) is a member of TMDs, with bandgap energy at 1.09 eV in the spectral range of near-infrared region [1]. We have performed spectroscopic measurement on different layers of MoTe2 exfoliated in silicon and quartz substrate. The layer thickness was confirmed by atomic force microscope (AFM) and Raman measurement. We performed temperature dependent reflectivity, photoluminescence (PL) measurement to understand the detail excitonic properties of monolayer and two layers MoTe2. The Raman spectra of MoTe2 with various layer thicknesses show significant frequency shift of $E^{1}_{2}g$ mode in monolayer $MoTe_2$. With decreasing temperature, the PL peak is shifted towards higher energy side. Moreover, two clear peaks (1.16 and 1.19 eV) are observed at low temperature (<40 K), which are assigned as the radiative recombination of free-excitons and charged excitons (trion), respectively. We will discuss the detail information of exciton relaxation dynamics and valley-polarization dynamics of $MoTe_2$ in the presentation.

Reference
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P165

Influence of electric double layer carrier injections on optical absorption spectra of CVD synthesized multi-layered MoS2 and WS2 thin films

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Transition metal dichalcogenides (TMDCs) are atomically thin two dimensional semiconducting crystals. TMDCs have a strong spin-orbit coupling originated from the d orbitals of the heavy metal atoms. The conduction and valence-band edges are located at the K points of the 2D hexagonal Brillouin zone, and the strong spin-orbit coupling induces the spin splitting at the valence band top. For the manipulation of electronic states of TMDCs, electric double layer carrier injection techniques are widely used, and various physical properties have been manipulated, such as superconducting states and circular polarized light emissions. However, whether the carrier injection can selectively inject holes on the one of the splitting electronic states has not been clarified yet. Such selective carrier injection will contribute to the valleytronic applications. To clarify the above question, in this study, we investigated the influence of electric carrier injections on optical absorption spectra, especially A and B exciton optical absorption bands, which are caused by the spin splitting, of multi-layered MoS2 and WS2 thin films, which were synthesized by chemical vapor deposition methods, and we found that electrons can be injected, inducing the disappearance of A and B exciton bands, but not be extracted in our CVD grown samples.

P166

One-shot K-region selective annulative pi-extention of polycyclic aromatic hydrocarbons for nanographene synthesis

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The optoelectronic nature of two-dimensional sheets of sp^2-hydridized carbons (e.g. graphenes and nanographenes) can be dramatically altered and tuned by altering the degree of pi-extension, shape, width, and edge topology. Among various approaches to synthesize nanographenes with atom-by-atom precision, one-shot annulative pi-extension (APEX) reactions of polycyclic aromatic hydrocarbons (PAHs) hold significant potential not only to achieve a growth from template synthesis of nanographenes, but also to fine-tune the properties of nanographenes.
Herein we describe one-shot APEX reactions that occur at the K-region (convex armchair edge) of PAHs by the $Pd(CH_3CN)_4(SbF_6)_2$/*o*-chloranil catalytic system with silicon-bridged aromatics as pi-extending agents. DFT calculations suggest that the complete K-region selectivity stems from the olefinic (decreased aromatic) character of the K-region. The protocol is applicable to multiple APEX and sequential APEX reactions to construct various nanographene structures in a rapid and programmable manner.

Ref: Ozaki, K.; Kawasumi, K.; Shibata, M.; Ito, H.; Itami, K. Nature Commun. **2015**, 6, 6251.

P167

Fabrication of densely aligned suspended graphene nanoribbons array by plasma CVD and its growth mechanism

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Graphene nanoribbons (GNRs) are candidate material for next-generation transistors because of their electrical transport gap. Up to now, we developed a novel plasma CVD method [1] with Ni nanobar for directly fabricating suspended GNRs devices [2]. However, the growth yield of suspended GNRs is low and understanding the growth mechanism is required to solve this problem. In this study, we found that the stability of Ni nanobars can be drastically improved during plasma CVD. Since GNRs nucleate during the cooling process, the Ni nanobar structure has to be maintained even under the high temperature condition (just before cooling) for the growth of suspended GNR. Our experimental results show plasma CVD can improve the thermal stability of Ni nanobar, resulting in the formation of suspended GNR. By following this growth model, precise adjustment of plasma CVD conditions was carried out. As a result, the yield of suspended GNRs growth can be improved (~ 90%) and the high density GNRs array has been successfully fabricated.

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P168

Fabrication of MoS_2 thin films on flexible substrates using water-based MoS_2 nanosheets dispersion

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Transition metal dichalcogenides (MCh2s) nanosheets have attracted interests as next-generation nanoelectronic materials for low-power/high-performance transistors, memory devices, thermoelectric devices, and solar cells, since their single-layer present large intrinsic bandgaps and large in-plane mobility. Moreover, MCh2s nanosheets are suitable to flexible devices due to their ability to reversibly undergo high strains. The preparation of large area and high quality MCh2 thin films is an important step in various applications. Using dispersion of MCh2 nanosheets can offer routes to mass production of MCh2s thin films at relatively lower energy and less time consuming. In this work, we present the results of fabrication and characterization of MoS2 thin films on flexible substrates using water-based MoS2 nanosheets dispersion.

MoS2 thin films on flexible substrates were fabricated by dropping of the dispersion with exfoliated MoS2 nanosheets. Poly ethylene terephthalate, polyethylene naphthalate, polyimide and printing papers were used for the substrates. Highly dispersed MoS2 nanosheets in water were prepared by the Li-intercalation method using n-buthyllithium in hexane. To remove excess Li atoms, purification by dialysis were performed after exfoliation. Morphology of the films was investigated by an optical microscope and an atomic force microscope. The detailed results including of electrical characterization will be discussed.

P169

Electrochemical exfoliation of graphite intercalated compounds

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Few-layer graphene intercalated compounds, such as one with FeCl3 (FLGraIC), are attractive materials for transparent conducting electrodes. For the bulk production of FLGraIC, exfoliation of FeCl3 intercalated graphite compounds (GICs) in solution is highly desirable. However, most intercalants are readily eluted by common solvents. In order to avoid elution, it is important to exfoliate GICs in a short time with a passivation layer over GICs. In this study, we report mass productions of FLGraIC by electrochemical exfoliation of GICs using surfactants, like carboxymethyl cellulose (CMC) and sodium dodecyl sulfate (SDS), as passivation layers. It was found that, whereas CMC reduced elution, SDS was not effective. We propose that the long chain of CMC coated on the surface of GIC is one of the important factors to prevent the elution of FeCl3 from the GIC. In addition, FLGraIC was successfully obtained within a potential window between +2 V and +4 V vs. Ag/AgCl. Also, the exfoliation had taken place slightly faster than the degradation of GICs.

P170

Electric field effect in layered strongly correlated materials A Ga_2S_4 (A = Ni, Fe)

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A Ga_2S_4 (A = Ni, Fe) are of considerable interest since they are candidates to exhibit novel spin liquid state due to their geometrically frustrated spin systems. A Ga_2S_4 (A = Ni, Fe) are two dimensional layered Mott insulating materials with triangular lattice of A site containing S = 1 and 2 spin, respectively. Each layer is separated by van der Waals gap as in the case of graphene and transition metal dichalcogenides. Recently, we have succeeded in fabricating the ultra-thin films of A Ga_2S_4 by mechanical exfoliation. In this study, we fabricated electric field-effect transistors with ultra-thin films of A Ga_2S_4 and investigated the electric field effect of them. We achieved carrier doping into Mott insulating state and found that both compounds show typically *p*-type field effect that the resistances of both compounds are decreased monotonously by applying negative electric field. Especially, it is also found that with increasing negative gate-voltage, the activation energy is decreased in $NiGa_2S_4$. These results suggest the Mott gap closing due to hole doping and the possibility of the observation of Mott transition.

P171

Control of optoelectrical property of few-layer tungsten diselenide with mild O2 plasma treatment

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Atomically-thin two-dimensional (2D) sheets attract intense attention for their superior electrical and optical features. Transition metal dichalcogenide (TMD) is known as a 2D material with excellent semiconducting properties. Monolayer TMD has strong Photoluminescence (PL) intensity for its direct band gap [1]. Although multi-layer (2-5 layers) TMD doesnt show bright PL because of its indirect band structure, its carrier mobility is higher than that of monolayer one. For the fabrication of high performance optoelectrical device, it is required to combine these optical and electrical properties of mono- and multi-layer TMD, respectively.

In this study, we investigated the electrical and optical properties of few-layer tungsten diselenide (WSe_2) before and after mild plasma treatment [2,3]. We found that mild O_2 plasma treatment can drastically enhance PL intensity of WSe_2, whereas the initial electrical properties of WSe_2 can be maintained even after the mild plasma treatment. This result indicates the mild O_2 plasma treatment can fabricate functionalized TMD including better optoelectrical features.

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P172

Atomically precise semiconductor graphene and hBN interfaces by Ge intercalation

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The integration of graphene and hexagonal boron nitride (*h* BN) into semiconductor technology requires their synthesis on semiconducting surfaces, which is still a challenge due to the low catalytic activity of these substrates in the chemical vapor deposition process. Here we report on the intercalation of monolayer Ge under epitaxial graphene (and *h* BN) on Ni (111). This results in atomically precise interfaces between these 2D materials and Ge with GeC_6 and GeB_3N_3 stoichiometry and sqrt3xsqrt3 reconstruction. Semiconductor interfaces prepared in this way decouple the 2D layer electronically from the substrate and lead to the restoration of the Dirac cone of graphene as well as the unperturbed electronic structure of h BN. Photoemission study of alkali-metal doped graphene shows that the intercalated Ge layer prevents charge leakage to the metal substrate, thereby allowing higher doping levels of graphene. This leads to an increase in electron-phonon coupling and thus raises the superconduction transition temperature. Moreover Ge intercalation leads to new adsorbate patterns, as compared to bulk GICs and graphene on metals (i.e. we have found a BaC_8 phase). Together with the application potential of Ge nanostructures this new interface is a path for the integration of graphene and *h* BN into state-of-the-art semiconductor technology.

P173

In-plane polarization in bilayer graphene nanoribbon induced by interlayer voltage

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We theoretically show that in a bilayer graphene nanoribbon, an in-plane polarization along the ribbon direction is induced by an external interlayer bias voltage. This transverse response appears for insulating bilayer nanoribbons with armchair edges, but not for those with zigzag edges. By using a tight-binding model, we show that the polarization exhibits different behaviors depending on the width in a novel way. Interestingly, when the interlayer bias voltage is weak, the polarization has opposite signs depending on the ribbon width modulo three. This difference can be understood by an effective two-band model, constructed from the tight-binding model. Furthermore, the results of our ab initio calculations well agree with the results of the tight-binding model. On the other hand, under a strong bias voltage, we find that the polarization takes one-third or zero depending on the width modulo three.

P174

Tunnel magnetoresistance in ferromagnetic layered dichalcogenide van der Waals junctions

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Various heterostructures based on different 2D materials can be fabricated by utilizing van der Waals (vdW) force. Here we demonstrate that magnetic tunnel junctions can be built by connecting flakes of layered ferromagnetic dichalcogenide $Fe_{0.25}TaS_2$. The crystal of $Fe_{0.25}TaS_2$ can be mechanically cleaved at the vdW gap and by using dry transfer technique, the $Fe_{0.25}TaS_2/Fe_{0.25}TaS_2$ junction can be fabricated. The cross-sectional transmission electron microscope image shows the presence of the well-defined vdW interface between the flakes and at the interface, the thin layer of oxide exists. We observe clear tunnel magnetoresistance (TMR) signals by measuring resistance under an external magnetic field perpendicular to the 2D plane. Comparing with the anisotropic magnetoresistance (AMR) of top and bottom $Fe_{0.25}TaS_2$ flakes, the observed TMR can be assigned to the switching between parallel and anti-parallel magnetic configuration at the vdW junction. Our results demonstrate the spin polarized tunneling through the vdW interface built from a layered material and open up the possibility of integrating layered ferromagnetic material Fe_xTaS_2 into the vdW heterostructures.

P175

PN-type photodiodes of large-area WSe_2 monolayer thin films

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Monolayer transition metal dichalcogenides (TMDCs) are promising materials for optical sensing applications owing to pronounced surface effects because of very high surface-to-volume ratios and Debye lengths comparable to their feature sizes. Although many excellent photodetectors with high photoresponsivity and light power conversion have already been fabricated, chemically formed PN-type photodetectors have not yet been performed due to lack of doping methodology. Here, we report the optoelectronic properties of large-area WSe_2 thin film PN photodiodes formed by freezing-while-gating technique, which is firstly demonstrated by Zhang et al. [1] Large-area WSe_2 thin film was prepared by chemical vapor deposition [2] and PN junctions were electrochemically formed by ion gels. Finally, these PN junctions were stabilized by freezing of biased ion gels. We successfully observed photo-current under monochromized light (730nm) and investigated internal quantum efficiency of 1.35%. This would open the route for the application of WSe_2 thin films as PN-type photoelectrical devices.

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Tuesday

K2

Overcoming historical challenges in carbon nanotubes and nanoribbons to enable their application in transistors and photovoltaics

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Carbon nanotubes and graphene-related materials are among the best charge transport materials ever discovered. The transformative potential of these materials in electronics and optoelectronics has already been demonstrated, on a single nanostructure level. However, implementing these exceptional materials in scaled, large-area, high-performance applications involving many nanostructures has been much more difficult. My work addresses challenges – in controlling the growth, processing, ordering, and heterogeneity of carbon nanomaterials and in understanding phenomena beyond the scale of single nanostructures – that must be overcome to exploit these materials in (opto)electronics technology.

Along these lines, I will present on 3 inter-related areas: (1) *Achieving highly monodisperse semiconducting carbon nanotubes without problematic metallic nanotubes and depositing these nanotubes into useful, organized arrays and assemblies*. We have recently pioneered a scalable approach for depositing aligned arrays of ultrahigh purity semiconducting nanotubes called floating evaporative self-assembly (FESA) that has allowed us to create the highest performance carbon nanotube field effect transistors (FETs) ever demonstrated, using on-conductance and on/off ratio as key metrics. (2) *Unlocking the potential of carbon nanotubes as light absorbers in macroscopic, thin film photovoltaic photodetectors and solar cells*. We have discovered how to efficiently harvest photons from thin films of nanotubes by driving the dissociation of photogenerated excitons using donor/acceptor heterojunctions. The efficiency of these devices is determined by the flow of energy in these films that we have temporally resolved and understood using a particularly broadband form of two-dimensional white light ultrafast spectroscopy. (3) *Creating graphene nanoribbons with smooth edges via a combination of top-down and bottom-up methods that can be extended to the large scales necessary for technology*. We have recently discovered a new CVD-based synthesis for high aspect ratio, self-aligned armchair nanoribbons that are < 10 nm in width but 100's of nanometers in length, with smooth edges.

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I3

Beyond carbon nanotube thin-film transistors: Logic circuits, memory, and heterostructures

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With the availability of large quantities of electronically monodisperse carbon nanotubes (CNTs), homogeneous semiconducting CNT thin films can be produced through a variety of solution-based methods including vacuum filtration, dielectrophoresis, evaporation-driven self-assembly, aerosol jet printing, and inkjet printing. Through careful integration of these thin films with high-k gate dielectrics, CNT thin-film transistors (TFTs) can achieve device metrics that are competitive with polycrystalline silicon and amorphous oxide semiconductors. Furthermore, with appropriate device geometries, doping schemes, and gate electrode materials, threshold voltage can be tuned to enable enhancement-mode p-type and n-type TFTs, resulting in CNT CMOS logic gates with subnanowatt static power dissipation and full rail-to-rail voltage swing. While these results suggest that very-large-scale integration (VLSI) should be possible for CNT thin-film circuits, further improvements are needed in CNT TFT large-area spatial homogeneity and long-term environmental stability. Towards these ends, this talk will introduce encapsulation schemes and automated measurement strategies that yield wafer-scale CNT TFT arrays with sufficiently tight control over on/off ratio, subthreshold swing, and threshold voltage for VLSI CNT thin-film circuits. Using this methodology, large-area arrays of fully functional CNT TFT static random access memory (SRAM) cells are demonstrated with desirable static noise and write margins.

I4

Recent advances in understanding carbon nanotube growth through atomic scale simulationss

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Although growth of materials is a pre-eminently experimental area of research, computational studies in general, and atomistic simulations in particular, have contributed significantly to our understanding of the metal-catalyzed CNT growth process. Such simulations have indeed resolved many key issues and revealed a manyfold of detailed insights in the growth mechanism, including e.g. an atomistic view on carbon dissolution and surface seggregation [1, 2], carbon polyyne formation at the surface [3], and cap lift off [4, 5]. First, I shall highlight a selection of simulations which have provided such insights and demonstrate how they have contributed to our understanding of the growth process [6]. Subsequently, a number of recent efforts will be highlighted which address previously uncovered areas, including ion bombardment [7, 8], growth from hydrogen containing growth precursors [9], and the application of accelerated atomic scale techniques for studying the dynamics of the growth process [10].

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I5

Computational Approach to Electrical Contacts in Carbon Nanotube Transistors

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Electrical properties of low-dimensional devices are dominated by the contact resistance. For carbon nanotube field effect transistors (CNT-FETs) [1], as for graphene [2] and MoS_2 transistors, the electrical contacts are a key factor limiting device performance. Contact resistance reflects a complex interplay of many factors. With advances in scaling, the contact resistance and transfer length are becoming even more critical. We have developed a general purpose CNT device simulator which is unique in including quantum-mechanical tunneling, both acoustic and optical-phonon scattering, as well as the crucial transfer of carriers between the CNT and metal contact. CNT-FETs integration requires closely-spaced arrays of tubes, with several tubes per device, to give adequate drive current. We find that with scaling of the tube spacing toward smaller pitch, there is a structural transition to a geometry in which the metal poorly wets the nanotube and substrate. This gives a sudden decrease in contact adhesion, and probably also an increase in contact resistance. Several interesting aspects of the wetting geometry will be discussed [3].

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C7

Structure of double wall carbon nanotubes by combining a robust HRTEM approach and tight binding calculations

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Single-walled carbon nanotubes (SWNTs) have shown oustanding capabilities in the realization of new functional devices but are extremely sensitive to any slight changes in their environment, altering their physical properties. A strategy to overcome this difficulty could be to use double-walled carbon nanotubes (DWNTs), consisting of two concentric tubes, provided to know how they interact each other. To this aim, we have developed a systematic and robust procedure using acHR-TEM (aberration corrected Transmitting High Resolution Electron Microscopy) and image simulations to study the atomistic structure of over one hundred CVD made DWNTs. Using these tools, we have established some interesting statistics on helicities and diameters of inner and outer tubes of the DWNTs inspected.

Results reveal the existence of a strong coupling between the two concentric tubes, resulting in favoring high helicity angle configurations for DWNTs with outer diameters below 2 nm. The nature of the coupling and the observed selectivity are discussed with the help of energy calculations based on a tight binding approach [1].

[1] A. Ghejatti et al, in preparation 2015

C8

Growth of high-density horizontally aligned SWNT arrays using trojan catalysts

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The applications of single-walled carbon nanotubes (SWNTs) based electronics require horizontally aligned SWNT arrays with the density more than 125 SWNTs μm^{-1}. During the past decades, significant efforts have been directed towards growth of high-density SWNT arrays. However, obtaining SWNT arrays with eligible density and larger area still remain a big challenge. Herein, we developed a rational approach to grow SWNT arrays with ultra-high density by using Trojan catalysts. SEM image and AFM image confirm that the density is as high as 130 SWNTs μm^{-1}. Also, by combining Trojan catalysts (release form substrate, assure ultra-high density) with Mo nanoparticles (loaded on surface, stabilize the released Trojan catalyst) as cooperating catalysts (We named the two synergetic catalysts as Trojan-Mo catalysts), the ultra-high density SWNT arrays with wafer-scale can be grown. These results confirm a high potential application of SWNT arrays in nano-electronics.

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C9

Selective cloning of (9, 4) carbon nanotubes by chemical vapor deposition

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For the applications of single-chirality carbon nanotubes such as nanotube-based devices and bioimaging, proliferation of chirality-sorted nanotube is highly desired. We used chirality-sorted (9, 4) nanotubes which were obtained by gel column chromatography [1] as the seeds for cloning, and optimized re-growth conditions of the seeds by chemical vapor deposition with ethanol as the carbon feedstock. The key for re-growth was activation of the seed edges by oxidation and water-vapor treatment as previously reported [2]. Re-grown nanotubes on a quartz substrate have an average length of ca. 50 um with a line density of 1/um. We also succeeded in growing suspended nanotubes between micro-pillar patterns and measuring photoluminescence from them. The chirality assigned by photoluminescence measurements was exactly (9, 4), confirming successful cloning. Since (9, 4) nanotubes have excitation and emission wavelengths of photoluminescence in the windows of absorption and scattering from tissues, the present method provides a route for production of the fluorescent material for bioimaging.

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C10

Origination of chirality selectivity in single-walled carbon nanotube growth catalyzed by tungsten-based intermetallic compounds: a theoretical study

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Synthesis of single-walled carbon nanotubes (SWNTs) with identical specific chirality is the paramount objective in the catalytic chemical vapor deposition (CCVD) method. Using tungsten-based intermetallic compounds as catalysts, we have achieved unprecedented high selectivity towards SWNTs with specific chiralities[1]. In this study, there are experimental evidences showing that the unique structure of the catalyst may act as the structural template for SWNT. Then we systematically studied the structural match between SWNTs and different catalysts with first-principles calculations. The structural match energy variations in the tungsten-based intermetallic compounds are universally higher than those in the corresponding monometallic catalysts, implying a higher specific selectivity towards certain chiralities. Anisotropic structures of the tungsten-based intermetallic compounds, i. e. lower symmetry and unique atomic arrangements are key factors for their high single-chirality selectivity towards SWNTs.

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P176

Real-space analysis of diffraction data as a tool of structural characterization of graphene-like materials

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In this study samples were obtained from chemically treated graphite, and chemically and heat treated saccharose and cellulose. Wide Angle Scattering whether Neutron (WANS) or X-ray (WAXS), can be a powerful tool to investigate graphene-like materials. However, data must be analyzed in real space too, thus adapting methods used for amorphous materials proves to be valuable. As such, Pair Distribution Function (PDF) should be calculated. If we combine PDF with computer simulations, we can obtain valuable information about sizes of coherently scattering regions and the presence of topological defects in the honeycomb lattice. In our study we combined the paracrystalline model with Molecular Dynamics (MD) simulations. The paracry-stalline model can quickly provide information such as number of layers or their size. It also allows estimation a degree of disorder within the system. As for physical implementation of that disorder MD simulations were performed. Point type defects such as mono-vacancies, di-vacancies and Stone-Thrower-Wales type of defects were considered. Such approach yielded good agreement between the model based simulations and the experimental data.

P177

Nitrogen ion implantation in carbon nanostructures.

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The grafting of functional groups in a controllable way is a feasible reproducible solution to tailor the electronic properties of sp^2-carbon nanostructures. In this frame-work, nitrogen doped graphene and carbon nanotubes have gained interest from both technological and fundamental point of view. A key issue, not yet solved, is the development of a strategy to control precisely over the possible different nitrogen atom configurations (pyridinic, pyrrolic and graphitic) in the carbon lattice, leading to difficulties in understanding how the C-N bond configuration impacts in their electronic properties.

We will discuss the nitrogen incorporation via plasma treatments in vertical aligned carbon nanotubes and suspended graphene through valence band photoemission spectroscopy (UPS) and scanning X-ray photoelectron spectromicroscopy (SPEM) measurements. The creation of defects induced by energetic particles drives the grafting of nitrogen. A different behaviour at the CNT tips with respect to the sidewalls was observed. On the tip, the presence of natural defects is involved in different bonding formation between carbon and nitrogen atoms, while at the sidewalls the bonding is similar to graphene. The effect of thermal heating was evaluated allowing the identification of the most thermal stable nitrogen species and the tuning of their presence in the lattice.

P178

Plasma fluorination of vertically aligned carbon nanotubes: tuning wettability

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There is interest in spatially selective wettability of surfaces at the micro- and nanoscale for controlling fluid flow in fluidics applications. In this context, carpets of vertically aligned carbon nanotubes (v-CNTs) provide a promising superhydrophobic surface coating, however to date it has proven difficult to tune their wettability.

Here we show that functionalization of v-CNT carpets performed via exposure to Ar:F_2 RF plasma provides a rapid, one-pot, scalable, spatially selective route to control the wettability/hydrophobicity of nanotube carpets. Rapid fluorination was observed via X-ray photoelectron spectroscopy (XPS) with surface fluorine concentration, bonding type, and patterning dependent on exposure time. Surface properties of v-CNTs forests can be controlled by the introduction of fluorine-containing groups, as demon-strated via surface wettability studies, while scanning electron microscopy shows that overall nanotube alignment and separation is conserved. Scanning X-ray photoelectron spectromicroscopy (SPEM) shows that the plasma treatment results in selective functionalization of the surface tips of the nanotubes. This opens the way to design nanotube carpet structures with tailored activated surfaces, which maintain the desirable conductive properties for the majority of the nanotubes length.

P179

Asymmetric dyes aligned inside carbon nanotubes yield a large nonlinear optical response

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Asymmetric dipolar molecules, acting as electric rectifiers with a large second-order nonlinear optical (NLO) response, find applications in ultrafast electro-optic switches for optical telecommunication networks and wavelength conversion of lasers. Such dipolar molecules tend to align in a pairwise anti-parallel way, thus cancelling each others directional properties.

By encapsulating such elongated dyes inside single-wall carbon nanotubes (SWCNTs), Coulomb interactions favor a polar head-to-tail alignment of the dipoles, leading to a cooperative enhancement of their second-order NLO responses.[1] The encapsulation is evidenced by fluorescence-excitation [2] and resonance Raman [3] experiments. Hyper-Rayleigh scattering experiments[4,5] (i.e. second-harmonic light scattering) show that the nanohybrids possess giant NLO responses, corresponding to ~70 aligned dyes. Their equally giant dipole moment and size promises a good and stable alignment in a polymer film, which opens up an entirely new route to the rational design of solution-processible yet stable NLO materials.

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P180

Chirality-dependent mechanical response of empty and water-filled single-wall carbon nanotubes at high pressure

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Single-walled carbon nanotubes (SWCNTs) combine a high mechanical resilience with a low density. We studied the mechanical stability of 18 different SWCNT chiralities (diameter range = 0.6-1.42nm) at high pressure by high-resolution resonant Raman and wavelength-dependent fluorescence-excitation spectroscopy. For small diameter SWCNTs (d<1nm) with a chiral angle of ∼12°, in particular for the (7,2) SWCNT, an anomalous behavior is observed, revealing an increased radial instability.

High-resolution spectroscopy of bile-salt solubilized SWCNTs [1] furthermore allows to resolve the different behavior of empty (closed, pristine) and water-filled (opened) SWCNTs [2-4] at high pressure, and reveals that water-filling exerts a stabilizing counter pressure on the SWCNT walls, leading to an increasing difference between the RBM frequencies of water-filled and empty SWCNTs at elevated pressures. We ascribe the longstanding contradiction between experiments and theory on the collapse pressure of SWCNTs to the presence of filling in most experiments to date, while empty SWCNTs follow the theoretically predicted collapse behavior.

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P181

Mechanical and thermal properties of graphene-polymer interfaces

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Graphene has been increasingly used as nano sized fillers to create a broad range of nanocomposites with exceptional properties. The interfaces between fillers and matrix play a critical role in dictating the overall performance of a composite. However, the load transfer mechanisms along graphene-polymer interface and interfacial thermal conductance have not been well understood. In this work, we conducted molecular dynamics simulations to investigate the influence of surface fictionalization and layer length on the interfacial load transfer in graphene-polymer nanocomposites. The interfacial thermal conductance and its dependence with surface fictionalization were also studied, taking into account the effects of model size and thermal properties of graphene. The simulation results show that oxygen-functionalized graphene leads to larger interfacial shear force than hydrogen-functionalized and pristine ones during pull-out process. Some models were established to demonstrate interfacial load transfer mechanisms and estimate the thermal conductivity in nanocomposites. These results are believed to be useful in development of new graphene-based nanocomposites with better interfacial properties.

P182

Third-order nonlinear optical properties in graphene oxide

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Nonlinear optical properties in nano-carbon systems such as single-walled carbon nanotubes are interesting topics for both fundamental material science and application of new optical devices. Many theoretical and experimental works have been done in nonlinear optical properties for single-walled carbon nanotubes. Recently, nonlinear optical properties in graphene oxide have been reported by several groups. However, these studies have been done only at 532 nm and 1064 nm. In order to clarify the mechanism of nonlinearity, we need to investigate the optical nonlinearity at various photon energies. In this study, we have measured third-order nonlinear susceptibility of graphene oxide by a Z-scan method around the absorption edge of 1.55-2.26 eV which corresponds to the energy region of photoluminescence band. The absolute value of imaginary part of third-order nonlinear susceptibility increases with increasing photon energy. On the other hand, the figure of merit of nonlinearity (the ratio of third-order nonlinear susceptibility to absorption coefficient) increases with decreasing photon energy. This result can be explained by the nanodisc model which is composed by the graphene nanodisc embedded in graphene oxide.

P183

True-color real-time imaging and spectroscopy of carbon nanotubes on substrate by enhanced rayleigh scattering

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Single-walled carbon nanotubes (SWCNTs) illuminated by white light should appear colored due to resonance Rayleigh scattering. Different colors imply different chiral indices, according to the Rayleigh spectra and the false color images of SWCNTs. However, the nanometer sized diameter and extremely small scattering cross-section of an individual SWCNT prevent its visualization under an optical microscope. Here we show that Rayleigh scattering can be enhanced by the near field of interface optical dipoles. Consequently colorful SWCNTs on various substrates can be directly observed under an optical microscope by wide field supercontinuum laser illumination. The true color image of SWCNTs provides the information of not only position and morphology, but also the chiral indices, which will greatly speed up chirality-related studies. Furthermore, Rayleigh imaging assisted spectroscopy (RIAS) is developed for in-situ characterization of SWCNTs, such as Rayleigh and Raman spectroscopy, which facilitates high throughput chirality assignment of individual SWCNTs.

P184

Momentum-resolved detection of the electron-phonon scattering in graphene by using ARPES

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We investigate the electron-phonon scattering in the single-layered epitaxial graphene on SiC by using the angle-resolved photoelectron spectroscopy (ARPES) in a similar way to a recent study of graphite[1]. In this study, we directly detect the indirectly photoexcited electron which is simultaneously scatted from the Dirac cone by the phonon. Due to the energy and momentum conservation-laws in the scattering process, the phonon which participates the electron-phonon scattering can be probed with resolving the momentum and energy by using ARPES. It is found only the TO-phonon is responsible for the scattering, and its dispersion near the K-point is deduced. The derived dispersion curve of the TO phonon in graphene is very similar to that in graphite. A striking difference between graphite and graphene is that interplane vibrations (ZA and ZO modes), which are clearly resolved in graphite by using the photon of about 7-eV, is not detected at any photon energies in graphene. We discuss the physical origin of this difference.

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P185

Raman spectroscopy on graphene-based multifunctional hybrid structures

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Integration of thin metal oxide films or nanowires, with interesting carbon nano-materials, such as graphene, offers a promising way to develop high-performance hybrid structures for optoelectronics, energy harvesting and battery applications. The overall properties and the device performance of these hybrids are strongly dependent on the interaction/interface between the graphene and the substrate material. Raman spectroscopy along with hyperspectral imaging was used to probe and understand the interfacial behavior between graphene and a number of substrates with varying thickness, surface roughness and crystallinity. Surface roughness induced strain at the graphene-substrate interface was studied using Raman spectroscopy, where peak position and intensity of G and 2D bands were investigated. Moreover, we developed graphene-nanowire heterostructures for Li-ion batteries by synthesizing a conformal graphene coating over vertically aligned Ge nanowires. The intensity and peak position of G and 2D bands present in the graphene Raman spectra were monitored as a function of the diameter of Ge nanowires. Lastly, Raman spectroscopy can be employed as a unique non-destructive probe to better understand the substrate/interfacial effects in graphene-based hybrids and hetero-structures for the development of new multifunctional devices with improved performance far-beyond that of the individual components.

P186

Structural and chemical evaluation of electrodes in nanotube-based electrical devices

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The use of carbon nanotubes (CNTs) as an alternative to silicon electronics has been a widely explored topic for the last two decades. In this respect, while much attention has been given to the transport properties of CNTs, less is known about the circuits parts that interact directly with them. To start with, there is less-than-desirable information on contamination of the objects of interest by the fabrication methods employed. Likewise, questions as to how do the contacts evolve with processing of the devices (e.g. contact curing) or throughout their lifetime are often overlooked.

Following the above, we have been studying the electrodes and contamination of simple carbon-based nanodevices. Of the commonly fabrication methods employed, we chose electron beam lithography (EBL), ion beam induced deposition (IBID) and electron beam induced deposition (EBID). Dispersed nanotubes were contacted on a four-probe configuration and analyzed before and after curing of the contacts, a trivial step to optimize the contact resistance. Spectroscopical and microscopical characterization shows that the contacts undergo a structural change upon curing, being particularly pronounced in the case of EBID. This situation will have repercussions in the interpretation of the electrical properties as well as in the assumptions made on device durability.

P187

Ballistic and diffusive thermal conductivity of graphene

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Thermal conductivity of graphene is calculated as a function of temperature and sample size in which a crossover from diffusive to ballistic thermal conductivity occurs. The diffusive thermal conductivity of graphene is evaluated by calculating the phonon mean free path for each phonon mode in which anharmonicity of the phonon and phonon scattering by 13^C isotope are taken into account. Here we show that phonon-phonon scattering of out-of-plane acoustic phonon mode by the anharmonic potential is essential for the largest diffusive thermal conductivity around 5000W/mK. The diffusive thermal conductivity monotonically increases with decreasing temperature. When the phonon mean free path is larger than the sample size (1 to 20 micron), the ballistic thermal conductivity appears at low temperatures (300 to 50K) in which the ballistic thermal conductivity increases linearly with increasing the temperature. When the sample size increases, the maximum thermal conductivity increases and the corresponding temperature decreases. We will design either large thermal conducting device for heat controlling materials or small thermal conducting materials for thermoelectric device.

P188

Characterization of hydrogenated carbon nanotubes by core level spectroscopy

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The nature of chemical bonding between carbon and hydrogen atoms on the surface and inside hydrogenated single-walled carbon nanotubes (H-SWNTs) was elucidated using the high-resolution near edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy. The experimental and theoretical investigations were done.

SWNTs (D=1.4-1.6 nm) were synthesized by an electro-arc method using Ni-Y catalyst. The SWNTs were hydrogenated at P ~ 5.0 GPa and T~500C and had 5.335 wt.% hydrogen. All measurements were performed using synchrotron radiation at the storage ring facility BESSY II of Helmholtz-Zentrum Berlin (Berlin, Germany). The possibility of H-SWNTs dehydrogenation was investigated also.

The C 1s x-ray absorption and photoelectron spectra showed formation of chemical bonding between the hydrogen and carbon atoms in H-SWNTs. In order to obtain a detailed understanding origin of the chemical bond between C and H atoms in H-SWNTs, semiempirical calculations were carried out.

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P189

Tunable thermal transport in suspended graphene and carbon nanotubes through strain wrinkling

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We study the influence of edge-strain-induced wrinkling [1] on thermal transport properties of suspended graphene nanoribbons and carbon nanotubes. The role of wrinkling in phonon scattering is calculated and illustrated by the phonon density of state. It was found that the ripples effectively scatter phonons of short wavelength. Such effect opens the ways to the control of thermal transport in low dimension materials and helps understanding experimentally measured thermal conductivity values always different from the theoretical limit.

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P190

Quantum optics of solitary covalent dopants in carbon nanotubes

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The discovery that nitrogen vacancy centers in diamond can serve as a solid-state analogue of trap ions has triggered the growth of a new branch in the field of Quantum Optics. By revealing the capability of NV centers for single photon generation and performing quantum processing/ storage operations, studies of this new branch have made far-reaching impacts in technologies that span from sub-diffraction imaging to photonic quantum information processing and quantum computing with defects. Recent studies have shown that such introduction of new optical transitions is also possible in single wall carbon nanotubes (SWCNTs) through the incorporation of low-level oxygen or diazonium covalent dopants on their side walls. However at this moment, there is no direct proof that these covalent dopant states can indeed behave as individual quantum emitters. Here, I will present a review of our recent low temperature single tube PL study that provides a first look into the electronic structure and chemical nature of oxygen doped SWCNTs. I will then present quantum optical experiments performed using state-of-the-art superconducting nanowire single photon detectors and report the observation of room temperature photon anti-bunching from a solitary dopant state emitting at wavelengths approaching 1300nm.

P191

Analysis of thermally induced C-N bonding in hydrazine-treated carbon nanotubes by synchrotron photoelectron spectroscopy

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In this study, the bonding properties of our non-oxidized carbon nanotubes (CNTs) treated with hydrazine vapor were investigated by synchrotron photoelectron spectroscopy. When the CNTs initially treated with hydrazine and then baked at 80℃ were probed by ultraviolet photoelectron spectroscopy (UPS), the results showed (i) damaged pi-bonding and (ii) the shift of the CNTs Fermi level toward the conduction band. A further 350℃-baking treatment on the hydrazine-treated CNTs could restore the damaged pi-bonding and shift the CNTs Fermi level back toward the valence band. When the CNTs treated with vapor-phase hydrazine and then 80℃-baking were probed by X-ray photoelectron spectroscopy (XPS), the results showed a significant increase in the signal corresponding to C-N bonding. A further 350℃-baking treatment on the hydrazine-treated CNTs could essentially eliminate the signal corresponding to C-N bonding. The fate of the thermally metastable C-N bonding could be related to the nitrogenous radicals, such as nitrene and amidogen, thermally decomposed from hydrazine. The chemical association of such nitrogenous radicals with CNTs generates metastable amino/aziridino derivatization on the surface of CNTs, which will disrupt the continuum of CNTs graphitic domains. Upon further baking, the disruptive functionalization can be eliminated to restore the graphitic sp^2-carbon bonding structure.

P192

Landau-Herring approach as applied to excitonic complexes in quasi-1D semiconductors

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A configuration space (Landau-Herring [1]) theoretical approach is developed to obtain the universal asymptotic relations for the lowest energy trion and biexciton binding energies in quasi-1D semiconductors [2]. Trions are shown to be more stable (have greater binding energy) than biexcitons in strongly confined quasi-1D structures with small reduced electron-hole masses. Biexcitons are more stable than trions in less confined quasi-1D structures with large reduced electron-hole masses. The theory predicts a crossover behavior, whereby trions get less stable than biexcitons as the transverse size of the quasi-1D nanostructure increases–quite a general effect which could likely be observed through comparative measurements on semiconducting carbon nanotubes (CNs) of increasing diameters. For a specific case of CNs with diameters ~1 nm, the trion binding energy is greater than that of the biexciton by a factor ~1.4, decreasing with the CN diameter, thus revealing the general physical principles that underlie recent experimental observations [3]. Supported by the US Department of Energy (grant # DE-SC0007117).

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P193

Electrical activation of dark excitonic states in carbon nanotubes

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Electric-field effects on exciton states in single-walled carbon nanotubes are investigated by simultaneous photocurrent and photoluminescence excitation spectroscopy. We utilize field-effect transistors with suspended carbon nanotubes in order to apply longitudinal fields [1]. Photoluminescence imaging and excitation spectroscopy are performed to locate individual nanotubes and to identify their chirality. When a bias voltage is applied, we observe an emergence of a new absorption peak near the first excited state in both photoluminescence and photocurrent spectra. With excitation at the new peak, photocurrent begins to flow above a threshold bias, while the luminescence intensity starts to decrease. Furthermore, we have found another bias-induced peak at a higher energy in the photocurrent spectra which has a threshold at a lower bias. Measurements of several nanotubes with different chirality reveal that the energy separation between these bias-induced peaks and the ground state of E_{11} excitons is inversely proportional to the tube diameter. The results suggest that the new peaks are the dark excited states of the E_{11} excitons which became optically active due to the applied fields.
Work supported by KAKENHI and APSA.

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P194

Improving the quality of carbon nanotube depositions through the use of mobile liquid interfaces

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We investigate the application of mobile liquid interfaces in improving the cleanliness of carbon nanotube (CNT) depositions. The samples are prepared on silicon substrates that have been rendered hydrophilic by a treatment in oxygen plasma, prior to CNT deposition by spin-coating from a solution of 1,2-dichloroethane. The CNT material is of the arch-discharge type, multi-walled variant that also contains irregular carbon-based debris stemming from synthesis imperfections.

In an experiment where such a freshly prepared sample is carefully immersed into a beaker containing ultrapure water, a radical cleaning effect is witnessed where most of the particulate debris is vacated from the surface due to the mobile contact line. Meanwhile, majority of the CNTs remain adhered onto the surface. Furthermore, apparent re-orientation of the CNTs is also seen in dedicated experiments.

In order to understand the processes involved on the macromolecular level, we explore the feasibility of a qualitative model to relate the interface forces and surface adhesion, based on earlier works including e.g. Joanny & DeGennes (1984), Gerdes et al. (1999) and Sharma et al. (2008). Implications of the discovery are demonstrated by utilizing the immersion cleaning technique in preparation of clean, semi-aligned CNT depositions on etched trench substrates.

P195

Dynamics of coherent phonons in metallic single-walled carbon nanotubes

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For understanding the ultrafast dynamics of electron-phonon coupling in metallic single-walled carbon nanotubes, we investigated coherent phonons by using a sub-10-fs ultrashort pulse laser. Coherent phonons of radial breathing, M, D, G, 2D, and 2G modes are clearly observed in time domain. By resolving the probe wavelength, we observed the resonance enhancement of the coherent phonon signals, which appears at different wavelength for different phonon modes. The energy difference between the peak wavelength and the excitonic resonance was approximately the same as the phonon energy, indicating the enhancement of stimulated Stokes Raman resonances. The amplitudes of these modes change drastically by applying the gate voltage, indicating the Pauli blocking of phonon excitation in these Raman resonances. The obtained results are analyzed by the windowed Fourier transformation, and the voltage and wavelength dependent frequency chirp was observed. The origin of the frequency chirping may be the change of the damping constant of G-mode phonons due to the Kohn anomaly. The relation to the relaxation dynamics of excitons will also be discussed. The results form a basis to understand the electron-phonon coupling in metallic single-walled carbon nanotubes.

P196

Interplay of electron-phonon and electron-electron interactions in gate modulated Raman spectroscopy of graphene

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The electron-phonon and the electron-electron interactions interplay in graphene and are observed in the Raman spectra around ∼ 1600 cm^{-1} (G band). The existence of the gapless linear energy bands (Dirac cones) in graphene modifies phonon energy, spectral broadening, and spectral lineshape of the Raman spectra. One of the well-known phenomena is the Kohn anomaly effect, in which the phonon energy (lifetime) becomes lower (shorter) due to the interaction between a phonon and an electron-hole pair in the linear energy band. The other phenomenon is the asymmetric spectral shape of phonon spectra, also known as the Breit-Wigner-Fano (BWF) lineshape, which long been observed in metallic nanotubes and recently observed in graphene as a function of Fermi energy. The origin of the BWF lineshape in graphene is due to the quantum interference effect of phonon spectra with the electronic Raman spectra (ERS) [1]. Taking both phenomena into account, we successfully reproduce the Fermi energy dependence of frequency shift, spectral linewidth, and spectral asymmetry of the G band Raman spectra [2].

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P197

In-situ synchrotron X-ray diffraction study of ion adsorption on single-walled carbon nanotube inner and outer surfaces

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Single-walled carbon nanotubes (SWCNTs) have been expected to be used as Li-ion battery (LIB) and electric double layer capacitor (EDLC) electrodes. However, it has not been understood very clearly how ions are adsorbed on the surfaces of SW- CNTs. Usually, some tens to hundreds of SWCNTs are gathered by van der Waals interaction and thereby bundle structures of SWCNTs are formed. It is well known that some broad X-ray diffractions of the bundle structure can be observed for well crystallized bundles. Therefore, by using the well crystallized SWCNT bundles whose SWCNTs have small diameter distribution, it is possible for us to observe the structural change with ion adsorption. Then we developed an electrochemical cell which can be used for the in-situ XRD measurements. We performed in-situ XRD measurements of SWCNTs using several kinds of electrolytes at beam-line BL18-C of KEK, Tsukuba, Japan. The detailed structural changes with ion adsorption will be discussed at the symposium.

P198

Graphene doping mechanisms by iodine molecules

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Since its discovery, significant researches have tried to understand and use the electronic transport properties of graphene to create more efficient new components. One way to improve significantly the conductivity of graphene is to put them in interaction with iodine vapor.

We have focused our computational effort including van der Waals forces, on the comparison of the adsorption modes and the induced modifications of the electronic structures (Fermi level shifts and hybridization of bands) by atoms and molecules belonging to the family of halogens, I and I_2 on a graphene layer. Our result confirm that the molecular state is more stable than the dissociated one and the molecule exhibits a transition phase from in-plane to perpendicular-to-plane of graphene when halogen concentration varies. It turns out that the primitive cell of graphene layer gives 5.55×10^{-3} electron to the I_2 and the hole areal density in surface unit cell is around 1.1×10^{13} cm^{-2}, corresponding to a Raman shift of 9 cm^{-1}. However experimentally charged complexes like I_3^- and I_5^- are detected. By looking at the interaction of agglomerated molecules with graphene, we propose a mechanism of formation of these ions compatible with the hole-doping observation of the carbon nanostructures.

P199

Electronic states in collapsed carbon nanotubes: Dependence on tube chirality and displacement

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We theoretically study effects of inter-wall interaction in collapsed carbon nanotubes, first directly calculating effective inter-wall interaction within an effective-mass scheme and second regarding collapsed tubes as ribbons of bilayer graphene with closed edges described by boundary conditions explicitly derived.

Within the effective-mass scheme, effects of inter-wall interactions are shown to be important in non-chiral nanotubes such as zigzag and armchair. In fact, with the increase in the width of the flattened region, the band structure approaches that of a bilayer ribbon in which the electron motion in the ribbon-width direction is discritized. In chiral nanotubes, inter-wall interaction can essentially be neglected except in the vicinity of non-chiral tubes. Inter-wall interactions diminish rapidly when chiral angle deviates from zigzag or armchair, although the decay is slower in the vicinity of the armchair tube. When the flattened region has the structure of AA and AB stacked bilayer graphene, the same results can be derived by calculating boundary conditions corresponding to the closed-edge structure in which the top and bottom layers are smoothly connected through a monolayer graphene.

P200

Chirality determination of carbon nanotubes using coherent phonon spectroscopy

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Using sub-10-fs pump-probe technique, we have extracted coherent phonons (CPs) of individual semiconducting carbon nanotubes (CNTs) from CNT aqueous solutions with mixed-chiralities. By resolving probe wavelength, we observed the CP oscillations of the radial breathing mode (RBM) throughout a wavelength range of 700 ~ 990 nm. By making two-dimensional (2D) Fourier transformed spectra as functions of the RBM frequency and probe wavelength, each chilarity component appeared at a specific point in the 2D plot, indicating the excitonic resonance of each RBM mode. The observed results are in good agreement with those observed in resonant Raman spectroscopy, indicating that our method allows a simple determination of the chirality distribution in CNT samples.

P201

Optical properties of substitutionally boron-doped- and thermally boron-dedoped graphenes

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Graphene has superior physical properties such as high electrical conductivity and carrier mobility. Such properties make graphene promising for the fabrication of electronic devices, supercapacitors, batteries, and sensors. However, graphene has a large difficulty in using as a semiconductor because of its zero-gap conducting property. In this sense, the introduction of foreign atoms, doping, has been commonly used to create the band gap in graphene.

In this work, we achieved p-type doping on graphite by substituting carbon atoms with boron atoms using high temperature thermal diffusion method, and then we have tried to extract boron atoms from boron-doped graphite sample. Because optical properties of graphenes strongly depend on the number of layers, we prepared mono-, bi-, and tri- layers of graphene using micromechanical exfoliation.The number of layer was identified by Atomic Force Microscopy(AFM). The effect of the boron-doping and the de-doping on graphene samples were evaluated by Raman spectroscopy and Kelvin Probe Force Microscopy. Interestingly, we observed two strong peaks(e.g., G- and G′-band) in the Raman spectra of graphene sample. Newly introduced Raman peaks such as D- and D′-bands were clearly identified in boron doped graphene. In case of thermally dedoped graphene, the intensity of D and D′ bands significantly decreased.

P202

Experimental detection of the squash mode and its polarization dependence in the extreme low vibrational frequency region of single walled carbon nanotubes

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There is considerable interest in the vibrational modes of carbon nanotubes (CNTs), in particular theory predicts the appearance of so called squash modes (SMs, with E2g symmetry representation) at very low frequencies. These SMs are predicted to be very sensitive to environmental changes and thus ideal as nanoscale probes.

Here we report clear experimental evidence for the existence of SMs of ordered, dry, single walled carbon nanotube (SWNTs) arrays with peaks as close as 18 cm-1 to the laser excitation. Furthermore, we confirm the theoretical predictions regarding the angular and polarization dependent variations of the SM's intensity with respect to the excitation. Additionally, using both SM and RBM data, we unambiguously assign the chirality and diameter of the SWNTs in our sample.

The novel Raman shifts and polarization dependent intensity cannot only be used to confirm the prediction of SMs but also to refine theory and to build up models which accurately reflect the ultra-low frequency behavior of SWNTs. Further investigations on these ultra-low frequency modes of SWNTs under high pressure will be discussed.

P203

Valley coupling in finite-length metallic single-wall carbon nanotubes

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Metallic single-wall carbon nanotubes (m-SWNTs) are ideal one-dimensional conductors of nanometer to micrometer length. Due to the confinement in finite-length, energy levels of electrons are quantized. Fourfold degeneracy of the energy levels has been considered as an intrinsic property of SWNTs reflecting the two non-equivalent, degenerate valleys of K and K' in the two-dimensional Brillouin zone together with two spins degrees of freedom. Recent measurements with ultraclean SWNTs have found fine structures of the order of sub-millielectronvolt in tunneling conductance spectra caused by spin-orbit interaction. On the other hand, the gate-dependent two- and fourfold oscillations in measurements may imply strong coupling of the two valleys.

We will show that the degeneracy of energy levels of m-SWNTs strongly depends on the chirality, boundary condition, length and the spin-orbit interaction by numerical and analytical calculations. The two valleys are strongly coupled for the so-called metal-2 nanotubes with both ends orthogonal-shaped edges as well as the armchair nanotubes. The effect of strong coupling combined with the asymmetric velocities appears as a vernier-scale-like spectrum, showing two- and fourfold oscillations as observed in experiments. For a so-called minimal boundary, fourfold degeneracy and its length-dependent lift are shown.

P204

Scanning electron microscopy imaging mechanisms of chemical vapor deposition grown graphene on Cu substrate

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The interaction of graphene and Cu is an important issue since Cu foils have been widely used as the substrate to synthesize monolayer graphene. In this presentation, the scanning electron microscopy (SEM) imaging mechanism of graphene on the Cu substrate is discussed. Graphene is formed by chemical vapor deposition on the Cu substrate. By treating the as-grown sample in different ambiences, the interaction of graphene and Cu substrate is varied. It is quite evident that the variation on their interaction affects the SEM contrast of graphene. Vacuum heating of as-grown sample leads to the coupling of graphene and Cu substrate, and the disappearance of graphene contrast from SEM. On the contrary, long time air exposure causes decoupling of graphene and Cu substrate, and enhanced SEM contrast of graphene domains. Detailed analyses suggest that several gases such as O_2 and H_2O or their mixtures intercalate between graphene and the Cu substrate as well as adsorb on the uncovered Cu surface areas at the boundaries of graphene domains after air exposure. This experimental observation suggests that the SEM contrast of graphene actually reflects its interaction with substrate, which might be applicable to other 2D materials.

P205

Effects of nanoshapes on energetics and spin polarization in nearly zigzag-edged graphene nano-ribbons

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It is known that peculiar edge states and then spin polarization emerge in zigzag-edged graphene nanoribbons (GNRs). This makes zigzag-edged GNR a promising material in spintronics applications. However, the ideal zigzag-edged GNR is rare in nature. It is thus imperative to consider more realistic shapes of GNRs and clarify the effects of nano-shapes on the edge states, the spin polarization and the energetics. In this study, we focus on the nearly zigzag-edged GNRs (NZE-GNRs) which have finite-length zigzag edges connected by another short zigzag edge (kink), and perform the total-energy electronic-structure calculations based on the density functional theory. Through the systematic calculations, we have clarified effects of nano-shapes of NZE-GNRs on its stability, the spin polarization, and the electron states. Edge states localized near the zigzag edge, the flat bands, and the consequent spin-polarized ground states exist when NZE-GNRs have long enough zigzag edge or enough width. In contrast, we have found that the large kink size hinders their appearance. Our results have also revealed that the relative stability of the edge is enhanced when the zigzag edge is short or the width is narrow.

P206

Evaluating bandgap distributions of carbon nanotubes via scanning electron microscopy imaging of the schottky barriers

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We show that the Schottky barrier at the metal-single walled carbon nanotube (SWCNT) contact can be clearly observed in scanning electron microscopy (SEM) images as a bright contrast segment with length up to micrometers due to the space charge distribution in the depletion region. The lengths of the charge depletion increase with the diameters of semiconducting SWCNTs (s-SWCNTs) when connected to one metal electrode, which enables direct and efficient evaluation of the bandgap distributions of s-SWCNTs. Moreover, this approach can also be applied for a wide variety of semiconducting nanomaterials, adding a new function to conventional SEM.

P207

Metal-film-assisted ultra-clean transfer of single-walled carbon nanotubes

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Transfer printing of nanomaterials onto target substrates has been widely used in the fabrication of nanodevices, but it remains a challenge to fully avoid contamination introduced in the transfer process. Here we report a metal-film-assisted method to realize an ultra-clean transfer of single-walled carbon nanotubes (SWCNTs) mediated by poly(methyl methacrylate) (PMMA). The amount of PMMA residue can be greatly reduced due to its strong physical adhesion to the metal film, leading to ultra-clean surfaces of both the SWCNTs and the substrates. This metal-film-assisted transfer method is efficient, nondestructive, and scalable. It is also suitable for the transfer of graphene and other nanostructures. Furthermore, the relatively low temperature employed allows this technique to be compatible with nanomaterial-based flexible electronics.

P208

Crossover between localization and delocalization in sub-100nm edge-disordered graphene nanoribbons

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Graphene nanoribbons (GNRs) is expected to be a channel material of field effect transistors (FETs) because of their high carrier mobility. However, a recent experiment reported that the resistance of GNRs increases exponentially with their length even at the room temperature. The underlying physics of this non-Ohmic behavior of GNRs remain to be elucidated yet. In this study, we have investigated the electronic transport in sub-100nm edge-disordered GNRs (ED-GNRs) using the nonequilibrium Greens function method combined with a tight-binding model. In our simulation model, the edge vacancy is modeled by adding or removing pairs of carbon atoms at the edges. We calculated electrical conductances of ED-GNRs by changing the roughness concentration from 0% to 50% and the ribbon-width from 0.74nm to 2.95nm. We confirmed that the electrical conductances G of ED-GNRs decrease exponentially with their lengths L, i.e., G is in proportion to exp ($-L$ / L_c), where L_c is the localization length. Moreover, we numerically determined the vacancy-concentration dependence of L_c and the ribbon-width dependence of L_c. In addition, we gave a physical interpretation of these dependences through theoretical analysis based on the perturbation theory. This result provides a guideline for developing GNR-based FETs.

P209

Gate-bias modulation of charge-transfer rate in hydrazine-adsorbed graphene

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The introduction of guest species to graphene has been extensively studied, since the electronic properties of atomic membrane are easily modulated by the surface adsorption. Hole-doping has been achieved by adsorption of oxygen (O_2) as electron accepter, where novel gate-tunable kinetics was observed for the hole injection to graphene. In this study, effect of the adsorption of hydrazine having electron-donating nature on graphene is investigated in terms of the charge transfer kinetics (CT kinetics).

Hydrazine monohydrate ($N_2H_4H_2O$) was adsorbed with changing EF of graphene by gate voltage to the channel region of graphene field effect transistor prepared by exfoliation on SiO_2 substrate, followed by rinsing in extra pure water. Raman spectroscopy was measured with the excitation wavelength of 532 nm in ambient condition as changing $N_2H_4H_2O$ adsorption time.

$N_2H_4H_2O$ adsorption on graphene is found to be chemisorption with the charge transfer interaction, giving electron carrier to graphene. CT kinetics is more rapid in the case of the lower EF of graphene for $N_2H_4H_2O$, as opposed to the case of O_2. This is explained by Electrochemical mechanism for the charge transfer by molecular adsorption on graphene.

P210

Fabrication and in-situ TEM characterization of freestanding graphene nanoribbons devices

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Edge-dependent electronic properties of graphene nanoribbons (GNRs) have attracted intensive interests. To fully understand the electronic properties of GNRs, the combination of precise structural characterization and electronic property measurement is essential. For this purpose, a new experimental technique using freestanding GNR devices has been developed, leading to the simultaneous characterization of electronic properties and edge structure of GNRs.

Graphene was first transferred on a Si substrate with an open slit covered by SiO2 layer. To fabricate a freestanding structure, we first made electronic contacts on isolated graphene by EBL and deposition of Cr/Au, and then SiO2 membrane underneath the graphene was etched away by buffered hydrogen fluoride acid. The so-prepared freestanding graphene device was assembled to a home-made TEM holder for in-situ characterization. The freestanding graphene was sculpted by a focused electron beam in TEM, purified and narrowed by Joule heating down to several nanometers width. Electronic properties including IV characteristics, differential conductance and transfer curve have been measured using the structure-defined freestanding graphene in TEM. We have observed significant increase in resistance and semiconducting behavior became more prominent with decreasing width of GNR. The details of device preparation and characterization of GNRs devices will be addressed in the presentation.

P211

Optical properties of high-purity single-chirality enantiomers of single-wall carbon nanotubes

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We have developed a new method for single chirality enantiomer separation of single-wall carbon nanotubes (SWCNTs) by combining overloading selective adsorption and stepwise elution for the gel column chromatography. In this work, we prepared high-purity enantiomers for nine distinct (n, m) species and measured their optical absorption and circular dichroism (CD) spectra. Single-chirality purity was estimated from optical absorption spectra, and all samples showed higher purity than 90%. CD peak intensity at E_{22} transition was normalized by E_{22} absorption and was compared with the previous work [1]. Our sample shows two times higher CD signal for (6,5), indicating much higher-purity of enantiomers. Recently, Castillo and Noguez theoretically demonstrated that not only $E_{i,i}$ but also $E_{i,i\pm1}$ transitions can be observed in CD spectrum [2]. We have analyzed CD spectra using the results of DFT calculations [3]. We found some CD peaks are assigned to $E_{i,i\pm1}$ transitions reflecting asymmetric valence and conduction bands. Detailed analysis will be shown.

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P212

Electron transmission through the stacking domain boundary on multilayer graphene

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We present a theoretical study on the electron transmission through the AB-BA stacking boundary in bi-, tri, tetra- and pentalayer graphene. Using the Green function method, we calculate the electron transmission probability through the stacking faults. In bilayer boundary, the system is almost insulating at the low energy, while the transmission sharply rises as the Fermi energy increases to higher energies. This suggests that the stacking fault crucially suppresses the electron transmission in the intrinsic graphene bilayer at the charge neutral. We also study the effect of the per-pendicular electric field which opens an energy gap, and find that the gap-opening and the Mexican-hat band deformation significantly enhance the electron transmission at the low-electron density. For the ABA-ABC boundary in trilayer graphene, we notice a similar behavior of electron transmission to the bilayer case, but in the tetralayer (ABAB-ABAC boundary) and pentalayer case (ABABA-ABABC), the low-energy transmission is not much suppressed unlike in bilayer and trilayer cases. We also notice the transmission shows some odd-even effect at high electron density, where the even-layer boundaries have better electron transmission than odd-layer boundaries. We find that the linear band in odd-layer cases causes this characteristic due to the high reflection rate of electrons coming from this channel.

P213

Chirality-selective fluorescence enhancement of ssDNA-wrapped single-walled carbon nanotubes coated with gold nanoparticles

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Using single-stranded DNA (ssDNA) for structure-specific recognition and separation of single-walled carbon nanotubes (SWNTs) has become an important method for chirality-selective separation of SWNTs. In this work, we modify the ssDNA-wrapped SWNTs with gold nanoparticles (AuNPs) and report the first case of chirality-selective fluorescence enhancement of the so-obtained AuNP-DNA-SWNT hybrids. In addition to the overall fluorescence enhancement of more than 10-fold, we observe with the (7,5) recognition DNA $(ATT)_4AT$ a higher fluorescence enhancement factor (EF) for (7,5) than for the other chiralities, showing chirality-selective fluorescence enhancement. This is likely due to the ordered and tightly wrapped structures of the recognition DNA-SWNT, which protect the SWNTs from direct contacting with the AuNPs. Similar selective fluorescence enhancement is also observed with (7,6) recognition DNA.

P214

Two-electron ambipolar double quantum dots electrostatically defined in carbon nanotubes

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Recently, a few experiments have been conducted which focused on spin manipulation in ambipolar carbon nanotube quantum dots [Nature Nano. 7, 630; Nature Nano. 8, 56] with results that remain partially unexplained. The attempts for description of the experimental data assumed that the ambipolar and unipolar dots have similar electron properties, however no comprehensive description of ambipolar QDs has been yet provided in literature.

We consider ambipolar n-p double quantum dot with one electron localized in n dot and three holes localized in p dot [PRB 91, 085312]-system investigated experimentally. We solve the problem of a confined electron pair using an exact diagonalization method within the tight-binding approach. We demonstrate that the electronic structure of the double n-p dot differs from the n-n dot, especially in the form of exchange interaction. We indicate that observed differences for n-n and n-p systems are an effect of opposite electron circulation in the conductance and valence bands for a given valley. We discuss universality of our results for CNTs of various chirality and quantum dots sizes.

P215

Rayleigh scattering spectroscopy of various single-walled carbon nanotube samples

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Understanding electronic structures of SWNTs is important to evaluate the quality and reliability of SWNT devices. Recently, Rayleigh scattering spectroscopy has attracted much attention as the efficient method to investigate the 1D electronic structure of SWNTs [1]. In this work, we have constructed the optical system and measured Rayleigh scattering from SWNTs. The attenuated continuum laser (the range of wavelength is 400 2500 nm) was focused on SWNTs and scattering light was measured with CCD array and InGaAs detectors. In order to cut off the incident light, the incident angle was 45 degree and the emission light at the reflection angle of 45 degree was collected. The confocal system was used in order to suppress stray light. Dispersed SWNTs in the surfactant solutions [2], dry-deposited SWNT films [3], suspended SW- NTs and so on, were measured in this work. We obtained Rayleigh scattering spectra with different characteristic features depending on the SWNT samples.

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P216

Highly selective and nondestructive purification of metal impurities from multi-walled carbon nanotubes using chloroform and acids

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Multi-walled carbon nanotubes (MWCNTs) have been produced in a large quantity for industrial applications. Metal impurities are inevitably introduced into CNTs during synthesis using metal catalyst. Some high-end applications including Li-ion batteries, super capacitors and high-voltage cables require highly pure CNTs. This study has developed gas-phase purification to remove selectively and nondestructively metal impurities from CNTs. The MWCNTs were purified in a quartz tube located in a vertical-type furnace at 800℃ by bubbling nitrogen gas through chloroform at 100 ml/min. Our chloroform purification removed effectively Fe/Co as much as 94% but eliminated only 53% of Al/Mg. On the other hand, conventional acid treatment (3M HCl) worked in an opposite manner as that of chloroform purification: 92% removal for Al/Mg; 46% for Fe/Co. Thus we combined the chloroform process and acid treatment to remove both Fe/Co and Al/Mg and thus removed 90% of metal impurities. The chloroform purification introduced a traceable amount of chlorine over MW-CNTs, which could be etched out by feeding nitrogen gas containing a small amount of hydrogen or other gases. We optimized further the purification processes and could obtain MWCNTs having only ~ 300 ppm level of metal impurities by removing them as much as 95%.

P217

Correlation between spin magnetism and catalytic activity in graphene oxide / nanographene

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The introduction of functional groups or edges to graphene, which exhibits spin magnetism, is popular way for giving the chemical activity to graphene. In this study, the correlation between the spin magnetism and catalytic activity for graphene oxide (GO) and activated carbon fibers (ACFs) as edge-riched nanographene assembly materials was investigated by the magnetic susceptibility and GC-MS. GO samples were synthesized by Brodie and Hummers methods (BGO and HGO). An oxidation reaction from benzyl alcohol to benzaldehyde was carried out by using ACFs and GO as catalyst to evaluate their chemical activities. Judging from the spin density, ACFs should contain the larger amount of the chemically active sites than that of BGO. This is supported by the larger GC-MS yield for oxidation of benzaldehyde by using ACFs than that BGO. However, the reaction by using HGO results in benzaldehyde as byproduct and even larger yield for benzyl alcohol than those with ACFs and BGO, where dibenzyl ether appears as major product. Moreover, HGO exhibits the extremely large spin density from oxidant reagent. The presence of impurity from oxidant reagent also significantly influences both the magnetism and the chemical activity of GO.

P218

Imaging the density and type of horizontal carbon nanotube arrays by polarized optical microscopy

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Fast determining the density of single-wall carbon nanotubes (SWNTs) with metallic/semiconducting (M/S) recognition is a longstanding target. Currently, scanning electron microscopy and atomic force microscopy are two most used methods to count the numbers of SWNTs in finite area (typically ~1 micron). However, these two methods lack the ability of M/S recognition and they even meet great challenges at lateral resolution as the density of SWNTs increases, spectroscopic methods, electrical measurement and transmission electron microscopy are adopted to determine the M/S type but usually with quite low throughputs. Here we demonstrate a density and type imaging of SWNTs with hundreds-micron field of view and sub-second display rate. This imaging is achieved through polarization induced dramatical contrast enhancement of SWNTs. The enhanced optical contrast is then used to determine the density of SWNTs and the image color is used for M/S recognition according to their distinguishable spectral responses. Our technique provides a routine to search and characterize the SWNT arrays on various substrates and in diverse environments. Its universality and practicability offer the opportunities not only to push forward the controlled growth of both high density and high M/S selectivity SWNT arrays, but also to promote the development of SWNT applications.

P219

Direct evidence for the quantized stepwise evolution of the chiral induces of individual single-walled carbon nanotube during its super-plastic deformation at high temperatures revealed by in-situ HRTEM

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An intramolecular plastic flow theory was proposed firstly by Yakobson group, where they considered the nucleation and migration of a dislocation dipole 5-7-7-5 as the main mechanism for the plastic deformation of single-walled CNTs (SWNTs). A breakthrough experiment was done by Huang et al reporting the so-called super-plastic deformation of individual SWNT at very high temperatures (close to 2000 degree C), where the SWNTs underwent an axial elongation over 280% and a 14-fold reduction in its diameter. In this presentation, we will give the first direct evidence for the quantized step evolution of individual SWNT during its plastic deformation at high temperatures by means of low-voltage in-situ aberration-corrected TEM. The atomically-resolved HRTEM images enabled us to analyze the evolution of chiral induces of the SWNT with high accuracy. The chiral induce (n, m) of the SWNT was found to change to (n, m) with (n, m)= (n, m)-(b1, b2), where (b1, b2) is the Burgers vector, which was experimentally assigned to be (0, 1), (1, 0) and (1, -1), consistent with the intramolecular plastic flow theory.

P220

Excitons in single-wall carbon nanotube revealed by ultrahigh magnetic fields of up to 350 T

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In general, application of an extremely high magnetic field simplifies a very complicated degenerate quantum state. Carbon nanotubes (CNT) are not the exception. The Aharanov-Bohm magnetic flux causes quantum state mixing of band-edge dark and bright excitons, and the optical activity is shared by both of them, which is expected to realize in magnetic fields above 100 T. It is predicted by theory that these exciton states split into two independent and simple excitons arising from the K and K’ points in the Brillouin zone and show a simple energy splitting that exhibits linear dependence in magnetic fields. The absorption intensity of the K and K’ point exciton showed asymptotic behavior to increase and decrease linearly, respectively, upon increasing magnetic fields. However, experimental verification requires intense magnetic field over 100 T as well as precise measurement techniques. We prepared highly- selected CNTs with its chiral index (6,5), which were separated from a mixture of HiPco-grown CNTs by single-surfactant multicolumn gel chromatography. The sample is stretch aligned CNTs which are dispersed in a PVA film. Results are presented from magneto-absorption spectroscopic measurements of the E22 exciton transition by the streak optical transmission spectroscopy carried out in magnetic fields up to 370 T.

P221

Optical absorption and luminescence of the half-fluorinated graphenes

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The structure and composition of graphite fluorides are determined by the synthetic conditions as reaction temperature and fluorinating agent. Interaction of graphite with a mixture of BrF_3 and Br_2 at room temperature produces bromine intercalated graphite fluoride with a composition of $C_2F_x{\cdot}0.13Br_2$, where x is less 1. It was shown that fluorine atoms form short chains, while non-fluorinated carbon atoms are organized in very narrow ribbons and aromatic pi-conjugated areas with a size smaller than 3 nm. These pi electron nanochains and nanoislands preserved after the fluorination process are likely responsible for the value of the energy gap of the compound of ~2.5 eV. Variation in the size and the shape of pi-electron regions within the fluorinated graphene layers could be a way for tuning the electronic and optical characteristics of the graphene-based materials. Incorporation of two kinds of carbon atoms, bonded with fluorine atoms and bare carbon, into graphite fluoride C_2F could give the various structures compositions. Here, from the comparison of the experimental NEXAFS spectrum of graphite fluoride C_2F_x produced at room temperature and theoretical spectra plotted for three different models.

P222

Mechanical behavior of few-walled carbon nanotubes within and beyond the linear regime.

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When carbon nanotubes (CNTs) are bent they will deform, in localized buckling or rippling deformations. The force-deflection relation is only linear up to a critical strain, where the deformation begins, and then the relation becomes non-linear with a concomitant drop in the mechanical stiffness. The nonlinear force-deflection relation and the reduced stiffness, has important implications for the design of future nano-electromechanical systems (NEMS) that utilize bending of CNTs.

Here we discuss our recent experimental findings of the mechanical behavior of few-walled, free-standing, carbon nanotubes made with different fabrication techniques. We find that the crystallinity of the tubes has a profound influence on the mechanical behavior, both within and beyond the initial linear regime. Tubes with a high crystallinity, grown by arc-discharge methods, are very stiff, they ripple early and loose most of their initial stiffness in the rippled regime. Tubes grown with catalytic methods on the other hand are much softer, ripple later, and retain most of their stiffness in the rippled regime. These findings are of high importance for applications, as highly cry-stalline materials are very hard to manufacture and most fabrication methods are not compatible with regular semiconductor device fabrication.

P223

Sign inversion of the Fano coupling factor when crossing the optical energy transition in Raman spectra of KC_8 and KC_{24}

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There is a renewal of interest in potassium graphite intercalated compounds as they could be used for scalable production of monolayer graphene. Due to charge transfer, the Fermi level strongly shifts. We perform an analysis of the shape of the Raman feature of potassium graphite intercalated compound at stage 1 (KC_8) and 2 (KC_{24}). By varying the excitation energy from ultraviolet to infrared, we observe a sign change of the Fano coupling factor below and above the optical transition equal to twice the Fermi level shift determined from first principle calculation neglecting the small shift due to the phonon energy. This behavior is explained by a sign change in the Raman matrix element of the electronic part. The optical indexes of graphite, potassium compound at stage 1 and 2 have been computed showing that specific features far from the transition energy are without strong effects to this coupling factor. The energies associated to this sign change for KC_8 and KC_{24} obtained experimentally are fully consistent with the values determined from first principle calculations

P224

Interface dipole enhancement effect and enhanced rayleigh scattering

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The optical effect of a nanometer or sub-nanometer interfacial layer of condensed molecules surrounding individual nanomaterials such as single-walled carbon nanotubes (SWCNTs) has been studied theoretically and experimentally. This interfacial layer, when illuminated by light, will behave as an optical dipole lattice and contribute an instantaneous near field to enhance the local field on neighboring atoms, molecules, or nanomaterials, which may lead to enhanced Raleigh scattering, Raman scattering, and Fluorescence. The theory of this interface dipole enhanced effect (IDEE) predicts that a smaller distance of nanomaterials to the plane of the interfacial layer, or a larger ratio of the dielectric constants of the interfacial layer to surrounding medium, will result in a larger field enhancement factor. This prediction is further experimentally verified by several implementations of enhanced Rayleigh scattering of SWCNTs as well as in-situ Rayleigh scattering of gradually charged SWCNTs. The interface dipole enhanced Rayleigh scattering not only enables true-color real-time imaging of nanomaterials, but also provides an effective mean to peer into the subtle interfacial phenomena.

P225

Single-electron transport and quantum interference effect in suspended CVD graphene nanoribbon

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We study the electron transport in suspended graphene nanoribbon, grown on copper foil by chemical vapor deposition (CVD) and then transferred to SiO_2/Si substrate. The wire width of graphene nanoribbon is varied from 50nm, 75nm and 245nm to 705nm for studying the size effect in electron transport. A single electron transport is observed in the smallest wire width 50nm by Coulomb diamonds. Weak localization (WL) and universal conductance fluctuations (UCF) phenomenon are observed by measuring magnetoresistance oscillations and the temperature dependence of resistivity is observed an enhance resistivity at low temperature, due to electron-electron interaction effect, with decreasing temperature. Both behaviors are due to quantum interference effect. Our results indicate electron transport from single electron transport, or ballistic transport to diffusion transport in weak-disorder CVD graphene nanoribbon with increasing wire width.

P226

Chemically modified absorption quenching of graphene

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Although optical properties in graphene are solely defined by the frequency-independent fine structure constant in visible region, some deviations have been observed in infrared region due to Pauli blocking phenomenon. Here, we report a complete absorption quenching in infrared (IR) region driven by bis(trifluoromethanesulfon)amine (TFSA), an optically transparent p-type chemical dopant. The Fermi level was downshifted by TFSA to provoke absorption quenching by Pauli blocking phenomenon. The transmission was enhanced in infrared region with increasing doping concentration. The extracted Fermi level shift in doped graphene, which is defined as an absorption quenching onset point, was in congruent with the Schottky barrier height change extracted from I-V characteristics of graphene/n-Si hetrojunction diode, which was further confirmed by Raman spectroscopy and X-ray photoelectron spectroscopy. The Fermi level shift is also related to the different substrates which can be understood by dielectric screening.

P227

Influence of hydrogen edge passivation on the properties of graphene systems

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The p_z tight binding theory and its Dirac low-energy approximation predict metallic dispersion relation for zigzag and armchair nanoribbons with 3n+2 atoms across the channel. For these ribbons formation of perfectly conducting channels is predicted by the theory [Carbon 47, 124]. However, the transport experiments show finite transport gaps [PRL 98, 206805, Phys. E, 40, 228] near the neutrality point for all types of nanoribbons. The finite band gaps originate from quantum confinement, edge disorder effects, and/orpassivation [PRL 99, 186801] of the dangling bonds at the edges of the ribbon. The ab-initio calculations for nanoribbons [PRL 97, 216803] report formation of energy gaps.

We study the transport properties of nanoribbons with hydrogen-passivated edges and discuss the effects of passivation for the systems based on nanoribbons as electron scatterers. We use the tight binding approach using three p/d orbitals per atom [J. Appl. Phys. 109, 104304] and develop a version of quantum transmitting boundary method [PRB 89, 165306] to study the transport with the Landauer approach. We confront the results obtained for the passivation model against the results of a single-p_z tight binging model. Our study involves graphene nanoribbons perturbed by external potentials and quantum point contact of various geometries.

P228

The Raman spectroscopy study of inter-layer coupling in individual index-identified double-walled carbon nanotubes

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We use 9 laser excitations energies, ranging from 458 nm to 1000 nm, to study the dependence of the frequencies of the Raman modes on the inter-layer van der Waals coupling in individual double-walled carbon nanotubes (DWNT), whose structures are independently identified by electron diffraction (ED) and high-resolution electron microscopy (HRTEM).

We show that the Raman features of the radial breathing-like modes (RBLM) and tangential modes (G-modes) obtained at different excitation wavelengths on several index-identified individual DWNTs can only be understood in a coherent way by considering the coupling between the two concentric layers. This coupling determines the conditions of observation of the modes in Raman spectra and affects the frequencies of the RBLM and G-modes. In particular, one demonstrates a clear downshift of inner-layer G-modes with respect to the corresponding G-modes in equivalent single-walled carbon nanotubes (SWNT) when the inter-layer distance is larger than the nominal van der Waals distance (close to 0.34 nm).

P229

Covalent versus non-covalent functionalisation of double-walled carbon nanotubes: a quantitative approach

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Many applications of carbon nanotubes involve the modification of the CNTs walls, through chemical functionalisation, in order to make possible the attachment of molecules of interest or to improve their interface with a matrix. There are two approaches, involving different interactions and more or less substantial modifications of the intrinsic properties of the CNTs. The most widespread is the covalent functionalisation, leading to stable covalent bonds but also modifying the structure properties of CNTs. CNTs can also be functionalised by a non-covalent way, which does not affect the structure of CNTs but involves much weaker interactions.

We compare here the covalent and non-covalent functionalisation of double-walled carbon nanotubes (DWNTs) synthesized by a Catalytic Chemical Vapour Deposition process developed at the CIRIMAT. We have selected a common fluorescent dye, FITC, which can be used in both ways of functionalisation, as well as a cyanine derivative. We will describe our approach to identify but also quantify the presence of these molecules on the surface of the DWNTs. Our results raise the question of the stability in time of the non-covalent interaction, and of what is really covalently grafted on the CNTs when this approach is targeted.

P230

Preparation and characterization of fibrous single-wall carbon nanohorn aggregates

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Single-wall carbon nanohorns (SWNHs) are single-graphene tubules with nanometer-scale diameters, and about 2000 of them gather and form a spherical aggregate with diameters of 50-200 nm. Many fundamental and application studies have been done since its discovery in 1998. SWNHs with high purity are usually produced by CO_2 laser ablation of graphite without using a catalyst at a high production rate of 1 kg/day. Here, we succeeded in preparing fibrous SWNHs by CO_2 laser ablation to iron-contained graphite target for the first time.

The CO_2 laser ablation was operated at 3.5 kW. During 30 seconds laser ablation, the iron-contained target was rotated at 2 rpm. The buffer gas and pressure were N_2 and 760 Torr, respectively.

From SEM and TEM of the obtained samples, the individual SWNH was 2-5 nm in diameter and 40-50 nm in length. The SWNHs have been assembled fibrously with 30-100 nm in diameter and several micro-meters in length, which is different entirely from normal spherical SWNH aggregates. From EDX, and XPS, the iron catalyst after CO_2 laser ablation existed mainly as Fe metal particles in SWNH aggregate. We believe that fibrous SWNHs become promising candidates for conductive materials, and electrode catalyst.

P231

Electronic properties of the closely-packed aligned carbon nanotube film

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Carbon nanotube (CNT) has excellent electronic, thermal, and mechanical properties. In particular, the electronic device applications using the random network of the CNTs are widely investigated recently. We have synthesized the closely-packed aligned CNTs on the SiC substrate. In this study, we investigated the electronic properties of the closely-packed CNTs, focusing on the effect of the CNT caps on the properties. We also tried to control its properties by boron-doping.

We prepared the CNTs film with its length of about 160 nm and the diameter of 2～3 nm. Our CNTs are only of zigzag-type and typically double or triple walled. Interestingly, the electric resistivity of the CNTs film with the CNT caps drastically increased with decreasing temperature, while the capless CNT had little temperature dependence in the resistivity. The CNTs with caps had the electron concentration of 5*10^16 /cm2, while the capless CNTs had 3*10^13 /cm2. This result suggests that the CNT caps have much more electrons than in the body of the CNTs. This is the first electric measurement of the effect of the CNT caps on its electronic properties. In addition, we succeeded to obtain the CNTs film with the p-type conduction realized by the boron doping.

P232

Ab Initio study of reaction paths of molecular oxygen with (6,4) and (8,6) carbon nanotubes

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Oxygen doping of single-wall carbon nanotubes (SWCNTs) exposed to ozone and light has attracted attention because of their greater luminescence quantum yield than that of pristine CNTs. The luminescence at E_{11}^*, which is red-shifted from E_{11} for pristine CNTs, originating from the oxidation appears to be also observed for small-diameter CNTs in chirality separation experiments without a particular oxidation treatment. To understand this phenomenon, we performed ab initio calculations for the adsorption of oxygen molecules (O_2) onto realistic models of chiral nanotubes. We found that the adsorption energy of the physisorption of O_2 does not depend on the chirality, whereas that of the cycloaddition product increases with increasing diameter of the SWCNTs. Furthermore, one of the final products was found to be the isolated ether structure as also proposed for ozone oxidation. The energy barrier from the physisorption of O_2 to the chemisorption is lower than that of the reverse reaction for (6,4) nanotubes, whereas the relation is opposite for (8,6) nanotubes, consistent with the distinct luminescence peak at E_{11}^* observed for (6,4) nanotubes and with the lack of a pronounced luminescence peak for larger-diameter (8,6) nanotubes in the chirality separation experiments.

P233

Magnetic interactions between nanographene host and guest molecules with localized d-electron

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Activated Carbon Fibers (ACFs) consisting of 3D random network of nanographenes is interesting host material because of its nanopores and localized spins. Ferrocene ($FeCp_2$) and methemoglobin (metHb) having localized *d*-electron are guest molecules expected to exhibit magnetic interactions with nanographene. In this study, we introduced $FeCp_2$ and metHb to ACFs, and evaluated magnetic interactions between nanographene host and magnetic guest materials. The guest molecules were introduced by vapor transfer ($FeCp_2$-ACFs), and soaking ACFs in metHb-dispersed saline (metHb-ACFs). The introduction of the guest molecules is confirmed by Fe2p peaks in XPS for $FeCp_2$-ACFs and metHb-ACFs. The increment in shake-up peak intensity of C1s spectrum for $FeCp_2$-ACFs indicates the increase of conducting electrons. So, the emergence of charge transfer host-guest interaction is suggested in $FeCp_2$-ACFs, which is also supported by Red-shift of G-band in Raman spectrum. The larger spin concentration than that of ACFs indicates the presence of cationized $FeCp_2$ in which chemical form spin magnetism of 3*d* electron appears. The magnetization for metHb-ACFs is smaller than that of ACFs at 2K, indicating the reduction in the spin magnetism of metHb in metHb-ACFs. The presence of antiferromagnetic interaction is suggested in metHb-ACFs, being consistent with the decreasing in the Weiss temperature.

P234

Chirality evaluation of horizontally aligned single-walled carbon nanotubes by Raman spectroscopy

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Detailed analysis of single-walled carbon nanotube (SWCNT) chiralities is re-quired toward understanding the mechanism of chirality-controlled growth. However, most of evaluation methods have shown only overall chirality distributions, which are affected by both populations and lengths of SWCNTs. In this study, we independently evaluated the populations and lengths of SWCNTs with different chiralities using aligned structures of individual SWCNTs together with Raman mapping measurements. Horizontally aligned arrays of SWCNTs were grown by alcohol chemical vapor deposition method [1] from patterned catalyst on crystal quartz substrates, transferred onto silicon substrates, and investigated by Raman mapping measurement. Chiralities of individual SWCNTs were assigned on a one-by-one basis using acquired radial breathing mode frequencies and excitation energy in comparison with Kataura plot. Lengths of chirality-assigned SWCNTs were determined by Raman mapping or scanning electron microscopy. Measurement results indicated that both the populations and lengths of the SWCNTs grown in this study have no dependence on chiral angle.

[1] S. Maruyama et al., Chem. Phys. Lett. 360, 229 (2002).

P235

The role of substrates in graphene field effect transistors

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In this study, we investigated what affects the electrical properties of graphene field effect transistors (GFETs). In order to fabricate GFETs for this study, monolayer graphene is first grown on Copper foil by chemical vapor deposition, then transferred to a SiO_2/Si substrate using Poly(methyl methacrylate) (PMMA) as a transfer medium. As-fabricated GFETs typically show p-type behavior which is usually associated with PMMA residue and its absorption of H_2O or O_2 in the air. Charge puddles in SiO_2 is also known to affect electrical characteristics of GFETs. For this study, we focused on the role of the substrates on the electrical properties of GFETs. After fabrication and characterization of GFETs on SiO_2/Si substrates, GFETs can be transferred to different substrates such as boron nitride or polymer substrates. We investigated how different substrates affect device characteristics. We also studied how chemical or mechanical modification of the substrates influence the electrical properties of GFETs.

P236

Transport property of highly aligned and chirality selected SWCNTs

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Single-walled carbon nanotubes (SWCNTs) are expected to have excellent transport property owing to their intrinsic high mobility. However, in typical network where SWCNTs are randomly distributed and connected, conducting carriers are scattered and localized on their junctions[1]. Therefore, in such a random network, transport property significantly degrades compared with that in a single rope of SWCNTs. One of approaches to improve the state of junctions is to produce aligned arrays of SWCNTs. We have reported producing of assembly of highly aligned and chirality selected SWCNTs by a crystal template method [2-3]. Since we have reported that tuning a Fermi-level is significantly changes the physical property of bulk system of SWCNTs[4-5], in this study, we report transport properties of highly aligned Metallic SWCNTs under high carrier injections through electric double layer techniques.

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P237

Onset potential for electrochemical oxidative corrosion on Sp^2-carbon

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The oxidative corrosion of carbon is an urgent problem because carbon is widely used as a platform electrode to immobilize catalysts. One of the factors in the gradual decrease of output power in fuel cell is the oxidative corrosion of the carbon supports. The oxidative corrosion of carbon is a complicated process that includes parallel oxidation pathways. Furthermore, the following electrochemical oxidation reaction of carbon by water molecules occurs at a much more negative potential than that thermo-dynamically expected, although the rate of this reaction is very slow.

We recently reported the oxidative corrosion potential vs. pH diagram for single-walled carbon nanotubes (SWCNTs). The current Raman spectroscopy studies based on the encapsulation of beta-carotene into SWCNTs revealed that there are three types of oxidative corrosion of SWCNTs: non-oxidized, end-cap oxidized (end-cap eliminated), and side-wall oxidized SWCNTs. SWCNTs are good models for experimentally analyzing the oxidative corrosion of sp^2-carbon.

P238

The study of fullerene dispersion stability in organic solvent

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This paper describes peculiar phenomena of fullerene in solvent in terms of particle size distribution. It is well known that fullerene is one of allotrope of carbon and still would be soluble to a solvent.

Three kinds of solvent were chosen, 1,2-dichlorobenzene, dichloromethane, oleic glyceride. Commercial powder nanom mix was used, mainly composed of C60, C70.

Instrument for the evaluation of solutions is Zetasizer Nano ZSP made by Malvern Instruments Ltd using dynamic light scattering, covering particle size is from 1nm to 1um. Saturated solution was made as follows: nanom mix was dissolved to a solvent and filtered by using opening of 0.1um. In the case of dichloromethane and oleic glyceride, particle bigger than 0.1um was observed after some interval of time, whereas in the case of 1,2-dichlorobenzene, solvent remain stable. If saturated solution was diluted to 1/2 of saturation concentration, this kind of big particle did not appear. The solution stability difference would be explained by dissolving mechanism. Solubility should be determined by Gibbs free energy. Solvent which have benzene ring dissolve fullerene by enthalpy effect, whereas solvent without benzene ring dissolve fullerene by entropy effect. Relationship between concentration of solution and particle size distribution would be discussed.

P239

Numerical study on inelastic electronic transport in submicron-length single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) can be either metallic or semiconducting depending on their chirality. Semiconducting SWNTs (s-SWNTs) are potential candidates for channel materials of FETs because of their high carrier mobility ($\sim 10^5$ cm^2/eV), whereas metallic SWNTs (m-SWNTs) are expected to be wiring materials of integrated circuits because of their stability for the current density (10^9 A/cm^2). Although electronic transport properties of SWNTs are subjected to influence of phonon scattering at room temperature, the effect is not fully understood. One of reasons is that atomistic simulation methods incorporating the electron-phonon interaction have not been established thus far. In this work, we have developed a new computational simulation method to investigate inelastic electronic transport in nanomaterials. Moreover, we applied the developed simulator to SWNTs, focusing on the tube-length dependence of electrical resistance of both s-SWNTs and m-SWNTs at various temperatures. In consequence, we found that (i) the electrical resistance of SWNTs decreases with temperature and (ii) submicron-length m-SWNTs exhibit quasi-ballistic transport even at room temperature in contrast to s-SWNTs. These results are in excellent agreement with recent experimental results.

P240

Molecular dynamics simulation on RBM frequency of bundled SWNTs

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Radial Breathing Mode (RBM) is one of the most important vibrational modes of single-walled carbon nanotubes (SWNTs), because the measurement of RBM frequency w_{RBM} allows us to uniquely assign the chirality of an individual SWNT by resonant Raman scatting. It is known that w_{RBM} responds sensitively to surrounding environment around an SWNT. Recently, we showed both experimentally and theoretically that w_{RBM} of an individual SWNT is up-shifted when the SWNT is exposed to water vapor. On the other hand, an SWNT embedded in bundled SWNTs is not exposed to ambient air, but it receives van der Waals force from the surrounding SWNTs. Thus, we can expect that w_{RBM} of bundled SWNTs is also up-shifted in comparison to that of an SWNT in vacuum.

We have computationally estimated the up-shift of w_{RBM} of bundled SWNTs using molecular dynamics (MD) simulation. In order to estimate w_{RBM} of bundled SWNTs, we prepared an SWNT bundle consisting of seven SWNTs which have the same chirality and close-packing structure. Here, we present MD simulation results of w_{RBM} for various chirality types of bundled SWNTs and discuss the diameter dependence of w_{RBM}. Finally, we compare the effect of bundle and water vapor on w_{RBM}.

P241

PL imaging spectroscopy of water adsorption and desorption on suspended SWCNT

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Recently we have reported that water molecules adsorb on the surface of the single-walled carbon nanotubes (SWCNTs) and they form stable adsorption layer [1].

However, the details of adsorption and desorption mechanism are still not elucidated. Here, we investigated the water adsorption phenomena on the SWCNT surface by PL imaging spectroscopy with controlling the water vapor pressure. The PL images were measured from suspended SWCNTs between a pair of quartz pillars, by using a 2D allayed detector and a tunable band-pass filter. The length of suspended SWCNTs was longer than 10 μm.

PL images showed that the spatial distribution of adsorbed water molecules on the outer surface of SWCNTs during water adsorption and desorption processes.

We will discuss the water adsorption and desorption phenomena on SWCNTs in detail based on the spatial distribution of PL spectra.

Reference
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P242

Photon energy dependence of angle resolved photoemission spectroscopy in graphene

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The dependencies of angle-resolved photoemission spectroscopy (ARPES) for different photon energies, light polarization, and incident light angle near Dirac point of graphene are calculated theoretically. We find that there is an unexpected sudden increase of ARPES intensity in the p-branch of graphene near the Dirac point in the presence of nearly s-polarized light, which is in contrast to the s-branch of graphene that becomes brighter when illuminated with the same light. The intensity of p-branch increases by increasing the angle between the incident light and the axis normal to graphene surface particularly for the incident photon energy around 50 eV. Using a first principle approach to calculate the initial and final electronic states, we explain the origin of this phenomenon by the existence of stronger dipole vector in the direction normal to graphene surface and parallel to p-polarized light if compared to the dipole vector in the direction of s-polarized light. Furthermore, such a behavior does not disappear by changing the initial electronic states. Therefore, the final electronic states should contribute more strongly to the photon energy dependence of the ARPES intensity.

P243

Theoretical proposal of determining crystal orientation in graphene by Raman spectroscopy

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Graphene has two typical crystal orientations: the zigzag direction and the armchair direction. Determining the crystal orientation of graphene is essential for graphene-based nanoelectronics. For example, electrical properties of graphene nanoribbons and graphene nanomeshs are known to depend strongly on the crystal orientation.

In this study, we have investigated G-mode modulation of graphene under small uniaxial strain using first-principles calculations based on the density functional theory. We found that the G-mode splitting depends on the strain direction: the splitting was 46 cm^{-1} at 2% strain along the zigzag direction whereas 28 cm^{-1} along the armchair direction. The difference of splitting between the two cases (18cm^{-1}) is experimentally observable. From these results, we propose that the crystal orientation of graphene can be determined by measuring the G-mode splitting of strained graphene using Raman scattering spectroscopy.

P244

Temperature dependence of momentum distribution in a correlated Dirac sea with the zero mode of a hydrogenated graphene vacancy V_{111}

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At a hydrogenated graphene atom vacancy, V_{111}, a zero-energy mode appears at the Fermi level. Based on evaluation of two-body interactions using DFT basis functions, we have derived an effective Hamiltonian of the system.[1] The model involves an on-site Coulomb correlation term U and an isotropic two-body magnetic scattering term J. By performing a unitary transformation of this model, we obtained a kind of Anderson impurity model with a correlation-induced renormalized Dirac sea. Applying a CT-HYB-QMC calculation to this model, we made an estimation of the electronic state of the system, and emergence of the Kondo effect was implied. In this presentation, we focus on the temperature dependence of electron occupation in the zero mode and an effective low-energy level deduced from the exchange scattering. The occupation numbers relate directly to the momentum distribution and the electron density of the system. Actually, the step-wise behavior in a correlated Dirac sea shows a characteristic temperature scale of O (10K) for the estimated anti-ferromagnetic exchange J. By reducing the temperature, the momentum distribution changes from the Fermi distribution, implying strong electron correlation developed around the Dirac point.

Keyword: Graphene, Kondo effect, Hydrogen, Topological zero mode

[1] N. Morishita, et al. arXiv:1412.8589.

P245

Spray coated graphene oxide/carbon nanotube films

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Graphene oxide is a water processable material which can be used in diverse composites and medical applications. However, many times reduction is used order to achieve electrical conductivity, thus changing its structure. In this work we report the use of the mixture of graphene oxide and carbon nanotubes that are spray coated on a substrate and its electrical conductivity is monitored at different content ratios. The films exhibit a well dispersed hybrid structure revealed by scanning electron microscopy and scanning probe microscopy. In addition, its surface chemical structure was determined by x-ray photoelectron spectroscopy. This technique is promising for an easy scale up for industrial applications.

P246

Energetics and electronic structure of graphene nanoribbons

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Graphene has attracted substantial attention not only in nanoscience but also in nanoelectronics because of its unique electronic and geometric properties. For the practical application of graphene in electronic devices, it is necessary to understand the fundamental behavior of graphene under the influence of electric fields. In the present work, using density functional theory with the effective screening medium method, we studied the electronic properties of graphene nanoribbons with several edge structures under a lateral electric field.

Our calculations showed that the stability of graphene edges strongly depends on the length of the zigzag edge portion. Near-zigzag edges are less stable than near-armchair edges because of the large number of states at the Fermi level in near-zigzag ribbons. Under the lateral electric field, we found that the nanoribbons with near-zigzag edges exhibit unusual electric field screening that electrostatic potential oscillates rapidly, leading to over-screening in the vicinity of edge C atomic sites. Moreover, our calculation also showed that a nearly free electron state emerges in the vacuum region outside the ribbons and shifts downward with increasing electric field.

P247

Structural stability and electronic band structure of defective graphene with Zn atom

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It has been reported that the electronic structure of graphene can be influenced by defect creation by beam irradiation, AFM tips as a mechanoelectrochemical pen, catalytic reaction using metal particles, etc. Notably, metal-substituted graphene has a different electronic structure from that of pristine graphene. And, it has been figured out that vacancies and metal adatoms on graphene play a role in tuning the electronic structure and magnetic properties. Nevertheless, defective graphene with metal atoms was not studied theoretically till now, to the best of our knowledge. Most of theoretical studies focused on metal atom having magnetic properties in pristine graphene. In this work, we studied the structural stability and electronic band structure of defective graphene with Zn atom by using QUANTUM ESPRESSO code. The band structure and formation energy of graphene were calculated along with the evolution of vacancies and Zn substitution. The calculated formation energy can determine energetically preferable structure of defective graphene with Zn atom. Additionally, this work demonstrates the effect of vacancy and metal substitution on the band structure of graphene, respectively.

P248

Valley hall effect in electrically spatial inversion symmetry broken bilayer graphene

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Valleytronics is a newly developed concept for electronics utilizing the occupation degree of freedom of valleys as an information carrier. Spatial inversion symmetry broken honeycomb lattice systems are ideal materials for valleytronics. Due to valley contrasting Berry curvature, these systems show valley Hall effect and its inverse effect, which enable generation and detection of a pure valley current. Valley Hall effect was demonstrated in structurally spatial inversion symmetry broken systems such as MoS_2 and monolayer graphene/h-BN superlattice. Here we used dual-gated bilayer graphene to break the spatial inversion symmetry electrically. At 70K, around charge neutrality point, we found that large nonlocal resistance emerges under displacement field and it scales cubically with the local resistivity by tuning the displacement field. This is an evidence of the pure valley current mediating the nonlocal transport and the valley Hall effect in spatial inversion symmetry broken bilayer graphene. The worth noting point is the observation of valley Hall effect in insulating regime. In the zero conductivity limit, non-dissipative conversion of an electric field to a pure valley current will be enabled. Finally, we discuss a self-consistent model of the nonlocal transport and development of the nonlocal resistance measurement technique in the high resistance regime.

P249

Metal-insulator transition induced by disorder in graphene patterned with a helium Ion microscope

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We have investigated the electrical transport properties of a patterned graphene device at low temperatures and high magnetic fields. The device consists of an exfoliated monolayer graphene on top of a SiO2/Si substrate processed as Hall bridge using standard electron beam lithography. Three regions of the main channel of the device were patterned with a series of periodic lines by using a beam of helium ions from a helium microscope. Different ion densities were used to bombard the lines in each region. We have measured both longitudinal and transversal magnetoresistances of each patterned regions at temperatures varying from 1.8 to 110 K using standard lock-in techniques. By fitting the magnetoresistance data with the weak localization theory for graphene, we were able to extract the phase coherence length for different carrier densities and for different temperatures. A transition between insulating and metallic behaviors was observed as the density of defects was increased. This behavior is consistent with the transition between the regimes of strong and weak localization for conductivities close to the minimal value at low temperature.

P250

Influence of the surface structure of substrate for proximity effect on graphene

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Modification of SiO_2 by Self-Assembled Monolayers (SAM) is one of the most promising strategy for tuning the Fermi energy of graphene through the proximity effect. However, the experimentally achieved tuning-range of the Fermi energy has been insufficient because of the non-ideal structure of the SAM on the substrate. In this study, the piranha pre-treatment of the substrate and post-annealing of the SAM were carried out in order to improve the tunability of graphene electronic structure by the proximity effects.

XPS C1s peak assigned to C-O bonding remarkably reduces for SAM-modified substrate by hydrophilic treatment on substrate surface by piranha solution. It is suggested that the improvement of the SAM structure by the formation of bonding to the substrate and removing non-reacted molecules from the surface.

AFM reveals that the SAM structure was rearranged and become dense one by post-annealing.

Enhancement in hole doping to graphene by annealing is confirmed by the blue shift of Raman G-band and the decreasing in G/G intensity ratio.

P251

Dynamics of nonequilibrium carriers in monolayer graphene probed by near-infrared photoluminescence

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We investigated the dynamics of nonequilibrim carriers in a monolayer graphene on a SiO_2 substrate by employing luminescence up-conversion technique. The decay time of the observed luminescence increases with decrease of photon energy, suggesting the slower cooling of the photoexcited carriers with lower energy. We analyzed the luminescence kinetics based on a carrier cooling model considering the carrier-optical phonon interaction. The model calculation reproduced well the luminescence decay curves in the photon energy range of 0.7-0.9 eV, while the curves in the range of 1.0-1.4 eV cannot be reproduced. The observed luminescence in 1.0-1.4 eV is much stronger than the calculated luminescence, indicating the existence of a luminescence component caused by other than thermal carriers: This component is attributed to nonthermal carriers. The decay time of the luminescence at 1.0 eV indicates that the nonthermal carriers last till ~300 fs. A possible scenario for the long duration of nonthermal carriers is that scattering between photoexcited carriers with the assistance of phonons excites the carriers to the high energy region above the linear dispersion, and the relaxation of these carriers takes several hundreds of femtosecond because of the low relaxation rate caused by the nonlinear dispersion.

P252

Energetics and electronic structures of substitutional B and N defects in bilayer graphene

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Since the discovery of graphene, atomically thin monolayer as well as few-layered sheets of graphene has received a lot of attention both scientifically and technologically since they exhibit interesting and important variations in their electronic structures depending on the number of layers. Doping with B and N atoms is one of the effective methods to modify the electronic structures of carbon-based nanomaterials. In this work, we report stabilities and electronic properties of B and N defects in bi-layer graphene using the first-principles density-functional theory. All kinds of dopant sites and stacking patterns (AA and AB) of bilayer sheets are examined and the site-dependent and independent behaviors of the dopants are shown. We also study the electronic structures and demonstrate the STM images of doped bilayer graphene. The B-doped and N-doped defects show distinctive STM images, whereas the STM images are shown to be similar for AA and AB stacking patterns in both B- and N-doped defect cases.

P253

Electronic structure of graphene nanomeshs with square, triangular and hexagonal nanoholes

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Graphene is a potential candidate for channel materials of field effect transistors (FETs) because of their high carrier mobility and good thermal conductivity. However, graphene has no band gap, which poses a serious problem for its application to FET technology. Recently, graphenes with a high-density array of nanoscale holes, which are called graphene nanomeshes (GNMs), are attracting much attention as a possible candidate to overcome the above problem.

In this study, we have systematically investigated the electronic structures of GNMs with periodic array of triangular, square and hexagonal nanomeshes by first principles calculation based on the density functional theory. In particular, we have investigated how the band gap and the effective mass of GNMs change with increasing the neck widths between neighboring nanomeshes. In addition, we discuss the difference of electronic structures depending on shapes of nanomesh such as triangular, square and hexagonal nanomeshes. Based on our simulation results, we propose the best structure of GNMs for FET application.

P254

Electronic structure of oxygen- and hydrogen- adsorbed graphene studied by angle-resolved photoemission spectroscopy

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Graphene has a linearly dispersive energy band near the Fermi level at the K point in the Brillouin zone, called Dirac cone with the massless carriers. In addition to the striking advantage of the massless nature for high mobility of carriers, creation of a band gap in graphene is an essential step to integrate it into Si-based semiconductor devices. It has been theoretically proposed that a band gap is created by atom adsorption on graphene and the gap size is controlled by the amount of adsorbed atoms. In order to examine this proposal and investigate the origin for opening the band gap, we have performed angle-resolved photoemission spectroscopy (ARPES) on hydrogen- or oxygen-adsorbed graphene grown on SiC(0001). We observe the two steep bands around the K point assigned to the pi and sigma; bands of graphene in oxygen-absorbed graphene. In addition, we also find two nearly dispersionless bands at around 5 and 7 eV attributed to the oxygen 2p orbital. In this paper, we report the atom (oxygen and hydrogen)-adsorption-induced creation of a band gap in the pi band, and discuss the origin of the band gap formation by adatoms on graphene.

P255

Effect of Si_3N_4 thickness on the optical characterization of graphene

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Optical detection of graphene on a specific substrate is important for the analysis of the physical or chemical properties of graphene. Si_3N_4, an oxygen free substrate with high dielectric constant, is a good candidate to replace SiO_2. In this letter, we report the optimization of the Si_3N_4 thickness for efficient optical characterization by means of the contrast, enhancement factor (F), and the Raman spectra of the graphene obtained on the selected Si_3N_4/Si substrate. The contrast (visibility) and enhancement factors (F, Raman intensity) of the graphene/Si_3N_4/Si structure were calculated as a function of the Si_3N_4 thickness and the wavelength of the excitation source. A suitable Si_3N_4 thickness generating high visibility and Raman intensities at the wavelength of the excitation source, 633 nm, was obtained.

P256

Nanoscale evaluation of elastic force of graphene by atomic force microscopy

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The mechanical properties (i.e., elastic modulus, adhesion, and deformation) of graphene for various numbers of layers on a SiO_2 substrate were evaluated on the nanoscale by atomic force microscopy. In the case of the multilayer graphene with 25 layers, the multilayer graphene began to be deformed at a pressure of 0.1 GPa, and the dent depth of the graphene reached 0.55 nm at a pressure of 3.5 GPa. This means that each interlayer of the graphene was compressed to 0.022 nm corresponding to a 6% compression of each interlayer of graphene, which is consistent with the results of the compression of bulk graphite in the previous report. However, in the case of single-layer graphene, the dent depth of an interlayer between the graphene and SiO_2 substrate saturated at 0.2 nm at a pressure of approximately 1 GPa. In addition, the higher elastic modulus part, which corresponds to a slightly lower part in the topography image, was locally observed in the two-dimensional elastic modulus mapping of single- or few-layer graphene. This might be due to the presence of water molecules between the graphene and SiO_2 substrate, because a first water adlayer is well known to form an ice structure.

P257

Anisotropic magnetotransport of epitaxial graphene grown on vicinal SiC substrate

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We have measured low-temperature magnetotransport of epitaxial graphene grown on vicinal SiC(0001) substrate, having roughly parallel steps with the height ~1.6 nm arranged with the period ~27 nm. Prominent anisotropy was observed between the directions parallel and perpendicular to the steps. Highly anisotropic appearance of the quantum Hall effect was accounted for by the presence of parasitic parallel conduction allowed virtually only parallel to the steps. The phase coherent time deduced from the weak-localization analysis also showed anisotropy. In addition, small amplitude low-field magnetoresistance oscillations were observed along the direction parallel to the steps. The oscillations can be interpreted as geometric resonances of open orbits resulting from the Bragg reflections due to the periodically arranged steps. The open orbits, composed of a series of arc segments cut out from the cyclotron orbits, run basically along the steps, explaining why the resonances were observed only parallel to the steps.

P258

Graphene-metal interaction investigated by raman spectroscopy

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An intensity ratio of G and 2D band (G/2D) is usually used to estimate the layer number of transferred graphene on SiO2. However, Raman spectra of as-grown graphene on various metals are affected by graphene-metal interaction. For example, G and 2D band intensities of graphen on Ni disappear because strong pai-d hybridization modifies resonance conditions [1].

This fact suggests that it is possible to analyze the graphene-metal interaction by Raman spectroscopy. However, a systematic study has never been performed due to a difficulty for identifying the graphene domains on metal by optical microscopy.

We used in-situ scanning electron microscopy to directly observe and control the graphene growth [1]. With following Raman scattering measurements at the graphene domains identified, we succeeded in collecting the vibration spectra on various metals. We will discuss the relationship between G and 2D intensities and the graphene-metal interaction.

[1] K. Takahashi, K. Yamada , H. Kato, H. Hibino, Y. Homma: Surf. Sci. 606 (2012) 728.

P259

Thickness dependence of magnetoresistance under high-magnetic fields in graphite

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An explosive success in graphene has revived interest in the study of electronic properties in graphite, which can be regarded as the multilayer of graphene. One of the notable features of graphite appears in the magnetoresistance (MR) under high-magnetic fields. Namely, the abrupt enhancement of MR shows up at $B \sim 34$ T at 4.2 K. Under such circumstances, all carriers populate only four quasi-one-dimensional Landau subbands (so-called quasi-quantum limit), and the electronic state goes into the density-wave state. The anomaly in MR is attributable to the emergence of this density-wave state. However, the detail of the subband structures and the nesting vector is not clear. On the other hand, such anomaly in MR is not identified in single-layer or bilayer graphene. These facts indicate that the essence of anomalous MR phenomenon surely lies in k_z dispersion, and if this dispersion can be controlled, the true nature of the density-wave state in the graphite is possibly unveiled. We employ the reduction of the thickness so as to affect k_z dispersion. In this presentation, we report the thickness dependence of MR in graphite up to 40 T with non-destructive pulse magnet, and discuss the quasi-quantum limit electronic state.

P260

Synthesis, characterization and photophysics of graphene donor-acceptor nanoensembles

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Graphene is an outstanding material with exceptional properties that make it an ideal candidate for energy conversion and storage systems. Herein, we present the liquid exfoliation of graphite to few layered graphene sheets together with the non-covalent supramolecular functionalization of exfoliated graphene sheets by the custom synthesized 1-N-methylpiperazinyl-N,N-di(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxydiimide (Pip-PDI). The planar aromatic Pip-PDI has the ability to non-covalently interact with exfoliated graphene sheets, stabilizing them and preventing re-aggregation. On the other hand, the presence of the piperazine moiety on the bay position of the PDI core in the Pip-PDI makes it an ideal electron donor, nicely coupled with electron accepting exfoliated graphene, hence forming a novel donor-acceptor nanoensemble. The new PDI-graphene ensemble was characterized by complementary spectroscopic and microscopy techniques. Furthermore, electronic communication between the counter-parts of the PDI-graphene nanoensemble was identified and probed by photophysical and redox assays, while prototype photoelectrochemical cells were constructed and evaluated.

Partial financial support from the Greek General Secretariat for Research and Technology and the European Commission, through the European Social Funds for Regional Development, NSRF 2007-2013, action ARISTEIA II project FUNGRAPH (3150) Functionalization of graphene with multichromophoric arrays of photoactive units for energy conversion is acknowledged.

P261

Decay patterns of localized states at reconstructed armchair graphene edges

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Using ab initio pseudopotential calculations, we investigate localized states in re-constructed armchair graphene edges. We also present complex band structures of graphene in the armchair and zigzag directions in both the tight-binding and first-principles frameworks. The extension of the conventional band structures to a complex band structure provides information on the energy-dependent decay lengths of the graphene edge states. By comparing the shapes of the complex bands in the armchair and zigzag crystallographic directions, we reveal that the decay behaviors of the edge state are strongly related to the crystallographic directions. Our analysis indicates that our theoretical approach to understanding the edge states through the complex band structure is quite general and can be applied to any graphene-based structure with edges or grain boundaries.

P262

Ab initio study of hexagonal boron nitride as a substrate for carbon nanotube-based devices

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Using first-principles calculations, we study the effects of an external electric field (E-field) and a metal impurity on the electronic properties of carbon nanotubes (CNTs) on the hexagonal boron nitride (hBN) sheet with and without vacancy defects. For each case, we obtained its electronic structures such as the band structure, projected density of states and local potential. We found that the electronic energy bands of the hBN sheet are shifted in response to the applied E-field, regardless of whether the hBN is perfect or defected with a vacancy, and whether there is a metal impurity or not. However, the shifted electronic states in the valence and conduction bands of the pefect hBN are located still far from the Fermi level under the field strength considered, suggesting that the hBN sheet can be considered as a suitable substrate material for CNT-based single-gate FETs, regardless of the existence of a metal impurity and/or a B_3N vacancy. However, hBN substrates with monovacancies and a metal impurity could exhibit poor performance since the imperfections impair electrical conductivity due to residual scattering when strong top-gate voltage is applied in dual-gate FETs.

[S.-H. Kang, G. Kim, and Y.-K. Kwon, Phys. Chem. Chem. Phys. **17**, 5072 (2015).]

P263

Oligothiophene/graphene ensembles managing photoinduced charge-transfer processes: Preparation, characterization, photophysical and redox properties

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Advances in organic synthetic chemistry combined with the exceptional electronic properties of carbon allotropes, particularly graphene, is the basis to design and fabricate novel electron donor-acceptor ensembles with desired properties for technological application. Thiophene-based materials, mainly thiophene-containing polymers, are known for their notable electronic properties. In this frame moving from polymer to oligomer forms, new fundamental information would help to the better understanding of their electrochemical and photophysical properties. Furthermore, a successful combination of their electronic properties with those of graphene is a challenging goal. In this work two oligothiophenes consisting of three and nine thiophene-rings were synthesized and noncovalently interacted with exfoliated few-layered graphene, forming donor-acceptor nanoensembles. Furthermore, the photophysical and redox properties of the oligothiophene/graphene ensembles were evaluated with electronic absorption and photoluminescence spectroscopy and electrochemistry, respectively.

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P264

Controlling growth modes of SWNTs

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A detailed understanding of the catalyst/nanotube interface, under actual growth conditions, is probably a key to a selective synthesis of single wall carbon nanotube (SWNT). Through careful Transmission Electron Microscopy observations [1], so called tangential and perpendicular growth modes were identified and Grand Canonical Monte Carlo simulations based on a tight binding model for nickel and carbon alloys [2, 3, 4], were used to analyze these growth modes at the atomic scale.

Further numerical investigations presented here show that, when catalyst nanoparticles are small enough to be (partially) molten under the synthesis conditions,- i. e. with a diameter below 3 nm -, these growth modes are directly related to the average carbon content in the catalyst nanoparticles. They also show that carbon incorporation energetics and statistics at the SWNT/nanoparticle interface depend on both nanotube helicity and carbon content, thus possibly indicating a route towards a full control of the nanotube structure during synthesis

[1] M.-F. C. Fiawoo et al., Phys. Rev. Lett. 108, 195503 (2012)
[2] H. Amara et al., Phys. Rev. B 79, 014109 (2009)
[3] M. Diarra et al., Phys. Stat. Sol. B 249, 12, 26292634 (2012)
[4] M. Diarra et al., Phys. Rev. Lett. 109, 185501 (2012)

P265

Size dependent phase diagrams of Ni-C nanoparticles

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Carbon nanotube synthesis critically depends on the chemical and physical states of the catalyst particle from which they grow. In the temperature range (600-1000℃) of SWNT synthesis, pure isolated Ni nanoparticles are solid. Under CVD synthesis conditions, reactive carbon may stay adsorbed on the surface, or diffuse to subsurface or in the core of the nanoparticle, thereby inducing a partial or complete melting.

On the basis of the tight binding model developed for the Ni-C system coupled with grand canonical Monte Carlo simulations [1, 2, 3], we calculate size dependent phase diagrams for Ni-C alloys. For NP sizes of about 3 nm, we find that i) the eutectic point lies around 1000K, much lower than the bulk one, ii) a large solid core/molten or amorphous shell domain is found instead of the two phase solid liquid region and iii) carbon segregation from a solid NP surface can take place only at temperatures below 850 K. We discuss the consequence of these findings on our understanding of the SWNT growth mechanisms.

[1] H. Amara et al., Phys. Rev. B 79, 014109 (2009)
[2] M. Diarra et al., Phys. Stat. Sol. B 249, 12, 26292634 (2012)
[3] M. Diarra et al., Phys. Rev. Lett. 109, 185501 (2012)

P266

Continuous production of few-wall carbon nanotubes by “floating-supported catalysts”

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In chemical vapor deposition (CVD), carbon nanotubes (CNT) are grown from catalyst particles floating in gases or supported on substrates/powders. Floating catalyst CVD has realized mass production of carbon fibers (∼100 nm in diameter). It has also realized production of high quality, small-diameter CNTs (a few nm in diameter), but at a small amount, because small catalyst particles rapidly aggregate if they are fed at high concentration. Here we propose “floating-supported catalyst”; each sub-micrometer-sized oxide particle supports thousands of catalyst particles and grows thousands of CNTs.

Al_2O_3 particles (∼300 nm in diameter, 0.5 wt%) were dispersed in $Co(CH_3COO)_2$ aqueous solution (0.15 wt%) and nebulized to yield droplets (∼3 um in diameter) containing one Al_2O_3 particle in each droplet on average. The droplets were carried by Ar to a furnace, dried, calcined and reduced to yield numerous Co nanoparticles (∼10 nm) supported densely on each Al_2O_3 particle. CVD is carried out successively and ∼3 um long CNTs with small diameter (<10 nm) were synthesized at 1073 K under 1.0 kPa C_2H_2/Ar at ambient pressure. Effects of C_2H_2 pressure, solvent and solute in the mother solution will be discussed in detail.

P267

Water encapsulation in a suspended SWCNT measured by photoluminescence imaging spectroscopy

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A single-walled carbon nanotube (SWCNT) has two surfaces, which are the outer surface with positive curvature and inner surface with negative curvature. We have shown that water molecules stably adsorbed on both surfaces of suspended SWCNTs by photoluminescence (PL) spectroscopy[1][2]. Since adsorbed water molecules increase the dielectric constant around the SWCNTs, the adsorption and desorption of water molecules on SWCNTs can be observed as changes of the optical transition energy.

Here, we measured PL spectra and PL images from suspended SWCNTs, whose length was longer than 10 um, controlling temperature and water vapor pressure. For PL imaging spectroscopy, a Ti:sapphire laser (the wavelength ranges from 700 to 840 nm), a tunable band-pass filter (from 1000 to 1600 nm) and 2D InGaAs detector were used.

PL spectra and PL images revealed the processes of adsorption, desorption and encapsulation. They also indicated the transition of water molecules encapsulated in SWCNTs to solid state (so called ice-nanotube).

We will discuss the phase transition of water encapsulated inside SWCNTs based on the PL measurements.

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P268

Role of gold catalyst structure for growing single-walled carbon nanotubes

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Au catalyst offers the potential of growing single-walled carbon nanotubes (SW-NTs) with chirality/diameter distribution differing from those grown on conventional catalysts. SWNTs with diameter up to 8.8 nm were successfully grown on Au nano-particles of 10 nm. The high population of large-diameter SWNTs allows the precise determination of the threshold diameter for an SWNT to collapse [1].

Despite the progress in SWNT synthesis, it remains a challenge to understand what factor determine the catalytic performances of Au particles for growing SWNTs, as only high-temperature annealed Au particles are active. By tracking the evolutions of Au nanoparticles upon calcination and growth of SWNTs, transmission electron microscopy studies show that the face-centered cubic single-crystal Au particles are the active phase for catalyzing SWNT growth. Grand Canonical Monte Carlo simulations demonstrate that icosahedral Au particles are less favorable for carbon dissolution. While single-crystal Au nanoparticles are favorable for dissolving carbon, leading to the nucleation and growth of SWNTs [2]. The studies highlight the importance of catalyst structures and significantly advance our understanding of SWNT growth mechanism, which is meant to guide designing structure-controlled nanoparticles for rational synthesis of SWNTs.

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P269

Synthesis and characterization of SWNTs using W-Co catalyst with low pressure CVD

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Chirality controlled growth of SWNTs is highly expected toward the applications of SWNTs. Recently, it was reported that W_6Co_7 alloy catalyst realized the growth of single-chirality SWNTs with purity over 90 % through pretreatment and growth at high temperature [1]. In order to investigate the controlled-growth mechanism and to conduct the experiment safely, we grew SWNTs using W-Co catalyst via ethanol CVD under much less hydrogen and lower pressure conditions. Owing to a narrow growth window of SWNTs at high temperature, we varied the growth parameters to search for appropriate conditions. We changed reduction temperature (800-1030 C), reduction time (3-10 min.), synthesis temperature (800-1030 C), synthesis time (10-20 min.), partial pressure of ethanol (100-1300 Pa), partial pressure of hydrogen by Ar/H_2 gas (0-150 Pa), and so on. As a result, we succeeded in growing SWNTs at over 1000 C under a condition where partial pressure of ethanol and hydrogen was 100 and 150 Pa, respectively, and total pressure was 5.0 kPa. Raman spectra of the grown SWNTs were measured to examine the chirality distribution.

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P270

Exciton-photon interaction in tip enhanced Raman spectroscopy of single wall carbon nanotubes

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The effect of exciton optical transition on the Raman intensity from tip enhancement Raman spectroscopy (TERs) is calculated for the armchair (5,5) single wall carbon nanotube in the presence of a metallic tip (gold or silver) . This calculation based on the near field factor from the incoming radiation predicts that the intensity of the Raman spectra will increase, this is due to E_{11} and E_{22} exciton transitions which give the main contribution to the Raman intensity. Moreover this calculation also confirm that without the near field factor the dipole vector near the Gamma-point remains zero, while close to K points it is maximum.

P271

Catalyst states during CNTs nucleation as revealed by in situ transmission electron microscopy

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Various catalysts were discovered to grow carbon nanotubes (CNTs), from traditional metals (Fe, Co, Ni), non-conventional metals (Au, Pt, Cu), to metal-free catalysts (SiOx, C60, SWCNT segments). The diversity urges an updated understanding on the nucleation mechanisms. We performed in situ transmission electron microscopy (1) observations on the catalyst states, by using a CNT tubular furnace. It was found that the growth of CNTs from iron oxide involves the reduction of Fe2O3 to Fe3C, nucleation of CNTs from partially liquefied Fe3C. In contrast, while changes in shape, size, and orientation were observed for the Au NPs, no chemical reactions occurred.(2) Furthermore, the active catalyst for metal-free silica was solid and amorphous, suggesting a vapor-solid-solid growth mechanism.(3) We developed a heteroepitaxial strategy to grow SWCNTs from a platelet boron nitride nanofiber. SWCNTs were found to grow epitaxially from the open (002) edges, and the diameters are multiples of the BN (002) interplanar distance.(4)

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P272

Observation of C60F18 polar molecules self-assembling on Ni(100)

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The present work presents the results of the first combined investigation of the C60F18 thin films on Ni(100) surface by X-ray absorption and photoelectron spectroscopies and DFT calculations. In our research, self-organization of polar molecules C60F18 with high electric dipole moments (EDMs) of ~10 D in a thin film on the Ni(100) surface was observed, interpreted and characterized. We have revealed the obtained film structure and traced its morphology modification under X-ray irradiation and thermal annealing. The photoelectron spectra exhibited the film morphology transformation from an as-deposited dielectric continuous 2D thin film to a 3D island film; the reconstruction was likely to be caused by preliminary surface charging that occurred due to X-ray irradiation and was enhanced by lateral intermolecular repulsion due to high EDM. The X-ray absorption spectra show that EDMs of the deposited C60F18 molecules are perpendicular to the surface, and the molecules are attached to the surface on the side of the fluorine atoms. Thus we have pioneered in observing for polar molecules formation of an irregular Ni(100) surface coating consisting in 3D islands with molecule ordering within them.

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P273

Beyond double-resonant Raman scattering: UV Raman spectroscopy on graphene, graphite and carbon nanotubes

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We present Raman spectra of graphite, graphene, and carbon nanotubes with UV excitation energies. Using excitation energies above 5.0 eV we can observe the vibrational density of states of these carbon materials. We get access to regions of the first Brillouin zone that are not accessible with Raman spectroscopy in the optical visible range. By simulations of the phonon density of states of graphene and graphite, we can assign peaks in the UV Raman spectra to certain phonon branches and high symmetry points in the first Brillouin zone. Tuning the excitation towards lower energies activates double-resonant Raman scattering processes with ultra-short wavevectors. We analyze and explain the origin of the scattering processes by simulating corresponding spectra for various excitation energies.

P274

High-yield synthesis and characterization of super-bundle single-walled carbon nanotubes using water-assisted chemical vapor deposition

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In the past two decades, the synthesis of SWCNTs has been studied using various techniques such as arc discharge, laser ablation, and catalytic CVD (CCVD). Extensive efforts have been made to increase the synthesis efficiency of SWCNTs during several years. Especially, introduction of water vapor or O_2 gas during synthesis have been important method for scale-up synthesis of SWCNTs. However, in general, the product yield of SWCNTs was less than 100 % until now. Among various synthesis methods, the CCVD method has attracted much attention because it promises a large-scale, high-purity, controllable, and cost-effective SWCNTs growth compared to other methods. In this work, a large-scale synthesis of water-assisted SWCNTs was investigated over Fe-Mo/MgO catalysts by CCVD of ethylene. Introduction of water vapor into a reactor induced a synthesis of super-bundle SWCNTs (SB-SWCNTs) and dramatically improved the product yield of SWCNTs from 40 to 206 wt%. By adding water vapor, the average diameter of the SB-SWCNTs was increased from 1.5 to 3.0 nm and distribution of the diameter became wider. The Raman peak intensity ratio (I_G/I_D) of the SWCNTs, which indicates the crystallinity and defect degree of SWCNTs, showed an almost constant value of 8 regardless of water vapor concentration.

P275

Temperature-driven exciton localization in carbon nanotubes

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Recent studies have established chemical charge-carrier doping [1,2], side-wall functionalization [2-4] and temperature-driven exciton localization [5,6] as means to modify the photophysics of semiconducting carbon nanotubes. Modified carbon nanotubes are particularly attractive for novel quantum applications by virtue of bright [5] non-classical [6,7] emission from localized excitons and spin-selective optical transitions of charged excitons [8]. In this context we present our recent experimental results on temperature-driven exciton localization in CoMoCAT, HiPco and as-grown carbon nanotubes.

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P276

Tuning the photophysics of localized carbon nanotube excitons with external fields

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Recent studies have established chemical charge-carrier doping [1,2], side-wall functionalization [2-4] and temperature-driven exciton localization [5,6] as means to modify the photophysics of semiconducting carbon nanotubes. Modified carbon nano-tubes are particularly attractive for novel quantum applications by virtue of bright [5] non-classical [6,7] emission from localized excitons and spin-selective optical transitions of charged excitons [8]. In this context we present our recent experimental results on the photophysics of localized carbon noanotube excitons in the presence of external electric and magnetic fields.

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P277

Visualizing the growth dynamics of individual single-wall carbon nanotubes

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In order to meet the increasing demand of faster and more flexible electronics and optical devices and at the same time decrease the use of the critical metals, carbon based devices are in fast development. Single walled carbon nanotube (SWCNT) based electronics is a way of addressing the environment friendly approach of faster and better electronics. In order to exploit the potential of SWCNTs in the electronic industry fully, selective growth of either conducting or semiconducting tubes is of high importance.

Understanding the mechanism for growth of SWCNTs is of great importance for maximizing the quality and yield, and for the ability to control structure including chirality. Transmission electron microscopy (TEM) gives unmatched detailed insight of the local chemical and structural state of the nanostructured materials. Adding the possibility of controlling the gaseous atmosphere around the studied sample at elevated temperature gives a unique way of monitoring gas-solid interactions such as CNT growth.

Here we show the direct experimental evidence on the growth dynamics of SWCNTs from Co/MgO catalysts using CO as carbon source inside the environmental TEM. The evolution of the interfacial structure of the catalyst and SWCNT are monitored during CNT growth.

P278

Quantifying the effect of carbonaceous impurities on the properties of single wall carbon nanotubes

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Carbonaceous impurities are ever present on carbon nanotubes (CNTs) at differing levels and is expected to affect the properties of single-walled carbon nanotubes (SWCNTs), a material composed solely of a rolled surface. We have quantitatively investigated the impact of carbonaceous impurities on the properties of SWCNTs, the ability to disperse, and their properties as an assembled form (buckypaper). We fabricated a family of SWCNT forests varying only the purity through post synthetic carbonaceous impurities deposition from ideally pure (97%) to exceptionally dirty (38%). Every property at each stage decreased nonlinearly with the greatest decrease (25-75%) occurring within the first 15% decrease in purity. These results indicate not only the exceptional sensitivity of properties to purity, but also that it is important as the SWCNT structure (i.e. crystallinity, length, etc.). Further, the strong and immediate effect of carbonaceous impurities demonstrates that even a small improvement in purity would result in a nonlinear increase in properties. Therefore, purity management (< 85%) at all scales is important to utilize the unique and advantageous properties of SWCNTs.

This study is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P279

Sputtering parameters of interval sputtering of catalyst deposition for the CNT growth

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High-area density placement of catalyst particles is required for the high-density growth of CNT forests. Sputtering deposition, widely used in industrial fields, are commonly utilized for the catalyst synthesis, which could enhance the agglomerations of catalyst islands compared with the thermal deposition methods. We have reported the increase in area density of catalysts islands by interval sputtering depositions.

In this paper, the effect of the interval sputtering deposition parameters (such as ON/OFF duty ratio, catalyst thicknesses, etc.) on the structure of CNT forests was investigated.

Fe of 2nm were deposited by interval sputtering of ON/OFF time ratio of 1/30 sec, or DC sputtering on AlOx(30nm)/th-SiO(100nm)/Si substrates, and kept in air for 3 days before CVD. CNTs were grown on them by thermal CVD with C2H2 gas at 730 degree C at 54 Pa for 30 min. Morphologies of grown CNT forests were observed by FE-SEM.

The height of CNT forest of 100 um grown on catalyst deposited by interval sputtering was higher than those of 40 um by DC sputtering. The oxidization of Fe catalysts during interval off time could reduce the diffusion of Fe catalysts into AlO buffer layers resulting in the long-duration catalytic reactions for higher CNT growth.

P280

Network density and electrical characteristics of semiconducting single-walled carbon nanotube networks at percolation threshold

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By virtue of the advances in the separating carbon nanotubes (CNTs), it is possible to use the highly pure metallic or semiconducting CNTs in electronics applications. In general, the CNT networks are preferred to individual CNTs. In this case, the formation of electrical path in the CNT networks is essential. In this study, we calculated the electrical percolation thresholds of semiconducting single-walled carbon nanotube (s-SWCNT) networks, and analyzed the electrical characteristics of the percolated s-SWCNT network. Employing the Monte Carlo method, s-SWCNT networks were randomly formed 100 times between the sourcedrain electrodes. Based on percolation theory, we obtained the percolation thresholds at various channel lengths (2, 6, and 10 um) by using percolation probability. And, we found the network density at electrical percolation threshold theoretically in each channel length. Also, we conducted SPICE calculations for each s-SWCNT network which constitutes electrical paths. At any case, the on/off ratio of the s-SWCNT network FETs was enhanced as network density increased. At last, we found out a power law relationship between the on/off ratio of the s-SWCNT networks and the network density at the percolation threshold.

P281

Gate-voltage induced trions in individual air-suspended carbon nanotubes

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The effects of electrostatically-induced carriers on photoluminescence spectra from air-suspended carbon nanotubes are investigated using field-effect transistor structures [1,2]. We observe an emergence of a peak below the E_{11} emission energy at gate voltages that coincide with the onset of bright exciton quenching. Excitation spectroscopy measurements show that emission intensities for the lower energy peak and the bright exciton peak are maximized at the same excitation energy, confirming that both peaks arise from the same nanotube. The energy separation between the bright exciton peak and the gate-induced peak becomes smaller for larger diameter tubes, as expected for trion luminescence. We obtain trion binding energies that are significantly larger compared to surfactant-wrapped carbon nanotubes, and the difference is attributed to the reduced dielectric screening in air-suspended tubes.

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P282

Thermomechanical behavior of CNF/ SMPU nanocomposites considering reinforcement damage

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In this paper, the effects of adding carbon nanofiber (CNF) to shape memory polyurethanes (SMPU) on the effective thermomechanical properties of the nanocomposite is investigated while he influence of the reinforcement damage mode (the debonding of the inclusions from the matrix) is considered. A thermo-elasto-plastic incremental constitutive equation of reinforced nanocomposite considering the debonding of the reinforcement and as well as the elastoplasticity using micromechanics principles is presented. This study is based on the more realistic engineering situation and the assumption of perfect bonding is not valid. The new approach is evaluated with experimental data and its accuracy is examined. The obtained results from proposed theory and experiments are in good agreement. The normalized thermal expansion coefficient (CTE) as a function of damaged evolution for the debonding damage is studied. The normalized CTE increases when the inclusions gradually turn into voids due to the reduction of reinforcement volume fraction. When all reinforcements are damaged, the CTE is close to that of the matrix in the debonding damage.

P283

Mist CVD method for millimeter-long dense MWCNT array

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For mass production of carbon nanotubes (CNTs), a floating catalyst chemical vapor deposition (CVD) method using a metal complex as a precursor of catalyst is widely used. In this method, it is possible to continuously carry out the production of CNT, however the growth of CNTs longer than a few millimeters is difficult. In this study, we conducted the growth of high density vertically aligned multi-walled CNT array using a mist CVD method.

In our CVD process, first catalyst particles were formed and then CNTs were grown on a substrate. In the catalyst formation step, a catalyst solution containing a precursor of metallic catalyst was supplied by way of mist. Ferrocene and ethanol was used as the catalyst solution. The catalyst solution was atomized by the ultrasonic nebulizer. Ar was used as a carrier gas. In the following CNT growth step, acetylene was flown as a carbon source. Grown CNTs were vertically aligned and densely grown on substrates. Grown CNT array was long, and its growth rate was very high.

P284

Magnetic properties of decamethyl C_{60} chain

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Chemical functionalization of fullerene molecules allows us to design the novel pi electron system with nanometer scale size and curvatures. These fullerene derivatives are known to have interesting diversity in their electronic structures. Indeed, decaorgano C_{60} possesses radical spins on two pentagonal rings surrounded by the functional groups, which prefer the antiparallel coupling than the parallel coupling. In the present work, we investigate the radical spin configurations in the column of decaorgano C_{60} for unraveling the intermolecular and intramolecular spin interactions based on the density functional theory with local spin density approximation. Our calculations show that the radical spins on decorgano C_{60} prefer antiparallel coupling within and between molecules. Calculated intermolecular and interamolecular spin interaction J are 11 meV and 44 meV, respectively.

P285

Investigation of catalytic supports for synthesis of multi-walled carbon nanocoils and nanotubes

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Muliti-walled carbon nanocoil (MWCNC) is a spirally-coiled multi-walled carbon nanotube and can be grown by chemical vapor deposition (CVD). MWCNC is applicable to electron field emission materials and electromagnetic wave absorbers. We have found that MWCNC was grown from the Fe and Sn catalysts loaded on zeolite and that Sn was not detected in the encapsulated catalyst nanoparticles in MWCNC by energy-dispersive spectroscopy equipped with transmission electron microscopy (TEM-EDS). In this study, we examined the CVD conditions using Fe catalyst solely and various kinds of porous materials.

We dropped the ethanol solution of Fe2O3 fine powder and porous materials on silicon substrate and calcined the substrate at 80oC in the air. Zeolite, Al2O3, and MgO were used as a porous material. The CVD conditions were as follows: C2H2/N2 gas flow rate ratio = 0.030.10, growth temperature = 660850oC, and growth time = 10 min.

MWCNCs and MWCNTs were observed with scanning electron microscopy. The composition ratio of MWCNC in the as-grown sample was raised to ～10% when zeolite and Al2O3 were used simultaneously. The averaged fiber diameter of MWCNCs in this sample was 40 nm, almost the same as that grown using Al2O3 solely.

P286

Effect of graphitization treatment on electrical properties of single carbon nanocoil

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Carbon nanocoil (CNC) is a spirally-coiled carbon nanofiber and is applicable to nanosprings and nanoinductors. In this study, we performed the measurement of 12 single CNCs. Furthermore, we compared the electrical properties of graphitized CNC (GCNC) with that of as-grown CNC.

CNC was synthesized by chemical vapor deposition (CVD) in our laboratory. A part of the sample was heat-treated in Ar gas at 2600℃ for 30 min and GCNC sample was prepared. The G/D ratio in the Raman spectra of GCNC and as-grown CNC were 2.4 and 0.94, respectively, which confirmed that GCNC is well graphitized. The focused ion beam (FIB) was employed for fabricating the measurement sample. Single CNC (or GCNC) was fixed on substrate and each of CNC ends was connected to the Au thin film electrode on substrate.

The resistivity of 12 single CNCs was ranged between 1.06×10^{-3} and 8.0×10^{-2} Ω cm and tended to have a dependence of coil diameter. We then measured 3 single GCNCs with a coil diameter range of 400 and 1230 nm and obtained the resistivity between 6.5×10^{-4} and 1.9×10^{-3} Ω cm, almost stable compared to those of CNCs.

P287

Optical transition of single-walled carbon nanotubes in transparent cellulose film

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Photoluminescence (PL) can be observed from single-walled carbon nanotubes (SWNTs) dispersed by DNA or carboxymethyl cellulose (CMC) on the substrate under the dry condition. A Transparent CMC-SWNT film can be fabricated by means of CMC as dispersant. It is important to understand the interaction between CMC and SWNT in order to apply CMC-SWNT films to optical devices.

PL from dried ensemble of CMC-SWNTs red shifted the same as those from dried ensemble of DNA-SWNTs. In this study, we fabricated a transparent CMC-SWNT film using CMC-SWNT solution diluted by 20000 times with pure CMC solution. PL could be obtained from the transparent CMC-SWNT film. The (n-m) mod 3 = 1 type showed increase in E11 and decrease in E22, whereas the (n-m) mod 3 = 2 type showed the opposite behavior. This type dependent behavior could be explained by compressive strain in the axial direction of SWNT. On the other hand, PL from mono-dispersed CMC-SWNTs showed no strain effect. The strain might be caused by the condensation of CMC during the drying process.

In conclusion, PL was obtained from a transparent CMC-SWNT film and the CMC film imposed compressive strain along the SWNT tube axis.

P288

Tuning of optical properties of carbon nanotube (CNT) forest grown using Taguchi method

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Simultaneous control of broad array of carbon nanotube (CNT) growth parameters is crucial to obtain desired properties of CNT forests. Standard procedure of CNT growth requires testing growth parameters separately and choosing values which gave the best results.

In this work, Taguchi method of designing experiment, applied for development of the plan of experiments and elaboration of obtained results, was used to tune optical properties of CNT forest. The method provides data that consist statistically significant factors of a huge number of process factors and allows to find optimum level of the parameters, using signal-to-noise ratio analysis and experimental data analysis.

Acetylene flow, temperature and additional parameters influencing absorbance, reflectance and refractive index were investigated. By simultaneous control of independent parameters of CNT growth, we found optimal levels of parameters for absorbance and reflectance (%R=0,085 ± 0, 15%\) improvement, in comparison to the results obtained during previous research. Furthermore, refractive indexes were measured to define their values for different CNT structures.

By using Taguchi method, we could define interactions between process parameters and their impact on optical properties of CNTs, drastically decreasing the number of experiments at the same time. This approach will support rapid development of future various applications of CNT forests.

P289

Characterization of carbon nanotube aggregates in liquids for making yarns

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Because of their superior mechanical, optical, thermal and electrical properties, carbon nanotubes (CNTs) have been paid particular attention since their discovery. Although much progress has been made so far, it is widely recognized that the bottleneck for applications is to prepare the homogeneous dispersion of CNTs. Indeed the functionality of a wide range of applications depends on the individual CNTs rather than the CNT bundles. The evaluation of dispersion states of CNTs in solutions has therefore been one of the serious issues in the CNT community. Here we examine the dispersion and the aggregation states of (CNTs) solution for making CNT yarns by the several characterization techniques such as centrifuge sedimentation analysis. The estimated particle size and distribution will be discussed as compared to the physical properties of the produced CNT yarns.

This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P290

Pt nanoparticles supported on carbon nanowalls with different domain sizes and their oxygen reduction reaction activity

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Vertically oriented two-dimensional carbon sheets called carbon nanowalls (CNWs) have been fabricated on substrates [1]. Each CNW is composed of nanographite domains with several tens of nanometers [2]. Recently we demonstrated that the unique structure of CNWs is useful as Pt support in fuel cells [3]. The domain boundaries in CNWs are effectively activated as absorbed sites of Pt nanoparticles. Furthermore, it was shown that the Pt/CNW has high electrochemical active surface area and utilization for hydrogen anode reaction.

In this paper, we report the Pt loading for CNWs with different domain sizes and their oxygen reduction reaction (ORR) activity for improving its performance. It is shown that the size of Pt-nanoparticles decreases with decreasing domain size. Additionally, the decrease of the particle size leads to the increase of the ORR activity. The highest value is about twice as much as that of commercial Pt/C. Thus, the high ORR activity of Pt/CNWs exhibits that they are more promising materials for practical application of fuel cells.

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[3] S.C. Shin et al., J. Appl. Phys. 110, 104308 (2011).

P291

Facile and controllable synthesis of heteroatom-doped carbon nanotubes under atmospheric pressure

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Here we demonstrate an atmospheric-pressure, solution-assisted substitution method to produce heteroatom-doped CNTs with varying heteroatoms including nitrigen(N), boron (B), sulfur (S), and phosphorus (P). Pristine multi-walled CNTs (MWCNTs) were used as starting materials. The heteroatom-doped CNTs were then produced by heating the mixture of heteroatom precursor and MWCNTs under argon (Ar) atmosphere from 300 to 1200℃ for 1 to 8 hr at atmospheric pressure. We found that the heteroatom concentrations in the nanotubes could be tuned by controlling the reaction temperature and time, confirming by the X-ray photoelectron spectroscopy (XPS) and Raman characterizations. Detailed XPS characterization indicated that the heteroatoms were successfully doped into the sp2 graphene lattice of CNTs. Raman characterization was performed and shown the ratio of the D- and the G- bands (ID/IG) was increased for the as-produced samples due to the doping process can be controlled in our method. Thin-film electrical conductance characterization suggested the electrical conductances of the heteroatom-doped CNTs were significantly improved by heteroatom doping, making them useful materials for electronics and electrochemical-base applications. It is also noteworthy from a practical point of view that the developed atmospheric-pressure synthesis method is amenable to industrial-scale production since it avoids the need for a vacuum system.

P292

Mechanism and applications of Far-infrared optical response of carbon nanotubes

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The optical response of carbon nanotubes (CNTs) in far-infrared (FIR) frequency range are intriguing for the origin of universally observed peak-like features. Recently, we reported the FIR optical response of Single- and Multi-Walled CNTs (SWCNTs and MWCNTs). The FIR peak-like features showed clearly dependence to their effective conductive channel length and geometrical structures[1,2]. These results are consistent with theoretical predictions by the model of one-dimensional plasmon excitation resonance. In this model, the FIR peaks should be directly reflected by the resonance length and quality of wall structures.

In this paper, we present the detail experimental results of various types SWCNTs and MWCNTs. We also show that these sensitive peak position and line-shapes are useful for inspecting CNT length, qualities and damages during sample preparation process.

This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

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P293

CNT cap nucleation from hydrocarbons: combined molecular dynamics and monte carlo simulations

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Cap nucleation and the effect of atomic hydrogen on the growth are still not fully understood. We here study the atomistic mechanisms of cap nucleation and the role of hydrogen atoms during the growth process from hydrocarbon species, i.e., C2H2, C6H6, CH4 molecules as well as C2H and CH3 radicals, by means of hybrid MD / force-bias MC simulations. Four nucleation stages are distinguished, including graphitic network formation and subsequent cap lift-off through the intermediate formation of vertically oriented, not fully dehydrogenated or/and rehydrogenated graphitic islands. In the intermediate nucleation stages, these vertical graphenes gradually lose their H atoms depending on the growth temperature and type of hydrocarbon species, as well as on their flux. Subsequently, dehydrogenation allows these graphene patches to curve over the surface, connect, and form a continuous graphitic network, which eventually leads to cap formation. The results indicate that controlling the extent of dehydrogenation offers an additional parameter to control the nucleation of CNTs. Overall results lead to a better understanding of the initial stages of hydrocarbon-based CNT growth at the atomic level.

P294

Plasma-assisted CNT etching mechanisms in the initial growth stage: combined molecular dynamics and monte carlo study

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Hydrogen enhances CNT growth by assisting in catalyst activation. It may, however, also hinder the formation of graphitic carbon, if its concentration is too high, e.g., in H2-plasmas. The precise etching behavior of the H2 plasma during the early stages of CNT growth is still not fully understood. We here study etching mechanisms of the cap and incipient (defective) nanotubes in comparison with ideal nanotubes to under-stand the effect of atomic H on the initial nucleation stage of the CNT growth. The hydrogenation and etching processes are investigated by combined MD and force-bias Monte Carlo (tfMC) simulations at 1600 K. In the initial etching stage, three specific stages can be distinguished, i.e., 1) CNT hydrogenation and H clustering on the surface; 2) breaking of the first C-C bond; and 3) hole creation or etch pit formation. Due to the hydrogenation, cap structures can also convert to vertical graphene patches. During the hydrogenation/etching process, different types of etching CxHy species in addition to desorbed H2 molecules are found in the gas phase. The results help to understand the etching behavior of H2-plasmas on the initial stages of CNT growth.

P295

Efficient CVD growth of single-walled carbon nanotubes smaller than (6,5)

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Ultra-small diameter SWNTs are grown by alcohol catalyst chemical vapor deposition (ACCVD) method by using USY-zeolite supported (Fe-Co, Cu-Co) catalysts. The temperature range of growing high-quality SWNTs is extended down to 430 degree C combining with very low partial pressure of ethanol down to 0.02Pa. SWNTs with diameters smaller than (6,5) are known to be very inefficient to grow unless inside of special zeolite pore or inside of an outer nanotube. By the low temperature growth with the conventional Fe-Co catalysts, we can extend the small diameter limit; ratio of smaller diameter tubes increased with lower temperature CVD with optimum low pressure. By using Cu-Co catalysts, diameter distribution can be narrower. Resonant Raman with 5 excitation laser lines, absorption and Photoluminescence (PL) are used to characterize abundance of small diameter nanotubes such as (6,4), (5,4), (8,0) etc.

P296

STM/STS investigation of Europium nanowires encapsulated in carbon nanotubes

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The discovery of carbon nanotubes (CNTs) and their fascinating properties have ignited intense research interests on one-dimensional systems. One-atom-thick nano-wires are ideal and ultimate one-dimensional system and have attracted a great deal of attention. Ultrathin nanowires are however fragile and readily depredated under normal conditions, which prevent us from investigating their properties. In this work, we have focused on one-dimensional ultrathin Eu wires encapsulated in CNTs (EuNW@CNT). Eu wires in EuNW@CNT are extremely stable and can be treated under atmosphere. In this presentation, we are going to present synthesis and investigation of spatially-resolved electronic structure of EuNW@CNT by scanning tunneling microscopy/spectroscopy.

EuNW@CNT was synthesized by direct nano-filling method and deposited on Au(111) surface by pulsed-jet deposition technique for preparing clean sample surface. We observed a new peak in a STS spectrum that arise from localized density states of the Eu wire nanowire. Spatially-resolved STS spectra indicate that the position of Eu atoms in EuNW@CNT directly, which leads to precise assignment of the STS peak and interaction between Eu nanowires and CNTs.

P297

Atmospheric Ions as the origin of phtoinduced degrading of photoluminescence from single-walled carbon nanotube

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Single-walled carbon nanotubes (SWCNT) is feasible materials for the nanoscale light source because of those unique one-dimensional structure, electrical and optical properties. Emission instability at high excitation regime such as photoinduced bleaching or blinking of photoluminescence from SWCNTs is one of the problems to be solved for the application of SWCNTs to such devices. We will talk about atmospheric ion as the origin of photoinduced bleaching and blinking of photoluminescence from SWCNTs.

Air-suspended SWCNTs exposed to dense atmospheric ions showed decreased intensity and a low energy shift of the photoluminescence. The amount of the decrease and shift were attributed to the sp3 hybridization of carbon atoms and dielectric screening of exciton due to chemisorption of water cluster ions, respectively. Important point is that this change is strongly accelerated by laser light excitation of SWCNTs. This means that atmospheric ions are the possible candidate for the origin of so-called photoinduced bleaching and blinking of the photoluminescence from SWCNTs.

P298

Magnetic susceptibility measurements on highly purified single-wall carbon nanotubes

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Single-wall carbon nanotube (SWCNT) was predicted to show novel magnetism originating from its quasi-one dimensional electronic structure, where orbital diamagnetism and Aharanov-Bohm effect give major contributions. It was shown theoretically that magnetic susceptibility depends on field direction, carrier doping, and types of electronic structures. Semiconducting SWCNT are diamagnetic in the direction both of parallel and perpendicular to the tube axis, while metallic SWCNT is para-magnetic (diamagnetic) for applied field parallel (perpendicular) to the tube axis. In particular, one of the main predictions of theory, which can be tested by experiments, is that magnetic susceptibility increases linearly with the nanotube diameter. However, because magnetic impurities are usually included in as-grown SWCNT sample, systematic experimental verification of intrinsic magnetic susceptibility is still not available. Here, we prepare almost ferromagnetic impurity-free SWCNT sample by combining acid treatment and ultracentrifuge density gradient (DGU) method. We observed that magnetic susceptibility of SWCNTs scales linearly with the nanotube diameter. Furthermore, we also estimated magnetic susceptibilities of purely semiconducting and metallic SWCNTs by measuring two SWCNT samples with different semiconducting SWCNT ratios, and the estimated magnetic susceptibilities are consistent with theory.

P299

Thermal properties of carbon nanowalls probed by Raman spectroscopy

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Carbon nanowalls (CNWs) fabricated by dc-plasma enhanced chemical vapour deposition (dc-PECVD) are composed of uniform nano-graphite domains with several tens of nanometers and high quality [1]. Such unique structure of CNWs has stimulated various applications for electronic devices. The understanding of the thermal properties is important for applications. In this paper, we report the temperature dependence of the Raman spectra of CNWs with different domain sizes in the temperature range of 298 K to 673 K.

The Raman spectra of CNWs exhibited G and D bands at ~1590 cm^{-1} and ~1353 cm^{-1} respectively. The G band peak monotonically decreases with increasing temperature. From the slope of the peak position as a function of temperature, the temperature coefficient (dw/dT) is estimated to be -0.019 cm^{-1}/K for G band. It should be noted that the temperature coefficients strongly depend on the domain size of CNWs. The temperature coefficients will be compared with CVD-derived monolayer graphene [2], and the origin will be discussed in light of the thermal expansion coefficient of CNWs [3].

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P300

Coherent phonon spectroscopy of single-walled carbon nanotubes: a quest for excited-state vibrational dynamics

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Coherent phonon spectroscopy has potential for revealing the electron(exciton)-phonon coupling of single-walled carbon nanotubes(SWCNTs) [1,2], especially that in excited states [3], in which the electron-phonon coupling is predicted to strongly depend on excitation energy and chirality [4]. However, extracting information on excited-state vibrational dynamics is not straightforward since pump-probe signals generally contain contributions of both ground and excited-state nuclear wavepackets. The issues are how we can distinguish the two contributions and to investigate excitation-energy dependence.

Here we utilize an effective linear response approach to femtosecond pump-probe vibrational spectroscopy based on a moment-analysis of pump-induced wavepackets [5,6]. This simulation provides oscillatory amplitude and phase profiles of either ground or excited state separately, which can be compared with experiments by using measured absorption or emission lineshapes, respectively, and pulse spectra. We will then present detailed comparisons between the simulation and experiment for (6,5)-enriched SWCNTs excited across either the first(E_{11}) or second(E_{22}) excitonic transitions.

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P301

Controlled synthesis of single-walled carbon nanotubes using sputtered W/Co

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Single-walled carbon nanotubes (SWNTs) have been widely recognized as promising building blocks for nanoscale electronics because of their unique structure-dependent electronic properties. However, one of the main obstacles to applications of SWNTs is the controlled synthesis of SWNTs with desired (n, m) structure. Recently, the tungsten-based nano-clusters have been used as catalysts to grow SWNTs with a single chirality of (12, 6), resulting in an abundance higher than 92% [1].

Here, we report an improved density of SWNTs with narrow chirality distribution by using sputtered W/Co. Alcohol catalytic chemical vapor deposition (ACCVD) was conducted for the selective growth of (12, 6) at low temperature, much lower than that of originally reported tungsten-cobalt clusters [1]. High-quality and uniform SWNTs were obtained. Raman spectroscopy with different excitation wavelengths shows narrow (n, m) distribution than that of monometallic cobalt system. The absorption spectroscopy reveals the abundant (12, 6) in the randomly collected samples. Further parametric study of the controlled synthesis of SWNTs will also be presented. The chirality distribution and growth mechanism will be discussed in detail.

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P302

Electronic transport properties of defective CNTs - A multiscale approach

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Mainly due to the high linearity of the current-voltage characteristic, carbon nanotube (CNT) field effect transistors (FET) have become potential candidates for high-frequency analogous applications essential for mobile system technology. Wafer-level compatible fabrication procedures (1) are therefor a promising tool to transfer CNTFETs into usage. Device simulations play the most important role to support these fabrication processes starting with understanding the device physics through to optimizing the circuit design.
In this work we investigate the influence of defects on the electronic transport properties of CNTs by using different abstractions levels. First, we use a simple orthogonal tight-binding representation in combination with the recursive Green's function method to calculate transmission spectra and local density of states for CNTs possessing randomly distributed defects with different densities. These results are then employed to calibrate the effective mass Schroedinger-Poisson solver (2) to study the output and transfer characteristics of a predefined CNTFET architecture.

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P303

3-Dimensional networks of carbon nanotubes and graphene

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We will first describe the synthesis of carbon nanotubes and nanotube networks using different dopants during chemical vapor deposition. We will discuss the effects of sulfur, boron and nitrogen. These dopants are responsible for significant changes in the nanotube morphology and electronic properties. For example, sulfur induces the formation of pentagons and heptagons, whereas boron aids the growth of heptagonal carbon rings, and nitrogen promotes the formation of pentagonal cusps. Thus, it is indeed possible to assemble/grow carbon nanotube networks if a careful control of dopants is achieved during chemical vapor deposition (CVD) growth. High resolution electron energy loss spectroscopy studies on nanotube materials will be presented, and locations of boron, sulfur and nitrogen within nanotubes will be shown. Theoretical calculations on nanotubes containing pentagon, hexagons and heptagons in the presence of these dopants will be discussed. Recent experiments on different doped graphene layers will also be presented. We will discuss the citotoxicity and applications as molecular sensors of these doped nanocarbons. We will also discuss the synthesis of 3-Dimensional networks of graphene and graphene-nanotube hybrids using chemical routes and controlled drying/annealing processes. The mechanical and electrical properties of these systems are outstanding and will be discussed in detail.

P304

A census of chirality population in a nist reference material of single-walled carbon nanotubes

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A reference material is essential to enable and accelerate the commercialization of a new material. The National Institute of Standards and Technology recently released the worlds first reference material (RM) of a single-wall carbon nanotube (SWCNT) dispersion known as RM8281. However, the accompanying User Information doesnt include chirality distribution, which is known as one of the most important structure parameters. Here, we present for the first time a quantitative chirality assessment of the RM8281 by using an enhanced method for absorption spectrum analysis. Our results show that approximately 75 % of SWCNTs in RM8281 have a diameter in the narrow range of 0.7 - 0.9 nm, and 69 % of SWCNTs have a chiral angle from 15° to 30°. Of significance, about 25 % of the total RM8281 SWCNT population was found to be the (6,5) species nanotubes. Transmission electron microscopy and electron diffraction techniques were utilized to complete an adequate statistical analysis of chirality distribution in RM8281, giving a satisfactory agreement with the above absorption spectra measurements. More importantly, the independent multiple characterization methods give a full quantitative chirality assessment of the RM8281, which significantly promote the application of the material as a SWCNT reference sample.

P305

Morphology and electrical conductivity of poly(2-vinylpyridine-co-styrene) composites with carbon nanofillers: multiwall carbon nanotubes and herring bone structures

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Dielectric properties and morphology of nanocomposites based on poly (2-vinylpyridine-co-styrene) (P2V-S) as a matrix and either multiwall carbon nanoubes (MWCNTs) or herring bone carbon structures (HBC) as nanofillers are investigated. The electrical conductivity measurements in the wide frequency (10-2-10-6 Hz) and temperature range allow to describe the dependence of electrical properties on the size, the type and the volume fraction of the carbon nanoadditive. Nanotube-polymer interactions are evaluated by Raman and Fourier Transform Infrared Spectroscopy (FTIR). The dispersion and distribution of carbon nanostructures in the polymer is studied by combination of Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM).

Acknowledgements
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P306

Nitrogen doped carbon nanotubes with encapsulated Fe3C Composites synthesized by a direct pyrolysis

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Carbon catalysts with encapsulated iron species have be considered as a novel non-precious metals oxygen reduction reaction (ORR) catalysts in acidic medium. In this paper, the nitrogen doped carbon nanotubes with encapsulated Fe3C (Fe3C@NCNTs) catalyst was synthesized by simply pyrolyzing a mixture of ferric chloride and melamine without high pressure. The EDS and XPS results reveal that Fe3C is mainly encapsulated in the interior of NCNTs and N species is mainly distributed on the outside surface of NCNTs. The growth mechanism of Fe3C@NCNTs has been demonstrated by TEM and XRD. Amorphous carbon dissolves in metal phase and graphitic layers are formed by the carbon-through-metal diffusion. Above 680 oC, Fe2O3 is completely transformed into Fe and Fe3C, and graphitic layers begin to grow into carbon nanotubes. Meanwhile, the hot liquid-like cementite particles axial move in graphitic layers. The as-prepared Fe3C@NCNTs catalyst exhibits superior ORR activity in acidic medium, revealing the synergetic active site of Fe3C.

P307

Vapor-condensation-assisted optical microscopy for ultralong carbon nanotubes and other nanostructures

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Here we present a simple yet powerful approach for the imaging of nanostructures under an optical microscope with the help of vapor condensation on their surfaces. Supersaturated water vapor will first form a nanometer-sized water droplet on the condensation nuclei on the surface of nanostructures, and then the water droplet will grow bigger and scatter more light to make the outline of the nanostructure be visible under dark-field optical microscope. This vapor-condensation-assisted (VCA) optical microscopy is applicable to a variety of nanostructures from ultralong carbon nanotubes to functional groups, generating images with contrast coming from the difference in density of the condensation sites, and does not induce any impurities to the specimens. Moreover, this low-cost and efficient technique can be conveniently integrated with other facilities, such as Raman spectroscope and so forth, which will pave the way for widespread applications.

P308

The shortest “ionic” fullerene peapod: Synthesis, characterization and specific charge transfer character of $\mathrm{Li^+@C_{60}}$ encapsulated [10]CPP

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It is well known that cycloparaphenylenes (CPPs), hoop-shaped pi-conjugated molecules, selectively encapsulate fullerenes. Because CPPs represent shortest sidewall segment of armchair carbon nanotubes, resulting CPP-fullerene complexes are regarded as shortest fullerene peapods. To understand the unique electronic properties of fullerene peapods, detailed studies of the electronic interaction observed in well-characterized CPP-fullerene complexes are quite important. Here, we report the synthesis and characterization of new type of shortest fullerene pea pod $\mathrm{Li^+@C_{60}}$ encapsulated [10] CPP, and its notable properties induced by the specific intermolecular interaction between $\mathrm{Li^+@C_{60}}$ and [10]CPP.

The complex $\mathrm{Li^+@C_{60}}$-encapsulated [10]CPP was immediately formed when $\mathrm{Li^+@C_{60}}$ and [10] CPP were mixed in dichloromethane. The 1:1 complex of [10]CPP with $\mathrm{Li^+@C_{60}}$ was unambiguously characterized by NMR, ESI-MS, UV-vis titration as well as X-ray crystal structure analysis. UV-vis-NIR spectrum showed new absorption band due to the charge transfer interaction between $\mathrm{Li^+@C_{60}}$ and [10]CPP. In addition, the complexation renders $\mathrm{Li^+@C_{60}}$ less reducible, which indicates the increase of electron density of $\mathrm{Li^+@C_{60}}$ induced by the electron transfer interaction. In the presentation, other interesting results such as photophysical property of the complex will be also discussed.

P309

Carbon nanotubes growth by thermal CVD from the ends of CNT forest on SiC

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We report the synthesis of carbon nanotubes by thermal CVD method from uncapped carbon nanotube forest as template. The CNT forest was formed by SiC surface decomposition (CNT forest on SiC) [1,2]. CNT forest on SiC consists of nearly ideally close-packed, well-aligned, and catalyst-free CNTs. The length of CNT forest was about 30 nm. Then, this CNT forest was treated to uncap CNTs by H2O2 solution treatment [3]. CNTs were grown from uncapped CNT surface by thermal CVD method with CH4 and H2 as source gases[4]. We explored the optimal proportion of these gases and temperature condition for growth. In thermal CVD method, CNTs were grown under wide range conditions. The best condition of these gases for non-catalytic CVD growth was CH4 ratio of 40%, 1000℃. Various diameters CNTs grew rapidly from the surface of CNT forest.

We will report the detail analysis of the synthesized CNTs.

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P310

In situ TEM study on electric transfer in a multiwall carbon nanotube; contact formation with a metal electrode and inter-shell conductance

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Multiwall carbon nanotubes (MWNTs) are expected to be applied to electrical wires and interconnect in nanoscale electronic devices. To integrate MWNTs into electronic devices, it is necessary to examine how the structural change by joining process of a MWNT and a metal electrode affects their electric conductive properties. In this study, the structural change of a MWNT contacted with a Mo electrode during the passage of electrical current was observed by in-situ transmission electron microscopy (TEM), and current-voltage characteristics to the MWNT were simultaneously measured. We found that inner-shells of the MWNT were retracted to the Mo electrode and total electrical conductance was decreased accordingly. This result shows that inner-shells being retracted to the Mo electrode contribute to the electric conduction of the MWNT. We thought that the change of electric conductive properties mainly results from the change of inter-shell transfer between the inner-shells being retracted to the Mo electrode and outer-shells adjacent to them.

P311

Enhanced optical response of gold-carbon nanohybrid colloidal systems

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Here we report on a new hybridization route of carbon nanotubes we introduced to overcome their low emission yield. Following a bottom-up method, we grew metallic nanoparticles in colloidal suspensions and used them to produce the hybrids as well. By rationally choosing the features of the metallic system, it is possible to combine and take advantage of both the proximity effects and of the localized surface plasmons. We will highlight the effect of the energetic overlap between tubes and metallic particles on the optical response of our hybrids.

P312

Carbon nanotube grafted carbon fibres - for CO2 capture construct

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Carbon nanotubes (CNT) continues to interest researchers for their exceptional mechanical, thermal, and electrical properties. These properties has led to tremendous applications in many fields.

Among various approaches for growing CNT, chemical vapour deposition method (CVD) has proven to be an effective method to generate large amount of CNTs as it allows direct growth on different substrates (MgO, SiC, Al2O3, Si and carbon fibre).

Among various, one of the most important applications is fabrication of constructs to capture CO2 emissions from power station. Currently, one of the major concerns regarding CO2 capture is its significant cost and CO2 uptake efficiency. The solution is to improve the efficiency of current capture technologies and develop new cost-effective and environmentally friendly technologies. Hence, this work presents the investigation of a novel CO2 capture technique using different constructs prepared from a mixture of carbon fibre (CF), CNT grafted carbon fibre, CF, CNT and resins. Methods of grafting CNTs on CF will be presented.

P313

Towards type-selective SWCNTs growth: Comparative study on characterization techniques for an effective CVD process development

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For direct integration of CVD grown SWCNTs in applications like FETs, it is of crucial importance to know the quality and composition of the material. Unfortunately for more advanced CVD process exploiting for instance multi-catalyst systems, it is in general a very time consuming procedure to access important details like content of amorphous or sp2/sp3 carbon as well as semiconducting to metallic ratio or even chiral distribution.

In search of an effective characterization method for CVD process developments, we performed a comparative study using several characterization techniques to investigate purity, structure and type of CVD grown vertically aligned SWCNTs (VA-SWCNTs). Therefore microscopic techniques such as AFM, SEM, and TEM as well as spectroscopic techniques like XPS, TGA, Raman spectroscopy and UV-Vis absorption spectroscopy were used. The advantage and disadvantage of these characterization techniques are balanced and a multi-technique approach is suggested to achieve a fast and reliable access to the essential information.

P314

Optical and THz properties of carbon nanotube forests

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Recently, black body absorption has been reported in high-density and vertically-oriented carbon nanotube (CNT) forests. Unique optical properties of CNT forests opened the next door of opt-electronics applications.

In this paper, we report anisotropic optical properties of vertically aligned CNT forests with varying structures (vertically alignment, height, area density and so on.) in UV-VIS, IR, and THz regions.

CNT forests were grown on Si substrates by catalytic thermal CVD using a C2H2 gas source utilizing Fe catalyst films on AlO or Al support layers at 480 730 degree C. Optical spectra in UV-VIS, IR, and THz regions were obtained by ellipsometry, FT-IR, THz absorption measurements, respectively.

The phase difference in ellipsometry increased for higher area density and higher degree of vertically alignment of CNT forests. CNT forests with higher degree of vertical alignment showed increasing of real and imaginary refractive index in lower freq. of 0.3 1THz.

Anisotropic optical index of vertically aligned CNT forests are interpreted by the anisotropic electrical conductance of nano-rods of CNTs.

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P315

Changes in structure and composition of Si nanoparticles on a multiwall carbon nanotube at high temperatures

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The structural dynamics of silicon (Si) nanoparticles supported on the surface of a multiwall carbon nanotube (MWNT) during Joule heating of the MWNT were studied by in-situ high-resolution transmission electron microscopy equipped with a spectroscopy system. The Si nanoparticles reacted with the outer layers of the MWNT to form silicon carbide (SiC) nanoparticles with increasing temperature. Note that the diffusion of carbon atoms from the MWNT into the Si nanoparticles leads to the formation of SiC nanoparticles, i.e., carburization occurs in the Si nanoparticles. Subsequently, silicon atoms were entirely sublimated from the SiC nanoparticles at temperatures of up to approximately 1900 K, and the remaining carbon atoms formed hollow carbon nanocapsules consisting of multilayered graphene shells on the MWNT surface. The present study provides a new approach toward the synthesis of carbon nanocapsules through the transformation of Si nanoparticles on an MWNT via SiC nanoparticles by Joule heating.

P316

Fundamental growth studies of single-walled carbon nanotubes synthesized using the floating catalyst method: Perpendicular growth and catalyst detachment?

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We report complementary differential mobility analysis (DMA), atomic force microscopy (AFM) and transmission electron microscopy (TEM) studies on the growth dynamics of SWNTs synthesized using the floating catalyst method using iron catalyst nanoparticles produced using a high-voltage spark discharge [1] and CO as the carbon feedstock.

The size distribution of the catalyst particles entering the CVD reactor can be precisely determined using DMA. Based on high-resolution TEM and optical absorption spectroscopy, the diameters of the grown SWNTs are 1.1-1.2nm, and the size of active catalyst nanoparticles varies between 1.97 and 4.85nm (mean 3.34nm), giving a mean diameter ratio of 3 between the catalyst and the SWNT and indicating a perpendicular growth process.

Additionally, we have performed tapping mode AFM and MFM on SWNTs deposited on mica using a thermophoretic precipitator [2]. Catalyst nanoparticles can be found attached to the ends of the SWNTs and freely on the substrate, with the attached particles following a log-normal size distribution with a mean of 2.7nm and the free particles following a bimodal distribution with peaks at 2.7 and 6nm. We postulate that the smaller mode corresponds to particles that have been detached from SWNTs, and the larger mode to agglomerated inactive particles.

P317

Upconversion photoluminescence properties of individual carbon nanotubes

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Since the first report of efficient near-infrared photoluminescence (PL) from individual carbon nanotubes [1], numerous distinctive luminescence properties of nanotubes have been revealed [2,3]. However, we have recently discovered an additional remarkable characteristic [4]: the ability of carbon nanotubes to efficiently emit high energy photons by absorbing lower energy photons in the near-infrared optical range. This type of luminescence phenomenon is known as upconversion photoluminescence (UCPL) [5], and has been intensively studied in other material systems because of its potential usefulness in various applications such as photovoltaic energy conversion and PL bio-imaging. Here, we performed direct observation of the UCPL from an individual (6,5) carbon nanotube by micro-PL spectroscopy/imaging techniques. Under epi-illumination of near infrared incident light of wavelength ~1100 nm, we clearly observed UCPL image (950-1000nm) of individual carbon nanotubes at room temperature. The mechanism, efficiency, and stability of UCPL in individual nanotubes will be discussed.

[1] M. J. O'Connell, et al., Science 297, 593 (2002) [2] Y. Miyauchi, J. Mater. Chem. C 1, 6499 (2013) [3] Y. Miyauchi, et al., Nat. Photon. 7, 715 (2013) [4] N. Akizuki et al., to be submitted [5] F. Auzel, Chem. Rev. 104, 139 (2004)

P318

Designed catalyst deposition for efficient growth of parallel aligned carbon nanotubes and their nanoparticle-assisted optical visualization

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Superlong carbon nanotubes (CNTs), which have perfect structures, extraordinary electrical, thermal and mechanical properties, have shown great potential for applications in nano/micro devices and superstrong fibers. However, the controllable preparation is still a big challenge. Compared with agglomerated CNTs and vertically aligned CNTs, superlong CNTs usually have low areal densities and narrow growth windows. Herein, we developed a series of strategy to improve the CVD growth efficiency of superlong CNT arrays. First, we introduced nanospheres to anchor catalyst nanoparticles and effectively improved the areal density of long CNTs. Then, we employed graphene/graphite layers to support the catalysts, and also observed increase of areal density of ultralong CNTs. Furthermore, we develop a rational ambush catalyst strategy for the high efficiency and reliable growth of horizontally aligned CNTs on surfaces. Besides, we realized the optical visualization of individual ultralong CNTs through a facile vapor deposition of nanoparticles on CNTs. A series of nanoparticles, could be deposited on the individual CNTs, leading to the observation and manipultion of individual CNTs with optical microscopes or even naked eyes. These efforts are expected to benefit the mass production and the practical application of superlong CNTs on surfaces.

P319

Modulating diameter of single-walled carbon nanotubes in alcohol catalytic chemical vapor deposition

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Modulating the diameter of a single walled carbon nanotube (SWNT) is essential for its applications in optical and electronic devices. We demonstrated in our alcohol catalytic chemical vapor deposition (CVD), that the average diameter of vertically aligned SWNTs can be successfully reduced down to 1.2 nm by changing component ratio in a CoMo bimetallic catalyst prepared by dip-coating or spray-coating. [1,2] Recently, Cu is found to be effective in reducing diameter, and sub-1-nm SWNTs are obtained using this CoCu combination. [3] To understand the underlying mechanism, an in-plane transmission electron microscopy (TEM) technique is proposed to investigate the structure and element distribution of the catalyst. This technique enables a direct characterization on SiO_2 film and thereby minimize the information change or loss from CVD chamber to TEM column. For example, in CoCu, small Co are found anchored epitaxially and kept metallic on large Cu particles. This structure results in a much better dispersion of active sites on the substrate and explains the formation of sub-1-nm SWNTs. SWNT Growth from Co, CoCu, CoMo, and the newly proposed CoW, are systematically studied.

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P320

Selective synthesis of semiconducting and metallic single-wall carbon nanotube films

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Single-wall carbon nanotubes (SWCNTs) can be either semiconducting or metallic, depending on their diameters and chiral angles. Semiconducting SWCNTs (s-SWCNTs) are potential channel material of high-performance field effect transistors, while metallic SWCNTs (m-SWCNTs) can be used for the fabrication of transparent conductive films. Therefore, it is highly important to prepare pure s-SWCNTs and m-SWCNTs selectively. We studied the growth mechanism and oxidation process of CNTs by using an in situ TEM method, from which, the structure-dependent stability of SWCNTs is revealed. Then, we developed an in situ selective etching approach by using suitable amount of oxygen or hydrogen as an etchant during the growth of SWCNTs by the floating catalyst chemical vapor deposition method. As a result, m-SWCNTs with relatively higher chemical reactivity are selectively removed, and s-SWCNTs with a concentration higher than 90% are obtained in large scale. Alternatively, by controlling the growth parameters and hence the diameter distribution of m- and s-SWCNTs, selective removal of small diameter s-SWCNTs is realized, and large diameter m-SWCNTs were preferentially synthesized. We also developed an approach and apparatus for the continuous collection of the grown SWCNT. As a result, large area, high quality SWCNT thin films are obtained in large scale.

P321

High purity synthesis of narrow-chirality distributed single-walled carbon nanotube and its growth mechanism by pulse plasma CVD

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Single-walled carbon nanotubes (SWNTs) are potential materials for future high performance opto-electric device application. Since the energy state of SWNTs depends on the chirality, it is important to control the chirality of SWNTs [1-3]. Based on our previous study, we developed novel plasma CVD named pulse plasma CVD, which can grow SWNTs with narrow chirality distribution. To improve the purity of chirality species, it is important to understand the effects of pulse plasma on the growth of SWNTs. In this study, we have investigated the correlation between pulse on/off time parameters and chirality-distribution of SWNTs. It is found that SWNTs chirality-distribution is influenced by the balance of pulse effect and Ostwald ripening effect, which is decided by pulse on/off ratio and total process time, respectively. Through the fine tuning of growth conditions by following this growth mechanism, we have succeeded in synthesizing SWNTs with very narrow chirality distribution, where only three chirality species ((6,4), (7,3), (6,5)) are dominant.

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[2] T. Kato and R. Hatakeyama, ACS Nano 4, 7395 (2010).
[3] B. Xu, T. Kato, K. Murakoshi, and T. Kaneko, J. Plasma Fusion Res. 9, 1206075 (2014).

P322

A transferable tight-binding model for boron and its application to B sheets

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A parameterized transferable tight-binding model to compute the total energy of a carbon system was developed by Xu et al. [1] which was later extended by Omata et al. [2] to better model structures with interlayer distances between sp2 layers larger than 2.6 angstroms. Both models are now widely used with molecular-dynamics simulations to study the conversion or transformation of phases in the nanostructured carbon materials.

There are growing interests in the study and research of compound nanostructured materials comprised of boron, carbon and/or nitrogen atoms and a transferable tight-binding model for BCN systems is an invaluable asset for the study of these materials. In the present work, a transferable tight-binding model for boron is developed by fitting a new set of transferable parameters with a carefully selected boron geometries given by the first-principles calculations as references. Using this model, we discuss geometries and stabilities of triangular and honeycomb B sheets.

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[2] Y. Omata et al. *Physica E: Low-dimensional Systems and Nanostructures* **29**, 454 (2005).

P323

Synthesis of semiconducting single-wall carbon nanotubes with narrow diameter distribution using uniform monodispersed Co nanoparticles as catalysts

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The unique physical and chemical properties of single-wall carbon nanotubes (SWCNTs) have triggered the exploration of SWCNTs toward a wide range of applications.[1] Owing to the bandgaps of s-SWCNTs are inversely proportional to their diameter, synthesis of narrow-diameter distributed s-SWCNTs is an alternative for chirality-selected synthesis in terms of the applications on nanoelectronics with stable performance. However, it is hard to tune diameter distribution especially for SWCNTs with big diameter (>1.5 nm) owing to difficulties in controlling both catalyst particle size and growth mode.[2] Herein, the uniform mono-dispersed carbon-coated Co nanoparticles with a mean diameter of 3.1 nm were prepared by self-assembled nanodomains of block co-polymer, in which the residual polymers were carbonized and partially coated on Co nanoparticles. Under etching atmosphere of hydrogen, s-SWCNTs selectively and per-pendicularly nucleate from the exposed surface of Co particles, and grow with perfect carbon layer structure at low temperature of 700°C. In consequence, high content of s-SWCNTs with a mean diameter of 1.7 nm and narrow bandgap difference of 0.08 eV were firstly synthesized under hydrogen atmosphere.

Reference:
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(2)Fiawoo, M. F. C.; et al. Physical Review Letters 2012, 108.

P324

Statistical investigation of SWNTs and catalyst nanoparticles by TEM

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Here we report our constant efforts in systematical investigations of size distributions of active and inactive nanoparticles, and of the SWNTs diameters and structures. Two synthesis reactors based on floating catalyst CVD have been used to synthesize the SWNTs. They differ by the way how the catalyst Fe nanoparticles are generated: chemical decomposition of a ferrocene precursor in the first case, and direct injection of nanoparticles formed by a spark discharge generator in the second one. Both use CO as a carbon source and Fe as catalyst nanoparticles. An aberration-corrected JEOL-2200FS transmission electron microscope was used to carry out the measurements. The results indicated that in the spark reactor the general size distribution of Fe nanoparticles is shifted towards smaller size compared to the ferrocene reactor while the average SWNT diameters in both cases show little difference from each other. HR-TEM imaging showed that under these growth conditions, nanotubes are clearly growing in perpendicular mode. It is also shown that with nanoparticles from the spark generator, one can better control the catalyst particle size and concentration, thus to control the nanotube concentration in the gas phase to prevent SWNT bundling, and fabricate sparse SWNT networks for high performance electronics.

P325

Raman Spectroscopy for Boron Nitride Nanotubes Crystallinity Analysis

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Boron nitride nanotubes (BNNTs) have many potential applications as structural material and reinforcing fibers due to attractive combination of their excellent mechanical characteristics and high thermal and chemical stabilities. Recent progress in BNNT reliable synthesis opened a way to first fabrication BNNT/metal composites [1-3]. During this work we have detected a new peak in the Raman spectra appearing certain sample preparation conditions which we attributed to partial BNNT amorphization [1].

In this work we present the results of Raman spectroscopy studies on multiwall BNNTs with intentionally introduced defects. We have modified using various doses of ion implantation, acid and plasma etching. Raman spectra of the initial samples consist of only one characteristic peak at ~1360 cm^{-1}. With the increasing quantity of defects in the samples a new broad peak is rising at ~1290 cm^{-1}. The relative intensity of the two spectral features can be used for the estimation of BNNT crystalline quality.

This work was supported by the Grant of Russian Federation Ministry for Science and Education. (NO. 11G34.31.0061)

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P326

Piezoresistive, electrical and environmental properties of hin film based intrinsically conductive polymer and carbon nanotubes

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Recently, intrinsically conductive polymer and nanomaterials are increasingly used in various research application, such as strain sensor, transparent electrode, field effect transistors, etc. Among others, poly(3,4-ethylenedioxythiophene): polystyrene sulfate (PEDOT:PSS) and multiwall carbon nanotubes (MWCNTs) and are fascinate with the great importance for its exquisite mechanical, and electrical conductivity. To improve the mechanical and electrical properties of the PEDOT:PSS, different MWCNTs content is blended into the polymer matrix. To understand the property of nanocomposite, the fabricated nanocomposite undergone various characterization techniques for example, UV-Vis, SEM, AFM, contact angle and surface tension. The electric conductivity of PEDOT:PSS/MWCNT shows drastic change under humidity and temperature as well as uniaxial tensile strain due to the strong change of their molecular structure i.e. electronic band gap. Accordingly humidity, temperature and strain distribution can be detected by measuring the change of electric resistance under those tests. The ultimate goal of this work is to fabricate a thin film based flexible strain sensor and to study the piezoresistive property of PEDOT:PSS/MWCNT nanocomposite. The strain sensitivity was found to be strongly dependent on the amount of MWCNT, and it reached k-factor of 25. In general, PEDOT:PSS/MWCNT films showed potential as highly strain sensitive material which can be used for structural health monitoring and aerospace application.

P327

J-aggregated dyes inside carbon nanotubes: giant raman diffusion and 1D absorption isotherms

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Here, we report the discovery of a giant Raman scattering effect from encapsulated and aggregated dye molecules inside single-walled carbon nanotubes (dyes@SWNTs) [1]. Measurements performed on rod-like dyes, such as alpha-sexithiophene and beta-carotene, assembled inside SWNTs as highly polarizable J-aggregates indicate a resonant Raman cross-section of ~10^-21 cm2/sr, which is well above the CS required for detecting individual aggregates at the highest optical resolution. This high scattering cross section enables the determination of the 1D encapsulation isotherms of the 6T inside carbon nanotubes [2]. The shape of the isotherms indicated two regimes depending on the temperature and consisting of single and pair of molecules aligned head-to-tail.

[1] Giant Raman scattering from J-aggregated dyes inside carbon nanotubes for multispectral imaging. E. Gaufrès, N Y-W Tang, R. Martel et al. Nature Photonics 8 (2014)

[2] One dimensional adsorption isotherms of 6T inside carbone nanotubes E. Gaufrès, N Y-W Tang, R. Martel et al. (submitted)

P328

Tuning the sensitivity of PFO/SWNT networks to their environment

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Single Wall Carbon Nanotubes (SWNT) properties are highly sensitive to their direct chemical, dielectric and mechanical environment. Depending on the application field, such as, photonics, electronics, sensors, the interaction strength with the environment has to be modulated and fully controlled. PFO (polyfluorene polymer), commonly used for wrapping carbon nanotubes in selective purification process acts also as an effective isolant due to its natural helicity matching with SWNT diameter and its wide bandgap in the UV. Here we report on a selective annealing process under a low pressure of oxygen to tune the PFO coverage of SWNT networks deposited on a substrate. The impact of the annealing on both SWNT network and PFO was probed by AFM, Raman, absorption, photoluminescence and electrical experiments.

P329

Structural analysis of single-walled carbon nanotubes synthesized from very thin nanodiamond layers

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Single walled carbon nanotubes (SWCNTs) can be synthesized from nanodiamond (ND) particles. However, very little is known about the growth mechanism since the growth window is much narrower than that for conventional metal catalysts, resulting in the very low growth efficiency. Thick (∼100 layers) NDs were required to improve amount of CNT growth. That makes structural analysis of SWCNTs and ND seeds very difficult. In this work, SWCNTs were successfully grown from very thin (several layers) ND by optimizing the growth conditions including the pre-heating process for ND particle cleaning and carbon feedstock materials. ND particles and grown SWCNTs can be clearly observed using atomic force microscope (AFM). Correlation between sizes of grown SWCNTs and ND was analyzed from the observed AFM images. The SWCNT diameter is significantly smaller than the diameter of the ND which works as the seed of SWCNT. This diameter correlation seems to be similar to that for the metal catalysts, but microscopic mechanism would be completely different because aggregation reaction which can happen for metal catalyst should be negligible for ND seeds. This finding is closely related to the growth mechanism and a key for improving the growth efficiency.

P330

Synthesis and characterization of SWNTs from open-end nanotube edges

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It is required to establish the method of chirality-controlled synthesis of single-walled carbon nanotubes (SWNTs) to realize the application of SWNTs. Recently, SWNT cloning [1,2], in which SWNTs are grown using not metal catalysts but existing SWNTs as templates, was reported. In this study, we grew SWNTs using open-end SWNTs as templates and investigated the growth mechanism. We grew horizontally aligned SWNTs on quartz substrates. Then the grown SWNTs were partially etched by photolithography and oxygen plasma treatment to prepare open-end SWNTs. We annealed the substrates in air and water vapor to activate the edges of the open-end SWNTs, and then grew SWNTs via ethanol CVD.

The conditions of water vapor treatment effected on the number of SWNTs grown from the open-end SWNTs. Raman mapping images showed the chirality of the grown SWNTs was the same as that of the template SWNTs.

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[2] J. Liu, et al., Nat. Comm., 3 (2012) 1199.

P331

Magnetic properties of nanoparticles encapsulated in nitrogen-doped multiwall carbon nanotubes grown on Co/Ag thin films

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Nitrogen-doped multiwall carbon nanotubes (N-MWCNT) were grown on Co/Ag bilayer thin films. These films were previously deposited on Si/SiOx substrates using the magnetron sputtering method. The N-MWCNT were obtained by chemical vapor deposition (CVD) at 850 ℃ during 30 minutes and using benzylamine (C6H5CH2NH2) as carbon and nitrogen source and Co/Ag films as catalytic source. Carbon nanotube forests were grown on Co layers also. Magnetic measurements of N-MWCNTs carpets grown on those substrates reveal that coercive fields show a strong dependence on the thickness of cobalt when it is less than 40 nm. Images of scanning and transmission electron microscopy show that the N-MWCNT are curved with mostly monocrystalline Co nanoparticles inside them. Energy-dispersive X-ray spectroscopy on nanoparticles shows that silver is detected only when its thickness is larger than 0.7 nm in Co/Ag film. The system consisting of nanoparticles inside of N-MWCNT could be used as drug delivery system taking advantage of its large surface area and biocompatibility

P332

Measurement of resistance induced by a single potassium atom on chiral-angle known nanotubes: understanding the impact of a model scatterer for nanoscale sensors

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Impurity-induced carrier scattering is expected to be dependent on the chirality of nanotubes and the nature of scattering potentials induced by impurities. Such scattering is still poorly understood because it has been impossible to measure the impact of impurities on resistance of carbon nanotubes with known chirality.

We have measured the scattering strength of charged impurities on semiconducting single-walled carbon nanotubes with known chirality. The resistivity of nanotubes is measured as a function of the density of adsorbed potassium atoms, enabling the determination of the resistance added by an individual potassium atom. Holes are scattered 26 times more efficiently than electrons by an adsorbed potassium atom. The determined scattering strength is used to reveal the spatial extent and depth of the scattering potential for potassium, a model Coulomb adsorbate, paving way for rational design of nanotube-based sensors.

P333

Fine control of graphene oxide structure by oxidation of graphite or reduction of highly oxidized graphene oxide

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Control of oxidation level in the graphite- and graphene-like materials is important to tailor the functionality to suit the relevant areas of applications that include opto-electronics, physical-, biological-, and energy-related materials. For example, carboxyl group-free graphene oxide (GO) would be desirable for the production of defect free graphene by reduction. In contrast, oxygen functional groups are necessary for the synthesis of GO composites with nanoparticles, organic molecules, and heteroatoms. Application for conductive films, electrodes for lithium ion battery, super capacitor, and catalyst for fuel cell would often require the functionalization processes to improve GOs performance.

We have achieved the fine tuning of the oxygen content by oxidation and reduction processes. The oxidation content was analyzed by elemental analysis, and properties of each GOs were measured by XPS, XRD, electron conductivity, oxidation ability, and cyclic voltammetry.

P334

Theoretical studies on the structures of carbon nanobelts

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Carbon nanotubes (CNTs), tubular molecular entities that consist of sp2-hybridized carbon atoms, are currently produced as mixtures that contain tubes of various diameters and different sidewall structures. The electronic and optical properties of CNTs are determined by their diameters and sidewall structures and so a controlled synthesis of uniform-diameter, single-chirality CNTs would provide access to pure samples with predictable properties.

Recently, we have reported the growth of CNTs from carbon nanorings, the shortest sidewall segment molecules of armchair CNTs. However, for precise control of the synthesis of CNTs, more rigid template molecules are required. Herein we report the theoretical studies on the structures and properties of carbon nanobelts, which are the class of molecules representing longer CNT segments than carbon nanorings. Theoretical prediction about strain energies, structural features, and photophysical properties of carbon nanobelts would be helpful for the design and synthesis of carbon nanobelts.

P335

Mechanistic insight of the synthesis of warped nanographene

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Graphite consists of pure carbon sheets stacked upon one another like reams of paper. Individual sheets, which are known as graphene, prefer planar geometries as a consequence of the hexagonal honeycomb-like arrangements of sp2 carbon atoms that comprise their two-dimensional networks. Defects in the form of non-hexagonal rings in the networks cause distortions away from planarity.

Recently we have reported an extreme example of this phenomenon: A 26-ring warped nanographene that incorporates five seven-membered rings and one five-membered ring embedded in a hexagonal lattice was synthesized by stepwise chemical methods, isolated, purified and fully characterized spectroscopically. Herein we report the mechanistic insight of the synthesis of warped nanographene by isolation and characterization of intermediates. In this presentation, structures and photophysical properties of these intermediates will also be discussed.

P336

Measurements of the transport gap in semiconducting multiwalled carbon nanotubes with varying diameter and length

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In this work, low temperature transport in multiwalled carbon nanotubes (MWNT) has been studied at different diameters and lengths, within 2-10 nm, and 0.3-3.5 micron, respectively. In a majority of the samples, semiconductivity showed up as a transport gap in the gate voltage controlled conduction, but metallic MWNTs are found in all diameters. The transport gap is seen to be quantitatively determined by a diameter dependent bandgap, and length dependent localization of charge carriers. The bandgap of semiconducting MWNTs is estimated to be smaller than that extrapolated from the conventional expression applicable to semiconducting single wall carbon nanotubes. Our results constitute the first systematical study on size dependent transport and especially of semiconductivity in MWNTs. These results have significant similarities to the current research on graphene nanoribbons (GRN). As graphene does not intrinsically possess a bandgap, GNRs are fabricated, where a gap is created via quantum confinement due to the narrow width of the channel/nanoribbon. The size of the gap is then roughly in a similar inverse relation with the width, as in the case of the diameter dependence of the MWNTs in our work.

P337

Selectivity in photochemical reactions of single-walled carbon nanotubes with organic compounds

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In recent years, much interest has been directed toward the photochemical properties of single-walled carbon nanotubes (SWNTs) because of evolution of their possible applications, such as photovoltaics. Herein we report the selective sidewall reaction of SWNTs with organic compounds.

As a practical application of photoluminescence of SWNTs, much attention has been focused on the biological probe. Recently, band gap modulation of semiconducting SWNTs (s-SWNTs) by photoreaction in the presence of O_3 was reported. The oxygenation reaction is useful to control their photoluminescence properties. Thus, photoreaction of SWNTs with disulfide in the presence of oxygen was carried out. Changes in the characteristic absorption and RBM peaks indicated that the helicity selective photoreaction proceeded. Photochemical reactions of unsaturated hydrocarbons with amines are well known to afford the corresponding adducts via an electron transfer process. However, the interaction of SWNTs with amines in the excited state has not been clarified. In this context, photochemical behavior of SWNTs in the presence of propylamine was investigated. Optical and Raman spectroscopic analyses and ESR experiments suggested that the reaction involves the photoinduced electron transfer from the amine to the excited SWNTs. In addition, subsequent sidewall functionalization of SWNTs having small-diameter proceeded.

P338

Synthesis of (2, 2) single-walled carbon nanotubes in SAPO-41 and $AlPO_4$-41 zeolites

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It has been reported that (2, 2) single-walled carbon nanotubes ((2, 2) SWNTs) could be synthesized in the channels of SAPO-11 zeolite. Herein, we synthesized (2, 2) SWNTs in the channels of SAPO-41 zeolite and $AlPO_4$-41 zeolite for the first time, for which the hydrocarbon molecules generated from the pyrolysis of the organic template dipropylamine (DPA) in the zeolite channels acted as the carbon source. (2, 2) SWNTs has the smallest diameter which is 0.3 nm and a characteristic RBM peak at about 760 cm^{-1} in the Raman spectrum. For obtaining (2, 2) SWNT array in the zeolite crystal with similar density and quality, our choice do not need such high crystalline quality of zeolite crystal compared with the situation of SAPO-11. And the vacuum in the preparation procedure is also lower than that in the past. The (2, 2) SWNT array in the ordered channels of zeolites are highly aligned and uniform in size, so they can be seen as ideal one-dimensional quantum wire array and have many potential theoretical values. Meanwhile, the (2, 2) SWNTs are also the possible precursor to synthesize a theoretical new carbon phase, tubulanes, which constituted with sp^3 carbon totally.

P339

Anomalous non-linear transport behavior in ambipolar field-effect transistors of semi-aligned polymer-wrapped nanotube network

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The utilization of single-walled carbon nanotube (SWNT) networks in electronic devices still strives to exhibit the true potential of the single strand semiconducting tubes. Recently we demonstrated high performing ambipolar field-effect transistors (FETs), with high mobility (>10cm2/V.s) and high on/off ratio values (~10^8), using networks of ultrapure large diameter semiconducting SWNTs (sSWNTs), separated and individualized using polymer wrapping. The luxury of having ambipolar FET is that we are able to evaluate precisely the transport mechanism of both charge carriers. Here we report the observation of non-linear charge transport behavior in semi-aligned large-diameter sSWNT network. The FETs are prepared using semi-aligned network of SO tubes, separated and dispersed using poly(9,9-di-n-dodecylfluorenyl- 2,7-diyl) (PF12) polymers. Low temperature transport measurements are performed for both conventional SiO2-gated and ionic-liquid-gated FETs. It is observed that variable range hopping mechanism could not explain the transport mechanism of both holes and electrons in polymer-wrapped SWNTs. We found a significant interplay and a transition between the intertube transport governed by the wrapping polymer and intratube transport that dominates at low temperature. Furthermore, the utilization of ionic-liquid gating enable us to observe possibilities of transition from semiconducting to metallic-like behavior for both holes and electrons in these purely semiconducting ambipolar FETs.

P340

Differences in dispersibility of diverse CNTs based on the individual tube and assembly structures

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As-grown materials of carbon nanotubes (CNTs) are powdery, granular, or flaky and differ in assembly structure due to different tubular structures for diameters, wall numbers, lengths and crystallinity. Depending on their unique structures, single-walled and multi-walled CNTs (SWNTs, MWNTs) possess different dispersed structures in solvent. Wet-dispersed structures from such various CNTs have not so far been comprehensively investigated. To clarify correlation between characteristics of as-grown CNTs and their dispersed structures is of importance in designing CNTs as nanoscale building blocks in matrices like liquid, polymer and metal. Here we present the tailorable, wet-dispersed CNT structures based on characterization of the as-grown CNTs, which can propose a fresh insight into development of both SWNTs and MWNTs applications. Wet dispersions were done in methyl isobutyl ketone (MIBK) using different dispersion mechanisms on turbulent flow, cavitation and mechanical force. According to types of CNTs and dispersion mechanisms, we were able to fabricate a wide variety of wet-dispersed CNT structures reflected by inherent CNT characteristics and highly stable CNT/MIBK dispersions. This article is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P341

Theory of double-walled carbon nanotubes

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Being multi-shell structure, the well-defined atomic periodicity is hardly realizable in double-walled nanotubes because the periodic units of individual tubes therein cannot match well except very few cases, posing a challenge to understand its physical properties. Here we show that moiré patterns generated by superimposing atomic lattices of individual tubes are decisive in determining its electronic structures [1]. By using double-walled carbon nanotubes as an example, we demonstrate that even the combination of semiconducting nanotubes with almost the same physical properties such as diameter and energy gap can end up with very different double-walled nanotubes, of which electronic properties vary from metallic to semiconducting and further to insulating states, depending on the interlayer moiré interference. Our study puts forth a new classification of nanotubes as the first example of one-dimensional moiré crystals and paves a firm ground to utilize superb technological merits of double-walled carbon nanotubes.

[1] Mikito Koshino,* Pilkyung Moon,* and Young-Woo Son,* Phys. Rev. B 91, 035405 (2015). (*All authors contributed equally to this work.)

P342

Preparation and properties of the composites of hydroxylated single-walled carbon nanotubes and fullerenols

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Owing to their excellent physical, chemical, electronic and mechanical properties, Single-walled carbon nanotubes (SWNTs) have been attracting research interests. As a result, SWNTs are regarded as potential candidates in various kinds of functional composite materials. Polyhydroxylated Fullerenes (fullerenol: C60(OH)x) also have been thought to have potential applications in proton conductive materials. It has been reported that C60(OH)12 solids by Oleum method have proton conductivity in a dry atmosphere.
In this study, SWNTs modified with hydroxyl groups were prepared with NaAlO2 as chemical oxidant and characterized with FT-IR spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscope (TEM) and solid-state NMR spectroscopy. We also prepared the composites of hydroxylated single-walled carbon nanotubes and fullerenols and their electronic properties, aggregation behavior and the properties of proton dynamics were characterized by solid-state 1H-NMR. The detailed results will be presented.

P343

Enhanced production of double-wall carbon nanotubes by high-temperature pulsed-arc discharge

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A high-temperature pulsed-arc discharge (HTPAD) has been developed to produce nano-carbon materials. The system utilizes width controlled pulsed arc discharge for the vaporization of electrode in temperature and pressure controlled ambient rare gas. With this wide-range controllability, novel materials such as high-quality double wall carbon nanotubes (DWNTs) have been produced. Here, we present the further enhanced production of DWNTs by optimizing the parameters.
The HTPAD system consists of a furnace with a ceramic tube inside, an Ar gas flow and pressure control system, an HV pulse voltage controller, and a water cooling trap. Electrodes made of graphite containing catalytic metals (Ni/Y 4.2/0.5 at. %:Toyo Tanso Co. Ltd.) were located in the ceramic tube. The pulsed arc discharges (0.6 ms, 50 Hz, and 100 A) vaporized the electrodes and produced nanotubes in the high-temperature (1250℃) and high-pressure (up to 4 atm) Ar gas in the ceramic tube. The products were collected on the trap and were characterized by Raman spectroscopy with excitation laser of 633 nm together with weight analyses.
The pressure control significantly enhance the DWNTs. The results and the mechanism are going to be presented.

P344

Local structure and properties of the alkali halide crystals encapsulated in single-walled carbon nanotubes studied by molecular dynamics simulations

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Single-walled carbon nanotubes (SWNTs) have a hollow space in the nanometer size that can be encapsulated various functional molecules. And synthesis of alkali halide encapsulated SWNTs and their structures have been reported. However, the systematic studies on the local structure and some properties (ion conductivity, melting point etc.) encapsulated in SWNTs with different diameters and chirality have not been reported. In this study, we report the effects of the diameter and chirality of SWNTs on the local structures of the encapsulated alkali halides by using molecular dynamics (MD) simulations. In our MD simulations, we used the Born-Mayer-Huggins-Tosi-Fumi intermolecular potential between the alkali halide ions and the Dreiding potential between carbon atoms in SWNT. One SWNT and any number of alkali halide ions (CsI, KI) around SWNT were set in a rectangular cell as initial configuration. Stable structure at 298 K was calculated with the NVT ensemble after the relaxation calculation at 1100 K. The relaxation calculation was conducted after temperature was increased by 10 K from 298K. The detailed systematic results on the local structures of encapsulated alkali halide crystals will be presented. In addition, their experimental results obtained by TEM and solid-state NMR spectroscopy will be presented.

P345

Structure and properties of the chalcogens encapsulated in single-walled carbon nanotubes studied by molecular dynamics simulations

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Single-walled carbon nanotubes (SWNTs) have a hollow space in the nanometer size that can be encapsulated various functional molecules. Recently, syntheses of sulfur encapsulated SWNTs and selenium encapsulated DWNTs have been reported by Fujimori et al. They have also reported to take a unique structures including one-dimensional sulfur chain structure and selenium helical structure. However, the systematic studies on the local structure and some properties encapsulated in SWNTs with different diameters and chirality have not been reported. In this study, we report the effects of the diameter and chirality of SWNTs on the local structures of the encapsulated chalcogen (S, Se) atoms by using molecular dynamics(MD) simulations. MD simulations were conducted by using SCIGRESS Ver2.3.0 (Fujitsu). We used the GE-AR method of the fifth order in the numerical integration and the speed scaling method in the temperature control. One SWNT and arbitrary number of sulfur atoms were set in a rectangular cell. First, the relaxation calculation were conducted at 1K with the NVT ensemble for the encapsulation of sulfer. Stable structure at 297 K was calculated after the relaxation calculation at 800 K.

The detailed systematic results on the local structures of encapsulated chalcogen crystals will be presented.

P346

Functionalization of multi-walled carbon nanotubes with nitrile N-oxides - scope and limitations

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Poor solubility (dispersibility) of Multi-Wall Carbon Nanotubes (MWNCTs) remains a significant barrier for their everyday-life applications in such different fields as inter alia medicine, materials science or electronics. Such an issue is usually considered as an effect of strong van der Waals interactions occurring between individual MWCNTs which lead to the formation of bundles. Among others the covalent functionalisation of carbon nanotubes has been recognised as a convenient tool to overcome this problem. However the methods developed up to date (excluding oxidative treatments) are rather far from generality.[1]
We investigated the scope and limitations of poorly explored 1,3-dipolar cyclo-addition of nitrile oxides to MWCNTs originally adapted from fullerene's chemistry by Poplawska et al.[2] The obtained pool of hybrid materials was characterised by means of thermo-gravimetric analysis, Fourier-transform infrared spectroscopy, scanning and transmission electron microscopy (SEM, TEM). Moreover we measured contact angles of synthesised nanohybrids to assess their affinity to solvents of various chemical polarity.

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P347

Effect of catalysts distribution on morphology of vertically aligned carbon nanotube films

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Depending on the properties desired in commercial applications, carbon nanotubes can be produced in bulk or thin film form. Vertically aligned carbon nanotubes (VACNT) which are carbon nanotubes grown on a substrate creates a CNT thin film and modifications can be made on this surface. Studies conducted in recent years shows us that micro-nano biomimetic hierarchical structures which are often used inorganic thin films can also be made with carbon nanotubes. Thus, with the unique features of carbon nanotubes advantages of hierarchical structure to systems is further improved. In this work, with chemical vapor deposition method vertically aligned multi-walled carbon nanotubes were produced. To examine the influence of the metal catalysts in production of VACNT, iron, cobalt and aluminum thin films were also stacked in layers in various combinations. System parameters such as reaction temperature, hydrocarbon type and concentration, catalyst concentration and catalyst calcination time are examined. Then the surface of carbon nanotubes produced in suitable properties were characterized. Characterization of the produced carbon nanotubes is performed using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Raman Spectroscopy and contact angle measurements.

P348

Silicon doped single walled carbon nanotubes: synthesis and characterization

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Carbon nanotubes (CNTs) have been in the limelight for several decades, owing to their outstanding properties.[1–3] However, it is often necessary to manipulate these nanostructures through chemical modification in order to exploit their interesting properties at a tangible scale. Elemental doping of CNTs has proven to be an effective route towards achieving this goal.[4] In this regard, the effects of silicon (Si) doping in single walled CNTs (SWCNTs) have not been explored in great detail previously. Theoretical calculations of Si doped SWCNTs[5] (Si-SWCNTs) showed that substitutional Si atoms protrude out from the carbon lattice due to the Si sp^3 pyramidal hybridization, longer Si-C bonds, as well as to its larger ion size. The stress induced by this protrusion makes the presence of smaller diameter tubes within Si doped samples more favorable, and it is also likely that the lone orbital from Si could act as an amphoteric center for inter-tube bridging. Here we report the successful synthesis of Si-SWCNTs by aerosol assisted chemical vapor deposition (AACVD). Si-SWCNTs were characterized via Raman spectroscopy and TEM. Analysis of the radial breathing modes in the Raman spectra suggests the incorporation of Si into the carbon lattice. Electronic transport measurements of the Si-SWCNTs bundles show drastically different electronic transport properties when compared to pristine SWCNTs, which corroborates the doping of Si atoms in the carbon lattice.

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Wednesday

K3

Bottom-up fabrication of graphene-related materials: From molecules to nanoribbons and nanotubes

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The properties of single-walled carbon nanotubes (SWCNT) and graphene nanoribbons (GNR) depend sensitively on the details of their atomic structure. For the case of SWCNTs, electronic and optical properties are directly related to the chiral index (n,m) that denotes the length and orientation of the circumferential vector in the hexagonal carbon lattice. For GNRs, the electronic states largely depend on nanoribbon width and edge structure (armchair or zigzag). Monodisperse "single-chirality" SWCNTs and atomically precise GNRs are thus needed to fully exploit the technological potential of these materials.

In a first part of this presentation, I will review a recently developed bottom-up approach to the fabrication of atomically precise GNRs [1]. It is based on a surface-assisted synthetic route using specifically designed precursor monomers, and has made available ultra-narrow GNRs and related graphene nanostructures for experimental investigations of their structural, electronic and optical properties [1-5]. In a second part, I will report on a closely related bottom-up strategy targeting the controlled synthesis of single-chirality SWCNTs [6].

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I6

Important factors in chirality-specific growth of single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) present structure-determined outstanding properties and may find important applications in many fields[1]. However, the chirality-controlled growth of SWNTs has been a great challenge for many years[2]. It is shown that the tube structure can be well controlled in a templated growth process[3-5]. Carbon nanotubes[6] and their caps[4] or catalysts[5] can all act as the structural templates.

SWNT growth via a catalyzed chemical vapor deposition CVD process is normally more efficient[7]. This is also true in the chirality selective growth processes. We used W_6Co_7 nanocrystals as catalysts and realized chirality-specific growth of SWNTs by optimizing the growth conditions[5]. As a kind of intermetallic compound, W_6Co_7 nanocrystals present unique structure and property, which are distinctly different from the normal alloy nanoparticles or simple metal nanocrystals. Besides the catalysts, the CVD condition is also very important. The factors which can influence the chirality selectivity and the mechanism of the process will be discussed from the thermodynamic and kinetic points of view.

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I7

Harvesting energy with semiconducting single-walled carbon nanotubes

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Semiconducting single-walled carbon nanotubes (s-SWCNTs) are promising materials for efficiently harvesting infrared radiation. Relatively narrow bands of NIR radiation can be harvested through absorption in diameter-tunable excitonic solar cells.[1,2] Alternatively, broad ranges of thermal energy (e.g. waste heat) can be harvested in SWCNT thermoelectric materials. In this talk, I will discuss our fundamental opto-electronic studies of thin s-SWCNT films with highly tunable electronic properties. I will first discuss time-resolved spectroscopic studies of exciton dissociation at s-SWCNT:fullerene Type II heterojunctions. We have measured ultra-fast (< 100 fs) photoninduced electron transfer across such interfaces, with trap-mediated recombination occurring on much slower (ns-μs) time scales.[3,4] Such studies provide insight into potential routes towards the development of efficient thin-film organic photvoltaics based on s-SWCNTs. Next, I will discuss electrical and thermal transport in s-SWCNT films with tunable electronic structure. Fine-tuning the s-SWCNT diameter distribution and carrier density allows us to find optimal ranges for the electrical conductivity, thermopower, and thermal conductivity. These studies provide crucial fundamental insights into the potential for SWCNTs in efficient energy harvesting devices.

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I8

Carbon nanotube transistors: toward fundamental limits

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The development of even more powerful computer systems are made possible by scaling of CMOS transistors, and this simple process has afforded continuous improvement in both the device switch time and integration density. However, CMOS scaling has become very difficult at the 14-nm node and unlikely to be rewarding beyond the 7-nm node. Among other new approaches, carbon nanotube devices are emerging as the most promising technique with unique properties that are ideal for nanoelectronics [1]. In particular, perfect n-type and p-type contacts are now available for controlled injection of electrons into the conduction band and holes into the valence band of the CNT [2], paving the way for a doping free fabrication of CNT based ballistic CMOS [3], high performance optoelectronic devices [4], and integrated circuits [5]. These results will be compared with data projected for Si CMOS toward the end of the roadmap at 2026, as well as with those thermodynamic and quantum limits.

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C11

Thermoelectric flexible film based on cobaltocene-encapsulated carbon nanotubes

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Direct conversion from heat to electricity is one of the important technologies for the sustainable society since large quantities of the energy are wasted as a heat. Here, we report the development of a high conversion efficiency, air-stable, and flexible thermoelectric device based on single-walled carbon nanotubes. We found the cobaltocene-encapsulated single-walled carbon nanotubes (CoCp2@SWNTs) showed negative-type (n-type) semiconducting behavior (Seebeck coefficient; -41.8 μV K^{-1} at 320 K), while empty SWNTs possessed positive-type (p-type) property (Seebeck coefficient; 45.3 μV K^{-1}). Notably, CoCp2@SWNTs showed high electrical conductivity (43,200 S m^{-1} at 320 K) and power factor (75.4 μW m^{-1} K^{-2}) with a remarkable stability under atmospheric condition at a wide range of temperature. The finding of the n-type CoCp2@SWNTs allowed us to fabricate the p-n type thermoelectric device by combining with p-type film based on the empty SWNTs. The device exhibited the highly efficient power generation close to the calculated values even without any air-protecting coating due to the high stability of SWNT-based materials (CoCp2@SWNTs and SWNTs) under atmospheric condition.

C12

Tuning of thermoelectric properties of single wall carbon nanotubes by electric doulbe layer carrier injections

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Thermoelectrics are a very important technology for efficiently converting waste heat into electric power. Hicks and Dresselhaus proposed an important approach to innovate the performance of thermoelectric devices, which involves using one-dimensional materials and properly tuning their Fermi level. To maximize the thermoelectric performance, understanding the relationship between the thermoelectric performance and the Fermi level is of great importance. Regarding single wall carbon nanotubes (SWCNTs), various types of chemical doping approaches have been proposed for controlling the Seebeck coefficient, however, in chemical doping approaches, fine-tuning of the Fermi level is difficult. Another approach is to control the Fermi level using an electric field, such as back-gating. However, by back-gating approach, the tuning of thermoelectric properties in SWCNT bulk networks was impossible. Here, we report continuous p-type and n-type control over the Seebeck coefficients of semiconducting SWCNT networks through an electric double layer transistor setup using an ionic liquid as the electrolyte [1]. The thermoelectric properties of semiconducting SWCNTs as a function of Fermi level were clarified. All-around gating characteristics by electrolyte gating approaches enabled to control the thermoelectric properties of bulk SWCNT networks.

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C13

Ice-assisted transfer of carbon nanotube arrays

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Decoupling the growth and the application of nanomaterials by transfer is an important issue in nanotechnology. Here, we developed an efficient transfer technique for carbon nanotube (CNT) arrays by using ice as a binder to temporarily bond the CNT array and the target substrate. Ice makes it an ultraclean transfer because the evaporation of ice ensures that no contaminants are introduced. The transferred superaligned carbon nanotube (SACNT) arrays not only keep their original appearance and initial alignment but also inherit their spinnability, which is the most desirable feature. The transfer-then-spin strategy can be employed to fabricate patterned CNT arrays, which can act as 3-dimensional electrodes in CNT thermoacoustic chips. Besides, the flip-chipped CNTs are promising field electron emitters. Furthermore, the ice-assisted transfer technique provides a cost-effective solution for mass production of SACNTs, giving CNT technologies a competitive edge, and this method may inspire new ways to transfer other nanomaterials.

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C14

Waveguide-integrated light-emitting carbon nanotubes

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Carbon nanotubes (CNTs) can be envisioned as waveguide-integrated light sources for future on-chip data communication due to their unique structural, electrical and optical properties. The challenge thereby is to integrate and electrically contact solution processed CNTs across CMOS compatible waveguide structures and to enforce efficient coupling of light from the CNT into the waveguide. We will show how light from an electrically-driven CNT can be coupled directly into a photonic waveguide [1]. We realize wafer scale, broadband sources integrated with nanophotonic circuits allowing for propagation of light over centimeter distances. Moreover, we demonstrate that CNTs can be used as fast waveguide-integrated light emitter with a Gbps response speed. The direct, near-field coupling of electrically generated light into a waveguide, opposed to far-field fiber coupling of external light sources, opens new avenues for compact optoelectronic systems in a CMOS compatible framework.

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Thursday

K4

Carbon nanotube thin films

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Indium is currently used as ITO (indium-tin oxide) to provide transparent conducting films (TCF) for a wide variety of consumer electronics devices, such as displays as well as touch screens of mobile phones and ipad-style portable computers. Polycrystalline silicon is the semiconductor material used in the thin film field effect transistors (TFT-FET) of the high quality display back planes. Recent introduction of bendable as well as flexible -and even stretchable – devices requires novel materials to replace both ITO and silicon, due to their rigid nature. In order to replace both indium and polycrystalline silicon, we have developed single-walled carbon nanotube (SWNT) thin films [1,2]. We introduce our industrial scale, ISO 9001:2008 certified direct dry printing (DPP) manufacturing of nanotube based TCFs, enabling the manufacturing of touch sensors with electrical properties on par with those of ITO-on-PET, and with optical properties better than those of ITO, metal nanowire and metal mesh. Similar dry deposition method has been used to manufacture TFT-FETs with properties comparable to those of polycrystalline silicon transistors [3,4].

We report recent studies on the synthesis of high quality single walled carbon nanotubes from CO with the ferrocene based floating catalyst chemical vapor deposition (FC-CVD) reactor and show that SWNT networks consisting of long, clean and highly individualized SWNTs exhibit substantially improved TCF performance. Interestingly, SWNT bundling has a strong effect on the tube growth rate. We introduce the novel FC-CVD reactor based on spark discharge catalyst generation to experimentally study the effect of bundling on the performance of TCF and TFT-FETs. The synthesis of SWCNTs relies on generation of iron catalyst particles in the diameter range of 4±3 nm with precisely tunable concentration into nitrogen carrier gas with a spark generator, allowing to grow individual and high-quality SWNTs from CO with well-defined diameter and length distributions. TCFs made from individual tubes with 4 micron mean length show 60 ohms/sq sheet resistance at 90 % transparency. TFT-FETs made of individual SWNT based thin films exhibit higher uniformity in terms of both mobility and ON/OFF ratio compared to the devices made with nanotube bundles. In addition, we compare TCFs made with direct dry deposition of the nanotubes using hydrocarbons as the carbon source [5] to those made from CO. Also, we discuss the conductive AFM-based studies on the SWNT network charge transport mechanisms [6].

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I9

Soft conductors from nanoscale carbon

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Certain materials properties are viewed as contradictory. For example, high electrical and thermal conductivity are associated to hard, crystalline materials like metals. Conversely, softness is associated with biological materials, polymers, and disordered structures, which are thermally and electrically insulating. We have accepted that certain ostensible contradictions cannot be resolved. For example, we have no material that is electrically conductive and can be sutured or sewn, despite obvious needs in medical devices and wearable electronics.

Nanoscale carbon — including CNTs and graphene — has remarkable electrical, thermal, and mechanical properties. I will discuss how CNTs and graphene can be assembled into soft conductors.

CNTs and graphene can be solution-processed in acids, their sole solvents [1, 2]. Low concentration solutions can be used for making flexible films [3] and porous, three-dimensional structures that combine conductivity and softness [4]. At high concentration, CNTs and graphene form liquid crystals that can be spun into high-performance multi-functional fibers [5, 6]. These fibers combine high conductivity, strength, and the emergent property of softness; they are finding applications in aerospace electronics, Hi-Fi cables, and field emission. As soft conductors, CNT fibers provide a natural interface to the electrical function of the body as restorative sutures for electrically damaged heart tissue and electrodes for stimulating and sensing brain activity [7].

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SP1

Resiponsible Production and Applications of Carbon Nanotubes
～ Promis for the future ～

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Carbon nanotubes have been attracted lots of attention from various fields of science and technology, because of their extraordinary physical and chemical properties due to the intrinsic nano-sized one-dimensional nature. It should be noted that various carbon nanotube-derived products have been developed, and thus their viability strongly depend on their large scale production by the most common CCVD process [1]. The hurdles in nanotube commercialization are considered to be the safety issue of carbon nanotubes [2-4]. By sharing the all informations on risks [4] and benefits of the materials with all the stakeholders, we are able to prove the carbon nanotubes to be the green and safe innovative materials, by the responsible productions and use. And further designing the safer nanostructure of CNT is becoming important. These are the promises for the future of CNT's as an inovative material for the 21st century.

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SP2

A road to carbon nanotube application and commercialization

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Super-aligned carbon nanotube(SACNT) arrays, films and yarns are materials that are made of pure and high quality carbon nanotubes, and have found applications in consume electronics, batteries, sensors, heaters, filters, chemical industry, and biomedical. But the prerequisite for any real products is the capability of producing these materials with stable and well defined quality, especially the SACNT arrays, as the SACNT films and yarns are dry spun form them and their qualities relies on that of the former. We have defined more than 10 quality specifications for SACNT arrays and thin films, and have developed specialized quality inspection equipment for production purpose. Unlike laboratory facilities (electron microscopes, for instance) that take long time to analysis micro scale samples, our equipment examine 8-inch-wafer sized SACNT arrays within minutes, thus provide fast feedback for inline quality control. These quality inspection equipment have brought consistent and high quality SACNT array production into practice. Base on that, SACNT touch panels production lines have been built and products were manufactured and went into market.

SP3

SWNT thin films for high optical quality flexible touch panels

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Indium is currently used as ITO (indium-tin oxide) to provide transparent conducting films for a wide variety of consumer electronics devices, such as displays as well as touch screens of mobile phones and ipad-style portable computers. Recent introduction of bendable as well as flexible-and even stretchable-devices requires novel materials to replace ITO, due to its rigid nature.

Conducting polymers, carbon nanotubes, graphene as well as metal mesh and metal nanowires are being developed for flexible touch panel applications. Here we discuss both the properties and the market development estimates of flexible transparent conductors required in high quality touch sensor applications. In addition, we introduce our industrial scale, ISO 9001:2008 certified direct dry printing (DPP) manufacturing mehod for carbon nanotube based transparent conductors developed at Canatu Ltd. (http://www.canatu.com), enabling the manufacturing of TCFs with electrical properties on par with those of ITO-on-PET, and with optical properties better than those of ITO, metal nanowire and metal mesh. We also discuss the future developments of nanotube based thin film manufacturing technologies.

SP4

Carbon nanotube x-ray: from scientific curiosity to patient imaging and commercial production

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X-ray radiation is widely used in many aspects of our lives including medicine, security, and industrial inspection. The way x-ray is generated however has not changed significantly since it was discovered over one hundred years ago. Utilizing the unique properties of the carbon nanotubes we developed a novel spatially distributed field emission x-ray source array technology [1]. After 10 years of intensive R&D efforts, the technology has been successfully translated from a scientific curiosity to commercial production. Its applications in medical imaging, radiation therapy [2], and homeland security [3] are being investigated, including for early detection of breast cancer [4] and lung cancer [5]. Some are in *in-vivo* patient imaging trials [6]. In this talk we will introduce the CNT x-ray technology and its applications.

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SP5

Putting the Carbon Nanotubes to Use as the Industrial Materials — Recent Progress in Development of Mass Production Method of Single Wall Carbon Nanotube and Development of Their Application in Japan.

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Single Walled Carbon Nanotube (SWCNT) Mass Production:
Industrial mass production technology is being developed based on highly efficient "Super-Growth" (i.e. water-assisted chemical vapor deposition) method [1] by combining large area with continuous process. On February 2011, a pilot plant of this method which is capable of producing 0.6 kg of SWCNT per day was established (in AIST) with Nihon Zeon Corp. On May 2014, Nihon Zeon Corp. started construction of commercial plant. Improvement of eDIPS (enhanced Direct Injection Pyrolytic Synthesis) method [2] was developed to control diameter of highly crystalline SWCNTs. As a result, the development of super-growth and eDIPS methods for mass production with low cost will promote the development of the industrial use of SWCNTs in the near future.

Development of SWCNT Application:
In 2010, the "Innovative Carbon Nanotubes and Their Applications Project" was begun which aims to develop applications utilizing the excellent properties of carbon nanotubes. We aimed to develop innovative applications of SWCNTs synthesized by Super-Growth method and eDIPS methods, and to build up methods of separating [3] and dispersing SWCNTs. In addition, we assessed the safety and the management of nanotube materials [4]. Moreover, we promoted R&D on ultra-light, super-strength, high-performance materials for application development through establishing a new industry on Carbon Nanotube (CNT) composite materials. In 2014, "Nano-carbon Application Project towards Low-carbon Society" project has been began to make further development of outcomes of "Innovative Carbon Nanotubes and Their Applications Project"

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SP6

Nano-carbon application activities in Korea

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The unique electrical, optical, and mechanical properties of carbon nanotubes and graphene have triggered diverse application efforts both in academia and industries. Some of these activities were successful, but others faded away. This talk briefly introduces carbon nanotube and graphene application activities in Korea. Firstly, major nano-carbon producers and suppliers will be introduced. Secondly, currently-available commercial products and near-future applications will be discussed. These include anti-static composites/films, electrically or thermally conductive composites/pastes, EMI shielding films, transparent conductive films, and energy storage materials. Finally, recent research activities targeting future markets will be discussed. Many of them are focused on flexible/stretchable electronics. The research activities in my group will also be briefly introduced. We employed 1-dimensional carbon nanotubes and/or functionalized silver nanoparticles to enhance conductivity or fluorescence for applications in flexible composites/pastes [1-3], stretchable films [4], flexible EMI shielding films [5], and stretchable fibers [6].

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C15

Hierarchically structured carbon nanotube-graphene fibers for micro-supercapacitors

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Micro-supercapacitors are promising energy storage devices for miniaturized portable electronics. Their main limitation, however, is the low volumetric energy density. We produced hybrid carbon fibers using the capillary chromatography column as a one-dimensional hydrothermal micro-reactor, in which reduced graphene oxide (rGO) and single-walled carbon nanotubes (SWCNTs) self-assembled into an inter-connected SWCNT network with rGO sheets interposed along the microfiber axis to create a mesoporous microstructure of a large surface area (396 m2/g) and a high electrical conductivity (102 S/cm). The resultant fiber showed capacity of 300 F/cm3. The fiber micro-supercapacitors exhibited a high volumetric energy density of ~ 6.3 mWh/cm3. Furthermore, the all-carbon hybrid fibers can be controllably functionalized to yield versatile composite fibers with either capacitive or Faradic characteristics. By matching the specific capacitances of one MnO2-coated rGO/SWCNT fiber as battery-type (positive) electrode and the other N-doped rGO/SWCNT fiber as capacitor-type (negative) electrode, we constructed fiber-based asymmetric micro-supercapacitors with a voltage window of 1.8 V and excellent cycling stability. These results demonstrate the great potentials of graphene and carbon nanotubes in miniaturized energy storage devices.

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C16

CNTs ; Devils or Angeles ?

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Mitsubishi identified Nano-Carbons as one of seeds for future business back in 1993, and has been struggling to start up new business over 20 years.

As so many scientists, technical people, business people might have been so, Mitsubishi has faced a lot of barriers, issues, technical or legal, and has experienced various failures by Nano-Carbons, especially by CNT.

Thanks to such struggles and failures caused by CNT as well as other Nano-Carbons, Mitsubishi learned invaluable lessons how to keep distance from dangers, what to find and & approach in a right way.

Not like in NT05, where Mitsubishi made presentation for industrial applications for the future, in NT15, however, 10 years later since then, Mitsubishi would present real applications/products with several types of CNTs, especially produced by KUMHO Petrochemicals in S. Korea.

People, Product, Money are 3 key factors to open up a new window for business, and Mitsubishi hopes to have any audience in NT15 NOT to repeat our failures, BUT to keep moving on their paths to accelerate product development.

CNT was born, but it is up to us how to bring up CNT to be recognized as superior material.

Look forward to seeing you all in NT15.

P349

Controlling the functionalization of carbon nanostructures for energy related materials

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Synthetic procedures that have been developed to functionalize carbon nanostructures (CNSs) such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) may require long reaction times and harsh conditions. In this context we have studied the continuous flow processing of carbon nanostructures with the aim not only to reduce reaction times but also to tune the properties of the functionalized carbon materials. Our methodology leads to derivatives with similar functionalization degree (FD) as those reacted in a flask but with reaction times dramatically reduced compared to batch conditions. The flow methodology was also extended to the fast and effective addition of diazonium salts to CNTs and to the functionalization of GNPs. The flow approach allows to control the degree of CNS functionalization, leading to derivatives with enhanced solubility that retain the electronic properties of pristine materials and can be used for organic electronics or photovoltaic applications. In this perspective, we observed how an increase of FD affects the electronic communication of CNTs with a conjugated polymer (P3HT). Our findings show that this is due not only to an increased density of defects, but also to the formation of multilayered organic structures that shield the conjugated carbon lattice.

P350

Synthesis of Pd nanoparticles decorated on Functionalized Graphene to Enhance Activity in Formic acid Electrooxidation

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The enhancement of anodic catalysts for low-temperature fuel cell technology such as formic acid oxidation fuel cells has been numerous explored by the combination of noble metals and carbon supports because of their catalytic properties and economic uses. Here, we introduce the nucleation of Pd nanoparticles (PdNPs) on modified graphene sheet with amino aniline groups compared with unmodified reduced graphene (rG). Functionalized graphene (fG) was performed by diazonium functionalization of surface-wrapped graphene method and confirmed by Fourier transform infrared spectroscopy (FTIR), Atomic Force Microscopy (AFM), Thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and Raman Spectroscopy. The results show high contained amino aniline moeities on graphene sheet, leading to a large amount of electron donating groups acting as PdNPs nucleation sites. PdNPs supported on fG and rG were confirmed by X-ray diffraction (XRD), and Transmission microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDS) techniques. The cyclic voltammetry of PdNPs/fG and PdNPs/rG were carried out in formic acid solution to investigate their catalytic activities. It was found that supported PdNPs on fG exhibit higher electrocatalytic activity shown by higher mass activity and durability than supported PdNPs on rG nanocatalysts. This can be envisaged that functionalized graphene can deliver higher activity and CO tolerance.

P351

Fuel cell performance and durability of newly functionalized carbon nanotubes-based electrocatalysts at high temperature and non-humidified conditions

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Among the most probable options of alternative energy sources are the fuel cells (FCs), in particular, polymer electrolyte membrane fuel cells (PEMFCs) that proffer instant power output with high energy conversion efficiency and CO2 emission-free. PEMFCs electrodes are usually consist of carbon based-electrocatalysts. Much effort has been devoted to the fabrication of a high performance and durable electrocatalyst. Multi-walled carbon nanotubes (CNTs) are receiving a broad attention as a FC catalyst support because it has a high electrical conductivity, a high surface area, a highly organized structure with a well-developed porosity, and a high electrochemical stability.

However, CNTs have a strong bundle structure and lack to binding sites for homogeneous loading of metal catalysts e.g. Platinum (Pt). Thus, it needs to be functionalized before its FC catalyst application. Here, we show a new functionalization process of CNTs in which CNTs were wrapped with proton conducting polymers before the deposition of the Pt metal catalyst. The fuel cell performance and the durability of the newly functionalized CNT-based electrocatalysts were evaluated at high temperature and non-humidified conditions in comparison with the current market carbon black-based electrocatalyst.

P352

Ultra-low platinum loaded-carbon nanotubes electrocatalyst with high fuel cell performance

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Fuel cells, in particular polymer electrolyte membrane fuel cells (PEMFC) are receiving a great deal of attention because of its practical use in transportation and commercial sectors. PEMFC that works without humidification at high temperatures became a market requirement because it offers several advantages over the currently available FCs, e.g. the higher activity of Pt based-electrode.

Cost reduction and improved durability are the two major targets for accelerating the commercialization of PEMFC. To achieve these goals, the development of a novel method to fabricate platinum (Pt)-based electrocatalysts with a high mass activity, deposited on durable conductive support materials, is necessary. Here, we describe a facile approach to grow homogeneously dispersed Pt nanoparticles with a narrow diameter distribution in a highly controllable fashion on polymer-wrapped carbon nanotubes. A PEMFC cell employing a composite with the smallest Pt nanoparticle size (2.3 nm diameter) exhibited a ~8 times higher mass activity compared to a cell containing Pt with a 3.7 nm diameter. This is the first example of the diameter control of Pt on polymer-wrapped carbon supporting materials, and the study opens the door for the development of a future-generation of PEFCs using a minimal amount of Pt.

P353

Investigation of carboxyl and hydroxyl groups at periphery of graphene

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The energetics of placing carboxyl and phenolic groups at the periphery of a graphene sheet are studied using density functional theory (B3LYP) with a 6-31G* basis set, augmented with diffuse functions on oxygen atoms. Individually both COOH and OH have the same preference for the corner sites, but in presence of COOH the smaller OH group opts for its second preference, the zigzag sites, leaving corner sites to the larger group. H-bonding acts to keep the two groups adjacent to one another, suggesting an interaction energy between the two groups of about 7.0 kcal/mol. However, π conjugation between these groups with the carbon network plays a decisive role in the stability as well. Vibrational analyses reveal strong features that are characteristic of each site, which may help in the assignment of experimental spectra.

P354

Carbon nanotube-templated synthesis of covalent porphyrin network for oxygen reduction reaction

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In the actual fuel cell devices, the reduction of oxygen is performed by platinum nanoparticles. The cost of platinum encourages the development of new catalysts based on non-noble metals. In nature, the reduction of oxygen is performed by iron porphyrins in the active center of enzymes. Thus bio-inspired catalysts based on cobalt or iron macrocycles have been extensively studied for oxygen reduction reaction (ORR). [1]

Here, we describe the formation of a covalent network of porphyrins around MW-NTs. Our approach is based on adsorption of ethynylporphyrins followed by the dimerization of the triple bonds. The nanotube acts as a template for the formation of the polymeric layer. The nanotube hybrids were characterized and tested for the ORR in a series of electrochemical measurements in acidic conditions. Compared to similar systems in which monomeric porphyrins are simply physisorbed, the nanotube hybrib showed a higher activity, a higher current density, a lower overpotential and a four electrons reaction pathway. [2]

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P355

Functionalization of carbon nanotubes for Li-sulfur batteries

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The development of rechargeable batteries with high energy densities has received an increasing attention over the last few decades. Li-ion systems are currently widely used in portable electronic devices; nevertheless, these systems will not meet the requirements for large-scale applications in electric vehicles.

Lithium-Sulfur batteries offer an interesting alternative, with a much higher theoretical specific capacity (1675 mA.h.g-1) and a lower cost due to the use of elemental sulfur as the positive electrode material. One of the main issues regarding Li-S accumulators is the progressive dissolution of the active material in the electrolyte, which causes an important loss of capacity, a self-discharge phenomenon and finally the end of the battery.

In this work, new positive electrode materials for Li-S accumulators have been developed, avoiding the dissolution of the active material in the electrolyte during the discharge phase. To this end, molecules bearing a disulfide bond were grafted to carbon nanotubes and graphene. The nanotube materials at once bring a good electronic conductivity to the positive electrode and serve as a template for a covalent immobilization of the active material. The resulting systems remain very stable over cycling and present a promising specific capacity. [1]

[1] G. Charrier et al. in preparation

P356

Transisitors based on double wall carbon nanotube and graphene hybrids for optoelectronics

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Double walled nanotubes (DWNTs) consisting of two concentric single walled CNTs, can be treated as structures of two twisted and stretched graphene bilayers that exhibit peculiar electronic properties, visible using molecule grafting on the outer wall [1].
Photo active molecules such as porphyrin molecules and terpyridine complex have the ability to reversibly switch between two or more stable states in response to external stimuli and can thus find application in molecular optoelectronics. A few studies have already demonstrated the efficient photo induced charge transfer in CNT/porphyrin hybrid systems by using electrochemical methods, photoluminescence excitation experiments [2].
Here we use Raman spectroscopy as a powerful tool both for the investigation of isolated DWNT and graphene and to study the charge transfer between the chemical dopants and sp2 carbon. We demonstrate field effect transistors based on isolated DWNT (or graphene) and functionalized with photo active molecules probed with combined Raman spectroscopy and electrical transport measurements. The role of light in the control of the state of the hybrid will be manifested and elucidated in terms of photo-induced charge transfer.

Reference: [1] D. Bouilly, et al. ACS nano 5, (2011), pp. 4927-4934. [2] F. Vialla, et al. Phys. Rev. Lett. 111 (2013), pp.137402

P357

Boronic acid-coated magnetic nanoparticles as a platform for carbon dots and doxorubicin conjugation

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Here, we describe the preparation of phenylboronic acid-modified magnetofluorescent nanoparticles (NPs), consisting of $MnFe_2O_4$ magnetic NPs and fluorescent carbon dots (Cdots), which could provide both optical and magnetic resonance (MR) imaging modalities as well as could further conjugate with Dox as a drug delivery vehicles. In this study, the hydrophobic $MnFe_2O_4$ NPs can be transferred from organic media into water by utilizing 4-carboxyphenylboronic acid, which serves as specific ligands for targeting cancer cells and active groups for the conjugation with fluorescent Cdots, resulting in phenylboronic acid-modified magnetofluorescent NPs. The designed NPs displayed colloidal stability at different pH value and salt concentration as well as exhibit negligible cytotoxicity with >85% cell viability in HeLa cancer cells. Confocal laser scanning microscopy results show that the specificity of the magnetofluorescent NPs internalized HeLa cells. The MR results show that magnetofluorescent NPs displayed excellent contrast effects in T2-weighted MR imaging. Moreover, in vivo zebrafish imaging is also demonstrated using phenylboronic acid-modified magnetofluorescent NPs as the fluorescence marker. The results also indicated that these magnetofluorescent NPs carried doxorubicin could efficiently induce an inhibitory effect on HeLa cells, as confirmed by confocal laser scanning microscopy and in vitro cytotoxicity assay.

P358

Experiments and modeling: advanced multifunctional polymer composites using graphene aerogels and carbon nanotubes

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Graphene aerogel (GA) PMMA composites are developed by backfilling PMMA into the pores of the GAs, providing uniform distribution of reduced graphene oxide (rGO) sheets in the PMMA matrix. Electrical, mechanical and thermal properties of the GA-PMMA composites are measured by two-probe, microindentation and comparative infrared techniques respectively. When graphene volume fraction increases, the electrical conductivity, microhardness and thermal conductivity of the composites are enhanced significantly more than those of pure PMMA and the graphenePMMA composites prepared by traditional dispersion methods. Thermal boundary resistance (TBR) between graphene and PMMA is estimated to be 1.906x10^8 m2K/W by an Off-Lattice Monte Carlo algorithm taking into account the complex morphology, size distribution and dispersion of rGO sheets. Also the Monte Carlo model is modified to investigate effective thermal conductivities (Keff) and thermal transport limitations of three-phase polymer composites containing CNTs and inorganic nanoparticles. The simulation results agree well with experimental data for PEEK composites having CNTs and WS2 nanoparticles. The modified model can predict Keff of three-phase composites more accurately than previous models. The effects of CNT and WS2polymer TBRs, CNT concentration, CNT morphology, CNT bundle and CNT orientations (parallel, random and perpendicular to the heat flux) on Keff are quantified.

P359

Freestanding macroscopic metal-oxide nanotube films derived from carbon nanotube film templates

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Aligned carbon nanotube films coated by amorphous carbon were developed into novel templates of atomic layer deposition. Freestanding macroscopic metal-oxide nanotube films were successfully synthesized by using such templates. The reactive amorphous carbon layer greatly improves the nuclei density, which makes sure the high quality of the films and the precise control of the wall thickness of the nanotubes. On the basis of the alumina nanotube films, we showed a humidity sensor with a high response speed, a TEM grid, and a catalyst support. The cross-stacked assembly, ultra-thin thickness, chemical inertness and high thermal stability of alumina nanotube films contribute to the high performance of these applications. In addition, it is expected that the metal-oxide nanotube films have great potentials owing to their functional richness, the macroscopic flexible appearance, the compatibility to the semiconducting technologies and the feasibility of mass production.

P360

Earth-abundant bifunctional 3D electrode based on nitrogen-doped carbon nanotubes for efficient water electrolysis in alkaline medium

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A 3D bifunctional electrode is developed for catalyzing both water electrolysis half reactions (OER and HER) in the same medium of 0.1 M KOH electrolyte solution. Our 3D electrode is prepared in a self-assembly process comprising Co_3O_4 nanospheres nucleated on the surface of nitrogen-doped carbon nanotubes (NCNTs) which themselves are grown directly on the carbon paper (CP) conductive substrate as the current collector. A higher stability compared to the similar material which was drop casted on glassy carbon electrode was achieved due to the firm anchoring of electrocatalyst to the surface of CP current collector. Our bifunctional electrode displays current density of 10 mA/cm^2 at overpotential of 0.47 V for OER and at overpotential of 0.38 V for HER.

P361

Hierarchical self-assembled structures based on nitrogen-doped carbon nanotubes as advanced negative electrodes for Li-ion batteries and 3D microbatteries

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A hierarchical self-assembled structure based on nitrogen-doped carbon nanotubes (NCNTs) was directly synthesized on the electrode surface (carbon paper) and tested as negative electrodes for Li-ion microbatteries. This structure was further functionalized with hematite nanorods attached on their outer walls. The electrochemical behavior and the footprint area capacities of these 3D architectures were also investigated to probe their applicability in Li-ion microbatteries. NCNTs showed excellent coulombic and energy efficiencies and footprint area capacities as high as 2.1 $mAhcm^{-2}$ at 0.1 $mAcm^{-2}$ after 20 cycles and up to 1.95 $mAhcm^{-2}$ after 60 cycles at 0.3 $mAcm^{-2}$. On the other hand, hematite nanorods modified NCNTs displayed footprint area capacity up to 2.25 $mAhcm^{-2}$ at 0.1 $mAcm^{-2}$. However, their coulombic and energy efficiencies were not as good as NCNTs electrode. This is due the difference in the nature of conversion reaction occurring in these two structures. A continuous rearrangement of the phase boundaries in hematite structures causes progressive electrochemical milling which lowers the efficiencies.

P362

SWNT paste for micrometer-thick, uniform, and wide-area SWNT film fabrication by coating

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Single-walled carbon nanotube (SWNT) films with thicknesses in the range of micrometers has a potential for use in a variety of applications. Vacuum-filtration of SWNT suspension has been often used to fabricate those films, but suffers in a limited production efficiency and quality. Therefore, the coating process for thick SWNT film is desirable. However, a low concentration (< c.a. 0.1 %) and viscosity of the suspension of SWNT previously reported has limited the coating thickness.

In this work, we have developed the high concentration (1 wt%) and high viscous suspension of SWNT (SWNT paste), by sonication of SWNT with a high aspect ratio (diameter: 3 nm, length: c.a. 0.1-1 mm) under extremely vigorous stirring. In SWNT paste, SWNTs are suspended to form agglomerates consisting of three-dimensional networks, and large amount of solvent are contained inside those networks. These structures of SWNT paste resulted in unique fluidic behaviors such as shape-retainability, plastic deformation, and fast recovery of viscosity. Consequently, thick (> 10 um), uniform (Ra < 0.5 um), and large-area (>A4 size) SWNT film has been easily obtained by conventional coating technique.

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P363

Graphene oxide selectively targets cancer stem cells across multiple tumor types: Implications for non-toxic cancer therapy

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Tumour-initiating cells (TICs), a.k.a. cancer stem cells (CSCs), are difficult to era-dicate with conventional approaches to cancer treatment, such as chemo-therapy and radiation. As a consequence, the survival of residual CSCs is thought to drive the on-set of tumour recurrence, distant metastasis, and drug-resistance, which is a significant clinical problem for the effective treatment of cancer. Thus, novel approaches to cancer therapy are needed urgently, to address this clinical need.

Here, we show that graphene oxide (of both big and small flake sizes) can be used to selectively inhibit the proliferative expansion of cancer stem cells, across multiple tumour types. More specifically, we now show that graphene oxide effectively inhibits tumour-sphere formation in multiple cell lines, across 6 different cancer types, including breast, ovarian, prostate, lung, pancreatic cancers, as well as glioblastoma (brain). In striking contrast, graphene oxide is non-toxic for bulk cancer cells (non-stem) and normal fibroblasts. Mechanistically, we present evidence that GO exerts its effects on CSCs by inhibiting key signal transduction pathways (WNT, Notch and STAT-signaling) and inducing CSC differentiation. Thus, graphene oxide may be an effective non-toxic therapeutic strategy for the eradication of cancer stem cells.

Reference: Fiorillo, M. et al, Oncotarget 6(6), 3553-3562 2015,

P364

Simple organic chemistry for wide functionalization of graphene as a strategy for incorporation in polymers

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The limited procesability of graphene is one of the main restrictions for the preparation of graphene-based materials, directly affecting many application types. To overcome this, graphene must be furnished with different functionalities that allow its combination with other compounds, leading to new materials with a compendium of interesting properties.

In our laboratory we design and develop simple organic chemistry approaches to the modification of graphene with a wide range of functional groups for its subsequent incorporation into polymer matrices. We focus on two main issues: i) the use of approaches based on covalent chemistry due to the greater stability of covalent bonds over supramolecular ones, which is of paramount importance for implementation in long life devices; ii) as a general rule we apply only very simple and well-established synthetic protocols, especially one-pot reactions, if viable.

Here we present the chemical modification of graphene with reactions including diazonium coupling, Friedels-Craft and diverse click reactions. By using these protocols graphene has been covalently modified with functional groups very different in nature, including SO3H, acetylene, SH, OH, etc., as well as with conjugated and con-ventional polymers.

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P365

Fabrication and properties of ultralight weight carbon nanotube yarn by dry spinning process

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Ultralight weight Carbon Nanotube (CNT) yarns are developed based on a CNT dry-spinning technology, free from a conventional wet-spinning process. The first efforts were concentrated to study and optimize the parameters for the growth of dense and tall CNT forest such as precursor feed, temperature, time as well as the interlinks of CNT bundles, number of walls and length of the individual CNT in the forest, which is appropriate for the continuous spinning from CNT forest. Very good reproducibility of rapid grown CNT forests were obtained through a chemical vapor deposition (CVD) process without water vapor. The forest here in this research consists of few walled CNT of up to some 0.4 mm lengths in a super-aligned array, and we are currently working with typical CNT yarn diameter and length of about 0.01-0.02 mm and 0.5 m, respectively. The tensile strength and electrical conductivity by optimizing the spinning parameters and treatment of the CNT yarn are in the range of typically 1 GPa and $5\text{x}10^2$ S/m. Our benchmark is to reach tensile strengths better than carbon fiber and an electrical conductivity as well as bulk metals.

P366

Lasagna-like electrode by painting method for flexible thin film LIBs

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The development of advanced flexible thin film batteries is a key step for flexible/stretchable electronics. In this work, we achieved a new type of electrode configuration by directly painting common battery materials (LiFePO4 and Li4Ti5O12) into the ultra-thin but robust carbon nanotube (CNT) films. This electrode resembles a lasagna-like structure by alternating electrode materials and CNT films layer by layer. The rich number of electron pathways and the highly porous structure of the CNT film result in full batteries (LiFePO4 cathode and Li4Ti5O12 anode) that exhibit a high areal capacity over 0.2 mA h cm−2, a stable output voltage of 1.82 V, plus excellent reversibility and light polarization. More importantly, the capability of such batteries working in both flat and bent conditions suggests great promise in the energy storage and delivery for revolutionary portable electronics.

P367

Template synthesis of nanodiamond polymers utilizing inner space of carbon nanotubes

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Carbon nanotubes (CNTs), nano-scale cylinders composed of rolled-up graphene sheets, provide an ideal platform to create one-dimensional (1D) nanostructures. Precursor species are filled into the cavities of CNTs, and then molded into linear structures via thermal annealing. To date, various kinds of 1D nanomaterials have been synthesized, including metal atomic wires, ultrathin boron-nitride nanotubes, and well-defined CNTs, which exhibit different properties from those of their bulk counterparts. As part of our exploring for novel 1D nanomaterials, we have studied the synthesis of linear forms of diamond crystal from diamantanes, the molecules in the diamond configuration.

Here, we report the synthesis of diamondoid chains from bridgehead-halogenated diamantane (a kind of diamondoids) inside CNTs. Our experimental and theoretical approaches revealed that the diamantane cages are linked with each other. The present synthesis of this new class of diamond nanomaterials offers a new direction for the nanocarbon research as well as a new strategy for the design and synthesis of 1D nanomaterials.

P368

Ultra-stretchable conductors based on buckled super-aligned carbon nanotube films

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Ultra-stretchable conductors are fabricated by coating super-aligned carbon nanotube (SACNT) films on pre-strained polydimethylsiloxane (PDMS) substrates and forming buckled SACNT structures on PDMS after release of the pre-strain. The parallel SACNT/PDMS conductors can be stretched to 200% strain with a normalized resistance increase of only 4.1%. The cross-stacked SACNT/PDMS conductors exhibit even lower resistance variation. The parallel SACNT/PDMS conductors exhibit high durability with resistance increase of less than 5% after 10,000 cycles at 150% strain. In situ microscopic observations reveal that the SACNT conductive network can be protected from fracture by the formation and straightening of the buckled SACNT structures during the loading and releasing processes with reversible morphology evolution. Due to the excellent stretchability, resistance stability and high durability of the SACNT/PDMS composite films, the ultra-stretchable conductors may find broad applications in stretchable interconnections and power devices.

P369

Functionalization of carbon nanotubes and their application to obtain conductive cotton textile

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We have developed a new and safe method to functionalize both single-walled and multiwalled CNTs (SWNTs and MWNTs) using a citric-acid-assisted RF oxygen plasma treatment, which is less destructive to their structure [1]. The treatment conditions in each step are optimized to attach large number of carboxyl (-COOH) groups onto CNT surfaces ensuring fewer damages to their structure, which significantly improves their dispersion in water.

By using the functionalized MWNTs, we have produced conductive cotton textile form coating. The oxygen-containing groups on the f-MWNTs significantly enhance their dispersion in water to produce highly stable MWNT-ink. 100 % cotton textile is repeatedly dipped into the ink and dried in air at room temperature. After several dip-drying cycles, the textile becomes uniformly coated with f-MWNTs, where they are strongly attached with the cotton fibers keeping the flexible nature of the textile. As a result, thermal and electrical conductivities of the textile are enhanced. This can be used in devices as flexible heater, flame retardant materials, pressure sensor, high frequency signal transmitter, electro-conductive fabric for smart textile, etc.

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P370

Self-doped conducting polypyrrole-grafted graphene sheets synthesized by a click chemistry reaction

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Graphene, a two-dimensional nanocarbon material may be an ideal candidate as a filler of polymer composites for conducting polymer-based bistable memory devices due to its extraordinary properties such as high surface area, broad electrochemical window, good electrical and mechanical properties. However, the major drawback in the fabrication of the conducting polymer-graphene composite-based electronic devices is the insolubility of conducting polymers and the aggregation of graphene sheets in organic solvents. We synthesized the self-doped conducting polypyrrole-grafted graphene sheets (GS-PPy) through click chemistry reaction, where the functionalized graphene oxide with a water-soluble polymer containing anionic dopants was used. The GS-PPy hybrids showed a uniform coating of PPy on the graphene sheets, good dispersion in aqueous solutions, and high electrical conductivity. We also demonstrated a fabrication of non-volatile memory device with a good write-once read-many times memory behavior using the GS-PPy.
Acknowledgement: This work was supported by the Defense Acquisition Program Administration (DAPA) and the Agency for Defense Development (ADD).

P371

Gate-controlled generation of optical pulse trains using individual carbon nanotubes

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We report on optical pulse-train generation from individual air-suspended carbon nanotubes under an application of square-wave gate voltages [1]. Electrostatically-induced carrier accumulation quenches photoluminescence, while a voltage sign reversal purges those carriers, resetting the nanotubes to become luminescent temporarily. Frequency domain measurements reveal photoluminescence recovery with characteristic frequencies that increase with excitation laser power, showing that photoexcited carriers quench the emission in a self-limiting manner. Time-resolved measurements directly confirm the presence of an optical pulse train synchronized to the gate voltage signal, and flexible control over pulse timing and duration is demonstrated.
Work supported by KAKENHI (24340066, 24654084, 26610080, 26870167), SCOPE, Canon Foundation, Asahi Glass Foundation, and KDDI Foundation, as well as the Nanotechnology Platform and Photon Frontier Network Program of MEXT, Japan. A.I. is supported by MERIT and JSPS Research Fellowship, and M.Y. is supported by ALPS.

[1] M. Jiang, Y. Kumamoto, A. Ishii, M. Yoshida, T. Shimada, Y. K. Kato, Nat. Commun. 6, 6335 (2015).

P372

Electromagnetic SERS effect in carbon nanotube systems

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Most of the applications of carbon nanotubes (CNs) to enhance Raman scattering have been to decorate them with metallic nanoparticles, to use metal plasmons as spectroscopic enhancers with CNs only serving as their supporters. In this work [1], the quantum theory of the resonance Raman scattering is developed for a hybrid quantum system of a dipole emitter, the two-level system (TLS), coupled to a CN interband plasmon resonance. Nanotubes are shown to be able to greatly enhance the Raman scattering effect under the strong TLS-plasmon coupling. This resonance Raman scattering effect is a manifestation of the general Surface Enhanced Raman Scat-tering (SERS) phenomenon, in which the strong near-surface field due to the interband plasmon excitation results in the resonance Raman scattering enhancement by the hybrid nanotube system. The work opens up paths for new design concepts of future generation CN based nanophotonics platforms for single molecule/atom/ion detection, precision spontaneous emission control, and optical manipulation, which will benefit from the extraordinary stability, flexibility and precise tunability of the electromagnetic properties of carbon nanotubes by means of their diameter and chirality variation.

Supported by the US Department of Energy (grant # DE-SC0007117).

[1] I.V.Bondarev, Optics Express 23, 3971 (2015).

P373

Demonstration of pressure sensor sheet using printed carbon nanotube transistor array

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Printed electronics is attractive because it leads to low-cost and eco-friendly device fabrication. It is suitable for large-area device fabrication such as sensor sheets. We fabricated 16 x 16 array of printed CNT transistors on plastic film. Semiconducting CNTs were purified and cast by an ink dispenser to form CNT channels. The CNT transistors had p-type characteristics with an on/off ratio of 1,000,000. Averaged ON-current was 1.37 uA with a sigma of 27 % and field effect mobility was 4.1 cm2/Vs. A pressure sensor sheet was assembled by stacking a pressure sensitive conductive rubber (PCR) sheet and an Al foil over the CNT transistor array. When the PCR is deformed, the resistance of PCR is reduced. A vial was put on the sensor sheet and a 2 kg weight was applied to the vial. The center of the vial bottom is hollowed and pressure concentrated at the vial edge. The vial edge was clearly detected by the measured current map. A pressure sensor sheet was successfully demonstrated using printed CNT transistors.

This work is based on results obtained from a project supported by the New Energy and Industrial Technology Development Organization (NEDO).

P374

Binder-free polymer encapsulated sulfur-carbon nanotube composite cathodes for high performance lithium batteries

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Binder-free polymer encapsulated nano sulfur/super-aligned CNT (PVP@S-SACNT) composite electrode is developed via a solution-based method. During the synthesis process, PVP not only facilitates better dispersion of SACNT bundles into a 3D continuous network, but also encapsulates the sulfur nanoparticles onto the SACNT network to ensure their tight electrical connection and prevent polysulfides dissolution.

Combining the advantages of the high conductive and porous SACNT network and the PVP surface encapsulation, the PVP@S-SACNT cathode possesses a robust composite structure with improved mechanical property and exhibits excellent cyclic stability (initial capacity of 1303 mA h g−1 and 856 mA h g−1 after 200 cycles at 1C) and highrate performance (590 mA h g−1 at 20C). Moreover, the PVP@S-SACNT composite presents excellent long-term capacity stability with a capacity decay of 0.052% per cycle during 1000 charge/discharge cycles at 2C. With these appealing performances, the PVP@S-SACNT composite becomes a promising cathode material for the next-generation rechargeable batteries.

P375

Graphene and single-walled carbon nanotube films for gas sensor applications

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Detection of environmental gases is becoming more and more important for various applications such as global warming, monitoring and control of environmental pollution, advanced diagnostics in medical applications, destruction of the ozone layer, etc. A high sensitivity and selectivity are very important for explosive gas leakage detection and for a real-time detection of toxic or pathogenic gases in industries. Single-walled carbon nanotubes (SWCNTs) and graphene are considered as the most promising materials due to their one atom-thick conjugated structures, a large specific surface area and a high sensitivity.

Thereby, in this work we present a detailed investigation of influence of various gases on the sensory properties of graphene and SWCNT films[1]. The performance of gas sensor was measured by using a relevant apparatus to register a continuous sensor electric resistance variation triggered by an exposure to different gases in air atmosphere at room temperature. We observed different reactions of sensor depending on donor or acceptor mechanism for redistribution of electrons between the gas used and the sensor films.

The work was supported by RFBR-14-02-31639 and Keldysh Research Center projects.

[1] I.Kondrashov, P.Rusakov, et al., Jrn. of Nanoelectronics and Optoelectronics 2 (2015) 00.

P376

Development of ordered structural carbon composed from the graphene oxide

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Ordered Structural Carbon (OSC) materials are expected to satisfy a lot of demands from whole range of fields such as energy storage device and fuel cell. However, a typical synthesis method of OSC has several issues. First, the filling process of carbon source to hard template is complex. Second, the template removing process needs HF or organic solvents. Finally, controlling of structural wall is difficult. Therefore, purpose of in this study is development more easily OSC synthesis method. We focused on Layer by Layer (LBL) method using polymer particles as a template and titanium oxide nanosheets as structural wall. In this method, thickness of structural wall can be controlled. Furthermore, it is possible to change the property of hollow shell by exchanging the nanosheets and combine a variety of nanosheets. We synthesized new OSC using graphene oxide nanosheets (GOns) as structure wall. Afterward its morphology and crystalline structure, electrochemical properties were characterized. Raman spectra and UV-vis spectra indicated that polymer spheres were covered by GOns. SEM images showed that the synthesized material maintained sphere after heat treatment. In addition, the hollow sphere was observed by TEM.

P377

Graphene/conjugated polymer composites and their properties

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Graphene has attracted enormous attention among scientists. As the precursor of reduced graphene oxide (RGO), graphene oxide (GO) is generally prepared by oxidation of graphite and possesses an abundance of oxygen-containing groups, which enable modification of GO sheets with desirable molecules or polymers covalently or non-covalently. In our research, we modified GO sheets using conjugated polymers, e.g. polythiophene derivatives. A higher grafting density of poly(3-hexylthiophene) (P3HT) on the surfaces of GO sheets leads to red shifted absorption maximum, which is beneficial to efficient use of sunlight in optoelectronics. The electronic coupling between RGO and P3HT in the RGO-g-P3HT composite results in tuned photoluminescence (PL) emission of the RGO component, leading to resolved dual PL emissions corresponding to RGO and P3HT components, respectively. The photoinduced electron transfer from P3HT to RGO in the composite leads to enhanced photothermal effect of graphene. In addition, the RGO/polythiophene films exhibit enhanced photoresponse due to the photoinduced electron transfer from polythiophene to RGO.

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P378

Terahertz sensing and imaging with graphene and carbon nanotube devices

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The advantageous properties of terahertz (THz) waves, such as the important energy spectrum in the meV range, enable various applications of imaging and spectroscopy. However, since the THz region is located between the electronic and photonic bands, even basic components like detector and source have not been fully established, compared to the other frequency regions. The THz wave also has the problem of low imaging resolution, which results from a much longer wavelength than that of the visible light. By employing graphene and carbon nanotube devices, we have developed a new type of THz sensing and imaging devices. We have succeeded in observing THz photoconductivity of graphene, ranging over a wide frequency band of 0.8-33THz. This result demonstrates that the graphene device works as a wide-band, frequencytunable THz detector. By using the graphene THz detector, we have further created a new designed THz imager, in which all the components: an aperture, a probe, and a detector are integrated on one chip. The development of this device has made it possible to perform nanoscale THz imaging and spectroscopy. Finally, other types of THz devices with carbon nanotubes will be also presented.

P379

The sheet resistance dependent electromagnetic interference shielding effectiveness of flexible conductive adhesives

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The electromagnetic interference (EMI) shielding materials made of polymers and conductive fillers have attracted great attention recently to replace metal based shields [1]. We previously reported flexible conductive adhesives made of micro-scale silver flakes, multi-walled carbon nanotubes coated with nano-scale silver particles, and nitrile butadiene rubber (NBR) [2]. The flexible adhesives also provided excellent EMI shielding effectiveness [1,2]. Our data as well as the data in literatures demonstrated a good correlation between shielding effectiveness and sheet resistance which was previously suggested by Zhang et al [3]. The conductivity and shielding effectiveness could be controlled by the concentration of conductive fillers and the maximum EMI shielding effectiveness was 75 dB at 1 GHz at the film thickness of 20 microns [1].

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P380

Fabrication of highly stable silver nanowire networks under current flow by in-situ interconnecting with single-walled carbon nanotubes

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One-dimensional (1D) nanomaterial, such as silver nanowires (AgNWs) or carbon nanotubes (CNTs) have been investigated as alternative electrode materials for transparent conducting films (TCFs) on plastic substrates instead of the brittle and expensive indium tin oxide (ITO). In addition, modulation of the junction resistance between metallic nanowires is a crucial factor for high performance of the network-structured conducting film. Here, we show that under current flow, silver nanowire network films can be stabilized by minimizing the Joule heating at the NW-NW junction assisted by in-situ interconnection with a small amount (less than 3 wt%) of single-walled carbon nanotubes. This was achieved by direct deposition of AgNW suspension containing SWCNTs functionalized with quadruple hydrogen bonding moieties excluding dispersant molecules. The electrical stabilization mechanism of AgNW networks involves the modulation of the electrical transportation pathway by the SWCNTs through junction in the network film. The SWCNT-induced stabilization of the AgNW networks was also demonstrated by irradiating the film with microwaves. The development of the high-throughput fabrication technology provides a robust and scalable strategy for realizing high-performance flexible transparent conductor films.

P381

Modulation of the Dirac Point Voltage of Graphene by Ion-Gel Dielectrics and Its Application to Soft Electronic Devices

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We investigated systematically Dirac point voltage modulation of graphene transistors by changing types of ionic liquids as a main gate dielectric component. Ion-gel was formed by ionic liquids and a non-triblock copolymer-based binder involving UV irradiation. With a fixed cation (anion), Dirac point voltage was shifted to a higher voltage as size of anion (cation) increases. Dirac point voltage modulation mechanisms of graphene transistors by designing ionic liquids were fully understood by molecular dynamics (MD) simulations, which excellently matched with our experimental results. It was found that the ion size and their molecular structure play an essential role in the modulation of the Dirac point voltage of the graphene. Using controlled position of its Dirac point voltage based on our findings, complementary metal-oxide-semiconductor (CMOS) -like graphene based inverters using two different ionic liquids were perfectly working even at a very low source voltage (VDD = 1 mV), which was not possible for previous works. These results can be broadly applied in the development of low-power consumption, flexible/stretchable, CMOS-like graphene based electronic devices in the future.

P382

Enhancement of thermoelectric performance of graphene nanoribbons by introduction of edge disorder

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To ease global energy problems, it is effective to develop ubiquitous thermoelectric materials that can change low-temperature waste heat below 200 degrees Celsius to electrical energy. Because of their ubiquitous, atoxic and flexibility, graphene nanoribbons (GNRs) are expected to be potential candidates for new thermoelectric materials. However, thermoelectric efficiency of pristine GNRs is not so large as GNRs have extremely high thermal conductivity. In order to deduct the thermal conductivity without reduction of high thermoelectric power factor (PF), we have proposed a method of introducing edge disorder to zigzag-edged GNRs (ZGNRs).
We have theoretically investigated PF of edge-disordered ZGNRs (ED-ZGNRs) with 1.78nm width, 8.7～100nm length, 0～40% edge disorder in 300K. In our simulation, the edge disorder was treated as removing edge atoms of ZGNRs. From the simulation results, we have found that PF of ZGNRs at the Fermi energy increases rather than decrease by introducing the edge disorder to ZGNRs. Within ED-ZGNRs we calculated in this work, the maximum value of PF was 200 microwatts/cm/K^2 that is almost 5 times larger than that of pristine ZGNRs. Thus we conclude that ED-ZGNRs are potential candidates for novel flexible thermoelectric materials with high thermoelectric power factor.

P383

High-throughput fabrication of highly conductive composite fibers with long carbon nanotubes and silver nanowires by wet spinning

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Nanocarbon-based conducting fibers have been produced by using solution- or dry spinning techniques. However, no one has succeeded to fabricate the highly conductive polymer composite fiber containing large amount of conducting nanomaterials without dispersant because of the severe aggregation of conducting materials in highly concentrated colloidal solution. Here we show that highly conductive (electrical conductivity ～1.5X105 S m−1) polymer composite fibers containing carbon nanotubes and silver nanowires were fabricated via conventional solution-spinning process without any other treatment. Importantly, the high electrical conductivity of the fiber was achieved by rearrangement of silver nanowires in the fiber skin during coagulation process because of a favorable interaction between silver nanowires and coagulation solvents.

P384

Addressing commonly overlooked specifications to produce high quality carbon nanotube TCFs

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Single Walled Carbon Nanotube (SWNT) transparent conductive thin films (TCFs) have been around for many years as an alternative to ITO, however they have not made the breakthrough into full commercial usage. Up until recently it was the transparency and resistivity values of these films that did not meet specification, however a number of different technologies based on carbon nanotubes have emerged to exceed the commonly quoted literature specification of 100 ohms/sq at 90% transparency. However in the drive to reach this point not enough focus has been given to the wider TCF properties of; hardness, adhesion, haze, environmental stability, flexibly and of course cost.

To address the full customer need Linde Nanomaterials has achieved the necessary values for the given specification parameters and here we talk about the specifications, the techniques used to address them and the current result for our SWNT TCFs. Using the ink produced by our unique SEER technology Linde Nanomaterials has produced transparent conductive thin films that can truly be considered as a viable alternative to ITO in current displays and also push forward the quest for fully flexible displays.

P385

Single-walled carbon nanotube film as electrode in indium-free planar heterojunction perovskite solar cells: investigation of hole-transporting layers, dopants, and flexible application

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Recent emergence of perovskite solar cells have drawn much attention owing to excellent power conversion efficiency arising from a long exciton diffusion length, high absorption and carrier mobility. Since ITO is indispensible in perovskite solar cells much like in other photovoltaic devices, there are numerous problems such as rising cost and inflexibility. Many organic solar cell researchers have been vigorously working on replacement of ITO by carbon nanotube. Yet, the same application in perovskite solar cells has not been reported to date. Therefore, in this work, we investigated diverse methodologies that can achieve carbon nanotube electrode in indium-free perovskite solar cells. We found that modified PEDOT:PSS function as both electron-blocking layer and dopant analogue to the organic photovoltaics while MoO_3 is not compatible which is unique to the perovskite system. We discovered that diluted nitric acid doping with a concentration of 35% serves as the most effective method to enhance optical conductivity of carbon nanotube in a safe manner. A PCE of 6.32% in an ITO-free planar heterojunction perovskite solar cell was recorded when its indium tin oxide based reference gave 9.05%. A further flexible application showed 5.38% on a PET substrate.

P386

Development of aqueous hybrid capacitor system using iodine storage reaction at carbon nanotubes electrode

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Owing to its high power density and good cycle stability, electric double layer capacitor (EDLC) has attracted much attention. However, energy density of EDLCs is much lower than that of batteries. In order to increase the energy density of EDLCs, many approaches have been proposed. Redox capacitor using redox reaction of electrode materials is one of such approaches. Lithium ion capacitor is a well-known example of the redox capacitors. However, lithium ion capacitor should use flammable organic electrolytes. Here we propose a new type of redox capacitor which can work with aqueous electrolyte. This capacitor consists of single-walled carbon nanotube (SWCNT) positive electrode and NaI aq. electrolyte. In the positive electrode, reversible redox reaction of iodine occurs at the inner surface of SWCNTs. On the other hand, physical Na ion absorption/desorption occur at the negative electrode. We found that the energy density of this system is three times higher than that of the conventional EDLCs device. Details of electrochemical properties of this system will be discussed in the conference.

P387

Hybrid electrodes of self-supporting carbon nanotube films with MnO_2 particles for electrochemical capacitors

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To enhance the performance of electrochemical capacitors, various capacitive materials have been extensively studied. Manganese oxide (MnO_2) is a relatively low cost and environmentally friendly pseudo capacitive material but its poor electric conductivity is a barrier for practical use. In this work, we use the “sponge” of sub-millimeter-long few-wall carbon nanotubes (FWCNTs) synthesized by fluidized bed as a 3D current collector and capture small (10-100 nm) MnO_2 particles inside its pores. To control the structure of MnO_2 and make the electric paths to CNTs, MnO_2 was electrodeposited on the FWCNT electrodes by oxidizing Mn^{2+} in 0.6 M $MnSO_4$/0.8 M H_2SO_4 aq. High potential is required for dense electrodeposition of small MnO_2 particles, which causes preferential deposition of MnO_2 on the outer surface of thick CNT papers. We examined electrodeposition at a constant potential, at a constant current, or applying high potential pulses, and obtained large number of small MnO_2 particles uniformly. Such thick CNT-MnO_2 hybrids realized high areal capacitance compared with previous studies. The effects of the reaction and mass transfer processes during electrodeposition on the microstructure of the hybrid electrodes and the microstructure on the charge-discharge characteristics of the hybrid electrodes are also discussed.

P388

Squeezed phonons in single wall carbon nanotubes

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In quantum mechanics, coherent states are known as a quantum state whose amplitude-phase uncertainty reach its minimum value. We may generally increase the uncertainty in the amplitude and at the same time decrease the uncertainty in the phase, or vice versa, while still holding the minimum uncertainty principle. These states are the so-called squeezed states. There is a possibility to generate squeezed states of phonons in single wall carbon nanotubes (SWNTs) via ultrafast spectroscopy using less than 10 femtosecond pulses, in which the coherent oscillations of G bands involving two-phonon process may be relevant as a particular example. In this study, we calculate the squeezed phonon amplitude of the G band for a given SWNT and compare it with the coherent phonon amplitude of the G band. We find that the ratio between the G band and G band intensities in ultrafast spectroscopy depend on the laser energy, laser pulse width, and SWNT chirality (electron-phonon coupling). This result might be useful for coherent control of phonon excitations so that we may be able to selectively excite a certain phonon mode in carbon nanotubes.

P389

Biodegradation of carbon nanohorns

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With the rapid development in the medical application of carbon nanomaterials such as carbon nanohorns (CNHs), carbon nanotubes, and graphene based nanomaterials, understanding the long-term fate, health impact, excretion, and degradation of these materials have become crucial. Here, the in vitro biodegradation of CNHs was determined using a non-cellular enzymatic oxidation method and two types of macrophage cell lines. Approximately 60% of the CNHs were degraded within 24 h in a phosphate buffer solution containing myeloperoxidase. Furthermore, approximately 30% of the CNHs were degraded by both RAW 264.7 and THP-1 macrophage cells within 9 days. Inflammation markers such as pro-inflammatory cytokines interleukin 6 and tumor necrosis factor alpha were not induced by exposure to CNHs. However, reactive oxygen species were generated by the macrophage cells after uptake of CNHs, suggesting that these species were actively involved in the degradation of the nanomaterials rather than in an inflammatory pathway induction.

P390

Properties of High-Performance Resin Nanocomposites Using Multiwalled Carbon Nanotubes and the Resin Cellulation

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Significant attention has been paid to CNTs as fillers for composite materials because of their properties. A CNT is an extremely long and thin tube that is made of fiber material; thus, the nanolevel uniform dispersion of CNTs has been extremely difficult to achieve because the CNTs exist as bundled and entangled aggregates. In the present work, we have recently succeeded in developing a resin composite in which disentangled CNTs are individually separated in the resin matrix by using a new method called as the resin elasto-milling method. In addition, the resin composite in which highly concentrated CNTs are separately disentangled exhibits excellent mechanical and thermal properties.

P391

Competition and cooperation between external and internal electric fields for carrier injection in carbon nanotubes with defects

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Carbon nanotubes (CNTs) are attracting much attention due to its possible material for semiconductor electronic devices in the next generation. It has been shown experimentally that CNTs work as a conducting channel of field-effect transistors (FETs). However, the fundamental properties of CNTs under an electric field are not fully understood. In this work, we aim to elucidate the fundamental electronic properties of CNT with defects under the electric field by using density functional theory. We consider (10,0), (11,0), and (12,0) CNTs with monovacancies, divacancies, C_2 adatoms, and Stone-Wales defects. To simulate the CNT-FET device, we consider a model system in which CNT is located above the planar electrode. We find that the gate voltage for carrier accumulations strongly depends on the position of the defects in CNTs relative to the electrode. We also find that the variations of the gate voltage depend on the defect species. These variations of gate voltages for carrier accumulations in CNTs are caused by the internal electric field induced by the defects.

P392

Characteristic field emission images reflecting atomic-scale structures in multilayered graphene electron emitters

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Intriguing field emission microscopy (FEM) images indicating sub-nanometer sized structures of emitting sites have been observed in nanocarbon materials such carbon nanotube (CNT) and graphene. FE properties and FEM images of multilayered graphene emitters with and without metal coating are reported. Exfoliated multilayer graphene attached on a tip of a tungsten needle was used as electron emitters. The graphene emitters with free edges (i.e., open edges) show a striped pattern (we dubbed a lip pattern); the direction of striations is perpendicular to the graphene sheet, and each stripe are divided into two wings due to a dark band which runs perpendicular to the striation in the center of pattern, indicating coherent interference of electrons from pi-orbitals with a phase difference of pi on either side of the graphene sheet. When graphene edge becomes closed, the stripe pattern changes to a dim (or blurred) pattern, like that from single-wall carbon nanotube. Aluminum coated graphene emitters gave FEM images of atomic clusters with a shape of truncated octahedron, suggesting electron emission from aluminum clusters. Similar images of polyhedral Al clusters have also been observed for Al-deposited CNT emitters.

P393

Electrochemical magnesium storage properties of quinone molecules encapsulated in single-walled carbon nanotubes

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Owing to recent industrial needs for large-scale applications such as smart grit networks and electric vehicles, improvements of energy density of rechargeable batteries are strongly desired. In this context, magnesium-ion batteries (MIB) with magnesium metal anode should be a promising candidate for the next generation energy storage device, because the theoretical volumetric capacity of magnesium (3837 mAh/cm^3) is about 5 times higher than that of the graphite anode in lithium-ion battery. However, the energy density of the previously reported MIB systems are not so high because of the low specific capacity of cathode materials consisting of ceramic materials. In order to increase the capacity of MIB, we developed new cathode materials based on quinone molecules. We found that electrochemical magnesium storage properties of quinone molecules are highly dependent on their chemical structure. For example, 9,10-phenanthraquinone (PhQ) showed large reversible capacity around 100 mAh/g, while 9,10-anthraquinone (AQ) could not store magnesium ions,. However, cyclability of the PhQ electrode was poor, probably due to the dissolution of PhQ molecules into electrolyte. In order to overcome this problem, we encapsulated PhQ molecules into single-walled carbon nanotubes. By the encapsulation treatment, cyclability of the PhQ electrode was clearly improved.

P394

Active silicon photonics devices by degenerated pumping of s-SWNT

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Nanophotonics is an emerging field where researchers look for potential application of carbon nanotubes (SWNT) in the framework of silicon photonics technology, due to SWNT ability to emit, modulate and detect light in the wavelength range of silicon transparency.
In this field of nanotube photonics, a first milestone was to couple light emission from SWNT into silicon waveguides. Current researches focus on coupling SWNT with optical cavities, either for enhancing nanotube photoluminescence (PL) or non-linear optical phenomena at the nanoscale, using microdisk resonators, or photonic crystal cavities. However, these kinds of cavities could not be easily coupled to silicon waveguides, hindering subsequent integration into more complex photonic devices.
Building up on our previous work, we propose to couple SWNT PL with silicon microring resonators in a fully integrated configuration. PL coupled to microring modes could be collected from the access waveguide, with efficient rejection on non-resonant photons. Emission quality factor up to 8000 were observed. This design allow for collinear excitation of SWNT through the access waveguide, leading to efficient excitation and collection of SWNT PL at different wavelengths. The requirement for out-of-the-plane SWNT excitation is lifted, underlining the pertinence of this approach for realistic carbon nanotube based photonic devices.

P395

Highly sensitive graphene photosensor toward single photon detection

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Graphene is a promising candidate for use in photodetectors for the ultra-wide wavelength region from ultraviolet to terahertz region. Nevertheless, only 2.5% light absorption of monolayer graphene and fast recombination time of photo-excited charge limit its sensitivity. To enhance the photosensitivity, combination of photosensitive material and graphene field-effect transistor (G-FET) are widely studied. The photo-excited charge is accumulated at charge traps adjacent to the graphene channel, which results in the modification of channel conductance of G-FET through gating effect. However, the charge accumulation process for gating leads to the slow response.
Here, we demonstrate highly photosensitive G-FET with ~25 pA/photon with response time within milliseconds at room temperature, which consists of Au oxide layer on contact electrodes without hybridization for photo-absorption on graphene channel. The output current induced by light illumination is proportional to the total number of irradiated photons owing to the charge accumulation function of our proposed structure. This enables us to realize the photon counting sensing using G-FET at room temperature. We believe that our finding opens a way to realize graphene photodetectors with high sensitivity in the order of single photon detection.

P396

Structured SWNT films as hole transporting layer and electrode for perovskite solar cells

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Low cost, high performance, and stability are being research challenges in the development of organic-inorganic perovskite solar cells. Single-wall carbon nanotubes (SWNTs) are promising materials that can have both metallic and semiconducting properties based on changing diameter and chirality. In this regard, SWNTs were employed as both hole transporting layers and electrodes for $CH_3NH_3PbI_3$ based perovskite solar cells. Different structured SWNT films were prepared seeking the higher power conversion efficiencies (PCEs) mechanism. The flexible, well-structured SWNT directly contacted to the perovskite substrate. The SWNT based perovskite solar cells were fabricated and compared to the common ones that have hole conducting layer and metal electrodes. We believe that the direct contact between SWNTs and perovskite substrate will significantly enhance the charge transport through the solar cell. The possibility of using SWNT films will reduce the energy and cost of fabrication of such promising type of solar cells.

P397

Double-walled carbon nanotube transparent conductive film for next generation flexible device

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We have developed double-walled carbon nanotube (DWCNT) transparent conductive film (TCF). Our DWCNT TCF has very high transparent conductivity, which are currently among the top in the world. And it has great characteristics such as high flexibility (bending and stretching durability) and high environmental stability.

In order to improve transparent conductivity, we focus on DWCNT, and developed flexible, high transparent conductive DWCNT TCF. We already have established mass production system.

Combining this CNT dispersion and our fine wet coating technology, we have developed DWCNT TCF. We also have established mass production roll to roll technology for this DWCNT TCF. The width of mass production DWCNT TCF is over 1000 mm.

One example of our DWCNT TCF commercialized product is twist-ball type e-paper display. DWCNT TCF is used as upper transparent conductive electrode. DWCNT TCFs neutral color and high light transmittance contribute to showing clear image. Large screen digital signage is realized using our DWCNT TCF.

We have also developed flexible touch screen using patterned Toray DWCNT TCF. Even if these devices are under bended situation, both work normally. Especially, touch screen detected the multi position across the folding line. These demonstrations are significant for future flexible device realization.

P398

Polymer organic-light emitting diodes on high-flatness transparent sheet with graphene films synthesized by plasma treatment

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Because graphene films have one atom-thickness, the morphology of the flatness of the transparent sheet could have a larger influence on the performance for organic light-emitting diode (OLED) devices using graphene films than indium tin oxide (ITO). Therefore, decreasing the surface roughness of the transparent sheet, which results in reducing the possibility of leakage current, is important factor to improve the performance for OLED devices with graphene films. In this study, we have evaluated the polymer OLED devices with graphene films synthesized by plasma treatment on polyethylene terephthalate (PET) sheet and polyethylene naphthalate (PEN) sheet having high flatness. The graphene-based OLED device on the transparent sheet with higher flatness shows high illumination (~8000 cd/m^2 at 15 V) and high current efficiency (6.71 cd/A) at area of 2 mm X 6 mm. The results suggest that the surface roughness of transparent sheet strongly affect the performance for OLED devices with thin transparent electrode such as graphene films.

P399

Carbon nanomaterials negatively affect cell viability and gene expression

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Carbon nanomaterials (CNMs), which include carbon nanotubes (CNTs) and their derivatives have diverse technological and biomedical applications. The potential toxicity of CNMs to cells and tissues has become an important emerging question in nanotechnology. To assess the toxicity of CNTs and fullerenol C60(OH)24, we in the present work used the budding yeast Saccharomyces cerevisiae, one of the simplest eukaryotic organisms that share fundamental aspects of eukaryotic cell biology. We found that treatment with CNMs, regardless of their physical shape, negatively affected the growth rates, end-point cell densities and doubling times of CNMs-exposed yeast cells when compared to unexposed cells. To investigate potential mechanisms behind the CNMs-induced growth defects, we performed RNA-Seq dependent transcriptional analysis and constructed global gene expression profiles of fullerenol C60(OH)24-and CNT-treated cells. When compared to nontreated control cells, CNP-treated cells displayed differential expression of genes whose functions are implicated in membrane transporters and stress response, although differentially expressed genes were not consistent between CNT-and fullerenol C60(OH)24-treated groups, leading to our conclusion that CNMs could serve as environmental toxic factors to eukaryotic cells.

P400

Carbon nanotube based Schottky diodes for terahertz radiation detection

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Increased sensitivity of detection of terahertz (THz) range radiation can be achieved by reducing the size of the sensitive element. Therefore recent advances in nanotechnology may result in cost-effective solutions for novel THz detectors. One particular route is the use of carbon nanotubes (CNTs) [1].

In this talk we report our recent results on individual CNT based asymmetric devices, made by using two different metals for the source and the drain electrode. We find a relatively strong response to terahertz radiation manifesting itself as a DC voltage across the sample. Our analysis shows that the response at room temperature comes mostly from the nonlinearity of the current-voltage curves, which is the consequence of the intrinsic device asymmetry. Photothermoelectric response similar to the one reported for CNT film devices [2] is also observed as inferred from the analysis of the dependence of the response on the gate voltage.

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P401

Development of a novel polymer cross-linked graphene gel for environmental applications

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Chemically modified graphene sheets can self-gel and this gelation behavior enables the formation of a freestanding gels. The resultant gels are porous and their unique structures offers a number of distinct advantages for environmental and energy applications. However, the mecahnical stability of such independent graphene gels is not sufficient to withstand the operational conditions of applications. Keeping this inview, we prepared the novel polymer cross-linked graphene gel (PCGG) by a simple approach. Graphene was suitably modified to involve in the cross-linking polymerizations. The successful formation of PCGG was confirmed by FT-IR spectroscopy, Raman spectroscopy and XRD measurements. Scanning electron microscope images of the side and top views of the interior structure were recorded to undestand the morphology of the gel. Chromium contamination of dirt and groundwater is one of the important environmental problems today. The PCGG was further utilized in the adsorption of Cr (VI), a widespread and toxic pollutant in industrial effluents. The adsorption behavior of Cr (VI) was systematically investigated by varying the contact time, solution pH, Cr (VI) concentration and ionic strength. Finally, desorption and recyclability of the adsorbent were also measured. Our work clearly shows that properly nanoengineering the gel microstructure is the key to realize its full potential.

P402

Semitransparent organic solar cells using single-wall carbon nanotube thin films as top anode

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Semitransparent organic solar cells (OSCs) have attracted a great attention for their possible use in photovoltaic applications such as energy-generating windows and multi-junction OSCs. Several semitransparent OSCs have been demonstrated using transparent electrodes, such as thin metals and indium tin oxide (ITO) on top of the active layers. However, most of the top electrodes are deposited by vacuum evaporation. For lowering production costs, solution-processable fabrications are desirable. In this work, we utilized solution-processed single-wall carbon nanotube (SWCNT) films as top anode for fabricating semitransparent OSCs.

SWCNT film was fabricated by a bar-coating on polyethylene terephthalate substrate and used as top anode of inverted-type OSCs. Transmittance of the film was 80% and sheet resistance was 500 ohm/sq. The active layer was fabricated by spin-coating low-bandgap polymer and fullerene derivative on ITO/Glass substrate pre-coated with a buffer layer. Finally, two substrates were laminated together by pressing. The fabricated OSCs showed a transparency of 34% at 550 nm and bifacial power generation at both front and backside illumination. In addition, the stability was improved compared with normal-type OSCs using Al top electrode. This work was supported by KAKENHI No. 26790021, 25220602.

P403

Applications and preparations of graphene-sandwiched-type environmental cells

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High-resolution transmission electron microscopy (HRTEM) observations provide real-time atomic-level structural information on various materials. HRTEM observation of liquids and solutions should provide a great impact on physics and chemistry of liquids and solutions. One of the critical issues to realize HRTEM observations of liquids is that samples have to be placed under a high vacuum condition, where the liquid samples are lost spontaneously through vaporization. To overcome this difficulty, we have focused on graphene-sandwiched-type environmental cells for HRTEM observation of liquids and have developed a facile preparation technique to prepare such environmental cells.

High quality graphene was grown on copper foil by using the atmospheric pressure chemical vapor deposition method using methane as the carbon source. The graphene so produced was directly transferred onto a SiN grid. Another graphene was then transferred onto the SiN grid to prepare a suspended bilayer graphene, whose interlayer space can be used to sustain liquids even under vacuum conditions. We expect that our method contribute to obtain brand new insights on various types of liquids including microstructure of liquids, interface between liquids and solids and structure and properties of low-dimensional liquids.

P404

Properties of bias-induced on carbon nanotube fibers

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Despite possessing great properties such as, mechanical strength, electrical conductivity, chemical stability, and lightweight, carbon nanotube (CNT) has not achieved the practical applications. One of the reasons that the CNT is tiny (normally in a few micrometers) to handle CNTs. In this presentation, we fabricate CNT fibers and improve its mechanical properties via applying high voltage (HV) in vacuum chamber. The CNT fiber is fabricated by dry-spinning technique from vertically aligned CNT substrate synthesized by thermal chemical vapor deposition (CVD) method. To avoid an effect of oxygen, the chamber is pumped less than $1.0x10^{-5}$Pa. The tensile strengths of as-spun and HV-treated CNT fibers were 624MPa and 955MPa, respectively. Also, the Youngs modulus improved from 34GPa to 75GPa by HV-treatment. A transmission electron microscope (TEM) study revealed the structural change of each CNTs inside CNT fiber after HV-treatment. Also, the crystallization behavior of the amorphous carbon on CNTs was confirmed. It is considered that residual amorphous carbons have significant effect on property of the mechanical strength after HV-treatment. Although HV-treated general carbon fiber becomes rigid, HV-treated CNT fiber shows flexibility.

P405

Fully solution-processed solar cells based on graphene anode and cathode

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An *in situ* doping process with polymer-free transfer for graphene has been demonstrated, allowing the integration of residue-free doped graphene with arbitrary substrates such as delicate organic thin films. The doped graphene/dopant intercalation stacks have been systematically investigated via photoemission and Raman spectroscopy to gain insight into their electronic structure and corresponding *e-ph* coupling, respectively. The doping effect on the optical and electrical properties of graphene, such as transmittance, sheet conductivity and morphology, has been studied in detail as well. The tunable work function of doped graphene from 3.25 eV to 5.10 eV modifying the interfacial energy barrier to provide a more energy-favorable band alignment for carrier extraction, enabling graphene anode and cathode for transparent electrode applications. In this way, the semi-transparent, high performance graphene-based photovoltaic cells obtained via fully solution process can be achieved with the incorporation of graphene andode and cathode. Therefore, the proposed facile strategy of vacuum-free process benefits the fabrication of photovoltaic cells to reach a time-saving, low-cost, large-area processing technology.

P406

Electropolymerized carbon nanotubes-polyaniline-3D graphene foam nanocomposite for supercapacitor applications

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In this work, we present a carbon nanotubes (CNTs)-polyaniline (Pani)-3D graphene foam (GP foam) composite prepared by electropolymerization process for supercapitor applications. GP foam was fabricated by chemical vapor deposition (CVD) on Ni foam using acetylene/hydrogen mixture (3/24 sccm) at 700oC for 3 minutes. Next, the foam was then etched in 3M HCl for an hour to partly remove Ni template. Next, multi-wall CNTs powder were dispersed in 1M HCl under sonication at 80oC for 2 hours and 0.2 M aniline monomer was added. Electrochemical polymerization in the CNTs-aniline monomer solution was then conducted on the GP-foam at 0.55 V vs. Ag/AgCl. Characterizations by electron microscopy and Raman spectroscopy confirmed the incorporation of CNTs in Pani/GP foam network with a number of nanowire features appeared on GP foam surface and dominant D and G carbons peaks compared with PANI peaks. Cyclic voltammetry results in 2M H2SO4 electrolyte showed that PANIs redox peaks were broadened due to the presence of CNTs, indicating enhanced pseudocapacitance. From galvanostatic charge-discharge measurement, CNTs-Pani-GP foam exhibits a high specific capacitance of 920 Fg-1 at a specific current of 0.8 Ag-1, which is more than twice higher than that of Pani-GP foam (430 Fg-1).

P407

Active site of nitrogen doped graphene for ORR in fuel cells

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The nitrogen doped graphene (NGr) has been reported to show a high catalytic activity for the oxygen reduction reaction (ORR) in polymer electrolyte fuel cells (PEFCs). We have previously assumed that the carbon atoms in the vicinity of the pyridinic nitrogen (nitrogen having two N-C bonds) are the active site for ORR as O_2 adsorption site based on analysis with scanning tunneling spectroscopy. To characterize the active site of NGr, here we have measured ORR activity in 0.1 M H_2SO_4, X-ray photoelectron spectroscopy (XPS) and the temperature programmed desorption (TPD) of CO_2 on NGr samples and model catalyst samples. It is then found that there is a clear correlation between the amounts of CO_2 adsorption and current density in ORR of NGr. It is also found that only pyridinic nitrogen dominant model catalyst shows CO_2 adsorption and high catalytic activity for ORR, while the graphitic nitrogen dominant model catalyst, carbon-edge dominant model catalyst and basal plane dominant model catalyst shows no CO_2 adsorption and low catalytic activity. These results suggest that the Lewis base sites on carbon created by the pyridinic nitrogen dopants are the active sites for ORR.

P408

High-conductive wire of carbon nanotubes by floating CVD method

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Felt a strong desire to use carbon nanotubes (CNTs) as vehicle wire harnesses and motor windings, and the producing lightweight cable of CNTs will replace copper wires widely used in the future. The electrical conductivity of CNTs is theoretically estimated to be superior to that of copper. The intrinsic properties of CNTs are yet to be well exercised today. We found that high conductive CNTs wire can be prepared by the floating catalytic chemical vapor deposition (FCCVD). We have achieved a CNTs wires conductivity of 1.6 x 10**5 S/cm (resistivity of 6.3 x 10**-6 Ohm*cm), close to that of copper (6.0 x 10**5 S/cm), by optimizing the fabrication of the CNTs, controlling structures of CNTs, and a surface treatment with acid. This fabricated CNTs wire will be applied to lightweight cable in the near future.

P409

Opening lids: modulation of lipase immobilizsation by graphene oxides

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Herein, we have for the first time demonstrated with both experimental and theoretical approaches that graphene oxide (GO) can be used for molecular tuning of lipase activity, as GO provides an elegant hydrophobic/hydrophilic surface for lipase immobilization and lipase lid-opening to expose its active site. The lid opening is assisted by lipases sophisticated interaction with GO, which allows the adsorbed lipase to enhance its enzyme activity. The lipase enzymatic activity can be further optimized through fine tuning of the GO surface hydrophobicity. Based on these findings, we have designed multilayered GO papers for long-term lipase storage with retained high activity. We expect that these results might provide new guidance for better tuning of lipase activity and practical applications in future.

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P410

Multi-wall carbon nanotubes - polypropylene composites produced by in situ polymerization method

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Multi-wall carbon nanotubes (MWCNTs) are widely used as a fillers of polymer based composite materials to provide the enhancement of their mechanical, electrical and/or thermal conductivity. In the present work the in situ polymerization technique was applied for preparation of MWCNT/polypropylene (PP) composites with various MWCNT loading. Original preparation procedure of titanium-magnesium catalytic species (TMC)/MWCNT with uniform distribution of TMC on the MWCNT surface was proposed. MWCNTs were synthesized by CVD ethylene decomposition over bimetallic Fe-Co catalysts at 680 C. The study was carried out using MWCNTs with an average diameter of 9.4 nm. MWCNTs both as produced and after oxidation pre-treatment were used. TEM, XRD, DSC were used for the characterization of the structure of MWCNT/PP composites. PP molecules demonstrate high wetting ability of nanotube surface. For the first time we have observed the Ti-Mg-containing catalyst species of the size 2-3 nm on the MWCNT surface, stabilized in polymer matrix. The results suggest promising directions for composite MWCNT/PP preparation via the catalyst distribution on the surface of MWCNTs followed by polymerization of propylene. MWCNT/PP composites with high concentration of homogeneously distributed nanotubes are perspective as polymer carbon nanotubes conductive masterbatches.

P411

S-doped carbon materials with superior electrochemical performance in lithium ion batteries and supercapacitors

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Here, we present the synthesis and electrochemical applications of S-doped porous carbons (SPCs) and 3D networks composing of S and N dual-doped graphene (SNG) and S-doped carbon nanotubes (SCNTs). SPCs with up to 29 wt % S were synthesized based on the S doping reaction between carbon and magnesium sulphate. The high concentration S doping was able to significantly enhance the electrical conductivity. In lithium ion batteries (LIBs), the S doping leads to a higher initial coulombic efficiency and higher Li storage capacities in comparison with the undoped PCs. Superior capacitive performance in supercapacitors was also observed for the SPCs. The SNG was obtained by a chemical vapor deposition using basic magnesium sulphate whiskers as both templates and S source, which has exhibited an extraordinarily high Li storage capacity and excellent rate capability. The SCNTs were prepared by a post-treatment S doping process, and were used as the aqueous conductive slurry for LiFePO4 cathode in LIBs. The SCNTs exhibited higher SSA, higher conductivity and better hydrophily as compared to the pristine CNT. The as-obtained LFP cathode exhibited much better electrochemical performance as compared to the LFP electrode fabricated by pristine CNTs.

P412

Pd/PdO nanoparticles supported on carbon nanotubes: a highly effective catalyst for promoting Suzuki reaction in water

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We report that the presence of PdO nanoparticles can enhance the catalytic performance of Pd catalyst for the Suzuki reaction in water. Heterogeneous Pd/PdO nano-particles supported on multi-walled carbon nanotubes (CNTs), weakly oxidized multi-walled carbon nanotubes (WCNTs) and strongly oxidized multi-walled carbon nanotubes (SCNTs) catalysts are synthesized by a one-pot gas-liquid interfacial plasma (GLIP) method using Pd(NO3)2·2H2O as precursor. Among these synthesized catalysts, the Pd/PdO supported on WCNTs (Pd/PdO/WCNTs) catalyst exhibits the highest catalytic activity during the Suzuki reaction in water. Moreover, the Pd/PdO catalyst shows higher catalytic activity during the Suzuki reaction than Pd catalyst. The asprepared catalyst displayed remarkable activity toward challenging substrates such as heteroaryl halides and ortho-substituted aryl halides as well as aryl chlorides using low Pd loading in good yields. Since the catalyst exhibits extremely low solubility in organic solvent, the product can be simply extracted with ethyl acetate while the catalyst remained in the aqueous phase. The catalyst can be simply and efficiently used for ten consecutive runs without significant decrease in activity.

P413

Gate-controlled photo-oxidation of graphene

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All carbon atoms of graphene belong to its surface, and thus electronic properties of graphene are sensitive to surface chemical modifications. In addition, an external electric field can penetrate into the graphene because the ultrathin body is insufficient to completely screen the field; in the configuration of a field-effect transistor (FET), an electric field from the bottom gate electrode can penetrate to the top surface of graphene. Therefore, the field-effect control of surface chemical reactions is expected to be feasible using the FET configuration.

In this presentation, gate-controlled photo-oxidation of graphene will be introduced [1]. Edge-selective photo-oxidation was observed only with negative gate voltages, and enhanced with the presence of water molecules [2]. The oxidation was found to proceed into the center region, which might enable us to fabricate graphene nanoribbons or nanoconstrictions.

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P414

Cavity enhanced light emission from electrically driven carbon nanotubes

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Nanoscale photonic emitters are essential elements for on-chip networks and optical interconnects. Besides preferred electrical trigger capability, tailored optical properties are highly desirable to engineer application specific light sources. Here we demonstrate electrically driven nanoscale emitters with exceptional narrow linewidth based on carbon nanotubes embedded into nanophotonic circuits. Using one-dimensional photonic crystal cavities we spectrally select desired emission wavelengths, enhance the signal intensity and efficiently couple light into the underlying photonic network with high reproducibility. Our approach holds promise for active photonic networks and localized sensing applications in a chip-scale framework, in particular since the emission linewith is determined by the quality factor of the photonic crystal, eliminating broadening due to hot-carrier injection, surface interaction and temperature.

P415

Flexible carbon nanotube composite heater

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Flexible electronics is one of emerging fields of recent electronic devices. A flexible heater with quick response is an important component for this application. The quick response heater with small heat capacity would provide lower energy consumption owing to the reduction of the excess energy for heating up to the heater itself. Here, we present carbon nanotube (CNT)-polyimide composite film heater that has rapid electro-thermal response.

The CNT film was formed by vacuum filtration method followed by transferring on to Si substrate. The CNT film on the Si wafer was then coated with polyimide precursor to form the CNT-polyimide composite film. After the curing process, the free standing CNT-polyimide composite film was obtained by exfoliation from the substrate.

The temperature of the heater with ~100 ohm/sq. was quickly raised to 250 ℃ by the application of 10 V. Based on the heat flow analysis with simplified lamped capacitance model with heat losses to air and support of the heater revealed that the obtained heater response corresponds to the small heat capacity of the CNT-polyimide composite. Thus, we have successfully fabricated the flexible CNT-polyimide composite film heater through simple fabrication process.

P416

Flexible strain sensor based on CNTs/poly-dimethylsiloxane/3D graphene foam composites

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In this work, we report a new flexible strain sensor based on carbon nanotubes (CNTs)-Poly-dimethylsiloxane (PDMS)-3D graphene foam composite. A three dimensional (3D) graphene foam (GF) was synthesized by chemical vapor deposition (CVD) with nickel foam as a template. Scanning electron microscope (SEM) image and Raman spectra confirmed a high-quality multi-layer graphene structure. CNTs was dispersed in PDMS solution under long stirring. CNTs/PDMS/GF composite was then formed by dip coating the graphene foam into CNTs/PDMS solution and the nickel template was removed by etching in a hot hydrochloric acid. The ratio of CNTs and PDMS was varied to obtain the optimum condition for the high conductivity and flexibility. The results from SEM showed that the moderate CNTs concentration produces uniform distribution of CNTs on GF surface and resulted in higher conductivity of CNTs/PDMS/GF. The mechanical test demonstrates that the moderate CNTs content of 1 mg/ml exhibits better flexibility than other CNTs concentration. In addition, the resistance change of the composite with increasing applied strain is highest for the optimal CNT content until the break at the strain of ~80%. Moreover, the resistance of the composite increases considerably under bending with increasing bending curvature and can be fully recovered after straightening.

P417

Monopolar charge fluctuation induced forces involving graphitic nanostructures

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All systems in thermal equilibrium exhibit fluctuations out of equilibrium, which in turn bring about attractive or repulsive forces. The best known fluctuation induced force is the Van der Waals/Casimir interaction force, whereupon dipolar fluctuations give rise to attractive or repulsive forces between objects. However forces due to other thermodynamic variables have been studied less. In this presentation, forces induced by fluctuating monopolar charges will be explained in a metal plate/carbon nanoribbon system.

P418

Highly selective and sensitive electrochemical sensor for L-cysteine detection based on graphene oxide/multiwalled carbon nanotube/manganese dioxide/gold nanoparticles composite

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A highly selective and sensitive electrochemical sensor for detection of L-cysteine based on a graphene oxide/multiwalled carbon nanotube/manganese dioxide/gold nanoparticles composite (GO/CNTs/AuNPs@MnO2) was developed. The distribution property which GO/CNTs/AuNPs@MnO2 was modified on the glassy carbon electrode contributed to increasing the sensing surface area and the electronic transmission rate. Besides, the addition of MnO2 could effectively improve the selectivity and specificity of L-cysteine determination. The morphology and composition of GO/CNTs/AuNPs@MnO2 were characterized by scanning electron microscope, energy dispersive spectrometer, fourier transform infrared spectroscopy and X-ray diffractometer. The morphological and structural characterizations evidenced that GO/CNTs/AuNPs@MnO2 with core-shell structure was efficiently synthesized. The determination results of L-cysteine in-dicated that the surface area, electronic transmission rate and sensitivity of GO/CNTs/AuNPs@ MnO2 sensor were highly increased. Under the optimal conditions, the electrochemical sensor exhibited excellent analytical performance with good selectivity, reproducibility and stability. The linear range of L-cysteine was from $1.0\times10-8to7.0\times10-6mol\mathrm{L}-1andthedetectionlimitwas3.4\times10-9mol\mathrm{L}-1.Theproposedelectrochemicalsensorwassuccessfullyap\ cysteineinrealsamples.$

P419

Encapsulation of materials inside carbon nanotubes based on a CNT nano-porous membrane

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In this presentation we report a novel inter-diffusion infilling method to efficiently encapsulate organic (polyaniline (PANi) chains) and inorganic (Au nano rods) species inside multiwalled carbon nanotubes (MWCNTs) with an inner diameter of 15nm based on CNT nano-porous membranes. A continuous PANi nanowire and a Au nanorod array infilling MWCNT structure was respectively verified by 3DTEM, EFTEM as well as Raman analysis technique. The new PANi@CNT hybrid exhibits excellent gas sensitivity towards NH3 or HCl in a wide concentration range. The Au-nanorods@CNT composite has potentials for new type of optical devices and catalysts. This new method (inter-diffusion encapsulation) is believed to be more efficient and tunable in preparing novel endohedral nanotube materials compared to traditional capillary infilling approaches.

P420

Formation of Pd and Au metal nanoclusters supported on graphene

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We have examined the formation mechanism of Pd and Au nanoclusters on graphene for preparing a size-controlled graphene-supported metal nanocluster catalyst. It is found that metal nanoclusters can be spontaneously formed by mixing graphene and metal precursors ($PdCl_2$ or $HAuCl_4$) without adding reductants in the water-solution. Based on the X-ray photoelectron spectroscopy (XPS) analysis, it is suggested that metal clusters (M) were reduced on the graphene surface by receiving an electron ($M^+ + e^- \rightarrow M$) which was produced by the oxidation of graphene with H_2O ($H_2O + C \rightarrow C\text{-}OH + H^+ + e^-$). Owing to the difference in the redox potentials, this type of electrochemical reaction is considered to occur on graphene in water solution to form metal nanoclusters without adding reductants. It is also found that the surface charge of graphene in the solution, that is, the zeta-potential of graphene, significantly affect the formation of metal clusters on graphene. In particular, small Pd nanoclusters with diameter of 1.0 nm were found to form on graphene uniformly with high dispersion at pH =1.0.

P421

Fabrication and characterization of transparent conductive thin films of single-wall carbon nanotubes coated with thin layer of conducting polymer

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Single-wall carbon nanotube (SWCNT) thin films have attracted much attention in recent years as transparent conductive electrodes for plastic electronic devices. Trans-parent conductive films of SWCNTs provide high flexibility and ease of processing at low temperatures. In addition to electric conductivity, stability is also important property to employ SWCNT thin films for practical applications. In this study, we report stability improvement of SWCNT transparent conductive films by coating thin layer of conductive polymer. Coating conductive polymer materials such as poly (3,4-ethylenedioxythiophene) : poly(styrenesulfonate) and polyaniline improves stability of electrical conductivity of SWCNT thin films in air. We also found that electrical conductivity of SWCNT films are enhanced by carrier doping from the coated polymer thin layer.

P422

Current-voltage behaviour of single-walled carbon nanotube transparent conducting films dependent on temperature & voltage

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Carbon nanotubes (CNTs) have many advantages with outstanding mechanical, optical, and electrical properties. Transparent conducting films (TCFs) fabricated using single-walled CNTs (SWCNTs) are widely explored in numerous applications. High purified SWCNTs were dispersed in water with the help of sodium dodecylsulfonate (SDBS) as surfactant. SWCNT-TCFs were fabricated by a spray coating using the SW-CNT solution. The thickness of SWCNT films could be easily varied by controlling the spray coating times. The produced uniform SWCNT-TCFs treated by nitric acid have a relatively low sheet resistance and high transmittance. The currentvoltage (I-V) behaviors of the TCFs were measured at heating or cooling process. The results indicated that the I-V behavior of SWCNT-TCFs strongly dependent on the temperature and applied voltage. The sheet resistance of TCFs showed simeconductor behavior at low temperature and low voltage and metallic behavior at high temperature and high voltage.The mechanism was proposaled and discussed.

P423

Redox processes in supercapacitance performance of iron-filled carbon nanotube arrays

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Arrays of vertically aligned carbon nanotubes (CNTs) grown on n-doped silicon substrates using an aerosol-assisted catalytic chemical vapor deposition (CCVD) technique have been tested as supercapacitor electrodes. The CNTs were synthesized from a ferrocene solution in toluene and contained encapsulated iron species. Mössbauer spectra revealed these species are the a-Fe, gamma-Fe, and Fe3C phases. X-ray photoelectron spectroscopy (XPS) detected that metallic nanoparticles are covered by the oxide shells. Electrochemical properties of CNTs were studied in 1M H2SO4 electrolyte using a three-electrode system, arrays on silicon substrates were used as working electrodes without additional processing. Cyclic voltammograms (CVs) showed large redox peaks corresponding to transition between Fe(II) and Fe(III) forms. Based on the XPS data we concluded that electric current flowing through a CNT promotes etching of the graphitic layers in a dilute sulfuric acid. The acid anions penetrate under the layers and interact with the encapsulated iron nanoparticles. To remove iron from the CNT samples, arrays were treated by a diluted hot sulfuric acid. As the result, intensity of the redox peaks decreased and CV curves acquired a near rectangular shape. Moreover, the electrodes from CNT arrays showed a good rate performance.

P424

Optical properties of hybrid materials based on separated metallic or semiconducting single-wall carbon nanotubes filled with CuCl

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Single-wall carbon nanotubes (SWCNTs) represent a very attractive material promising in various fields of application. One of them is utilization of nanotubes as a transparent conductive material for the future photovoltaic. Functionalization can significantly improve SWCNT properties. Using the nanotubes as nanoscale reactors for filling them with other materials is a prospective approach for functionalization. Materials with a strong acceptor/donor behavior should be used for formation of transparent conductive films. Filled SWCNTs become highly doped, which leads to increase of both transparency and electric conductivity.

In this work, we show the simple and efficient method of improving performance of SWCNT media by filling them with CuCl molecules through a gas phase [1]. The electrical and optical properties of nanotubes strongly depend on a metallic/semiconducting type of SWCNTs. To verify the effect of nanotube conductivity type on the properties of hybrid material the films containing sorted metallic or semiconducting SWCNTs were functionalized with CuCl. The specific optical features of produced material have been obtained.

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P425

Field emission properties of TiO2 coated CNT studied by in-situ transmission electron microscopy

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Field emission (FE) characteristics of a multiwall carbon nanotube (MWNT) are influenced by their tip structures and materials deposited on its surface. Though a few research reports claim that TiO2 coating on MWNTs improves FE uniformity, stability, lifetime and low turn-on-field, it is still unclear how physical properties and morphology of TiO2 films affect the FE properties, and behavior of TiO2 coating-MWNT during field emission is not yet uncovered. In order to clarify the role of TiO2 deposited on MWNT, we have studied field emission properties of TiO2-coated MWNT emitters by in-situ transmission electron microscopy. We have found that an appropriate amount of TiO2 coating reduces the threshold field. An increase in the emission area indicated by the Fowler-Nordheim analysis may to be the reason of this reduction of threshold field. Emission stability is also improved, which may be caused by the suppression of adsorption and desorption of residual gas molecules by TiO2 and the enlarged emission area that averages out the local instabilities. In addition, a phenomenon of TiO2 breakdown observed during the field emission from MWNTs with various tip shapes is discussed.

P426

Higly conductive and transparent SWCNT film produced by easy removable Zn/Al complex dispersant

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Achieving high dispersibility of SWCNTs in water with easy removable agents after drying is one of urgent research issues in the science and technology of carbon nanotubes. Coating of SWCNTs with organic surfactants suppresses excellent properties of SWCNTs, which is a serious obstacle for the application of SWCNTs in various electronic devices. Here, we report Zn-Al complex as an efficient inorganic dispersant for SWCNTs and transparent and conducting film (TCF), prepared using SWCNT-Zn/Al complex dispersion. The complex is synthesized from Zn-acetate and Alnitrate, coupling at Zn to Al molar ratio of 1 to 0.5 in aqueous medium. Examination with FTIR and XPS indicates the presence of Al-O bonding attributed to Al-acetate frame structure. EXAFS analysis demonstrate the presence of the complex structure around Zn2+ ion coordinated with water molecules. In addition to desirable dispersibility of SWCNTs without foam formation, we achieved on-demand selective removability of the inorganic dispersant from SWCNTs film, which is not possible for conventional SWCNTs dispersing agents such as surfactants and polymers. The Zn-Al complex dispersant is a prime candidate for the TCFs fabrication.

P427

Array of 1024 LG-CNTFET biosensors integrated an a CMOS microsystem

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Liquid-gate carbon nanotube field-effect transistors (LG-CNTFET) have been shown to be highly sensitive and selective as electronic biosensors when functionalized with specific biomolecules [1]. Nevertheless, to be used in a complex environment, a multiplicity of sensors and corresponding addressing or multiplexing is required. To solve this issue, we have integrated a high number of LG-CNTFET sensors into a dense array of 1024 independent devices by using CMOS technology and on-chip current readouts [2]. The CNTs have been specifically assembled using floating electrode dielectropho-resis (DEP) and connected after deposition to the CMOS circuits.

Scanning electron microscopy data have shown that the DEP integration provides a yield of 90% of connected devices, in which about 70% are small bundles of three or less CNTs. Up to 80% of the final devices have been independently used as sensors with resistances ranging from few kΩ to few MΩ.

Here we present an integration method that is independent of the synthesis or purification of the CNTs, and we present, for the first time, large-scale and high-yield integration of LG-CNTFET on CMOS devices. The CNT-CMOS platform opens new opportunities for various sensing applications.

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[2]. Rothe et al. (2014). Analytical Chemistry

P428

Control of Q factors of carbon-nanotube mechanical-resonators induced by electrostatic force

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Carbon Nanotube (CNT) mechanical resonators (MR) are expected to be high sensitivity force sensors because of their minute mass and high mechanical strength. The Q-factor control is essential to improve their sensitivity. Here, we demonstrate the improvement of Q factors of CNT-MRs using electrostatic force induced by electron beam inside a scanning electron microscope (SEM). Cantilevered CNTs sandwiched by SU-8 layers on a Si substrate were used, where the CNTs were synthesized by chemical vapor deposition with post annealing treatment. It should be noted that both of the SU-8 and Si substrate surface with thin native oxide layer are electric insulator, so that the surface charge on the insulator can be varied by changing the emission current and acceleration voltage of the electron beam of the SEM. We found that not only the resonance frequency but also the Q-factor increase with increasing the emission current. At the optimum condition, the Q-factor reached to 12000, which is ～20 times higher than that for original Q-factor. Furthermore, the softening nonlinear effect was also found at high acceleration voltage. Finite element analysis revealed that these phenomena were explained by the electrostatic attraction induced by the surface charge.

P429

Contraction of anion-anion and cation-cation distances of ionic liquids in nanometor pores of carbon materials by coulombic screening effect

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Elucidation of inter ionic structure inside nanometer size spaces is one of the most essential subjects for the future science, relating to ion channeling in living cells, capacitive deionization and high energy storage with supercapacitors. In these limited spaces, ions can be condensed because of desolvation or electroadsorption so that inter-ion interaction can play important role on ion transport and high energy storage performances. Therefore, the study of ionic liquids inside carbon nanospaces could be a great model for the understanding of unique phenomena relating to ions.

Here, we report the clear structural evidence of unprecedented ionic state of 1-ethyl-3-methylimidasorium bis(trifluoromethanesulfonyl) imide (EMI-TFSI) ionic liquid inside pores of carbide derived carbons (CDCs) and single walled carbon nanotubes. Using X-ray scattering technique combined with hybrid reverse Monte Carlo simulations, we show the distance between TFSI-and TFSI-(or EMI+ and EMI+) is shortened from 0.9 nm to 0.5 nm in the case of the smallest pore of 0.72 nm size of CDC nanospaces. Our results indicate the conductive pore wall compensate repulsive interactions between the same ions.

The unusual ionic state is one of the outstanding merits of carbon nanoscale pores in the supercapacitor technology, because same ions can be effectively adsorbed in highly condensed state.

P430

Wafer-scale transfer of vertically aligned carbon nanotube arrays

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The first critical step in making vertically aligned carbon nanotubes (VACNTs) based thermal interface materials (TIMs) is to transfer the VACNTs in a large scale. Although VACNTs have been transferred by several methods, they were only transferred inadvertently in most cases. Here, we report well-controlled weak oxidation-assisted transfer of VACNTs. Specifically, after a short time of weak oxidation, we found that VACNTs could be easily detached from the native growth substrates and thus a freestanding VACNT film was obtained. Then, the VACNTs could be assembled onto specific substrates for its real applications. More importantly, the repeated, growth-transfer synthesis of the VACNT arrays can be realized in one batch by introducing an additional process of weak oxidation in chemical vapor deposition, which makes the strategy more effective. Surprisingly, no degradation in the quality was observed before and after the weak oxidation according to the thermal gravimetric analysis and Raman spectra of VACNTs. Enhanced thermal and mechanical properties were achieved after reaction ion etching and subsequent metallization of the surfaces of the VACNTs. These findings provide an efficient approach for transferring VACNTs, which are important for the application of VACNTs in thermal management.

P431

Overcoming the quality-quantity tradeoff in dispersion and printing of carbon nanotubes by a repetitive dispersion-extraction process

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Dispersion-printing processes are essential for the fabrication of various devices using carbon nanotubes (CNTs). Insufficient dispersion results in CNT aggregates, while excessive dispersion results in the shortening of individual CNTs. To overco-me this tradeoff, we propose here a repetitive dispersion-extraction process for CNTs. Long-duration ultrasonication (for 100 min) produced an aqueous dispersion of CNTs with sodium dodecylbenzene sulfonate with a high yield of 64%, but with short CNT lengths (a few um), and poor conductivity in the pinted films (~450 S cm^{-1}). Short-duration ultrasonication (for 3 min) yielded a CNT dispersion with a very small yield of 2.4%, but with long CNTs (up to ~20 um), and improved conductivity in the printed films (2200 S cm^{-1}). The remaining sediment was used for the next cycle after the addition of the surfactant solution. 90% of the CNT aggregates were converted into conductive CNT films within 13 cycles (i.e., within 39 min), demonstrating the improved conductivity and reduced energy/time requirements for ultrasonication. CNT lines with conductivities of 1400-2300 S cm^{-1} without doping and sub-100 um width, and uniform CNT films with 80% optical transmittance and 50 ohm/sq sheet resistance with nitric acid doping were obtained on polyethylene terephthalate films.

P432

Electrical burning of metallic single-walled carbon nanotubes in full length assisted by water vapor exposure and polymer film coating

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Logic circuits based on semiconducting single-walled carbon nanotubes (s-SWNTs) are expected to offer an improvement in both performance and energy efficiency, due to their superior electrical properties and ultrathin body. Dense arrays of exclusively s-SWNTs in large-scale are required to maximize the potential of SWNTs. Although high-density aligned growth and selective growth/removal techniques have been improved, the methods for preferential removal of metallic (m-) SWNTs which offer sufficient selectivity, scalability, and dense-array-compatibility are still not established.

We discuss an electrical burning method to remove full length of m-SWNTs with the assistance of polymer film coating [1] and additional water vapor exposure. SWNT arrays grown on crystal quartz substrates were transferred onto the Si/SiO$_2$ substrates on which Ti/Pd electrodes were photolithographically defined. The SWNTs (〜7.2 um) embedded in polymethyl methacrylate films were electrically ignited in ambient air or in oxygen saturated with water vapor (wet oxygen) at room temperature. Average removed length of SWNTs in wet oxygen was 6 times larger (〜4.8 um) than that in ambient air, and the ratio of full-length removal was 〜25 %. This suggests that water molecules adsorbed on SWNT surfaces assisted the propagation of SWNT burning.

[1] K. Otsuka et al., Nanoscale 6, 8831 (2014).

P433

Phase slips in superconducting NbN nanowires based on suspended carbon nanotubes

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NbN nanowires are promising for application to a superconducting device such as a superconducting single-photon detector, and have been actively studied. In addition, fabrication of superconducting quantum bits based on NbN nanowires was reported [1]. On the other hand, a new method of obtaining ultrathin nanowires by coating carbon nanotubes (CNTs) with desired material has been developed in recent years [2]. In this study, NbN nanowires were fabricated by using CNTs as molecular templates. The electrical transport measurements were carried out at low temperatures under 20 K. The superconducting transitions broaden with decreasing cross-sectional area of nanowires and the residual resistance in the nanowire of 10 nm width remains at 3 K, which is well below the superconducting transition temperature T_c. The data are in very good agreement with models of thermally activated phase slips just below T_c and quantum phase slips at lower temperatures.

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P434

Pressing mold and volatile urethane solution assisted fabrication of highly-densified vertically-aligned carbon nanotube membranes and their normalized water permeability and high pressure durability

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This study combined the densification and polymer filling process with addition of urethane monomer in volatile solvent and showed simultaneous densification by simple polymer filling process. The densification was maximized by mold pressing and the highest pore density of VA-CNT membrane which had $300*10^{10}$ pore/cm^2 was acquired. The ends of nanotubes were open by mechanical cutting and membrane pore size was analyzed by PEO (polyethylene oxide) rejection test in aqueous solution as well as verifying membrane integrity and it showed average pore size was 4.1 nm. Membrane compaction and water permeability were tested with UF membrane as control and compared with former studies. VA-CNT solid and forest membranes showed 328-fold and 159-fold water permeability compared to commercial UF membrane. In comparing water permeability to the results of former studies, there needed additional normalization by membrane structure because all VA-CNT membranes had too different dimensions. Water permeability of each membrane acquired by experiment was normalized by membrane structural parameters originated from Hagen-Poiseuille theory. Normalization showed water permeability of VA-CNT membranes did not have linear relation with inverse of membrane thickness and it might be starting point of building new equation of water permeation through CNT hole.

P435

Control photoluminescence of carbon nanotube with silica toroid microcavity

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Semiconducting carbon nanotube emits light at room temperature with telecom wavelength band by light irradiation. Silica toroid microcavity has circular structure with edge formed ultra-smooth surface by CO_2 laser, and its ideal quality factor is more than 10^8 [1]. Light propagate along circumference of silica toroid microcavity, and this propagation mode is called whispering gallery mode. In this study, we grow carbon nanotubes on silica toroid microcavity, and measure the optical properties of the fabricated microcavity with carbon nanotubes. We deposited cobalt on silica toroid microcavity with resistance heating deposition method, and grew carbon nanotubes by CVD method with ethanol. We measured the quality factor of this device with taper fiber. The quality factor decreased to the order of 10^3. Then, we removed carbon nanotubes selectively with O_2 plasma etching, and measured quality factor again. The quality factor recovered to the order of 10^4-10^5. This indicates that light propagated inside the silica toroid microcavity was absorbed by carbon nanotubes.

[1] D. K. Armani, T. J. Kippenberg, S.M. Spillane, K. J. Vahala. Nature 421 (2003) 925-928

P436

Thermoelectric properties of graphene heterostructures with carbon isotopes

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Since the main heat carrier in graphene is phonon, the thermal conductivity of graphene can be reduced by introducing carbon isotopes in its structure. Recently, we demonstrated the artificially controlled synthesis of isotopically-modified graphene heterostructures, and characterized the electrical and thermal properties of graphene heterostructures [1]. The heterostructures are electrically well connected at the junctions, whereas they are thermally more disconnected due to the phonon frequency mismatch. These properties are especially suitable for thermoelectric device application because the performance of a thermoelectric material is negatively correlates with its thermal conductivity. In this study, we measured the thermoelectric properties of graphene heterostructures. The thermoelectric power of graphene with the heterojunction is similar to that of graphene without the junction, suggesting that introducing isotope heterojunctions does not modulate the thermoelectric property of graphene. The power factor measured for the isotopically modified graphene heterostructure is 2.8×10^{-3} $\mathrm{Wm^{-1}K^{-2}}$. Our results strongly support that the reduction in total thermal conductance by heterojunctions is directly associated with the performance of graphene-based thermoelectric devices without affecting their thermoelectric properties.

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P437

Influence of metal contacts on graphene transport characteristics and its removal with nano-carbon interfacial layer

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Due to high mobility and atomic thickness, graphene is a promising candidate for the next-generation electronic material. While considerable effort has been devoted to achieve higher mobility in graphene films, relatively little attention has been paid to the effect of forming contacts between graphene and metal, which are indispensable to the electric devices. In general, at a graphene/metal interface, mainly due to the difference in work functions, carriers are injected from the metal to graphene. The resulting shift of local Dirac point is not limited at the graphene/metal interface but extends by ~1 micron into the graphene channel. This carrier doping affects more significantly the performance of graphene field effect devices with shorter channel, as well as may conceal Dirac physics at the graphene/metal interface such as the relativistic superconducting proximity effect.

Here, we experimentally investigate the channel length dependence of graphene transport properties and extract the effect of metal contact. Several metal species are investigated and results are compared with numerical models. The origin of electron-hole asymmetry is revealed. Furthermore, we succeed in reducing the influence of metal contact by inserting a thin nano-carbon layer (amorphous carbon or multilayer graphene (MLG)) at the interface.

P438

Switching of electromagnetic wave by graphene

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Undoped graphene is well known to absorb 2.3% of visible light at normal incidence angle. Here we demonstrate theoretically that for 10 -100 GHz electromagnetic wave the absorption can almost be perfect and can be tuned from nearly 0 to 100% by varying the Fermi energy of graphene when the incident angle of electromagnetic wave is kept within a total internal reflection geometry. Using a simple theoretical framework, we calculate absorption probability of the electromagnetic wave as function of Fermi energy and incident angle of electromagnetic wave. The high absorption is caused by the strong interaction between electromagnetic wave and graphene at low energy (around GHz frequency). This is related to the excitation of low energy (around GHz frequency) surface plasmons with very small wave vector (near $q=0$). These results may open up possibilities to develop simple electromagnetic wave switching devices operated by gate voltage.

P439

Graphene oxide as a multifunctional platform for raman and fluorescence imaging of cells

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Graphene oxide (GO), which presents nanoscaled size, 2D structure, hydrophilic property, and functionalizability, is unique in bioapplications. It acts as a vehicle to load nanoparticles and various molecules and to transport the loaded materials into cells. Meanwhile, it can be used as a Raman probe for cell imaging [1]. Therefore, GO is a good multifunctional platform. Here, using GO as a multifunctional platform, fluorescence and Raman bimodal imaging of cells was realized by the preparation of GO/gold nanoparticles (AuNPs, a SERS material)/aminoethanethiol (AET)/fluorescein isothiocyanate (FITC, a fluorescent dye) hybrids. In addition, GO/ AuNPs/p-aminothiophenol (p-ATP, a Raman Probe) hybrids were also prepared to perform multi-frequency Raman imaging of cells by using several Raman fingerprint peaks of GO and p-ATP. These two GO-based hybrids both presented very low cytotoxicity [2].

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P440

Excellent Field Emission Properties from Triangular-Shaped Carbon Nanotube Field Emitters

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We have proposed a new approach to fabricating 2D triangular-shaped CNT point emitters using freestanding CNT films, and have investigated the field emission properties as a function of the emitter tip angle. The turn-on electric field and the maximum emission current were increased as the tip angle of the CNT point emitter increased, while the size of a electron beam spot was reduced. The CNT point emitter with a wide tip angle of 150° demonstrated an extremely high emission current of up to 22.4 mA and a corresponding to an emission current density of over 10^5 A/cm^2 with excellent long-term emission stability over 20 h. We also investigated electron beam shapes of the triangular-shape field emitters according to the tip angle, the emission area and the emitter-anode gap. The triangular-shape field emitters exhibit round shapes of the electron beams regardless of the tip angles when the emission area is confined near the tip apex, even though the triangular-shape does not have a rotational symmetry. The outstanding emission performance has been attributed to the 2D shape of the CNT point emitter because it concentrates the electric field at the tip and distributes the mechanical stress effectively.

P441

Fabrication of air-stable n-type carbon nanotube thin-film transistors on flexible substrate using bilayer dielectrics

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Single-walled carbon nanotube (SWNT) thin film transistors (TFTs) hold great potential for flexible electronics. However, fabrication of air-stable n-type device by method compatible with standard photolithography on flexible substrate is challenging. For carbon nanotube thin-film transistors, our contrast experiments between oxygen doping and electrostatic doping demonstrate that the doping-generated transport barriers do not introduce any observable suppression of electron conduction. Based on the above observation, we conclude that the environmental adsorbates work by more than simply shifting the Fermi level of the CNTs; more importantly, these adsorbates cause a poor gate modulation efficiency of electron conduction due to the relatively large trap state density near the conduction band edge of the carbon nanotubes. Based on this results, we fabricated air-stable n-type device using a bilayer dielectric structure of MgO and atomic layer deposited (ALD) Al2O3 or HfO2 both on flexible substrate and silicon substrate. The key advantage of the method is the relatively low temperature 120 or 90℃ required here for ALD process. The mechanism for conduction type conversion is elucidated and attributed to hole depletion in SWNT and the decrease of the trap state density by MgO assimilating adsorbed water molecule in the vicinity of SWNT.

P442

CVD graphene/lead (Pb)-based cooper-pair splitter

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Electrons in a superconductor naturally form entangled singlet pairs. A device that effectively splits Cooper pairs can therefore be used as a source of entangled electrons. We demonstrate a Cooper pair splitter based on the superconductor-two quantum dots design. The efficiency of our device is up to 62%; meaning 62% of the current through the device is due to Cooper Pair splitting. CVD grown graphene is used as the base material with superconductivity induced via the proximity effect (a measured gap Delta=0.5-1meV) using a central lead (Pb) electrode. Quantum dot constrictions (with a charging energy $E_C \sim$ 5meV) are created by patterning the CVD graphene into two nanoribbons with self-aligned side-gates, and placed in a Y-shape relative to the central lead. Using a DC measurement we see an enhanced (correlated) current through the quantum dots when both quantum dots are gated to be on-resonance. (This result is contrary to the classical picture of three resistors where the current though one channel is expected to decrease as the conductance of the other channel increases.) Applied magnetic field higher than the critical field of Pb (B_C =770mT) destroys the enhanced current correlations, supporting the claim that the signal is due to Cooper-pair splitting.

P443

Preparation of carbon nanotube/ultrathin cross-linked polymer hybrids by using the interior of surfactant micelle on carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) are attracting increasing attention in biological applications because of their unique thermal, physical and optical properties. As-produced SWNTs are not soluble in many solvents and form aggregation due to the strong intertube van der Waals interactions. Since the aggregation of SWNTs has a risk of toxicity *in vivo*, a functionalization of SWNT surfaces is important in biological applications. Here, as a novel functionalization method, we demonstrated a method to prepare SWNTs/ultrathin cross-linked polymer hybrids by the polymerization in the interior of surfactant micelle encapsulating around SWNTs. *N*-isopropylacrylamide was used as a monomer. The composite materials obtained in this method are highly stable in aqueous solution upon heating, freeze-drying and the addition of a large amount of surfactant. Furthermore, from the absorption and emission measurement of the composite materials, the absorption and emission peaks of the isolated SWNTs were observed in the near-IR region. These results show that the SWNT structures are kept almost intact. This method also enables further functionalization to the composite materials by utilizing a variety of monomers in cross-linked polymer around SWNT surfaces [1].

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P444

Theoretical analysis of the quantum capacitance of charged bilayer graphene with applied electric field

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Bilayer graphene (BLG) is one of the promising materials for the channel in the field effect transistor (FET) due to the controllability of band gap by electric field. In FET structure, the electronic states of the BLG are determined by the doping from the source electrode, the modification of the band structure and the electronic polarization by the gate voltage. Some of us measured the quantum capacitance, the Fermi level shift to store the doped charge in the finite DOS, to estimate the DOS around the Fermi level. However, separation of the quantum capacitance from other capacitive properties is impossible experimentally. Thus, we calculated the dielectric property of BLG without doped charge using the density functional theory (DFT), and electronic structures of BLG with doped charge under applied electric field by the effective screening medium method within the DFT. We reveal that the BLG should not be regarded as a pair of metallic sheets but as a single dielectric material, and that the energy for modification of the band structure is very small.

P445

Improved field emission properties of carbon nanotube field emitters after thermal annealing

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Carbon nanotubes (CNTs) have been considered as a good field emission material due to their unique morphology and excellent properties. CNTs field emitters with a small size have attracted much attention for miniature x-ray source applications. Especially the point-type CNT field emitters can be a powerful candidate for x-ray sources and electron beam sources because it is suitable to get a focused electron beam from the CNT emitters with a few focal lenses. In this work, we fabricated a point-type CNT emitters, in which CNTs were attached on the graphite rod using graphite adhesive material between the CNTs and the graphite rod. Thermal annealing at 900℃ in vacuum ambient was applied to encourage crystallinity of CNTs and reduce unwanted residual organic material at the CNT emitters. The CNT field emitters showed much improved field emission properties after high temperature thermal annealing, such as the low turn-on electric field of 1.3 V/um and the threshold electric field of 1.8 V/um. A high emission current of over 10 mA was achieved from the CNT field emitter with a diameter of 0.5 mm. Moreover, the CNT field emitter indicated quite good emission stability after high temperature thermal annealing.

P446

Solution processing micrograms of carbon nanotubes into films and fibers

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A quick and simple slide coating method for production of carbon nanotube (CNT) aligned thin films and fibers has been developed which can be performed on microgram quantities of materials from any CNT source. The shear induced alignment results in homogenous films with anisotropic electrical, mechanical, and optical properties. Quantification of alignment by polarized Raman spectroscopy and birefringence measurements reveal shear dependent order parameters above 0.4. Substantial alignment in the thin film structure provides high mechanical strength, allowing for transformation of 2-D films into 1-D fibers which exhibit properties that compete with CNT fibers produced by solid-state and solution spinning. The electrical resistivity of these fibers is nearly equivalent to those achieved through full scale solution spinning from chlorosulfonic acid, reaching values as low as $2*10^{-5}$ ohm-cm. Utilization of high aspect ratio CNT materials yields tensile strengths above 3.0 GPa, which is larger than what has been achieved by solution spinning (2.4 GPa). The high throughput of this method and ultra-low mass requirement enables efficient exploration of possible film or fiber properties from different processing techniques or nanotube materials so that strength and conductivity can be readily optimized.

P447

Optical communication with graphene light emitting device

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Graphene is an ideal two-dimensional materials with interesting electrical, optical and thermal properties, and these unique properties have been utilized for the novel application in optoelectronics and photonics. In this study, we fabricated blackbody light emitters based on graphene. These devices have high-speed modulation speeds with the rise time of ∼ 100 ps, which is $> 10^6$ times higher than that of a conventional incandescent emitter with a filament and is higher or comparable to a light-emitting diode and a laser diode. We used mechanical exfoliation technique to deposit graphene onto SiO_2/Si substrate, and the Ti/Pd electrodes were deposited on it. Using this device, we measured real-time modulation of the emission from graphene under square voltage and made eye-diagram with photo-receiver and oscilloscope. We demonstrated receiving waveform measurement at real-time with 3 layer graphene at 50 MHz and made eye-pattern with about 100 layer graphene at 1 Mbps. This electrically driven, small footprint and ultra-high speed emitter may open novel applications of blackbody emission such as an integrated light source for integrated photonic or optoelectronic circuit, an ultrafast white light source and so on.

P448

Electrical and mechanical properties of polymer-free carbon nanotube fibers based on various carbon nanotube dispersed solutions by wet spinning

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Fibers composed of carbon nanotubes (CNTs) have the potential to form high strength, lightweight, thermally and electrical conducting materials. Wet spinning, CNT dispersed solution injecting into a coagulating solution, is well known method for fabricating continuous CNT fiber. Recently, we develop polymer-free CNT fibers with high performance by wet spinning. For the success of these continuous polymer-free CNT fibers, striking a balance between the dispersibility of CNTs in CNT dispersed solution, and the cohesive attraction between them by the van der Waals attraction at the moment after injecting into coagulating solution, is considered important.
Here we report electrical and mechanical properties of polymer-free CNT fibers based on various CNT dispersed solutions where the dispersibility of CNTs varied by using different types of CNTs and sonication time.

This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P449

Load characteristics of suspended carbon nanotube film heater and the fabrication of a fast response thermochromic display prototype

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The influence of heating load on the thermal response of CNT film heater has been studied. Two kinds of heat dissipation modes, thermal radiation in vacuum and convection in atmosphere, are investigated respectively. It is found that the thermal response slows down with the load quantities in the both cases. We have further studied the thermal response of the CNT film loaded with thermochromic pigment, which is a kind of phase change materials. Except that the thermal response slows down with the load quantity, it is also found that the phase change of the thermochromic pigments can also slow down the thermal response. With the suspended CNT film heater structure, we have fabricated a thermochromic display prototype, which can switch from room temperature to 50℃ in about 1 seconds with a brightness contrast of 4.8 under the normal indoor illumination. A 16 by 16 pixel thermochromic display prototype can dynamically display Chinese characters driving by a home-made circuit.

P450

Highly ordered one-dimensional fullerene crystals for concurrent control of cellular orientation and differentiation

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One of the most important factors in tissue engineering is a cell scaffold. Cell scaffolds must be biocompatible and must also promote adhesion, growth, and differentiation of cells with concurrent control of their morphology. Here, we show that cell scaffolds composed of highly aligned microscale fullerene-crystals, also known as fullerene whiskers (FWs), can be used to control cell morphology, orientation and differentiation. These cell scaffolds were prepared in a single step using the Langmuir-Blodgett (LB) approach. The aligned FWs cause elongation of deposited myoblast cells and induce cell differentiation to muscle cells. Our aligned FW substrate is made by a facile method of the LB approach, and hence our substrate is a promising alternative to other recently reported cell scaffolds for tissue engineering.

P451

Electronic structure of carbon nanotubes on GaN-(0001) surface

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Gallium nitride (GaN) is a direct gap semiconductor commonly used as optical devices such as light-emitting diodes in these decades. Recently, carbon nanotubes (CNT) are proposed as a possible electrode to realize the quite low interface barrier without Fermi level pinning in forming the contact on the GaN surface. In this work, we investigated the electronic properties of the interface between (12,3) CNT and GaN-(0001) surface using density functional theory. To impose the open boundary condition normal to the interface, the effective screening medium method is applied. The optimized spacing between CNT and GaN is found to be 2.04 A caused by the substantial overlap between electronic states of CNT and topmost Ga atoms. According to the hybridization, charge redistribution occurs at the interface that leads to the substantial modulation in electrostatic potential of both CNT and GaN surface. We also found that the CNT no longer retains their characteristic electronic structure in their isolated case due to the hybridization.

P452

Fabrication of perovskite solar cells with single-walled carbon nanotube cathodes

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Perovskite solar cells, which were invented in 2009 [1], are attracting a lot of attention. The power conversion efficiency (PCE) was 3.8 % at that time, but it has increased to about 20 % [2] only in these 5 years. As cathodes, gold electrodes and hole transport material (HTM) including Spiro-MeOTAD are used in conventional perovskite solar cells. The Spiro-MeOTAD is expensive and unstable in ambient. The gold electrodes are also expensive and needs vacuum deposition process, which requires high-cost. Hence it is desired to replace them with inexpensive and stable materials, which do not need vacuum processes. We propose that single-walled carbon nanotube (SWNT) can substitute for both Spiro-MeOTAD and gold electrodes. In this study, we fabricated perovskite solar cells using vertically aligned SWNT (VASWNT)/FTO cathodes and evaluated their properties. Perovskite solar cells using VASWNT/FTO cathodes showed the PCE of 4.49 %, while solar cells using Au without Spiro-MeOTAD resulted in 0.42 %. This indicates SWNTs can effectively act as HTM. We also fabricated perovskite solar cells using dry-deposited SWNT film cathodes which showed the PCE of 5.13 %.

[1] A. Kojima et al. JACS 131, 6050 (2009).
[2] H. Zhou et al. Science 345, 542 (2014).

P453

Quantum dots (QDs) mediated dye sensitized solar cells (DSSC) with self-assembled honeycomb photoanode of multi walled carbon nanotube (MWCNT) forests

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Carbon nanotubes (CNTs) have drawn a lot of attention due to a large surface area, high electron transport, and stable chemical properties. Moreover, CNTs are able to play an important role as an electron carrier from charge generating nanoparticles/materials to an electrode area. Recently, quantum dots (QDs) have been utilized for application in photovoltaic by means of the tunable band gap of particle size selection to generate multiple electron-hole pairs from a single photon. This has motivated the development of strategies to utilize QD additives onto CNTs to achieve the performance of high electron affinity. In this study, QDs and deformed MWCNT on dye-sensitized solar cell (DSSC) was expected to improve the power conversion efficiency (PCE). We expect to enhance multiple electron-hole pair performance of QDs in QD-MWCNT DSSC.QD-MWCNT forests utilizing CdSe/ZnS (core/shell) quantum dots were achieved not only to characterize the morphology of QD-deformed MWCNT, but also to represent optical characteristics. QD-treated MWCNT forests showed self-assembled honeycomb (HC) patterns as Maruyama reported which those are expected as a photoanode part of DSSC. The honeycomb size dependence will be investigated for efficiency comparison on QD-HC-MWCNT sensitized solar cell (QD-HC-MWCNT SSC) and QD-HC-MWCNT DSSC.

P454

Vertically aligned carbon nanotube membranes composite with polyethylene for membrane distillation process

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Accessible surface freshwater is distributed unequally. To solve this problem, there have been many studies about desalination technology. Unfortunately one has a problem that uses too much energy, the other has a low productivity. To untangle this complicated situation, it needs carbon nanotube (CNT) having outstanding potential properties such as extraordinary water permeability, high mechanical strength, and hydrophobicity.

In this study, vertically aligned (VA) CNT-based membrane of that space between CNTs was filled with hydrophobic polyethylene was used to test membrane distillation process for desalination. VA-CNT structure allows more water gas molecule move through the inside CNT hole than any other commercial membrane pore structure. In the entire water temperature range, VA-CNT membranes performed 16 to 25 times higher water permeability than commercial PTFE membrane. The highest water flux was 364.8 L/m^{2}h at 20/60°C of permeate/feed water. These results might be caused by the transport of water molecules through CNT cores at very high speeds. Furthermore, in response to the increase in feed in NaCl concentration from 0.5 to 3.0 M, water flux decreased only from 11.7 to 14.8 %. This is the first study demonstrating high water flux by distillation process based on VA-CNT membrane.

P455

Synthesis of carbon nanotubes in porous stainless steel block and application to glucose fuel cell

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Carbon nanotubes (CNTs) can be synthesized on complicated surfaces of some metallic alloy materials, such as stainless steel and other industrial alloys, by the following three steps: oxidation in air, reduction in hydrogen and chemical vapor deposition. In this study, ethylene, ethanol, methanol were employed as carbon source to grow CNTs on inner surfaces of a stainless steel porous block. In addition, the stainless steel porous block, in which CNTs were synthesized, was used for electrode in glucose fuel cell. It was found that the diameter synthesized from ethanol and methanol became significantly smaller than from ethylene, and the power generation efficiency at the glucose fuel cell by CNT-stainless electrodes synthesized from these alcohols was significantly higher than that from ethylene. Radial breathing mode in Raman spectra was observed in CNTs synthesized from the alcohols, while all CNTs synthesized from ethylene seemed multi-walled.

P456

Foldable aluminum-air battery based on carbon nanotube paper

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With the growing interest in flexible and wearable devices, the necessity of developing foldable battery is raising in parallel with the technical advance in flexible displays. In this work, we demonstrated a simply method to fabricate foldable aluminum-air battery by using conductive carbon nanotube paper (CNT paper). The CNT paper was prepared by mixing and grinding shredded A4 paper and multi-walled carbon nanotube in water, followed by filtering and rolling process. The paper was soaked with a saturated solution of sodium chloride and assembled with a layer of Kimwipes and aluminum foil which was used for anode of the foldable battery. As a result, the aluminum-air batteries in series connection lighted light emitting diode lamp even in the folded status.

P457

Polyglycerol-functionalized graphene and SWNT complexes for photodynamic therapy

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For biomedical in vivo applications of nanocarbons as drug carriers, they have to be dispersed well in a physiological environment. Recently, we have found that poly-glycerol (PG) grafted onto diamond and iron oxide nanoperticles, and afforded very good hydrophilicity and biocompatibility. In this study, we applied this methodology to synthesize PG functionalized graphene (G-PG) and SWNTs (SWNT-PG), and employed them for photodynamic therapy (PDT) after a photosensitizer was loaded on their hydrophobic surface.

Since we exfoliated graphene in water from graphite under sonication in the presence of hydroxytriphenylene, the resulting graphene was functioned with PG after removal most of the exfoliant. A photosensitizer, chlorin e6 (Ce6), was loaded on the hydrophobic surface of G-PG through hydrophobic interaction. The obtained G-PG-Ce6 exhibited good aqueous dispersibility. After incubating HeLa cells in the presence of G-PG-Ce6 under light irradiation, the G-PG-Ce6 complex showed remarkable PDT effect as compared to Ce6 itself. In the case of SWNTs, they were functionalized with PG after cutting and Ce6 was loaded on them. The resulting SWNT-PG-Ce6 also ex-hibited similar photodynamic activity.

P458

Thermally conductive epoxy composites using expanded graphite and multi-walled carbon nanotubes

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Efficient heat management has been important in electronic devices due to their miniaturization and integration. Owing to high thermal conductivity, expanded graphite (EG) and carbon nanotubes (CNTs) have emerged as promising fillers for polymer composite to replace the metal-based heat spreaders. This study investigated a synergy effect of hybridizing EG and multi-walled CNTs on thermal conductivities and mechanical properties of epoxy composites. The composites were fabricated by ultrasonically and mechanically treating EG and CNTs with epoxy in acetone. After adding curing agent and drying acetone under vacuum, the resulting slurry was cured in a hot-pressed mold. The hybrid epoxy composites were prepared to have the filler contents of 10 and 20 wt.%, where the ratios of EG:CNTs were systematically changed. At the filler content of 10 wt.%, thermal conductivity reached the maximum value of 1.89 W/m·K (0.2 W/m·K for neat epoxy) at the EG/CNT ratio of 9.9:0.1 while at 20 wt.%, the maximum of 4.42 W/m·K at the EG/CNT ratio of 9.7:0.3. Mechanical properties of the composites were also measured by varying the EG/CNT ratios to optimize the hybrid filler contents in terms of both thermal conductivities and mechanical properties.

P459

Electrochemical processing of single-walled carbon nanotubes

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Electrochemical methods are highly-versatile and useful ways to process single-walled carbon nanotubes. Individualised carbon nanotube solutions can be obtained on reductive or oxidative charging using a simple three-electrode system [1, 2], thereby eliminating damaging ultrasonication treatment, non-scalable ultracentrifugation or the use of undesired surfactants. This electrochemical dissolution approach can purify carbon nanotube mixtures, since unwanted amorphous carbon and defective nanotubes preferentially dissolve and leave behind purer nanotubes. Shorter nanotubes can also be separated from the longer ones through preferential charging and dissolution. The electrochemically obtained nanocarbon anions and cations can be readily grafted with functional side-chains. In particular, nucleophilic grafting of amine has been demonstrated on nanotube cations for surface modification of silicon substrate. In a reverse process to electrochemical dissolution, solubilized carbon nanotube ions can be electrochemically deposited on an electrode surface through selective ion discharge. These electrochemically deposited nanotubes are useful in a range electronic and energy storage device applications.

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P460

Efficient, absorption-powered artificial muscles based on carbon nanotube yarns

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Thermally driven, twisted carbon nanotube yarns and twisted high strength polymer fibers generate impressive tensile actuation, providing large strokes and vastly exceeding the work and power capabilities of natural skeletal muscle. However, operating temperatures can be high when giant strokes are required and energy conversion efficiencies are presently below 2%. We here report chemically powered, high performance artificial muscles comprised of twisted and coiled carbon nanotube fiber infiltrated with silicone rubber which can contract up to 50% , generate up to 1.2 kJ kg^{-1} of mechanical energy and support a 45 MPa mechanical load. The mechanism for actuation is swelling of the rubber during exposure to a nonpolar solvent. During solvent absorption, (time span < 0.25 seconds), the helical structure of the coiled fibers converts the expansion of rubber inside the yarn into contraction along the coil axis, thereby allowing a full cycle of actuation at 1 Hz. This new actuation mechanism also exhibits a natural catch state, so energy is not required to retain actuator stroke. Scalability of muscle yarns over a 20 fold diameter range is demonstrated. The theoretical conversion efficiency between chemical and mechanical energy is estimated to be as high as 16%, based on experimental results and the initial and final states of the system.

P461

Carbon Nanotube-based high selective tactile pressure and temperature sensor arrays for an artificial skin application.

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Artificial electronic skin (e-skin) has been developed widely as one of flexible device applications. However, conventional tactile sensors recognize not only a touch, but also a bending of a substrate. In this study, we propose a high selective tactile sensor using carbon nanotube (CNT)-based strain sensor fabricated on a cantilever structure to address the problem. In addition, utilizing unique electrical and mechanical properties of CNTs, CNT-based temperature sensor was also integrated with the tactile sensor array. For the strain sensor, CNT and silver nanoparticle inks were screen-printed to form resistive strain sensors. For the resistive temperature sensor, CNT and PEDOT:PSS inks were printed. Tactile and temperature sensors have the sensitivities of ~ 6 %/N and ~ 0.78 %/℃. More importantly, selectivities between tactile pressure (temperature) and the substrate bending is ~ 23 (~ 13). Compared with a conventional pressure sensitive rubber (selectivity ~ 0.5), which is often used for e-skin device, 46 times improvement is realized. This high selectivity allows it to measure the tactile pressure and temperature more precisely. Finally, 4×4 tactile pressure and 3×4 temperature sensor arrays were integrated, resulting in that two-dimensional tactile pressure and temperature distributions are successfully demonstrated like a human skin.

P462

Low schottky barrier height at carbon nanotube and silicon carbide interface for power epectronic devices

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Electrical contacts to silicon carbide with low contact resistivity and high current durability are crucial for future SiC power devices, especially miniaturized vertical-type devices. A carbon nanotube (CNT) forest formed by silicon carbide (SiC) decomposition is a densely packed forest, and is ideal for use as a heat-dissipative ohmic contact in SiC power transistors. The contact resistivity and Schottky barrier height in a Ti/CNT/SiC system with various SiC dopant concentrations were evaluated in this study. Contact resistivity was evaluated in relation to contact area. The Schottky barrier height was calculated from the contact resistivity. As a result, the Ti/CNT/SiC contact resistivity at a dopant concentration of 3×10^{18} cm^{-3} was estimated to be $\sim 1.3 \times 10^{-4}$ ohmcm^2 and the Schottky barrier height of the CNT/SiC contact was in the range of 0.40-0.45 eV. The resistivity is relatively low for SiC contacts, showing that CNTs have the potential to be a good ohmic contact material for SiC power electronic devices.

Inaba et al., Appl. Phys. Lett. 106, 123501 (2015)

P463

Mechanical and electrical characteristics of highly aligned CNT/polymer composite materials

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Carbon nanotubes (CNTs) have good mechanical and electrical properties. Recently, dry spinning from a multi walled CNT (MWCNT) array has been attracting much attention as a good technique to fabricate highly aligned CNT sheet materials. Focusing on the mechanical and electrical properties of CNTs, many studies on CNT/polymer composite materials have been reported. In this study, we investigated mechanical and electrical properties of unidirectionally aligned MWCNT/epoxy composites. A CNT sheet was spun from a CNT array, and then mixed with a thin epoxy film to prepare the composite material. With varying volume fraction of CNT in composites, mechanical and electrical properties were investigated. In mechanical properties, tensile strength and Youngs modulus increased as the CNT content increased. This result shows that MWCNT is functioning as a reinforcing material. In electrical properties, electrical conductivity also increased as the CNT content increased. It was found that good conductivity of a CNT sheet maintained even after impregnating epoxy resin in between CNTs. The remaining connections of millimeter-long CNTs resulted in rather high conductivity with low CNT concentration.

P464

Catalytic applications of carbon nanotubes as metal-free catalysts for the aerobic oxidation of cycloalkanes, cycloalkenes, aromatics and alcohols

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Catalytic oxidation is a key technology for upgrading petroleum-based feedstocks to value-added chemicals. Recently, it was found that CNTs display excellent performances in the aerobic oxidation as a metal-free catalyst.

Our interests were initiated from the discovery of excellent activity of CNTs and N-doped CNTs for the oxidation of cyclohexane. So far, it has been demonstrated that CNTs can be applied for the aerobic oxidation of aromatics, cycloalkenes and benzyl alcohol. Herein, we discuss the catalytic mechanism of CNTs in the oxidation reactions. CNTs promote the radical reactions through stabilizing the alkyl, alkoxy and peroxy radicals via electronic interaction with them. Hence, the electron transfer ability of CNTs is potent, which results in the worse performance of detective and oxidized CNTs. N dopants significantly enhance the activity, because of the modified electronic structure. N-doped CNTs are very active for the decomposition of peroxides, which increases the overall reaction rate and modify the selectivity patterns of the oxidation reaction. This feature enables us tune the selectivity of cycloalkene oxidation products from allylic oxide to epoxide, and tune the products of cumene oxidation from cumene hydroperoxide to acetophenone and 2-benzyl-2-propanol. The metal-free catalysis of CNTs paves a new way to the efficient manufacture of oxygenates.

P465

Pt nanoparticles selectively anchoring at graphitic nitrogens of N-doped carbon nanotubes and their electronic property and catalytic activities

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Nitrogen atoms incorporated into CNTs can form a variety of functionalities, including graphitic(N_G), pyridinic(N_P), pyrrolic nitrogen and nitrogen oxides, which anchor metal nanoparticles (NPs) with high dispersions. However, it is still under debate which type of nitrogen functionality on NCNTs is responsible for anchoring metallic NPs.

In this contribution, we aimed to verify if there is any preferential interaction of metal NPs with nitrogen functionalities of NCNTs. Because N_G behaves as a donor, and N_P as an acceptor of electrons, the interaction between Pt and N_G or N_P can be revealed by the shifting of Pt4f7/2(0) and N1s peaks measured by XPS. By this mean, it was found that N_G plays a potent role in stabilizing Pt NPs prepared by the ethylene glycol (EG) reduction method. The electron enrichment of Pt on N_G improves the activity of Pt/NCNT in the oxidation of glycerol and electro-oxidation of CO. The intrinsic activity is well correlated with the Pt4f7/2(0) binding energy, suggesting a promising approach to improved catalytic activity by maximizing the interaction between Pt NPs and N_G sites. By the same methodology, we also investigated the effects of synthesizing method of Pt NPs and oxygen containing groups on the electronic property and catalytic activity.

P466

The role of oxygenated functional groups on the surface of carbon nanotubes in liquid oxidation reaction

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Recently, carbon nanomaterials have been developed as an important type of metal-free catalysts due to their superior catalytic performance. Many researches reported that quinone-type oxygen functional groups on the surface of carbon nanotubes(CNTs) are responsible for their catalytic performances in gas phase oxidative dehydrogenation. But in our previous studies, we found that the oxygen-containing functional groups have a negative influence in liquid oxidation reaction of cyclohexane. In this study, we further study the role of surface oxygen functional groups on carbon nanotubes in selective oxidation of cumene.
Based on a variety of liquid phase reaction, we summarize the following conclusions: (1) in general, surface oxygenated groups have a negative effect on the liquid phase oxidation of radical-based carbocatalysis, because they act as radical scavengers that inhibit the chain length of radical reactions, such as oxidation reactions of cyclohexane or ethylbenzene; (2) for the liquid phase oxidation of non radical-based carbocatalysis, if surface oxygenated groups involve in reaction, they have a positive effect, such as oxidation of benzyl alcohol on GO; (3) if surface oxygenated groups do not involve in reaction, they have little effect, such as oxidation of benzyl alcohol in HNO3 assisted carbon-catalyzed oxidation system.

P467

High performance electromagnetic wave shielding and absorbing materials based on graphene

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Due to its unique physical properties and structural features, graphene is emerging as a rising star in the field of material science. In this paper, functionalized graphene materials, have been used as efficient energy transfer unit in construction of a new type of electromagnetic wave shielding and absorbing materials. The results show that graphene is an excellent candidate for lightweight microwave absorption materials with very high performance. Moreover, the large aromatic network and good solubility of functional graphene make it a good choice for novel smart materials and devices.

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P468

Touch sensor based on a SWNT thin film transistor with a corona-poled P(VDF-TrFE) layer.

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Single walled carbon nanotubes (SWNTs) combined with piezoelectric materials work as excellent mechanoelectrical transducers because SWNTs have an ultra-high sensitivity to polarization charge density surrounding them. This work presents touch sensors based on the SWNT thin film transistors (SWNT-TFTs) covered with a piezo-electric polymer, poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)]thin film. The devices were fabricated by spin-coating of P(VDF-TrFE) solution on backgate type SWNT-TFTs, followed by in-situ corona poling to pole the P(VDF-TrFE) layer. Negative corona poling induced a highly hole-doping of SWNTs and enhanced the piezoelectric effect of the P(VDF-TrFE) layer. The poled devices showed stable and positive drain current modulations to repetitive press/release sequences and the modulated currents were proportional to the applied pressures. Conversely, positive corona poling did not induce such changes. We ascribed this asymmetrical effect to the difference in the Schottky barrier height between SWNTs and electrodes for electrons and holes. Pd contact used in the devices is known to provide good Ohmic contact for hole injection into SNWTs and forms large Schottky barrier for electron injection. Therefore, the negative poling provides a strong electric field between corona ions attached on the P(VDF-TrFE) surface and injected holes in SWNTs, resulting in effective poling of the P(VDF-TrFE) layer.

P469

Application of oxygen-doped carbon nanotubes as imaging probes and fluorescent labels

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Optical imaging using near-infrared (NIR) fluorescence is a new imaging modality that has recently emerged in the fields of biology and medicine. Especially, above 1300 nm, tissue autofluorescence is much low and the fluorescence of molecular probes escapes from the light absorption of water. Single-walled carbon nanotubes (CNTs) show fluorescence in the wavelength region of 1000-1400 nm. Recently, it is reported that stable covalently oxygen-doped CNTs, prepared by exposure to ozone and then light, showed extreme enhancement in fluorescent efficiency as compared to the pristine CNTs.

Here, we report the synthesis method of a new oxygen-doped CNTs in bulk. The oxygen-doped (6, 5) CNTs show NIR fluorescence at a much longer wavelength than that of the oxygen-doped CNTs reported previously, which is just advantageous for NIR imaging (~ 1280 nm). Immunoassay and gastrointestinal contrast imaging using the CNTs as the NIR fluorescent labels and imaging agents, respectively, are demonstrated.

P470

Ion irradiation effects on single-walled carbon nanotubes on polymer substrates

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Ion irradiation is commonly used to sputter materials, create defects, or modify surface properties of materials. In this study, we studied ion irradiation effects on Single-Walled Carbon Nanotubes (SWCNTs) when they are placed on top of polymer substrate, a substrate with high sputtering yield compared to SWCNTs. SWCNTs are grown by thermal chemical vapor deposition and transferred to poly(methyl methacrylate) (PMMA) film. SWCNT/PMMA film, then, is exposed to Ar ion plasma. After the exposure, we found that nanowalls with thickness of SWCNTs are formed on PMMA substrates, which indicate that SWCNTs can act as an sputtering etch mask due to the difference in the sputtering yields. Nanowalls as high as 20nm can be formed this way. We also investigated the progress of nanowall formation by atomic force microscopy(AFM), I-V measurement, and Raman spectroscopy, which shows progressive formation of defects in SWCNTs with each exposure to Ar ions.

P471

High conductive mesoporous graphene nanofibers and its capacitance performance at 4V

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We reported the fabrication of one dimensional highly electroconductive mesoporous graphene nanofibers (GNFs) by a CVD method using MgCO33H2O fibers as the template. GNFs showed to be a 1D material on macroscopic scale, but a 2D material composed of graphene with average 2 layers on microscopic scale. The average length of GNFs was about 10 micrometers and average diameter was 100-500 nm. As a result of this special structure, it exhibited a SSA of 1280 m2/g and mesopores in large amount. The electrical conductivity of GNFs was 3 times that of carbon nanotube aggregates. This kind of special one dimensional structure made it have a huge advantage as a supercapacitor electrode material, compared to microns or larger size of bulk graphene with the similar specific surface area and pore size distribution. It exhibited high energy density in wide range of high power density and excellent cycling stability at 4V. Energy densities of GNFs were 103.5 and 70 Wh/kg at 1 and 10 kW/kg, respectively. The drop of the capacitance was only 1.81% after 5000 time test.

P472

Full capacitance potential of single walled carbon nanotube at 4V ionic liquids

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We studied the full capacitance potential of single walled carbon nanotube (SWCNT, 1250 m2/g) in EMIBF4 at 4V by a new charge mode with certain dwelling time at 4 V. This allowed the accessible surface area of SWCNT, in monodispersed state and with macropores in large amount, was fully explored to exhibit capacitance of 16 uF/cm2 in wide range of current density, higher than that (9.1 uF/cm2) of a graphene (5 um in size and 2200 m 2/g). In situ Raman characterization upon charge and discharge validated the enhanced doping of ions of EMIBF4 on SWCNT wall with the increased potential. The energy density is 107 Wh/kg at power density of 20 kW/kg, far exceeding that (64 Wh/kg) in conventional galvanostatic charge and discharge mode. The new capacitance charge method is also effective to study the potentials of electrodes with different pore structures.

P473

Electric-driven fishlike actuator based on graphene-Poly-(vinylidene fluoride) bimorph material

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Smart actuators have many potential applications in various areas, such as microrobotics, ultrafast switches, artificial muscle and so on, and the studies for novel materials, facile fabricating methods and overall excellent performances are still urgent needs. In this work, a novel electromechanical bimorph actuator, constituted by a graphene layer and a PVDF layer, is presented through a simple yet versatile solution approach. The bimorph actuator can deflect toward the graphene side under electrical stimulus, due to the differences in coefficient of thermal expansion between the two layers and the converse piezoelectric effect or electrostrictive properties of PVDF. Under low voltage stimulus, the actuator can generate large and fast actuation motion and produce high actuation stress (> 235 MPa/g). The bimorph actuator also can display reversible swing behavior with long cycle life under high frequencies. On this basis, a fish-like robot which can swim at a high speed, is designed and demonstrated.

P474

Single-walled carbon nanotubes and graphene as highly efficient hole extraction and transport layer for photovoltaics

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Here structured single-walled carbon nanotubes (SWNTs) and millimeter-scale monocrystalline graphene are investigated as an advanced hole extraction and transport layer in various kinds of solar cells [1-2]. We found out that three-dimensional honeycomb structured SWNTs fabricated by breath figure directed self-assembly de-monstrated higher fill factor and low serial resistance compared with random network. We also obtained a ten-fold increase in the power conversion efficiency (PCE) by using millimeter-scale monocrystalline graphene compared with polycrystalline graphene, with the PCE of 11.6% before any intentional doping process. The hole collecting and transport function of SWNTs was also demonstrated in perovskite solar cells with high PCE. More importantly, all these solar cells have high stability in the ambient.

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P475

Individual single-walled carbon nanotubes for applications and fundamental studies

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SWCNTs inherently form bundles due to Brownian diffusion and strong van der Waals interaction, whereas the impact of bundling on many applications is poorly understood. Here, we present a novel concept of aerosol synthesis and direct deposition of predominantly individual single-walled carbon nanotubes for electronic applications and fundamental studies. The nanotube synthesis relies on iron catalyst particle generation via physical evaporation by a nitrogen driven spark discharge system. The floating catalyst particles are mixed with carbon monoxide (CO) and hydrogen and fed to a vertical laminar flow reactor tube held at 880 ^{o}C, where the SWNCTs form via catalytic decomposition of CO on the catalyst surface. The as synthesized nanotubes can be deposited on various substrates, including temperature sensitive ones, using a purpose-built thermophoretic precipitator. Based on atomic force and transmission electron microscopy studies, the as deposited SWCNTs were up to 80% individual (non-bundled) and of high quality and purity. The observed SWCNT mean diameters and lengths were 1.10 nm and 2.97 microns, respectively, and based on diffraction studies, 70% are semiconducting and 30% metallic. SWCNT transparent conductive films with sheet resistance of 65 Ohms/square @ T=90% and network transistors with ON/OFF current ratio up to 10^8 are presented.

P476

Thin-film transistors fabricated using the semiconducting fraction of DNA-wrapped SWCNTs

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Single-walled carbon nanotubes (SWCNTs) have been investigated for the application of thin film transistors (TFTs) due to their excellent transport properties. Recently, the progress of their separation techniques leads to obtaining highly pure semiconducting SWCNTs, that results in improving the performance of SWCNT-TFTs such as on/off ratio and mobility.

In our previous work, SWCNT-TFTs with high on/off ratio were fabricated by using electronically unsorted DNA-wrapped SWCNTs[1]. However, the optimization of the density of SWCNTs in TFT channel was needed not to form the conductive pathways by metallic SWCNTs, which caused low mobility in the SWCNT-TFTs. In this study, DNA-wrapped SWCNTs were sorted by their electronic structures by ion exchange chromatography (IEX)[2], and SWCNT-TFTs with semiconducting SWCNTs were fabricated.

Three chralities of semiconducting SWCNTs, (7, 5), (7, 6), and (8, 4), were mainly enriched by using IEX. SWCNT-TFTs after IEX showed the on/off ratio of around 10^6 and carrier mobility of 10 cm^2/Vs. This result indicates that IEX method clearly improves the performance of SWCNT-TFTs due to the reduction of metallic SWCNTs pathways.

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P477

The limit of specific surface area and capacitance for sp2 carbon materials

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As one of the most studied and used highly porous electrode materials for carbon supercapacitors (SCs), sp2 carbon materials have attracted ever-increasing interests for high efficiency energy storage and conversion devices. Improvements have been made in the design of increasing the specific surface area (SSA) and controlling the pore size distribution (PSD) in order to enhance SCs performance. Up to date it is still unclear where the limit is for the SSA of bulk sp2 carbon materials and the corresponding best capacitance performance in practice. With this perspective, in this work, we have investigated these limits both experimentally and theoretically using a series of bulk sp2 carbon materials from different carbon sources, and found the possible limit for Brunauer-Emmett-Teller SSA would be around 3500-4000 m2 g-1 and the corresponding best capacitance would be around 230, 200 and 300 F g-1 when ionic liquid, organic electrolyte and aqueous KOH are used as the working electrolyte. An excellent agreement between theoretical capacitance and experimental capacitance is observed, indicating that our model for the calculation of theoretical specific capacitance is appropriate for SCs based on various carbon materials in all electrolytes.

P478

Air-tolerant n-type thermoelectric properties of single-walled carbon nanotubes with salts

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Solid-state thermoelectric materials will become prevalent in our daily lives in the near future. Their common metallic, heavy, and stiff nature can also be removed using nanocarbon materials. However, the absence of air-stable n-type nanocarbons has hindered the development of practical PN junction-type thermoelectric modules. Here we solve this challenge by using single-walled carbon nanotubes and ordinary salts with crown ether. The measurement of thermoelectric properties revealed that various ordinary salts convert p-type carbon nanotubes to n-type forms efficiently. n-Type carbon nanotubes were stabilized by forming their interfacial complexes with counter cations composed of stable alkali metal-crown ether host-guest complexes. This fact resulted in the creation of air-, and heat-stable n-type carbon nanotubes.

P479

Modelling of nanoelectromechanical memory cell switching

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We propose a model for nanoelectromechanical switching of the current state of carbon nanotube memory cells. We employ charging energies plus nanotube densities of states to produce electrostatic addition energies of the cell, simulating separated layers of the cell as a pair of attracting nanoparticles. The opening and closing of the gap between the nanoparticles constitutes the memory switching. Using also mechanical restoring forces and van der Waals attraction, we derive the equations for the electrostatic force between the nanoparticles, each in electrochemical equilibrium with its own lead, as a function of the lead chemical potentials. We show that a bi-stability exists in the system configuration, with one state representing a “SET” state and the mechanically relaxed state representing the “RESET” state. We show that the switching between states is in general asymmetric with respect to top and bottom contacts because of the geometric asymmetry and also the location of the gap in the nanotube material. Finally, we demonstrate that the dynamics of the system in the presence of current are highly nonlinear which feature is crucial for the RESET operation.

P480

Increasing the thermoelectric performance of carbon nanotubes upon conjugation with a one-dimensional coordination polymer

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Thermoelectric materials based on single-walled carbon nanotubes (SWCNTs) are the promising candidates of power generators. They serve various beneficial features such as lightness, physical flexibility, and high electrical conductivity. In addition, incorporation of additive substances can enhance the thermoelectric abilities of SWCNTs by controlling their electronic structures and carrier transport. Selection of the dopant is crucial to maximize the thermoelectric performance.

One-dimensional coordination polymers (1D-CPs) possess infinite structures composed of metal ions and organic ligands. Their bottom-up construction proceeds by self-assembly and also allows diversity in composition and electronic structures. However, no example have demonstrated the thermoelectric properties of 1D-CP/SWCNT hybrids.

We synthesized a 1D-CP comprising a bis(dipyrrinato)zinc complex motif. The 1D-CP was crystallized by means of a liquid/liquid interfacial synthesis and analyzed by X-ray diffraction. Isolated fibers of the coordination polymer could be exfoliated from the single crystal upon ultrasonication in dichloromethane, and AFM confirmed that the fibers were more than several micrometers long. The exfoliated 1D-CP wires featured good processability, realizing the formation of a conjugate SWCNTs. The conjugate featured a thermoelectric power factor of 33 microW m^{-1} K^{-2}, which is greater than that of pristine SWCNTs.

P481

Electronic properties of vertical graphene/hexagonal boron nitride heterostructures with intercalated defects or vacancies

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The electrical properties of graphene may be extremely sensitive to the environment. Therefore, any external contamination easily degrades the conductance of graphene. Although tremendous efforts have been made to prevent contamination at the interfaces, it is very difficult to completely remove the contamination. In the present study, we investigate the influence of metal impurities or vacancies, on the structural and electronic properties of the graphene/hexagonal boron nitride (hBN) heterostructure. A boron (nitrogen) monovacancy in the hBN layer creates p-doped (n-doped) graphene and metal atom impurities may increase the energy of the Fermi level of graphene. Boron and nitrogen monovacancies as well as Mn and Co impurity atoms produce deep levels due to in-gap states. In contrast, V_{B+3N} and V_{N+3B} defects are expected to contribute less than monovacancies (V_B and V_N) to electronic scattering in the deposited graphene since their localized defect states are quite far from the Fermi level. Consequently, the graphene/hBN system with extrinsic contamination or intrinsic vacancy defects could exhibit poor performance since the imperfections impair the electrical conductivity due to residual scattering in applications such as field effect transistors.

P482

Universal method of aligning carbon nanotubes in thin films

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The alignment of carbon nanotubes in thin films parallel to a surface is a current topic of widespread research interest. This is because when carbon nanotubes are present in a randomly ordered bulk, many of the often-touted electronic and optical properties of individual nanotubes are not observed, or are significantly suppressed, which confounds their exploitation in various devices and applications. It is only when the nanotubes are present in the highly ordered regime that many of the properties of individual carbon nanotubes become accessible in the bulk material. As well, there are several new and interesting properties that are predicted to arise when the nanotubes are present in the form of a fully ordered bulk crystal. A number of methods of producing aligned carbon nanotube thin films have been reported with varying degrees of complexity, difficulty, and scalability, as well as resultant nanotube alignment. These include the use of Langmuir-Blodgett troughs, vacuum filtration, solution shearing, evaporation-driven self-assembly, and exfoliation of CVD grown forests. Whilst successful, all of these techniques require very specific preparation and have limited applicability. In contrast, we have found a universal method of nanotube alignment in thin films that is both inherently scalable and exceedingly simple.

P483

Application of vertically aligned carbon nanotubes-based composite electrodes as a fine bubble generator

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Fine bubble shows diameter-dependent characteristics such as sterilization. More detailed investigation of size effect on their fundamental properties is required for further development, but they are generally obtained as a suspension with wide diameter distribution by conventional methods. Here we propose an application of vertically aligned carbon nanotubes (CNTs) for a tool to operate individual fine bubbles. In our study, individual CNTs are utilized as electrodes for water electrolysis, which may enable to generate bubbles with controlling diameters. It may be also possible to hold isolated bubbles at specific sites on the electrode continuously, so that array of size-controlled bubbles can be generated applicable to various size-selective measurements. However there is a technical problem that neighboring bubbles at tips of individual CNTs easily coalesce due to aggregation of CNTs by capillary action in water. Therefore, we fabricated composites with resin to make individual CNTs work as independent electrodes. Atomic force microscopy (AFM) confirmed numerous protrusions consisting of CNT tips on their surface, and bubbles selectively generated at such protrusions by electrolysis with 5% sodium chloride solution. In situ AFM observation also showed time-dependent growth of nanobubbles in 10 seconds order to be a certain size, and gradual shrinking in 10 hours.

P484

Erosive wear resistance of carbon nanotube reinforced epoxy composites

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Aligned carbon nanotube (CNT) polymer composites are envisioned as the next-generation composite materials for a wide range of applications. In this work, we investigate the erosive wear resistance of epoxy matrix composites reinforced with aligned CNT arrays[1] and CNT films[2]. Results have shown that the composite with vertically aligned CNT-arrays exhibits superior erosive wear resistance compared to any of the other types of composites, and the erosion rate (by mass loss) reaches a similar performance level to that of carbon steel at 20° impingement angle. The erosive wear mechanism of these composites, at various impingement angles, is studied by Scanning Electron Microscopy (SEM). In the case of aligned CNT arrays as the reinforcement material, the erosive wear performance shows strong dependence on the alignment geometries of CNTs (i.e., horizontally and vertically aligned) within the epoxy matrix under identical CNT loading fractions. However, the incorporation of multi-layered CNT films does not show significant improvement on erosion resistance which may be attributed to the relatively poor interaction between CNTs and matrix as well as porosity. Overall, this work demonstrates methods to fabricate CNT based polymer composites with high loading fractions of the filler, alignment control of nanotubes and optimized erosive wear properties.

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P485

MWCNT/Fe-based hybrids as a potential nanomaterial for biosensors and multimodal bioimaging tools

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Multi walled carbon nanotubes (MWCNTs) are a promising material for various biosensors due to their unique physicochemical properties, abilities to chemical oxidation and further biofunctionalization. We present the MWCNT/Fe-based magnetic-fluorescent nanohybrid as a multifunctional cellular imaging agent for magnetic resonance imaging (MRI) and fluorescence microscopy. The MWCNTs were synthesized by CVD method using ferrocene as the catalyst [1]. Magnetic properties of iron particles embedded in MWCNT were verified as T2-weighted contrast agents for MRI. Moreover, the outermost wall of MWCNT/Fe system was chemically oxidized [2] and covalently functionalized with polyethylene glycol (PEG) to improve its solubility and biocompatibility. The MWCNT-PEG complex was characterized by TEM, SEM, FTIR and Raman spectroscopy. The PEGylated nanostructures were also labeled with organic dyes (DAPI, MDC) and internalized inside HeLa cells for cellular imaging. Additionally, the minimal cytotoxicity effect of PEGylated complexes in comparison to non-PEGylated samples were revealed (In Cell Analyzer, confocal microscopy).

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P486

Floating catalyst-CVD based processing of SWCNTs for high uniformity TFT arrays

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Single-walled carbon nanotube networks can be used as transparent electrodes and thin film transistors. We report use of aerosol characterization techniques to control floating catalyst-CVD synthesis and deposition for improved uniformity of SWCNT TFT arrays. We used high voltage electric discharge between to Fe-electrodes to directly evaporate iron vapor to an inert gas jet, leading to formation of iron catalyst nanoparticles with controlled size and number concentration. The catalyst particles are mixed with carbon precursor (CO) in a synthesis reactor operating at 880°C. The well-controlled catalyst particle formation improves the control over the SWCNT synthesis, leading to formation of SWCNT networks consisting of high fraction of individual tubes. In addition to high individual fraction, these SWCNT networks exhibit small mean tube diameter of 1.1nm and mean length up to 4um. Furthermore, on-line concentration monitoring enables deposition of SWCNT networks with pre-determined SWCNT density, thus enabling controlled tuning of TFT characteristics, such as the ON/OFF current ratio. The SWCNT networks are highly uniform and can be used to realize SWCNT TFTs with excellent uniformity and high fabrication yield of 99%. The SWCNT TFTs exhibit excellent characteristics with high charge carrier mobility of 100 cm^2/Vs and high ON/OFF-ratio up to 10^5.

P487

Electromechanical properties of PDMS/MWCNT nanocomposites

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Dielectric elastomers exhibit the most promising properties that mimic natural muscle for use in advanced robotics and smart materials, as well as in haptic and microfluidic devices. Silicone elastomer actuators were investigated to develop a simple and industrially scalable product with improved mechanical properties, such as low modulus, high tearing strength and good resilience, and enhanced electromechanical actuation property. Silicone elastomers were fabricated via hydrosilylation addition reaction using vinyl end-functionalized poly (dimethylsiloxane) (PDMS), multi-vinyl functionalized silicone resin and a cross-linker in presence of platinum catalyst. For the larger electromechanical actuation response, silicone dielectric elastomer actuator had to have larger molecular weight of PDMS, smaller hardener content, resin-free composition, and composite with silicone grafted multi wall carbon nanotube (MWCNT)s. As the molecular weight and filler of MWCNTs increased, electromechanical actuation strain increased. And dielectric constant increased with increasing the MWCNTs until certain concentration.

P488

Unidirectionally aligned-carbon nanotube/polymer composite strain sensor

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We have conducted the growth of ultra-long dry-spinning capable carbon nanotube (CNT) array. By drawing CNT webs, unidirectionally aligned CNT sheet structures are easily fabricated. CNTs are well aligned in the drawing direction in the sheet. In this study, the CNT sheet was used for strain sensor devices. The CNT sheets were mixed with low-modulus polymer layers. In the composite, CNTs are aligned in the stretched direction. With changing length of the CNT/polymer composite, resistance between both ends changed. The stretching limits is larger than 200 %. Depending on the size of devices, the sensing distance ranges from several millimeters to centimeters. Our CNT based strain sensors show a good response faster than 1 sec. By analyzing the composite structure, it was found that during expansion process, number of CNT connections decreased, and in the contraction process CNTs returned to almost the original positions with recovering the electric connections.

P489

Bound-states in continuum in carbon nanotubes

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We study a theoretical model of a long carbon nanotube with two attached impurities and an external magnetic field. We show that, by tuning the magnetic field, an electron released from one of the impurities can be forced to be in a “bound-state in the continuum” (BIC), where the electron remains trapped between the two impurities, forming a standing wave. The magnetic field can be adjusted to significantly alter the absorption line shape of the impurities in the vicinity of the BIC.

P490

Improved response of thin film transistor biosensors by controlling synthesis conditions of carbon nanotube channel

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Sensitivity of sensor using carbon nanotube thin film transistor (CNT-TFT) was effectively improved by controlling the density, diameter and length of channel CNTs. Nanodiamond was used as the CNT growth seed since the nanodiamond maintain a solid state even in chemical vapor deposition condition and CNT density can be controlled by nanodiamond density. Nanodiamond is also applicable for synthesizing thin and long CNTs which is suitable for improving TFT performance. Growth procedure with two step conditions was applied for diameter and length control of CNTs. Carbon concentration was optimized separately at initial growth stage for thin CNT cap nucleation and at stationary growth stage for longer activated lifetime of nanodiamond growth seeds, resulting in the growth of thin and longer CNT films with higher carrier mobility. The response of TFT with the CNT grown under the optimized condition was notably improved for the selective sensing operation of human immunoglobulin E (IgE). Lower detection limit observed for IgE (0.1 ng/ml) was significantly lower than the reference values of allergy test (0.8 ng/ml). Analysis of sensor response indicated that charge distribution of target protein and Debye length affect current variation drastically. Appropriate Debye length is required for quantitative detection of protein.

P491

High-thermal-resistance CNT/rubber composite derived from radical scavenging effect of CNT

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Elastomer shows soft and elastic properties, therefore one of their main application is sealing materials. However, elastomer is weak for heat derived from thermal degradation with heat-radical. The low-heat resistance of elastomer limit the wide-range application of elastomers. The key to increasing thermal resistance of elastomer is scavenging heat radical in elastomer. CNT have been known as a radical scavenging materials. We provide high-thermal resistance elastomer by adequately adding small amount of carbon nanotubes for elastomer. The heat resistance was estimated by time dependence of storage modulus under isothermal condition (200 oC). The high thermal resistance of CNT/rubber composite have achieved by excellent radical scavenging effect of CNT. By adding 1 wt% of CNT, the heat resistance of elastomer increase in 100K compared with pure elastomer. This CNT/elastomer composite have big possibility for oil-sealing material of oil drilling, sealing material of gas engine as a private power generator and sealing materials for automobiles.

P492

Solar cell utilizing semiconducting SWNTs as exciton generators

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Single-walled carbon nanotubes (SWNTs) have superior electrical, chemical and physical properties compared to conventional materials being used in nanoelectronics, photovoltaics and sensors. SWNTs are composed of metallic SWNTs and semiconducting SWNTs. In order to use SWNTs as nanoelectronics and photovoltaic devices, we need to separate semiconducting SWNTs from mixtures, because metallic SWNTs cause recombination of electron-hole pair and trap electron transferred from active layer. To separate semiconducting SWNTs, density gradient ultracentrifugation (DGU) method has been used after attaching diazonium reagent to metallic SWNTs, thus making metallic SWNT heavier for those to be separated by density induced separation technique. But this method demand considerable time and energy. In this study, we investigated if we can turn off metallic SWNTs by selectively attaching diazonium reagent onto metallic SWNTs, while maintaining semiconducting SWNTs intact, therefore making semiconducting SWNTs device without separating metallic SWNTs. We fabricated semiconducting SWNT photovoltaics using semiconducting SWNTs prepared by the method above and compared their performance with the device made with pure semiconducting SWNTs, in which metallic SWNTs are separated by DGU method.

P493

Performance of solar cell fabricated with Cs encapsulated semiconducting single-walled carbon nanotube films

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Single-walled carbon nanotubes (SWNTs) are one of the most attractive materials for future high performance solar cells due to their excellent properties. It was also predicted that multiple exciton generation (MEG) can be possible in SWNTs, indicating the efficiency of solar power generation can be drastically improved with SWNTs. For the fabrication of solar cell with SWNTs, it is necessary to establish a controllable doping method. Environmental stability is also another important issue for the practical use of SWNTs in solar cells. In contrast with the p-type transport property of pristine SWNTs, we demonstrated very stable n-type SWNTs-thin film transistors (TFTs) by Cs encapsulation into SWNTs based on a plasma ion irradiation method. In this study, the optoelectrical transport properties were investigated for the controllably Cs doped stable semiconducting SWNTs films. It was found that the clear rectifying drain-source current vs. drain-source voltage characteristics can be observed after the position selective Cs encapsulation into semiconducting SWNTs thin films. Furthermore, a short-circuit current and an open-circuit voltage can be also detected under light illumination using a solar simulator, indicating the solar power generation has been successfully realized by pure junction of p-type and n-type SWNTs films.

P494

Molecular absorption and desorption dynamics on Tow-dimensional nanosheets observed by laser terahertz emission spectroscopy

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Two-dimensional (2D) nanosheets such as graphene and WS2 are known to be susceptible to its environment, including defects and phonons in the substrate as well as gas molecules that surround it. Thus, any device design using 2D nanosheets has to take into consideration all surrounding components, and device performance needs to be evaluated in terms of environmental influence.

In this study, we present a rapid and non-contact method for visualizing the distribution of molecular adsorbates on 2D nanosheets using terahertz time-domain spectroscopy and imaging. We found that the waveform of terahertz radiations emitted from 2D nanosheet-coated semiconductors sensitively changes with the type of atmospheric gas, laser irradiation time, and ultraviolet light illumination. These results demonstrate that terahertz emission serves as a local probe for monitoring adsorption and desorption processes on 2D nanosheet, suggesting a novel two-dimensional sensor for detecting local chemical reactions.

P495

Lithographically patternable and lightweight CNT-Cu composite interconnects showing longer lifetime and comparable conductivity to pure Cu

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Emerging lithographically processable materials with high conductivity and high stability at high current and high temperature are in demand for high current electronic devices used at high temperature. Here, we will demonstrate that a patterned CNT-Cu composite which exhibits a two times longer lifetime when current is applied at high temperature and comparable conductivity to Cu. In addition, it is patternable on the arbitrary substrates by lithographic processes and electroplating. As we have reported previously, it has 100-times higher ampacity than Cu. We also found that coefficient of thermal expansion (CTE) is approximately 5 ppm/K, which is comparable to that of silicon (3 ppm/K). The comparable CTE between CNT-Cu composite and Si substrate is effective to reduce mechanical strain arising due to the similarity in CTE between the substrate and patterned components during thermal cycling. Therefore, we attribute the longer lifetime to the high ampacity and low mismatch of thermal expansion coefficient of the CNT-Cu composite with the silicon substrate. Highly stable, conductive and lightweight CNT-Cu composite synergizing the advantages of Cu and CNT is promising as future interconnects, enabling highly reliable electronic devices for harsh environment. This presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P496

Developing reliable and stable CNT micro-supercapacitors on flexible substrates

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Over the past few years, the development of the electric double-layer capacitor (i.e. supercapacitor) has attracted increased attention due to its high power density, durability and safety compared to batteries. Recently, with the development of novel materials, including carbon nanotubes (CNTs) and graphene oxide, large strides in the improvement of the supercapacitor energy density has been demonstrated. Furthermore, these novel materials have enabled a route toward the miniaturization of capacitors which have remained unchanged in size over the past 50 years. We have recently demonstrated a CNT-micro supercapacitor which has demonstrated both high energy density and high power density while being 1000-times smaller than current aluminum electrolytic capacitors. However, for this technology to reach commercial applications, the individual CNT-micro supercapacitors must demonstrate stable and uniform operation which is largely determined by a stable and uniform production process. Here, we report the development of a stable production process for these CNT-micro supercapacitors on flexible substrates including flexible current collectors. In so doing, we have created a new flexible and durable micro-energy device which widens its potential ap-plications. This presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

P497

Flexible microelectrode based on CNT thin film and its electrochemical sensor applications

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Carbon nanotubes (CNTs) have shown promising properties as electrochemical electrodes such as rapid electron transfer kinetics, wide potential window, and bio-compatibility. Flexible devices based on CNTs have been investigated extensively for varieties of applications such as gas sensors, electronics devices, and electrochemical sensors. However, conventional solution-based process to form CNT thin film may degrade the performance and uniformity in electrochemical activity on electrode surface due to contamination associated with dispersal substances. Here, we demonstrate high-performance flexible microelectrodes based on an as-grown CNT thin film for electrochemical sensor applications to detect dopamine, an important neurotransmitter.

CNT microelectrodes were fabricated on a PEN substrate by dry transfer method based on the floating-catalyst CVD and standard microfabrication process. In electrode structure, only CNT surface is exposed to electrolyte and performs electrochemical reaction. To minimize the contamination of CNT surface, CNT surface was covered with an oxide film during fabrication process.

The electrochemical properties of flexible CNT microelectrodes showed high uniform, and high electron transfer rate with the quartile potentials | E3/4 E1/4 | ~ 60 mV, close to ideal value (59 mV). Electrodeposited gold on electrode confirmed the high uniformity in electrochemical activity of CNT surface, especially after an activation process. These CNT microelectrodes also exhibited high sensitivity in detection of dopamine.

P498

Carbon nanotube/graphene epoxy composites with superior electrical conductivity

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Highly conductive epoxy composites reinforced with a combination of carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) have been fabricated by controlled shear mixing process. The electrical conductivity studies of epoxy composites were based on the varied combinations of GNPs and CNTs with different aspect ratio, length and diameter. Given specific processing routes, a remarkable synergistic effect was found on the epoxy based composite with addition of GNPs into the CNT network. Such synergistic effect arises from the use of large-size CNTs and GNPs with optimized loadings. In addition, planar GNPs deliver the ability to maximize contact areas and increase the size of CNT agglomerates by means of non-covalent interactions. On the other hand, the conductive network formation for small-size CNTs (i.e., reduced aspect ratio, diameter and length) with GNPs lies in the continued growth of agglomerates accompanied with increasing filler loading fractions. This work demonstrates an effective method to fabricate macroscopic epoxy composites using fillers with enhanced electrical conductivity and paves the way into composite manufacture with low cost, lightweight and ease of processability.

P499

Magnetic and water soluble MWCNT/Fe composites as potential MRI contrast agents

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An increasing number of scientific reports state that carbon nanotubes (CNTs) and magnetic particles have a potential for medical applications like contrast for Magnetic Resonance Imaging (MRI) or guided drug delivery. Functionalised, multi-walled carbon nanotubes are usually considered to be less toxic than the long and pristine ones. Additionally, such nanotubes make a water-soluble shell for pure iron nanoparticles.

Multi-walled CNTs (MWCNTs) with three selected amounts of ferrocene were synthesised by a floating catalyst CVD route. Consecutively, three oxidation protocols were explored in order to select the most efficient route for the production of a highly soluble and biocompatible material with defined length [1], [2].

A highly effective and simple MWCNT/Fe dispersion technique, resulting in particles that remained suspended for months, was developed. Magnetic properties of nanocomposite were verified and significant enhancements in MRI contrast were observed. Moreover, the cytotoxicity of the MWCNT-Fe nanocomposites was studied in two cell lines.

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P500

Assessment of characteristic variation in carbon nanotube thin film transistors

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Carbon nanotubes (CNTs) have exceptional intrinsic electrical and mechanical properties, and CNT thin-film transistors (TFTs) are considered as promising components for flexible electron devices such as rollable displays and wearable healthcare devices. Though great efforts have been made to achieve high-performance CNT TFTs, one of critical issues for practical applications is to suppress device-to-device variation in their electrical characteristics. In this study, we have statistically investigated the variation in on-current, on/off ratio, and mobility of CNT TFTs by measuring over 500 devices. Here, we used high-purity semiconducting single-walled CNTs. The film was formed by the vacuum filtration and transfer method. The overall variation in oncurrent was about 20 % for a large area of 200 mm^2. The main cause of the variation is the non-uniformity in CNT density due to the filtration process. However, we have found out that quite small variation as ~ 5 % can be obtained in a small area of 9 mm^2.

P501

High performance natural rubber nanocomposite by surface modification of multi-walled carbon nanotubes

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We aim to develop high-level applications of natural rubber (NR) through the innovative use of multi-walled carbon nanotubes (MWCNTs) to improve reinforcing performance and thermal resistance. In this study, we examined the structures and characteristics of composite materials in which NR was the matrix and MWCNTs were the fillers. We studied the properties of composites containing surface-activated MWCNTs with three different diameters. The results show that the reinforcing performance improves as MWCNT diameter decreases, while thermal resistance improves as we decrease the heat-treatment temperature. The latter occurs because adherence between MWCNTs and NR becomes stronger at lower heat-treatment temperatures. We also found that for practical applications, we need to control active sites on MWCNTs to balance adhesion against thermal resistance.

P502

Impurity effect on edge-modes of graphene

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We theoretically examine the impurity effect on the edge modes in graphene. It is known that the zero-energy modes appear at the zigzag edge of graphene. The energy and wavefunction of the modes are numerically evaluated with gradually changing the on-site energy at an A- or B-site at the edge in the tight-binding model. We find that one of the zero-energy edge modes merges into the bulk band, whereas a new edge mode is created from the bulk band. The new edge mode is localized around the impurity site. Its localization length is independent of the impurity position at A- or B-site.

P503

A theoretical proof for electrically enhanced desorption of hydrogen chemisorbed on graphene

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Fermi level tuning of graphene had been experimentally shown to have ability realizing the bias-voltage-controlled adsorption of oxygen [1]. To show that bias-induced local charge can enhance a desorption rate of chemisorbed species, we performed the nudged-elastic-band-method simulation for charged hydrogenated graphene. The desorption barrier is clearly affected by the Fermi level shift in the electron rich side, although a rather large bias-induced doping of an electron per a few tens of carbon atoms would be required to achieve about 10% reduction of the desorption barrier. The desorbed hydrogen molecule is always kept in a neutral state, except for highly positive-charged condition. The present result may imply a construction method of information device, in which the electrical stimulation produces a flow of neutral chemical molecules emitted from graphene surface.

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P504

Change in raman spectrum of single-walled carbon nanotubes including iodine molecules with temperature

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We have developed new encapsulation method of iodine molecules into single-walled carbon nanotubes (SWCNTs) using electrolysis. It was found that the iodine doped SWCNTs show very good dispersibility in water at low temperature. Interestingly, it was also found that the dispersed SWCNTs become to re-aggregate with increasing temperature. This temperature dependency of the dispersion could be explained by temperature dependent charge transfer from iodine molecules to host SWCNTs. However, so far, we do not have any experimental evidences for that hypothesis. In the present study, we have performed in-situ Raman measurements of I@SWCNTs at several temperatures.

P505

Molecular dynamics study of water permeability for carbon membrane

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The flush water is fundamental and important for human life. The flush water can be obtained by desalination of seawater using semipermeable membranes. New carbon membranes as Diamond Like Carbon (DLC), Graphene, CNT, CNT composite etc., have been recently attracting scientists and engineers as reverse osmosis (RO) membrane Therefor we studied the water permeability and desalination ability of Carbon Membrane by Molecular Dynamics (MD) calculation. As the results, Carbon Membrane, such as DLC, Graphene, etc, are permeated water molecules only and block NaCl flow efficiency. But the loss of water flow for DLC is larger than Graphene. We found that a flow was reinforced by processing the surface.

P506

Transport of ions along the exterior of single walled carbon nanotubes

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Single walled carbon nanotube (SWNT) is an excellent material for studying the transport phenomenon at nanoscale due to their atomically smooth surface, small diameter (1-2 nm), and extremely high aspect ratio. The tubular nature of the material allows efficient molecular transport both externally and internally. Due to challenges in setting up a reliable experimental platform experimental studies on the transport has started only recently. Here we show experimentally the evidence of the ionic transport along the exterior of SWNTs. When an electrical bias is applied to droplets of salty water placed on each side of carbon nanotubes, nanocrystals are formed along the nanotubes. This result is a direct evidence of the exterior transport of ions and helps one visualize individual nanotubes under an optical microscope. Surface analyses show the distribution of cations and anions during the transport. We also investigate using Raman spectroscopy how the transport of ions depends on the diameter and metallicity of nanotubes. Recent studies in this area have largely focused on the interior of nanotubes, but our study suggests there still remain many questions to answer and opportunities to explore in the exterior of nanotubes.

P507

Electrocatalytic activities of Pt-based nanoparticles on carbon nanomaterials by one-step electrodeposition

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Direct methanol fuel cells (DMFCs) are one of the most promising transportable power sources which can be used in mobiles, laptops, and small power generation. The basic operation principle of DMFCs involves methanol oxidation and oxygen reduction on the precious metal catalysts, which are loaded on the support surfaces. As is well-known, the dispersion of Pt-based alloys on carbon supports as well as catalyst particle size and shape plays a dominant role in the electrochemical performance for fuel cells. We have explored the electrocatalytic properties of Pt-based nanoparticles supported on the carbon materials by one-step electrodeposition. In this study, we investigated the effects of electrodeposition conditions on the shape and dispersion state of Pt-based nanoparticles and their electrocatalytic properties supported on Single walled Carbon Nanotubes(SWNTs) or highly ordered pyrolytic graphite(HOPG). The detailed results on the relationship between the deposition conditions, the shape and dispersion state of Pt-based nanoparticles and their electrocatalytic performance for methanol oxidation will be presented.

P508

Non covalent oligothiophene-graphene hybrid materials

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Graphene is an outstanding material, with unique electronic and mechanical properties. Due to these exceptional properties, graphene is characterized as an ideal candidate for the construction of transparent conducting electrodes suitable in energy conversion and storage systems. Oligothiophenes in general are readily accessible organic chromophores with interesting electronic properties, have been used as p-bridges in energy transfer processes between photoactive molecules and as electron donors in donor-acceptor carbon-based nanohybrids. The stiff skeleton of oligothiophenes and the presence of the sulfur atom generate a stable p-conjugated chain, which can interact through multiple p-p stacking forces with the sp^2 graphene lattice.

In this context, non covalent oligothiophene-graphene hybrid materials have been produced and fully characterized through Raman and IR spectroscopy, TEM imaging and TGA analysis. Currently, we are exploring the nature of these interactions focusing in electron and/or energy transfer processes.

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P509

Graphene based material for Lithium ion hybrid supercapacitor

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A graphene-based 3D bulk material has been synthesized by the in-situ hydrothermal carbonization of biomass or industry carbon sources with GO followed by chemical activation (4M KOH). The obtained 3D graphene based material present high SSA (up to 3300-3523 m2 g-1) and conductivity (up to 303 S m-1) with most of the pore size in range of 1 to 10 nm, which is very suitable for the electrolyte to migrate. Using this 3DGraphene as the positive electrode material, we have designed three types of hybrid supercapacitor systems with Fe3O4/Graphene composite, LTO/graphene composite and FRGO film as the negative electrode, respectively. They all deliver high energy and power density, with the maximum energy density of 204, 148.3 and 95 Wh kg-1, respectively.

P510

Extremely high electron transparency of carbon nanotube films

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We report on the extremely high electron transparency of ultrathin CNT films. A CNT film with an average intertube distance of 20 nm was prepared using the vacuum filtration method [1] and deposited on a 3.4-nm-thick layer of thermal oxide on a 1 cm2 silicon chip. Symmetrical electrical connections were made to the CNT mesh and the silicon substrate underneath. The sample was mounted inside a high vacuum chamber and bombarded with 100-eV electrons from an EK-30-R STAIB Electron Source. The CNT mesh and the substrate were connected to two separate Keithley electrometers and the current through each was measured by sweeping the voltage from negative to positive values. The applied biases of the electrometers were changed concurrently to ensure no net bias was applied across the thin oxide separating the mesh from the silicon substrate. The current through the silicon substrate varied from 2 nA to 150 nA depending on the applied bias, whereas the current through the CNT mesh remained negligible during the entire experiment (less than 1.5 pA, the resolution of the measurement circuit). This suggests an extremely high electron transparency for the CNT mesh with transmissions higher than 99.999 % in the low-landing-energy range of 0-150eV.

P511

Controlled deposition of SWNT film suspended over nanostructured dielectric

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Nanoscale thermionic energy converters and thermionic refrigerators are attractive due to the addition of quantum tunnelling to the otherwise classical limitations on these devices [1-2]. However, maintaining a uniform nanoscale vacuum gap under large temperature gradients and thermal stresses remains challenging. Here, we present a precisely controlled metallic single-wall nanotube (SWNT) film suspended over a nanostructured dielectric on a metallic substrate for a uniform nanoscale vacuum gap. The nanostructured dielectric was fabricated using a focused ion beam to achieve large arrays of 100-nm-diameter holes in a 30-nm-thick dielectric film. The SWNT grid was deposited using a method based on the vacuum filtration technique [3]. In order to densify, i.e. decrease the inter-nanotube distance in the SWNT film, the vacuum filtration technique was modified as follows. First, a sufficiently thin film was deposited, in which individual tubes distinguishable from the dielectric substrate, then individual thin films were subsequently stacked by repeated vacuum filtration and deposition, rather than depositing as one thick film. This method provides a degree of independent control of the SWNT spacing and film thickness, which are conventionally inseparable. Therefore, a higher degree of uniformity in terms of vacuum gap between individual CNTs and the metallic substrate can be achieved.

P512

Light induced thermionic energy conversion using in-situ intercalated carbon nanotube forests

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Carbon nanotube (CNT) forests can be effectively heated to thermionic emission temperatures when irradiated by a focused beam of light [1]. We have shown that a reduction of the CNT forests workfunction by 2 eV can improve the thermionic conversion efficiency by several orders of magnitude [2]. Here, we present the results of in-situ potassium intercalation of CNT forests under thermionic conversion conditions. The potassium target was placed inside a custom-built ceramic crucible on a resistive heater in a nitrogen ambient. The CNT forest was then mounted directly on the potassium reservoir. At about 100μm from the CNT forest sidewall, a stainless steel mesh with an overall 85 % transparency was placed as the anode. The potassium reservoir was heated resistively by passing various amounts of current for a duration of 72 hours under 1 uTorr vacuum. The current-voltage characteristics of the thermionic cell were measured while the CNT forest was illuminated by a laser beam with varying levels of intensity. Following the method described in our earlier work4, the workfunction of the CNT-based thermionic cathode was extracted from the current-voltage characteristics and a reduction of 1.1 eV at 1500 K was observed, improving the efficiency by four orders of magnitude.

P513

Vertically Aligned Carbon Nanotubes (VACNT) materials for ultracapacitor electrodes

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Vertically Aligned Carbon Nanotubes have attracted major interest as electrodes materials for the elaboration of Ultracapacitors with high specific capacitance and power compared to conventional Electronic Double Layer Capacitors (EDLC). Although theoretical studies predict very high capacitance for VACNT alone, their manufacturing process is still far from being competitive with classical EDLC. The idea to use cost-effective VACNT, made by Atmospheric Pressure CVD [1,2], serving as template for a host material with higher intrinsic capacitance than carbon is presented in this paper. For instance, Electronically Conductive Polymer (ECP) is known to exhibit high specific capacitance [3-5] for which a composite material is obtained through electrochemical polymerization which is performed on the VACNT structured substrate [4].

The aim of this article is to present the basic design of nanocomposite electrodes made from poly(3 - methylthiophene) (P3MT) as ECP electrodeposited onto VACNT. The study will present initial simulation studies, processes for VACNT growth and ECP electrodeposition, optimization of the nanocomposite as electrode. Finally storage performances of the resulting nanocomposites will be reported and discussed based on electrochemical studies. The electrochemical performances of the nanocomposites in symmetric and asymmetric ultracapacitor using Ionic Liquids (IL) based electrolytes will be exposed and compared to conventional EDLC.

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P514

Improvement of transparency and conductivity with CNT micro-bundling

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Carbon Nano Tubes (CNTs) have attracted much attention since it was discovered in 1991. However, their industrial application has been hindered, mainly due to the lack of ease of processability. Dispersing CNTs has proven to be challenging as they tend to aggregate and become foreign materials in the final product. Lintecs DryDraw^{TM} technology offers an elegant solution where CNTs are continuously dry-drawn directly from a CNT forest producing a CNT sheet or cSlik^{TM} eliminating the need of dispersions of CNTs into solvents. The resulting cSilk^{TM} is transparent ($T_{total} \nabla 65$ to 85%), light weight and conductive (Resistivity ~ 650-1200 Ω/sq). However, for commercial product development, the need for higher transparency and higher conductive films is a must. Lintecs exclusive micro-bundling technology allows manipulating cSilk^{TM} s morphology by bundling CNTs within the cSilk^{TM}. Such method improves the conductivity of the film by more than 15% while increasing the transparency by 30% resulting on a film that has a resistivity of about 500 Ω /sq and with a transparency of $T_{total} \nabla 90\%$.

These high transparent and conductive films are highly flexible allowing for a wide range of applications suitable for commercialization.

P515

Multifunctional architectures based on cellulose nanocrystals and carbon nanotubes hybrids

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The dispersion of carbon nanotubes (SWNTs) through ultrasound treatment and stabilized by surfactants is a well-known technique. Here, we report the use of solid particles to fill this goal [1]. The cellulose nanocrystals (CNCs) are rod-like particles (120 nm long and 10 nm wide) and show great interest because of their renewability and abundance. We show by TEM and AFM experiments that it is possible to form hybrids of SWNTs and CNCs in aqueous media after sonication by a self-assembly process. Dispersions are obtained with a long term stability and the noncovalent approach allows to preserve the SWNTs properties. We have also shown that it is possible to use these dispersions to build multilayered thin films by the layer-by-layer method. Those films exhibit interesting multifunctional properties. Moreover, the CNCs show amphiphilic properties which offer the possibility to stabilize CNCs oil-in-water Pickering emulsions [2].

The aim of the present work is to explore more in details the CNCs/SWNTs dispersions and the conditions of their formation and to investigate the possibility to prepare 3D structures based on these dispersions or on the emulsions using SWNTs/CNCs hybrids.

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P516

Bioengineering applications of multi walled carbon nanotube based carpets

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Multi Walled Carbon Nanotubes (MWCNTs) due to their unique physical properties have been successfully applied in biomedicine. The novel approach is to use MWCNTs as scaffolds for tissue engineering i.e. in bone reconstruction, dentistry and oral regenerative medicine.

In this study, MWCNT based carpets were prepared and verified as potential scaffolds in tissue engineering. The quality of MWCNT based carpets were characterised by means of Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Infrared and Raman spectroscopy.

The analysis of cell attachment to MWCNT based scaffolds was studied by SEM and confocal microscopy. The osteosarcoma cell lines (U2OS), human skin fibroblasts (Detroit 551) and gingival fibroblasts (HGF-1) were used. In our research we investigated the cell adhesion, cell morphology as well as cytoskeleton organisation.

The physical structure of MWCNTs was compatible for adhesion of cells and no cytotoxic effect was observed. The difference between cell adhesion with MWCNT carpets and the type of used cell line was indicated. Moreover, the modification of MWCNT based carpets can improve the cell adhesion and growth. Therefore, the MWCNTs can be a suitable scaffold in cell culturing and dental tissue engineering.

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P517

Engineering the hot-carrier photoresponse in graphene heterostructures

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Graphene hosts a unique combination of electronic and thermal properties that sets it apart from any other optoelectronic material. Weak electron-lattice cooling allows an unusual kind of photo-response mediated by long-lived photogenerated hot carriers which can proliferate across the entire system [1,2]. Properties also include the exposed nature of graphenes two-dimensional electronic states and fast intraband Auger-type scattering, which allows photon energy to be efficiently captured as heat by ambient carriers. These features can be exploited to design novel transport regimes in graphene-based photoactive heterostructures [3].

Here we propose theoretically how the photoresponse in graphene Schottky junctions can be dominated by a new channel for energy transport: hot carrier advection. In this channel, electronic cooling occurs via thermionic emission of graphene hot carriers into a semiconductor material. Large hot carrier energy currents can overwhelm conventional diffusive electronic energy transport and dominate over electron-lattice cooling. Importantly, this regime features strongly coupled energy and charge currents that run vertically out of the graphene plane. This yields clear experimental signatures, such as large and tunable responsivities of graphene Schottky-junction photodetectors with a non-monotonic temperature dependence.

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P518

Developement of MoOx-CNT combinated buffer layer for performance improvement in organic solar cells

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Metal-oxide thin films have recently become good candidates as buffer layers for solving the contact problem in organic photovoltaic devices. Among the commonly used materials organic (e.g. PEDOT: PSS) and metal oxide semiconductors (MoOx, WO3, V2O5) are very promising because of their suitable optical and electrical properties, ambient stability, high work function, and practical solution processability. Instrinsic n-type behavior of MoOx enhances p-type dopping effect on carbon nanotubes (CNT) which have absorption in near-IR region, this makes significant improvement in solar cell efficiency. In this study, MoOx-CNT combinated buffer layer structure was developed and characterized.

MoOx thin films were prepared by spin and spray coating techniques on ITO/glass substrates and annealed at different temperatures and atmospheres. Single-Walled Carbon Nanotubes (SWCNT) used in this work were synthesized in fluidized bed reactor using chemical vapor deposition of acetylene gas at 800℃ for 30 min with Fe catalyst deposited on MgO support. Produced SWCNTs were coated on MoOx thin film to make the MoOx-CNT combinated buffer layer system. Organic solar cells consist of glass/ITO/MoOx-CNT /P3HT:PCBM/Al device structure. Thin films and OPVs were characterized with Scanning Electron Microscopy, Atomic Force Microscopy, X-Ray Diffraction, Raman Spectroscopy, UV-NIR Absorption Spectroscopy and device current-voltage measurements.

P519

Effect of structural parameters on transport properties of carbon nanotube networks

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We present non-invasive scanning probe methods to study the effect of structural parameters on the transport properties of carbon nanotube (CNT) network. We find the contact resistance of CNT scales inversely with nanotube diameter and having values in the range of mega Ohm; at diameters of less than 1.2 nm. Interestingly these contacts also modulate the source drain current up to 4 orders of magnitude. Larger diameter nanotubes form low resistive contacts and are characterized by high off current values. These findings highlight the importance of controlling structural homogeneity and reducing bundling of CNT for better device performance.

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P520

Sodium ion storage property of phosphorus molecules encapsulated in single-walled carbon nanotubes

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Lithium ion battery (LIB) has been widely used especially for portable electronic devices such as cell phones and notebook computers. Furthermore, in recent years, LIBs were begun to be used in electric vehicles and hybrid vehicles.With such increasing demand for LIBs, we would face cost problem of LIBs, because lithium resource is limited. Sodium ion battery (SIB) has attracted much attention as an alternative secondary battery. However, since graphite anode cannot be used for SIB, we have to develop new anode materials. We have investigated phosphorus materials as an SIB anode. It was elucidated that bulk phosphorus does not work well probably due to its low electric conductivity. Then we tried to use phosphorus molecules encapsulated in single-walled carbon nanotubes (P@SWCNTs). P@SWCNTs were prepared by heat treatment of the sealed glass tube in which SWCNTs and phosphorus powder samples were inserted. The obtained P@SWCNT samples were characterized by TEM, XRD, Raman and so on. It was found by electrochemical measurements that P@SWCNT works very nicely as an anode of SIB.

Friday

K5

When nanotube dreams come true

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Nanotubes of carbon and related materials are more than long nanowires with excellent charge and thermal transport properties [1]. The constrained cylindrical volume inside, with diameters around 1 nm, may be filled with atoms or molecules that often arrange in a very different way than in free space. In this way, selenium or sulfur atoms may reconnect inside the nanotube to helical or linear chains that may become metallic [2]. Nanotubes even act as natural pressure containers that selectively drive particular chemical reactions, including a transformation of functionalized diamonoid molecules to a diamond nanowire inside a nanotube [3].

Recent interest in layered black phosphorus and other potential 2D phosphorene allotropes [4] that connect to non-planar structures with virtually no energy penalty [5] suggests that phosphorene nanotubes should display a superior stability over their strained carbon counterparts [6].

Whereas individual nanotubes are straight, bundles of nanotubes are often observed as helical ropes. Natural coiling may traced back to combinations of chiral indices within the bundle [7]. Even more interesting is the possibility to twist nanotube ropes to reversibly store nanomechanical energy [8]. As a superior counterpart of twisted rubber cords, twisted nanotube ropes have the potential to store permanently and reversibly up to ten times more energy than Li-ion batteries within an unsurpassed temperature range.

Nanotube arrangement within a rope may be replicated in a complex carbon foam that could grow from carbon-saturated transition metal surfaces [9] and, while intrinsically semiconducting, displays a topologically protected conducting state at the surface [10].

The unique geometry of nanotubes inspires ideas about limitless phenomena that have not been imagined before. The enormous progress in the field is owed to scientists, who dared to try following unconventional ideas. Predictive calculations I will present offer a sound theoretical ground for imagining what has not been imagined before and for understanding, which nanotube dreams have a high potential of coming true.

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I10

Near-field and ultrafast optical microscopy of carbon nanotubes and graphene

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We report on our efforts to study the optical response of CNTs and graphene on nanometer length and femtosecond time scales. Sub-diffraction spatial resolution is achieved using tip-enhanced near-field optical microscopy. In this approach a sharp metal tip acts as an optical antenna enhancing both excitation and emission of a nearby object [1]. Photoluminescence, Raman scattering as well as photocurrent and electroluminescence images with sub 30 nm are obtained [2,3]. This allows us to visualize spatial heterogeneities of the optical responses hidden in confocal measurements and to investigate their microscopic origin.
We study the excited state dynamics and non-linear response of single CNTs and graphene on a time scale of 15 fs by laser pulse shaping. Spectral amplitude and phase shaping is used to control the emission spectrum of graphene and to follow the charge carrier relaxation dynamics [4]. We now aim at combining pulse shaping and near-field microscopy to obtain new insight into the ultrafast phenomena in nanocarbons.

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I11

Variance Spectroscopy Studies of Single-Walled Carbon Nanotubes

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A new experimental technique called Variance Spectroscopy will be described. It probes spectral variations among small regions of bulk samples resulting from statistical variations in composition. The method is applied to liquid suspensions of unsorted SWCNTs, which contain several distinct structural species emitting photoluminescence at characteristic near-IR wavelengths. Using dilute suspensions, focused excitation, sensitive multichannel detection, and quick data collection, we capture several thousand emission spectra representing independent spatial regions of the sample. The data sets are analyzed to find emission intensity mean and variance at each wavelength. We then combine the mean and variance spectra to obtain information unavailable from conventional methods, including abundances of different emissive species and their relative emission efficiencies. The data are further analyzed for correlations between intensity fluctuations at different wavelengths. This gives novel two-dimensional maps with off-diagonal peaks showing spatially correlated concentration variations for nanotubes of different types. These are from fragile “loose” aggregates of spectrally unperturbed SWCNTs, which may be precursors of familiar nanotube bundles. Results will be presented showing SWCNT loose aggregates under different conditions. We also use the method to study sonication-induced sample changes. Variance spectroscopy should prove a valuable tool for characterizing samples of carbon nanotubes or other nanoparticles with spectral heterogeneity.

I12

Comparing advanced functionalization routes to tailor 1D and 2D nanocarbons

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In this contribution I will present recent progress on unraveling the influence of charge transfer, local strain and hybridization on the electronic transport properties of single walled carbon nanotubes and graphene with special emphasis on the influence of basic correlation effects on the two particle excitation and the nature of the metallic ground state. In order to tailor their properties I will compare different functionalization routes and use resonance Raman, photoemission and x-ray absorption spectroscopy as probes. I will first briefly discuss recent results on charged and strained 2D graphene layers in graphite intercalation compounds and substitutionally doped graphene as well as intercalated and substituted 1D SWCNT. Then I will present a gas sensing model based on external functionalisation shows how reactive gases like nitric oxides are predominantly physisorbed on ultrapure SWCNT. I will also highlight the pathway how this interaction can be tailored by advanced filling reactions with metallocenes and metalacetylacetonates towards room temperature selectivity and sensitivity. As a last example I will review how such encapsulation inside SWCNT can be used for confined nanochemical reactions to stabilize new hybrid systems with novel electronic and optical properties.

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Ultra-long carbyne inside double-walled carbon nanotubes

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Angel Rubio[3,4], Kazuhiro Yanagi[5], Zachary Lapin[6], Lukas Novotny[6],
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4 Max Planck Institute for the Structure and Dynamics of Matter
5 Department of Physics, Tokyo Metropolitan University
6 ETH Zürich, Professur für Photonik

The extreme instability and strong chemical activity of carbyne, the infinite sp^1 hybridized carbon chain, are responsible for its low possibility to survive at ambient conditions.We successfully synthesized extremely long carbyne inside thin double-walled carbon nanotubes (as nanoreactor and protector). Their existence, structure, lengths and yield have been proved by Raman, HRTEM, STEM and XRD. The results show that the single-triple bonded carbyne including hundreds of carbon atoms have at least six new Raman peaks, some of which are even stronger than the G-band. Particularly, more than 200 nm carbynes were observed inside individual double-walled carbon nanotubes by near-field Raman microscopy. The optimum growth conditions, for example, diameter of the host tubes, annealing temperatures and time were carefully studied. The interaction and charge transfer between the carbynes and their host nanotubes were explored using resonance Raman, low-temperature Raman and also DFT calculations. Extracting the carbyne from the nanotubes was done by density gradient ultracentrifugation method, and the separated solutions were measured by Raman and absorption spectroscopies.

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NT15 Satellite Symposia

The NT15 Satellite Symposia and their Organizers

CCTN15: Tenth International Symposium on Computational Challenges and Tools for Nanotubes

Chief Organizer : David Tománek (Michigan State University, USA)
Local Organizer : Stephan Irle (Nagoya University, Japan)

MSIN15: Ninth International Workshop on Metrology, Standardization and Industrial Quality of Nanotubes

Chief Organizer : Ado Jorio (Federal University of Minas Gerais, Brazil)
Local Organizer : Hiromichi Kataura (AIST, Japan)
Organizers : Stephen Cronin (University of Southern California, USA)
Mildred S. Dresselhaus (MIT, USA)
Jin Zhang (Peking University, China)
Ming Zheng (NIST, USA)

CNTFA15: Third Carbon Nanotube Thin Film Electronics and Applications Satellite

Chief Organizer : Esko I. Kauppinen (Aalto University, Finland)
Local Organizer : Yutaka Ohno (Nagoya University, Japan)
Organizers : Hui-Ming Cheng (IMR, China)
Chongwu Zhou (University of Southern California, USA)

GSS15: Sixth Graphene and 2D Materials Satellite Symposium

Chief Organizer : Pertti Hakonen (Aalto University, Finland)
Local Organizer : Masataka Hasegawa (AIST, Japan)
Organizers : Katsunori Wakabayashi (NIMS, Japan)
Chun Ning (Jeanie) Lau (UCR, USA)

CNBMT15: Sixth Symposium on Carbon Nanomaterials Biology, Medicine & Toxicology

Chief Organizer : Masako Yudasaka (AIST, Japan)
Local Organizer : Yoshinori Sato (Tohoku University, Japan)
Organizers : Alberto Bianco (CNRS, France)
Emmanuel Flahaut (CNRS, France)
Kostas Kostarelos (University of Manchester, UK)
Dal-Hee Min (Seoul National University, Korea)

CCTN15

9:00 - 9:30

I1 **Understanding catalytic carbon nanotube growth through density functional theory calculations** (Andreas Larsson) ………… 374

9:30 - 10:00

I2 **Discussion on carbon precursor dissociation at initial stage of carbon nanotube growth** (Yasushi Shibuta) ………… 374

10:00 - 10:15

C1 **Quantum theory of the plasmon enhanced Raman scattering effect in hybrid nanotube systems** (Igor Bondarev) ………… 378

10:15 - 10:30

C2 **UV to terahertz signal conversion using graphene nanoribbons** (Yoshiyuki Miyamoto) ………… 378

10:30 - 11:15 **Coffee Break, Posters**

11:15 - 11:45

I3 **Geometric and electronic structures of nanocarbon hybrid materials** (Susumu Okada) ………… 375

11:45 - 12:00

C3 **Interplay of electron-phonon and electron-electron interactions in gate modulated Raman spectroscopy of graphene** (Eddwi Hesky Hasdeo) ………… 379

12:00 - 12:15

C4 **Controlling growth modes of SWNTs** (Yann Magnin) ………… 379

12:15 - 12:30

C5 **Relative Stability and local curvature analysis in carbon nanotori** (Jie Guan) ………… 380

12:30 - 13:30 **Lunch**

13:30 - 14:00

I4 **Recent progress and applications of the chiral-symmetry density-functional-theory program code for nanotubes** (Susumu Saito) ………… 375

14:00-14:30

I5 **Recent advances in understanding carbon nanotube growth through atomic scale simulations** (Erik C. Neyts) ………… 376

14:30-14:45

C6 **Prediction of dirac cones in 2D binary nanosheets** (Xuming Qin) ‥ 380

14:45 - 15:00

C7 **Atomistic simulation of the growth of defect-free carbon nanotubes** (Ziwei Xu) ······ 381

15:00 - 15:15

C8 **Electronic properties of twisted MoS2-nanotubes** (David Teich) ···· 381

15:15 - 15:30

C9 **Quantum chemical study on the excitation and optical properties of pi-stack aggregates of open-shell polycyclic aromatic hydrocarbons** (Ryohei Kishi) ······ 382

15:30 - 16:15 **Coffee Break, Posters**

16:15 - 16:45

I6 **Calculating core level binding energies for graphene and azafullerenes** (Toma Susi) ······ 376

16:45 - 17:15

I7 **Size dependent phase diagrams of Ni-C nanoparticles** (Christophe Bichara) ······ 377

17:15 - 17:30

C10 **Self-consistent approach to analysis of nanostructured-thermionincs** (Amir H. Khoshaman) ······ 382

17:30 - 17:45

C11 **Towards chirality-control: catalyst-free growth of single-wall carbon nanotubes on SiOy nanoparticles** (Teng Yang) ······ 383

Posters

MSIN15

15:30 - 16:30 **Coffee Break, Posters**

16:30 - 17:00

17:00 - 17:30

17:30 - 17:45

Posters

CNTFA15

16:15 - 16:45

I11 **Moldable and flexible double-walled carbon nanotube transparent conductive film and its application for next generation device**
(Takashi Oi) ········· 407

16:45 - 17:15

I12 **Flexible films of carbon nanotubes nanocomposites with graphene, nanowires and layered superconductors for functional applications** (Anvar A. Zakhidov) ········· 407

17:15 - 17:30

C1 **Single-carbon-nanotube photonics and optoelectronics**
(Yuichiro K. Kato) ········· 408

17:30 - 17:45

C2 **Mapping charge transport in semiconducting carbon nanotube networks by electroluminescence and Raman microscopy**
(Jana Zaumseil) ········· 408

17:45 - 18:00

C3 **Lithographically patternable and lightweight CNT-Cu composite interconnects showing longer lifetime and comparable conductivity to pure Cu** (Atsuko Sekiguchi) ········· 409

Posters

GSS15

9:00 - 9:45

K1 **Atomic imaging and spectroscopy of low-dimensional materials** (Kazu Suenaga) ········ 426

9:45 - 10:15

I1 **Moiré superlattice** (Pilkyung Moon) ········ 427

10:15 - 10:30

C1 **Revealing the mechanical properties of two-dimensional materials by direct in situ transmission electron microscopy** (Daiming Tang) ········ 430

10:30 - 11:15 **Coffee Break, Posters**

11:15 - 11:45

I2 **Solution processing and device integration of two-dimensional black phosphorus** (Mark C. Hersam) ········ 427

11:45 - 12:00

C2 **Probing spectroscopic properties of BN and black phosphorous layers** (Etienne Gaufrès) ········ 430

12:00 - 12:15

C3 **Effective switching of graphene-boron nitride nanotube heterojunctions** (Yoke Khin Yap) ········ 431

12:15 - 12:30

C4 **Exploring atomic defects and their dynamic behaviors in monolayer MoS_2 by ADF-STEM** (Chuanhogn Jin) ········ 432

12:30 - 13:30 **Lunch**

13:30 - 14:15

K2 **Advances in raman spectroscopy of graphene and layered materials** (Andrea C. Ferrari) ········ 426

14:15 - 14:45

I3 **Transport studies in black phosphorus field effect transistors** (Barbaros Oezyilmaz) ········ 428

14:45 - 15:00

C5 **Optical properties of high-quality WS_2 monolayers grown on graphite** (Yu Kobayashi) ········ 432

15:00-15:15

C6 **Substrate effect on photoluminescence properties of tungsten disulfide atomic layers** (Mitsuhiro Okada) ········ 433

15:15 - 15:30

C7 **Polymer organic-light emitting diodes on high-flatness transparent sheet with graphene films synthesized by plasma treatment** (Yuki Okigawa) ···························· 433

15:30 - 16:15 **Coffee Break, Posters**

16:15-16:45

I4 **Heterostructures based on CVD transition metal dichalcogenides** (Lain-Jong Li) ···························· 428

16:45-17:15

I5 **Catalytic growth of monolayer graphene on Ge surface** (Dongmok Whang) ···························· 429

17:15-17:30

C8 **Creation of boron-doped graphene by thermal decomposition of B4C thin film on SiC (000-1)** (Atsushi Masumori) ···························· 434

17:30-17:45

C9 **Layer-by-layer oxidation of atomically thin WSe_2: Implications for two-dimensional MOSFETs** (Mahito Yamamoto) ···························· 434

17:45-18:00

C10 **Gap states analysis in gapped bilayer graphene by conductance method** (Kosuke Nagashio) ···························· 435

18:00-18:15

C11 **Edge-channel interferometer in a graphene quantum Hall pn junction** (Tomoki Machida) ···························· 435

Posters

CNBMT15

9:00 - 9:45

K1 **Biomaterial applications and safety of carbon nanotubes**
(Naoto Saito) ······ 468

9:45 - 10:00

C1 **Carbon nanotubes-polymer electrospun nanofibers as biocompatible scaffolds for neuronal cells differentiation**
(Teresa Gatti) ······ 472

10:00 - 10:15

C2 **Carbon nanohorns boost alkaline phosphotase activity in co-culture of macrophages and mesenchymal stem cells**
(Eri Hirata) ······ 472

10:15 - 10:30

C3 **Biodegradation of carbon nanohorns in macrophage cells**
(Minfang Zhang) ······ 473

10:30 - 11:00 **Coffee Break, Posters**

11:00 - 11:30

I1 **Safety evaluation of fullerene and development of new drugs containing fullerene derivatives** (Hisae Aoshima) ······ 469

11:30 - 12:00

I2 **Fullerene as a new cosmeceutical: From nanotechnology to cosmetic nanomedicine** (Shigeki Inui) ······ 469

12:00 - 12:15

C4 **Synthesis of polyglycerol-functionalized graphene and SWNTs, and their application to carrier of a photosensitizer in photo-dynamic therapy** (Hongmei Qin) ······ 473

12:15 - 12:30

C5 **Application of oxygen-doped carbon nanotubes as imaging probes and fluorescent labels** (Yoko Iizumi) ······ 474

12:30 - 13:30 **Lunch**

13:30 - 14:15

K2 **Photothermal therapy with single-walled carbon nanotubes to treat cancer metastasis** (Zhuang Liu) ······ 468

14:15 - 14:45

I3 **Compared environmental impact of different carbon nanoparticles**
(Emmanuel Flahaut) ······ 470

14:45 - 15:00

C6 **Highly ordered one-dimensional fullerene crystals for concurrent control of macroscopic cellular orientation and differentiation towards large-scale tissue engineering** (Kosuke Minami) ·················· 474

15:00 - 15:15

C7 **Fingerprinting in vivo protein corona-carbon nanohorn interaction** (Srivani Veeranarayanan) ·· 475

15:15-15:30

C8 **Carbon nanomaterials negatively affect cell viability and gene expression** (Kyoungtae Kim) ··· 475

15:30 - 16:15 **Coffee Break, Posters**

16:15 - 16:45

I4 **Biosensors based on graphene oxide for drug screening** (Dal-Hee Min) ·· 470

16:45 - 17:15

I5 **Photothermal conversion of functional nanocarbons for biotechnological applications** (Eijiro Miyako) ····································· 471

17:15 - 17:30

C9 **Bio-mimetic membranes and bio-functionalization of graphene by dip-pen nanolithography** (Aravind Vijayaraghavan) ······························ 476

17:30-18:00

I6 **Magnetic manipulation, imaging and therapy using carbon nanotube/metallic nanoparticle hybrids** (Alberto Bianco) ················· 471

Posters

CCTN15

I1

Understanding catalytic carbon nanotube growth through density functional theory calculations

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To utilize the unperturbed inherent electrical properties of carbon nanotubes it's necessary to produce the single-walled type (SWNTs) of specific diameter and chirality (index). Catalytic CVD growth has scored tremendous advances in controlling the diameter and, using template catalysts and seed-molecules, product with one single index. Only certain metals act as catalyst and we have shown through density functional theory (DFT) computations that specific for CNT growth is its ability to stabilize the growing end and to prevent it from closing.

Thus the catalytic metal-CNT binding strength follows a 'Goldilocks criterion' where the tube-end cannot bind too weak or too strong to the metal. Our recent DFT work show which of all 1st, 2nd and 3rd row transition metals are in this zone, and could be used as catalysts in CVD. We also show how metals outside the zone (non-catalytic) can be combined to work as catalysts. In addition, we will present work where we have compared experimental product with SWNT stability from DFT, for which we surprisingly find strong correlation. We will shed light on how armchair and zigzag ends form bonds that are individually equally strong, but collectively show huge stability differences.

I2

Discussion on carbon precursor dissociation at initial stage of carbon nanotube growth

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The growth mechanism of carbon nanotubes (CNT) has been widely discussed both from experimental and computational studies. Regarding the computational studies, most of the studies focuses on the aggregation of isolate carbon atoms on the catalytic metal nanoparticle, whereas the initial dissociation of carbon source molecules should affect the yield and quality of the products [1]. Under such circumstances, we have studied the dissociation process of carbon source molecules on the metal surface by the ab initio molecular dynamics simulation [2,3]. In the study, we investigate the ethanol dissociation on Pt and Ni clusters by ab initio MD simulations to discuss the initial stage of CNT growth by alcohol CVD technique. In the presentation, our recent studies will be introduced after a brief review of this issue.

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I3

Geometric and electronic structures of nanocarbon hybrid materials

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Hybrid structures of nanocarbon materials with foreign materials usually exhibits interesting variations arising from dimensionality of constituents, interunit spacing, and structural hierarchy. In the present paper, we will discuss the geometric and electronic structures of various nanocarbon hybrid structures consisting of fullerenes, nanotubes, and graphene using the first-principles total-energy calculation based on density functional theory.

I4

Recent progress and applications of the chiral-symmetry density-functional-theory program code for nanotubes

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We have studied systematically the electronic properties of carbon nanotubes using explicitly the chiral symmetries of the system within the framework of the density functional theory. While in the past CCTN6 symposium, we reported systematically the electronic structure of carbon nantoubes without the geometry optimization [1], we now can optimize the geometries of carbon nanotubes using chiral-symmetry program code [2]. In this talk we report the presence of the "intrinsic twisting" in chiral nanotubes and the effect of the external twisting on the electronic properties of carbon nanotubes. In addition, we will report the extension of the present program code to the boron-nitride nanotubes.

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I5

Recent advances in understanding carbon nanotube growth through atomic scale simulations

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Atomistic simulations have contributed significantly to our understanding of the metal-catalyzed CNT growth process. Such simulations revealed detailed insights in e.g. carbon dissolution and surface seggregation [1, 2], carbon polyyne formation at the surface [3], and cap lift off [4, 5]. First, I shall highlight a selection of simulations which have provided such insights and demonstrate how they have contributed to our understanding of the growth process [6]. Subsequently, a number of recent efforts will be highlighted which address previously uncovered areas, including ion bombardment [7, 8], growth from hydrogen containing growth precursors [9], and the application of accelerated atomic scale techniques for studying the dynamics of the growth process [10].

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I6

Calculating core level binding energies for graphene and azafullerenes

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X-ray photoelectron spectroscopy (XPS) combined with first principles modeling is a powerful tool for determining the chemical composition of novel materials, such as graphene and carbon nanotubes doped with heteroatoms [1].

As a model system, we calculated the C1s binding energy of graphene using two methods based on density functional theory total energy differences: a calculation with an explicit core-hole [2], and an all-electron extension of the delta self-consistent field method [3], with the latter giving absolute energies close to graphite measurements.

Furthermore, we analyzed spectra of C_{60} and $C_{59}N$ fullerene powders [4], elucidating the identity of the oxygen signal. The calculations also allow us to quantify the effect of $C_{59}N$ dimerization on its N1s core-level shift (0.4 eV), with implications for interpreting other nitrogen-doped systems.

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I7

Size dependent phase diagrams of Ni-C nanoparticles

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Carbon nanotube synthesis critically depends on the chemical and physical states of the catalyst particle from which they grow. In the temperature range (600-1000°C) of SWNT synthesis, pure isolated Ni nanoparticles are solid. Under CVD synthesis conditions, reactive carbon may stay adsorbed on the surface, or diffuse to subsurface or in the core of the nanoparticle, thereby inducing a partial or complete melting.
On the basis of the tight binding model developed for the Ni-C system coupled with grand canonical Monte Carlo simulations [1, 2, 3], we calculate size dependent phase diagrams for Ni-C alloys. For NP sizes of about 3 nm, we find that i) the eutectic point lies around 1000K, much lower than the bulk one, ii) a large solid core / molten or amorphous shell domain is found instead of the two phase solid liquid region and iii) carbon segregation from a solid NP surface can take place only at temperatures below 850 K. We discuss the consequence of these findings on our understanding of the SWNT growth mechanisms.

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C1

Quantum theory of the plasmon enhanced Raman scattering effect in hybrid nanotube systems

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The quantum theory of resonance Raman scattering is developed for a dipole emitter, the two-level system (TLS), coupled to an interband plasmon resonance of a carbon nanotube (CN) [1]. The model used belongs to a broad class of driven four-level quantum systems [2], with an important distinction that instead of being driven by an external periodic field, scattering by the interacting TLS-CN system is controlled by plasmon-induced quasi-static electric fields in the CN near-surface zone. The analytical expression obtained for the Raman cross-section covers both weak and strong TLS-plasmon coupling, and shows a dramatic enhancement due to the formation of hybridized (dressed) states when two subsystems, the TLS and the CN, enter the strong coupling regime. The theory applies to atomic type species such as atoms, ions, molecules, or semiconductor quantum dots that are physisorbed on the nanotube walls. The model provides a unified description of the near-field plasmon enhancement effects, and can be used in designing nanotube based electromagnetic sensing substrates for single atom detection, precision spontaneous emission control, and manipulation.

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C2

UV to terahertz signal conversion using graphene nanoribbons

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In this presentation, we propose a signal conversion from UV light into terahertz (THz) radiation by performing the first-principles simulations. By employing the real-time propagation time-dependent density functional theory (rtp-TDDFT) with Ehrenfest molecular dynamics (MD), we monitored induced electric field (E-field) near a sheet of graphene nanoribbon under applying alternating E-field with frequencies of UV region. We have selected armchair nanoribbon as our target due to their thermal stability compared to zigzag nanoribbons.

We applied alternative E-field on armchair graphene nanoribbons, with several ribbon widths N=7, 9, 11, where N expresses a number of C-C dimers parallel to the ribbon axis along with the ribbon width. When frequency of applied E-field is above 6 eV, the induced E-field suddenly increases beyond the intensity of the applied one. Meanwhile the increased intensity is not sustainable, but shows modulation of E-field in a period around 100 fs corresponding to 10 THz oscillation.

The increase and modulation can be interpreted as resonant response and interference of several electronic states and we expect current finding would be useful for THz radiation by applying graphene nanoribbon.

C3

Interplay of electron-phonon and electron-electron interactions in gate modulated Raman spectroscopy of graphene

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The electron-phonon and the electron-electron interactions interplay in graphene and are observed in the Raman spectra around ～1600 cm^{-1} (G band). The existence of the gapless linear energy bands (Dirac cones) in graphene modifies phonon energy, spectral broadening, and spectral lineshape of the Raman spectra. One of the well-known phenomena is the Kohn anomaly effect, in which the phonon energy (lifetime) becomes lower (shorter) due to the interaction between a phonon and an electron-hole pair in the linear energy band. The other phenomenon is the asymmetric spectral shape of phonon spectra, also known as the Breit-Wigner-Fano (BWF) lineshape, which long been observed in metallic nanotubes and recently observed in graphene as a function of Fermi energy. The origin of the BWF lineshape in graphene is due to the quantum interference effect of phonon spectra with the electronic Raman spectra (ERS) [1]. Taking both phenomena into account, we successfully reproduce the Fermi energy dependence of frequency shift, spectral linewidth, and spectral asymmetry of the G band Raman spectra [2].

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C4

Controlling growth modes of SWNTs

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A detailed understanding of the catalyst/nanotube interface, under actual growth conditions, is probably a key to a selective synthesis of single wall carbon nanotube (SWNT). Through careful Transmission Electron Microscopy observations [1], so called tangential and perpendicular growth modes were identified and Grand Canonical Monte Carlo simulations based on a tight binding model for nickel and carbon alloys [2, 3, 4], were used to analyze these growth modes at the atomic scale.

Further numerical investigations presented here show that, when catalyst nanoparticles are small enough to be (partially) molten under the synthesis conditions,- i. e. with a diameter below 3 nm -, these growth modes are directly related to the average carbon content in the catalyst nanoparticles. They also show that carbon incorporation energetics and statistics at the SWNT/nanoparticle interface depend on both nanotube helicity and carbon content, thus possibly indicating a route towards a full control of the nanotube structure during synthesis.

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C5

Relative stability and local curvature analysis in carbon nanotori

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We introduce a concise formalism to characterize nanometer-sized tori based on carbon nanotubes and to determine their stability by combining ab initio density functional calculations with a continuum elasticity theory approach that requires only shape information. We find that the high strain energy in nanotori containing only hexagonal rings is significantly reduced in nanotori containing also other polygons. Our approach allows to determine local curvature and link it to local strain energy, which is correlated with local stability and chemical reactivity.

C6

Prediction of dirac cones in 2D binary nanosheets

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The formation of Dirac cones in electronic band structures via isomorphous trans-formation is demonstrated in 2D SiC, GeC, and GeSi monolayer sheets.We combined density functional and tight-binding calculations to show that 2D SiC featuring C-C and Si-Si atom pairs possesses Dirac cones (DCs), whereas an alternative arrangement of C and Si leads to a finite band gap. The origin of Dirac points is attributed to bare interactions between Si-Si bonding states (valence bands, VBs) and C-C antibonding states (conduction bands, CBs), while the VB-CB coupling opens up band gaps else-where. A mechanism of atom pair coupling is proposed, and the conditions required for DC formation are discussed, enabling one to search for a class of 2D binary Dirac fermion systems solely by performing DF calculations for pure and alternative binary structures.(Xuming Qin, Yi Liu et al., J. Phys. Chem. Lett., 6, 1333-1339, 2015)

C7

Atomistic simulation of the growth of defect-free carbon nanotubes

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Atomistic simulation of defect-free singlewalled carbon nanotube (SWCNT) growth is essential for the insightful understanding on the SWCNTs growth mechanism. Despite the extensive efforts paid in the past two decades, the goal has not been completely achieved, due to the huge time scale discrepancy between atomistic simulation and the experimental synthesis of SWCNT, as well as the lack of accurate potential energy surface (PES). Here, we report atomistic simulations of defect-free SWCNT growth by using a new generation of carbon-metal potential and a hybrid method, in which a basin-hopping strategy is applied to facilitate the defect healing during the simulation. The simulations reveal a narrow diameter distribution and an even chiral angle distribution of the growth of SWCNTs from liquid catalyst, which is in agreement with most known experimental observations.

C8

Electronic properties of twisted MoS_2-nanotubes

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During the last years, intensive research has been done on electronic properties of inorganic nanotubes (INT) built by metal dichalcogenides. They possess desirable intrinsic band gaps and intrinsic stick-slip behavior (1) indicating their potential for nanoelectro-mechanical devices.

Here, we present a theoretical study on the electronic properties of MoS2-nanotubes suspended to mechanical strain and torsion. To minimize computational cost, we performed DFTB (2) calculation with helical boundary conditions (3) allowing us to choose the size of the unit cell independent from the applied twist angle, although the initial translational symmetry is broken. We show that twisting an MoS2-nanotube leads to a decrease in the energy gap and therefore an increase in conductivity, following the phenomenological transport model. Our calculations are verified through experimental studies on twisted INTs exhibiting a highly repeatable response to torsion and strain.(4)

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C9

Quantum chemical study on the excitation and optical properties of pi-stack aggregates of open-shel polycyclic aromatic hydrocarbons

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Geometric features and physical properties of the pi-stack type one-dimensional aggregates of polycyclic aromatic hydrocarbons (PAHs) incorporated in carbon nanotubes have been investigated intensely as novel multi-functional materials. On the other hand, several PAHs and their related molecules having unpaired electron(s), i.e., open-shell PAHs, have attracted much attention since they are expected to show unique covalent-like interactions between the monomers in solution and/or in crystal phase. In this study, we investigate the relationship between the structures and electronic excitation properties of molecular aggregates composed of open-shell PAHs, and then discuss the open-shell character dependence of their static and dynamic optical response properties. We here employ several PAHs, such as a phenalenyl, as the monomer unit, and then we evaluate the excitation properties of several pi-dimers and -tetramers with different inter-monomer distances and orientations by using the quantum chemical calculations. The linear and third-order nonlinear optical response properties of these systems are evaluated by the sum-over-states method, and then we discuss the structural dependences of open-shell characters and optical response properties of molecular aggregates composed of open-shell PAHs.

C10 **CCTN P1**

Self-consistent approach to analysis of nanostructured-thermionincs

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There has been a surge of interest in the field of thermionic conversion due to promising features offered by nanomaterials and nanotechnology [1]. The current models, which were initially obtained for macroscopic devices, are incapable of capturing all the aspects of nanostructured devices. We report on a model that calculates the output characteristics of thermionic converters with a higher precision and range of applicability than the existing models. The model is based on coupling the Poisson and the Vlaslov equation and solving for the potential profile. This model can be applied to a wider range of parameters, including temperatures, surface areas, inter-electrode distances and workfunction. More importantly, this methods high numerical precision and flexibility can be used to solve the reverse problem and to obtain the internal parameters of the device from experimental data. As an experimental case, a carbon nanotube forest was used as the emitter of a thermionic converter and heated to thermionic emission temperatures using a low-power focused laser beam. The current-voltage characteristics were measured and used to solve the reverse problem. The values of internal parameters, such as the workfunction of carbon nanotubes and the temperature, were consistent with the values measured through other methods.

C11

Towards chirality-control: catalyst-free growth of single-wall carbon nanotubes on SiOy nanoparticles

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Chirality control (CC) during CNT growth becomes increasingly important along with the tremendous success of CNT in so many applications. The metallic catalysts which have demonstrated their important role in CC have its unavoidable limitations such as pollution. Therefore non-metallic catalyst becomes appealing. The chirality control of catalyst-free growth of single-wall carbon nanotubes on SiOy nanoparticles have been demonstrated to be possible. Some vague experimental demonstrations from the literature seem insufficient. In this talk, we show how we understand the mechanism behind it by combining ab initio molecular dynamics simulations and pair distribution function (PDF) analysis.

CCTN P1 ※ Please refer to **C10**

CCTN P2

Quantification of carbon nanotube film properties from scanning electron microscope images

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We report a strategy for quantifying the inter-tube spacings in semi-random[1] CNT films based on scanning electron microscope (SEM) images. First, image editing software is used to calculate the average apparent CNT diameter and to paint the intertube regions with a distinctive color (color A) absent in the CNT pixels. This image is inputted into MATLAB and analyzed via the following algorithm. The program sweeps along each column of the image. In order to determine the position of each CNT along the scan line, the program searches for stretches of non-A pixels with lengths equal to or greater than the apparent diameter of the CNTs. The position of the topmost edge of every CNT along the scan line is then recorded. The procedure is repeated for all columns of the image and the resulting matrix contains the position of each CNT along each column. Finally, the distances between the adjacent CNTs are extracted from this matrix. The same procedure is implemented on the transpose (inverted) image to minimize the error caused by CNTs parallel to the scan line. The probability distribution is plotted from the combination of these data, and the real CNT diameter is used in the final calculation.

CCTN P3

Plasma-assisted CNT etching mechanisms in the initial growth stage: combined molecular dynamics and monte carlo study

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Hydrogen enhances CNT growth by assisting in catalyst activation. It may, however, also hinder the formation of graphitic carbon, if its concentration is too high, e.g., in H2-plasmas. The precise etching behavior of the H2 plasma during the early stages of CNT growth is still not fully understood. We here study etching mechanisms of the cap and incipient (defective) nanotubes in comparison with ideal nanotubes to understand the effect of atomic H on the initial nucleation stage of the CNT growth. The hydrogenation and etching processes are investigated by combined MD and force-bias Monte Carlo (tfMC) simulations at 1600 K. In the initial etching stage, three specific stages can be distinguished, i.e., 1) CNT hydrogenation and H clustering on the surface; 2) breaking of the first C-C bond; and 3) hole creation or etch pit formation. Due to the hydrogenation, cap structures can also convert to vertical graphene patches. During the hydrogenation/etching process, different types of etching CxHy species in addition to desorbed H2 molecules are found in the gas phase. The results help to understand the etching behavior of H2-plasmas on the initial stages of CNT growth.

CCTN P4

CNT cap nucleation from hydrocarbons:combined molecular dynamics and montecarlo simulations

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Cap nucleation and the effect of atomic hydrogen on the growth are still not fully understood. We here study the atomistic mechanisms of cap nucleation and the role of hydrogen atoms during the growth process from hydrocarbon species, i.e., $C2H2$, $C6H6$, $CH4$ molecules as well as $C2H$ and $CH3$ radicals, by means of hybrid MD / force-bias MC simulations. Four nucleation stages are distinguished, including graphitic network formation and subsequent cap lift-off through the intermediate formation of vertically oriented, not fully dehydrogenated or/and rehydrogenated graphitic islands. In the intermediate nucleation stages, these vertical graphenes gradually lose their H atoms depending on the growth temperature and type of hydrocarbon species, as well as on their flux. Subsequently, dehydrogenation allows these graphene patches to curve over the surface, connect, and form a continuous graphitic network, which eventually leads to cap formation. The results indicate that controlling the extent of dehydrogenation offers an additional parameter to control the nucleation of CNTs. Overall results lead to a better understanding of the initial stages of hydrocarbon-based CNT growth at the atomic level.

MSIN15

I1

3D electron tomography for the structural quantification of carbon nanotube networks in unidirectional nanocomposites

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Recent advances in fabricating controlled-morphology aligned carbon nanotube assemblies with ultra-high volume fractions create unique opportunities for markedly improving the performance of next-generation advanced materials, with tailored anisotropic properties. However, the expected improvements in performance of the CNTs have proven difficult to realize. There is a considerable gap between theoretical predictions and the experimentally-determined properties of advanced polymer nanocomposites. The divergence between theory and experiment strongly suggests that the initial assumptions about the PNC structure may be inaccurate. The purpose of our work is to provide precise, quantitative data on the PNC morphology to resolve this discrepancy and to provide detailed process-structure-property relationships.

We have developed a novel imaging protocol, using energy-filtered electron tomography, for the fast and accurate morphological characterization of aligned carbon nanotube reinforced polymer nanocomposites. This rich, high-quality 3-dimensional (3D) microstructural data can be used to perform a detailed quantitative analysis of important parameters such as volume fraction, alignment, bundle/network topology, 3D waviness, etc. Our analysis reveals a non-linear evolution of the underlying CNT structure with increasing CNT volume fraction, which helps to explain the previously-measured nonlinear trends in property enhancements at high packing fractions.

I2

Accuracy of test methods for determination of resistance of carbon nanotubes

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Carbon nanotubes (CNTs) possess extraordinary electric transport phenomena. The promising applications have been proposed. For example, CNT-based interconnects are a prospective alternative for conventional Cu interconnects. On the other hand, the resistive characteristics have not yet been systematically investigated. This is because these characteristics are very sensitive to the protocol and the measurement conditions. The resistance changes not only depend on the length and the diameter of CNT, but also the current density, the substrate to hold the individual CNT, and the circumstances. Furthermore, the individual CNT reaches to the nanometer dimension, the contact resistance has a large impact on the measurement. These bottlenecks impede not only the practical interconnect application but also developments of various nano-electronic applications.

We report four-probe resistance measurements on individual multi-walled CNTs. The measurement was performed in scanning electron microscope (SEM). The choice of the probe was crucial in order to obtain the accurate result. The current-voltage (IV) characteristics changed during the SEM observation, probably due to the electronbeam induced charge-up phenomena. These results prove that the international standardization of the test method is indispensable for the accurate and reproducible measurement. We show the protocol which has been proposed in the International Electrotechnical Commission, IEC.

I3

Toolset for characterizing polymeric nanocomposites

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As nanotechnology based on carbon nanomaterials is approaching maturity with widespread applications, it begins to require significantly improved measurements with higher resolution and accuracy than has previously been practiced. Measurement methods provide a support throughout the innovation process from initial idea, through design manufacture, conformity assessment and marketing to the finished product. One of the key markets today is for materials with improved thermal, mechanical and electrical performance. Conventional and advanced techniques such as spectroscopies, thermal analysis, electron and probe microscopies, mechanical tests, electrical and electrochemical measurements, among others, should be taken in consideration when developing a material. The objective is to show our choice of techniques in the process of develop each individual application in the field of polymeric nanocomposites. The results obtained for epoxy and polyurethane composites produced with carbon nanotubes and graphene will be presented in the effort to understanding the intercomparability of different techniques.

I4

Simple synthesis of oxygen-doped single-walled carbon nanotubes and their application as fluorescent probes

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It has been found that the photoluminescence (PL) efficiency of single-walled carbon nanotubes (SWCNTs) can be enhanced by substituting oxygen atoms to the carbon network of the tube wall [1]. The oxygen-doped SWCNTs (o-SWCNTs) have been mostly prepared by the exposure of ozone to the SWCNTs solution under the light. This method can provide only a small amount of o-SWCNTs, and the surfactants are normally adsorbed on the surface of the obtained o-SWCNTs, which prevents further applications of the material. Recently, we found a very simple method for obtaining o-SWCNTs in bulk. In this meeting, the synthesis method and the characterization of the o-SWCNTs, and their application as in-vivo and in-vitro near-infrared imaging probes will be reported.

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I5

Photophysics of localized excitons in carbon nanotubes

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Recent studies have established chemical charge-carrier doping [1,2], side-wall functionalization [2-4] and temperature-driven exciton localization [5,6] as means to modify the photophysics of semiconducting carbon nanotubes. Modified carbon nanotubes are particularly attractive for novel quantum applications by virtue of bright [5] non-classical [6,7] emission from localized excitons and spin-selective optical transitions of charged excitons [8]. In this context we will discuss the spectral signatures of exciton localization in different carbon nanotube materials and present our most recent experimental studies of carbon nanotubes in field-effect devices.

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I6

Probing luttinger liquid in metallic carbon nanotubes

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Metallic carbon nanotubes provide an ideal platform to explore Luttinger liquid physics due to the strong quantum confinement in carbon nanotubes. Although electrical measurements has observed transport behavior consistent with the Luttinger liquid, no spectroscopy signature of Luttinger liquid has been observed previously. Here we will report our recent progress to probe Luttinger liquid plasmon excitation in metallic carbon nanotubes using single-tube spectroscopy.

I7

Measurement of resistance induced by a single potassium atom on chiral-angle known nanotubes: understanding the impact of a model scatterer for nanoscale sensors

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Impurity-induced carrier scattering is expected to be dependent on the chirality of nanotubes and the nature of scattering potentials induced by impurities. Such scattering is still poorly understood because it has been impossible to measure the impact of impurities on resistance of carbon nanotubes with known chirality.

We have measured the scattering strength of charged impurities on semiconducting single-walled carbon nanotubes with known chirality. The resistivity of nanotubes is measured as a function of the density of adsorbed potassium atoms, enabling the determination of the resistance added by an individual potassium atom. Holes are scattered 26 times more efficiently than electrons by an adsorbed potassium atom. The determined scattering strength is used to reveal the spatial extent and depth of the scattering potential for potassium, a model Coulomb adsorbate, paving way for rational design of nanotube-based sensors.

I8

Efficient semiconducting single-walled carbon nanotube sorting with a removable solubilizer based on dynamic supramolecular chemistry

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As-produced single-walled carbon nanotubes (SWNTs) contain semiconducting- and metallic-tubes, and it is still a great challenge to develop an efficient technique to purify the semiconducting-tubes. Synthetic polymers such as polyfluorenes have advantages, such as non-destructive, simple and versatile modifications in their chiral-selectivity by design. Although, the polymers are usually tightly hold onto the tubes, which make it difficult to remove them from the extracted SWNTs. For the achievement of ultra-pure purification of semiconducting-SWNTs, any wrapping polymers should be removed.

In an effort to develop a removable polymer with high semiconducting-SWNT-selectivity, we have designed and synthesized a family of supramolecular polymers based on metal-ligand coordination[1] and hydrogen-bonding. The building-blocks consist of fluorene moieties to achieve chiral selectivity and they are linked via reversible bonding. The purity of the obtained semiconducting-SWNTs was up to 99% in the Raman spectroscopy and the polymers were easily removed just by adding external stimuli, such as acid treatment or changing solvents. The X-ray photoelectron spectroscopy revealed that the resulting semiconducting-SWNTs were free from the used surfactant molecules.

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I9

High throughput methods for evaluating the chirality distributions of SWCNTs

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High performance field effect transistor (FET) will be the killer application of carbon nanotubes (CNTs). However, according to the International Technology Roadmap for Semiconductors (ITRS 2011 edition), Key challenges for carbon nanotubes to be viable in high performance FETs is the requirement for processes that provide a tight distribution of semiconductor bandgaps, and A methodology to evaluate a purity of semiconducting CNTs with a ppt-level precision should be developed. Here we show our efforts on developing high throughput methods for evaluating the chirality distributions of SWCNTs, which will greatly speed up the successful application of CNTs in high performance FETs.

The first high throughput method is low voltage SEM (LV-SEM). The LV-SEM image of CNTs possess the contrast comes from the conductivity and bandgap, which enables direct and efficient evaluation of the conductivity and bandgap distributions of CNTs.

The second high throughput method is the Rayleigh imaging microscopy, in which true-color real-time imaging of CNTs can be easily achieved via enhanced Rayleigh scattering. Consequently colorful CNTs on substrates can be directly imaged under an optical microscope, which facilitates high throughput chirality assignment of CNTs.

The aforementioned approaches are not restricted to SWCNTs, which can also be applied to other nanomaterials.

C1 **MSIN P11**

TEM investigations of SWNTs and catalyst nanoparticles

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In this work, we report our constant efforts in systematical investigations of size distributions of active and inactive nanoparticles, and of the SWNTs diameters and structures. Two synthesis reactors based on floating catalyst CVD have been used to synthesize the SWNTs. They differ by the way how the catalyst Fe nanoparticles are generated: chemical decomposition of a ferrocene precursor in the first case, and direct injection of nanoparticles formed by a spark discharge generator in the second one. Both use CO as a carbon source and Fe as catalyst nanoparticles. An aberration-corrected JEOL-2200FS transmission electron microscope was used to carry out the measurements. The results indicated that in the spark reactor the general size distribution of Fe nanoparticles is shifted towards smaller size compared to the ferrocenen reactor while the average SWNT diameters in both cases show little difference from each other. HRTEM imaging showed that under these growth conditions, nanotubes are clearly growing in perpendicular mode. It is also shown that with nanoparticles from the spark generator, one can better control the catalyst particle size and concentration, thus to control the nanotube concentration in the gas phase to prevent SWNT bundling, and fabricate sparse SWNT networks for high performance electronics.

C2 **MSIN P12**

Redox sorting of carbon nanotubes

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This work explores the role of redox chemistry in a number of SWCNT sorting processes. Using a polyethylene glycol (PEG)/dextran (DX) aqueous two-phase system, we show that electron-transfer between redox molecules and SWCNTs triggers reorganization of the surfactant coating layer, leading to strong modulation of nanotube partition in the two phases. While the DX phase is thermodynamically more favored by an oxidized SWCNT mixture, the mildly reducing PEG phase is able to recover SWCNTs from oxidation and extract them successively from the DX phase. Remarkably, the extraction order follows SWCNT bandgap: semiconducting nanotubes of larger bandgap first, followed by semiconducting nanotubes of smaller bandgap, then non-armchair metallic tubes of small but nonvanishing bandgap, and finally armchair metallic nanotubes of zero bandgap. Furthermore, we show that redox-induced surfactant reorganization is a common phenomenon, affecting nanotube buoyancy in a density gradient field, affinity to polymer matrices, and solubility in organic solvents. These findings establish redox modulation of surfactant coating structures as a general mechanism for tuning a diverse range of SWCNT sorting processes, and demonstrate for the first time that armchair and non-armchair metallic SWCNTs can be separated by their differential response to redox.

Reference: Gui et al. Nano Letters, doi:10.1021/nl504189p, 2015

C3 **MSIN P13**

The role of surfactants in aqueous two-phase and density gradient ultracentrifugal separations

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Solubilization of single-wall carbon nanotubes (SWCNTs) with bile salt surfactants [1] has enabled major advances in their processing, purification and spectroscopic characterization. These surfactants enable the structure sorting of SWCNTs by density gradient ultracentrifugation (DGU)[2] and aqueous two-phase (ATP) extraction [3], as they determine both the relative density[4] and hydrophobicity for different chiralities. [5,6] We present wavelength-dependent fluorescence-excitation and Raman spectra measured directly after DGU, in situ, as a function of height in the centrifuge tube. These in situ DGU experiments provide an easily interpretable observable, i.e. buoyant density as a function of chiral structure. We combine this in situ characterization with concentration-dependent ATP separations for different surfactants and, as such, obtain a more detailed understanding of and control over both separation mechanisms.

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C4 **MSIN P14**

Influence of crystallinity on the mechanical behavior of carbon nanotubes

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The future exploitation of carbon nanotubes relies on well-known material properties such as their mechanical behavior and electrical conductivity. While small volumes of highly crystalline materials can be fabricated using arc-disharge methods, it is not scalable for commercial fabrication. Instead chemical vapour deposition (CVD) methods and subsequent purification is commonly used for large-scale production. Unfortunately the crystallinity is rather low is such materials and there is currently no well defined way to characterize and document the level of crystallinity in these materials.

Here we discuss the differences in the mechanical behavior of free-standing carbon nanotubes that have been fabricated using different techniques. We have studied both arc-discharge produced materials and commercially available materials (CVD growth). The difference in crystallinity is clearly visible with transmission electron microscopy (TEM), and the differences in the mechanical behavior is even more striking. The CVD grown tubes have about an order of magnitude lower Youngs modulus than one would expect from ideal carbon nanotubes, and their behavior during deflection is also very different from highly crystalline materials. This illustrates the need for a classification system for different qualities of carbon nanotube materials, similar to what is currently done for carbon fibres.

MSIN P1

Threshold control of printed CNT transistors by polymer cap containing phthalocyanine pigment

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Printed CNT transistors were fabricated on plastic film with purified semiconducting CNT ink. The CNT transistors were p-type characteristics with on/off ratios of about 100,000. However, the averaged threshold voltage was 8.9V by natural doping. Then, a polymeric cap layer which contains phthalocyanine pigment was printed. The cap layer was dried and cured by exposing UV fluorescent lamp. Then, electrical measurement was carried out for the second time and the threshold voltage shifted by 30 V. Phthalocyanine pigment is known as electron-donor-acceptor complex material, and it has two absorption bands, Soret (350 - 450 nm) and Q (600 - 800nm) bands. A 409 nm laser was irradiated for 4 seconds and transfer characteristics were measured. This cycle was repeated 32 times, and the ON-state current decreased as integral time of irradiation increased. It is thought that electrons were provided from phthalocyanine by photo irradiation, and they killed holes in CNT channel. Consequently, the thres-hold voltage shifted and the ON-state current decreased. The recovery process from the irradiated state is very slow, and it was under investigation. This work is based on results obtained from a project supported by the New Energy and Industrial Technology Development Organization (NEDO).

MSIN P2

Electrical activation of dark excitonic states in carbon nanotubes

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Electric-field effects on exciton states in single-walled carbon nanotubes are investigated by simultaneous photocurrent and photoluminescence excitation spectroscopy. We utilize field-effect transistors with suspended carbon nanotubes in order to apply longitudinal fields [1]. Photoluminescence imaging and excitation spectroscopy are performed to locate individual nanotubes and to identify their chirality. When a bias voltage is applied, we observe an emergence of a new absorption peak near the first excited state in both photoluminescence and photocurrent spectra.With excitation at the new peak, photocurrent begins to flow above a threshold bias, while the luminescence intensity starts to decrease. Furthermore, we have found another bias-induced peak at a higher energy in the photocurrent spectra which has a threshold at a lower bias. Measurements of several nanotubes with different chirality reveal that the energy separation between these bias-induced peaks and the ground state of E11 excitons is inversely proportional to the tube diameter. The results suggest that the new peaks are the dark excited states of the E11 excitons which became optically active due to the applied fields.
Work supported by KAKENHI and APSA.

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MSIN P3

Mechanism of band-gap dependent adsorption of single-wall carbon nanotubes onto hydrogels

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Single-wall carbon nanotubes (SWCNTs) have been reported to be separated into each chiral species in hydrogel columns in the presence of sodium dodecyl sulfate (SDS). SWCNTs with smaller band-gap tend to have lower affinity for the hydrogels in the columns. Recently, we have shown that the adsorbability of SWCNTs onto the hydrogels depends on pH values which are known to affect the redox reaction of the SWCNTs with an O_2/H_2O redox couple. Such redox chemistry has been demonstrated to be associated with band-gap. These facts indicate that the band-gap dependent adsorbability of the SWCNTs onto the hydrogels is ascribable to the oxidation of the SWCNTs. We provide here a mechanistic model for the separation. In the model, the SWCNTs with smaller band-gap are more readily oxidized, so that they have more positive charges. Such positively charged SWCNTs enhanced their electrostatic interaction with SDS, resulting in condensation of SDS molecules on the SWCNT surfaces. That is why the adsorbability onto the hydrogels is more reduced for the SWCNTs with smaller band-gap, leading to the band-gap separation in the hydrogel columns.

MSIN P4

Precise structure sorting of SWCNTs using two-step liquid chromatography

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Single-wall carbon nanotube (SWCNT) takes a variety of electronic structure depending on its chirality denoted by chiral index (n, m). Therefore, high-purity single-chirality SWCNT is very important for fundamental studies and advanced applications. For this purpose, we have developed a two-step liquid chromatography method using a mixed surfactant. In this method, overloading selective adsorption [1] was combined with a stepwise elution chromatography. As the first step, raw SWCNTs were dispersed in a sodium dodecyl sulfate (SDS) solution and overloaded into the gel column to adsorb a limited chirality distribution [1]. Then the solution in the column was changed to a mixture of SDS and sodium cholate (SC). As the second step separation, sodium deoxycholate (DOC) was added stepwise to the SDS/SC mixed solution for elution. Individual chirality species were eluted out for each concentration of DOC. As a result, nine kinds of high-purity single-chirality SWCNTs were obtained. Estimated purity of the single-chirality was ranged from 90 to 98 %, which is much higher than that of previous reports [1, 2].

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MSIN P5

Single-chirality separation of SWCNTs using mixed surfactant gel chromatography

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Single-chirality separation is highly desired to clarify chirality-dependent physical properties of single-wall carbon nanotubes (SWCNTs). Previously, we reported an overloading gel chromatography method that realized a separation of 13 singlechirality SWCNTs [1]. In this work, we have investigated effects of mixed surfactant on chiral separation for an improvement.

After adsorption of SWCNTs to a gel column using mixture of sodium dodecyl sulfate (SDS) and sodium cholate (SC), selected SWCNTs were eluted by slightly different surfactant composition. We found that larger chiral angle species were eluted out at lower concentration of SDS in the SDS/SC mixture system. On the other hand, when we added sodium deoxycholate (DOC) to the SDS/SC mixture, smaller diameter species were eluted out at lower concentration of DOC. By combining these two different selection rules, we successfully separated six single-chirality species (6,4), (7,3), (6,5), (9,4), (8,6) and (10,3). Importantly, this method can be easily applied to large-scale separation because of its conventional HPLC procedure.

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MSIN P6

Gate-voltage induced trions in individual air-suspended carbon nanotubes

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The effects of electrostatically-induced carriers on photoluminescence spectra from air-suspended carbon nanotubes are investigated using field-effect transistor structures [1,2]. We observe an emergence of a peak below the E11 emission energy at gate voltages that coincide with the onset of bright exciton quenching. Excitation spectroscopy measurements show that emission intensities for the lower energy peak and the bright exciton peak are maximized at the same excitation energy, confirming that both peaks arise from the same nanotube. The energy separation between the bright exciton peak and the gate-induced peak becomes smaller for larger diameter tubes, as expected for trion luminescence. We obtain trion binding energies that are significantly larger compared to surfactant-wrapped carbon nanotubes, and the difference is attributed to the reduced dielectric screening in air-suspended tubes.

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MSIN P7

X-ray spectroscopy and quantum chemical modeling to study atomic structure of fluorinated carbon nanotubes

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Double-walled carbon nanotubes (DWCNTs) have been fluorinate by three different methods using fluorine gas, gaseous trifluoride bromine and carbon tetrafluoride plasma. Transmission electron microscopy revealed that all used methods of fluorination preserve double-wall architecture of nanotubes but separate DWCNTs in bundles related to each other depending on the fluorination degree. X-ray photoelectron spectroscopy analysis was performed to estimate fluorine content on the surface of DWCNTs. It was shown that near edge X-ray absorption fine structure (NEXAFS) spectroscopy as well as quantum chemical modelling of NEXAFS spectra can be effectively used to study the nature of chemical bonding between carbon and fluorine atoms and to suggest the fluorine pattern on graphene surface of DWCNT fluorinated by different techniques. According to profile of theoretical NEXAFS FK-spectra constructed based on DFT calculations, we assume that alternate zig-zag chains of C and C-F were formed in DWCNTs fluorinated by trifluoride bromine, while samples fluorinated by fluorine gas and CF4-plasma consist of divided C=C and CF-CF groups and CF area, respectively.

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MSIN P8

Structural and morphological control of nitrogen-doped carbon nanotubes using Ni/Mo, Co/Mo and Fe/Mo bimetallic nanoparticles

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Very important factor in the catalytic chemical vapor deposition (CCVD) growth of carbon nanotubes (CNTs) is a nature and a dispersion of a catalyst. The catalyst influences diameter, morphology, and defectiveness of nanotubes. On the other hand, there is a possibility to control properties of carbon nanomaterials using replacement of carbon by a heteroatom.

Usually nitrogen-doped carbon nanotubes (N-CNT) are synthesized using both nitrogen precursor during CNT synthesis procedure and post-treatment of CNTs by nitrogen containing molecules at high temperature. There are three main forms of nitrogen inserted into CNTs structure such as graphitic, pyridinic and pyrrolic. Temperature is a key parameter for control of nitrogen content and the nature of nitrogen species.

Here, we use polyoxomolybdates as a source of catalyst nanoparticles of N-CNTs growth. TEM investigation indicated that the CCVD products contained individual CNTs with porous carbon. EDX analysis showed formation of bimetallic nanoparticles inside CNTs. It was found how the catalyst composition influences the concentration and the nature of species of inserted nitrogen according to XPS data. The obtained carbon materials are expected to demonstrate improved properties as electrode materials.

This work was supported by the Russian Foundation of Basic Research (grant 14-03-32089).

MSIN P9

Imaging the density and type of horizontal carbon nanotube arrays by polarized optical microscopy

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Fast determining the density of single-wall carbon nanotubes (SWNTs) with metallic/semiconducting (M/S) recognition is a longstanding target. Currently, scanning electron microscopy and atomic force microscopy are two most used methods to count the numbers of SWNTs in finite area (typically ~1 micron). However, these two methods lack the ability of M/S recognition and they even meet great challenges at lateral resolution as the density of SWNTs increases, spectroscopic methods, electrical measurement and transmission electron microscopy are adopted to determine theM/S type but usually with quite low throughputs. Here we demonstrate a density and type imaging of SWNTs with hundreds-micron field of view and sub-second display rate. This imaging is achieved through polarization induced dramatical contrast enhancement of SWNTs. The enhanced optical contrast is then used to determine the density of SWNTs and the image color is used forM/S recognition according to their distinguishable spectral responses. Our technique provides a routine to search and characterize the SWNT arrays on various substrates and in diverse environments. Its universality and practicability offer the opportunities not only to push forward the controlled growth of both high density and high M/S selectivity SWNT arrays, but also to promote the development of SWNT applications.

MSIN P10

The characterization of defects in graphene with raman spectroscopy

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In this contribution, I review our work on the use of Raman spectroscopy to characterize defects in graphene. The Raman spectroscopy technique can be used to quantify the amount of defects through the intensity of the defect induced peaks, but the formalism depends whether the defects are punctual (like vacancies or dopants) or line-defects (like flake borders or grain boundaries). Geometrical models are used to correlate the amount of defects with the D band intensity, ruled by physical properties of the inelastic light scattering in graphene. The information has been calibrated using microscopy techniques, including scanning tunneling microscopy, transmission electron microscopy, tip enhanced Raman microscopy, as well as X-ray scattering.

MSIN P11 ～ **MSIN P14** ※ Please refer to **C1** ～ **C4**

CNTFA15

I1

CVD growth of randomly-oriented and vertical-aligned single-walled carbon nanotubes with bimetallic catalysts

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We grow vertical-aligned arrays of single-walled carbon nanotubes (SWNTs) with sub-nanometer diameter on Si/SiO2 substrates by chemical vapor deposition (CVD) using Co/Cu bimetallic catalysts. We can use lower growth temperature for randomly aligned SWNTs. The random network of SWNT formed at 650 degree C shows the major absorption peak at (6,5) position. The diameter of SWNTs can be further reduced by loading Fe/Co or Co/Cu catalysts on zeolite support at low CVD temperature of 430 degree C. The absorption peak of (6,4) is strong in this extreme condition; and we can identify (6,4), (5,4), (8,0) etc. by Raman scatterings. The quality of SWNT determined by D-band is better for Fe/Co and the diameter range is narrower for Co/Cu system. TEM observation indicated that the diameter of Co nanoparticles in bimetallic Co/Cu system is much smaller than that in mono-Co system. Finally, the chirality specific growth of SWNTs using W/Co catalysts from molecular precursors and from sputtered metals are also discussed.

I2

Direct synthesis of high-quality, large-area single-wall carbon nanotube thin films

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Single-wall carbon nanotubes (SWCNTs) are considered to be promising candidate for fabricating various high-performance electronic and opto-electronic devices. SWCNT-based thin film devices, such as thin film transistors and transparent conductive films have demonstrated desirable properties and are hopefully to be used in the near future. To realize high-performance thin film devices, it is essential to synthesize high quality SWCNT films in a controllable way. In this presentation, we report the direct growth of high-quality, large-area SWCNT films by a floating catalyst chemical vapor deposition (FCCVD) method. By tuning the growth parameters, high purity SWCNTs are obtained in bulk. Then, we introduce suitable amount of oxygen or hydrogen as etchant during the growth of SWCNTs by the FCCVD method. As a result, m-SWCNTs with relatively higher chemical reactivity are selectively removed, and s-SWCNTs with a concentration higher than 90% are obtained in large scale. Alternatively, by tuning the growth parameters and hence the diameter distribution of m-and s-SWCNTs, selective removal of small diameter s-SWCNTs is realized, and large diameter m-SWCNTs were preferentially synthesized.We also developed an approach and apparatus for the continuous collection of the grown SWCNT. As a result, highquality, large-area SWCNT thin films are controllably prepared.

I3

Aerosol synthesis of tunable surface density SWCNT networks for uniform thin film transistor arrays

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We report fabrication of SWCNT networks with tunable surface density by using a spark generator based floating catalyst CVD reactor for SWCNT synthesis. The uniform and tunable density SWCNT networks were realized by on-line SWCNT concentration monitoring at the reactor outlet by using a condensation particle counter and by estimating the appropriate volumetric flow thorough membrane filter for desired surface density SWCNT network. The controlled deposition process enables feedback-based compensation of synthesis process variations. The SWCNT networks consist mainly of individual SWCNTs with mean diameter close to 1 nm, forming extended Y-contacts. Thin film transistor characteristics were evaluated for devices fabricated from the SWCNT networks for different SWCNT network densities ranging between 0.4 1 #/um^2 - 1.8 #/um^2, channel lengths between 5 um - 100 um and channel widths between 100 um - 500 um. Back-gated SWCNT thin film transistors exhibit excellent performance with mobilities up to 100 cm^{2}V^{-1}s^{-1}, ON/OFF-ratios > 10^5, high uniformity and yield up to 99%.

I4

Organic solar cells using carbon nanotube films as transparent hole-selective electrodes

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Organic solar cells (OSCs) are now put into practical use in public space (train stations) and so on. Flexible OSCs are highly desired on the viewpoint of differentiation from conventional solar cells. Carbon nanotubes (CNTs) electrode is an excellent substitute for inorganic metal oxide electrode to realize highly flexible OSCs because of high flexibility of CNTs films. In this work, we developed a methodology for making CNT-utilized OSCs. For this purpose, we utilized direct and dry deposited single-walled (SW) CNTs films, which were doped by MoO3 to cover bumped CNT networks and to enhance conductivity of CNT electrodes. Hence, doped CNTs serve as transparent hole-selective (electron-blocking) electrodes. The CNTOSC, glass/SWCNTs/MoOx/PEDOT:PSS/PTB7:PC71BM/LiF/Al showed power conversion efficiency (PCE) of 6.04%. Flexible application using a PET substrate showed 3.91% PCE.

I5

Photovoltaic application using carbon nanotube thin film

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Carbon nanotubes have attracted much interest from the viewpoint of optical science[1] and applications[2,3]. The novel electronic and optical properties, including the ability to tune their band gaps, high carrier mobilities and high optical transparency values with low resistivity, are useful for photovoltaic applications. Here we showed a significant improvement of the carbon nanotube solar cells by the use of high quality carbon nanotube thin film with low resistivity[2] and metal oxide layers for efficient carrier transport[3]. The metal oxides also serve as an antireflection layer and an efficient carrier dopant, leading to a reduction in the loss of the incident solar light and an increase in the photocurrent, respectively. As a consequence, the photovoltaic performance of both p-single-walled carbon nanotube (SWNT)/n-Si and n-SWNT/p-Si heterojunction solar cells using MoOx and ZnO layers is improved, resulting in very high photovoltaic conversion efficiencies of 17.0 and 4.0%, respectively[3]. Moreover, the application of carbon nanotube thin film for different types of solar cells will be discussed.

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I6

Fabrication of thermoelectric devices using precisely fermi level tuned single wall carbon nanotube films

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Thermoelectrics are a very important technology for efficiently converting waste heat into electric power. As Hicks and Dresselhaus have proposed,[1] for realization of high-performance thermoelectric devices, it is important to use low-dimensional materials and to tune their Fermi level. In this context, we have reported across-bandgap p-type and n-type control over the Seebeck coefficients of semiconducting single wall carbon nanotube network films by Fermi level tuning through electrolyte gating.[2] All-around gating characteristics by electric double layer formation upon the surface of the nanotubes enabled the tuning of the Seebeck coefficient of the nanotube networks by the shift in gate voltage, opening the path to Fermi-level-controlled three dimensional thermoelectric devices composed of one-dimensional nanomaterials. By freezing the motion of the electrolyte, we fabricated thermoelectric devices using the precisely p-type and n-type tuned semiconducting SWCNT films.

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I7

Carbon nanotube film based light emission devices

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Semiconducting carbon nanotubes (CNTs) have direct, diameter-dependent bandgap, and are thus ideal materials for nanoscale optoelectronic devices. And the reduced dimensionality related quantum confinement effect further enriches their interesting exciton physics, which is closely related to the performance of the devices. By taking advantages of large binding energy between trion and triplet exciton, all trion (that is, charged exciton) emission can be realized using carbon nanotube films, which may open a new radiation pathway for the CNT-based optoelectronic devices, providing a new degree of freedom in controlling the device to extend potential application in spin optoelectronics field. The CNT films devices can also be readily integrated into microcavity to provided tunable emission characteristics, with narrow emission peak width, almost symmetric spectral profile, optional emission peak energy, low driving voltage, and broad tunable wavelengths.

I8

Carbon nanotube-based printed flexible electronics: material, fabrication, and applications

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Carbon nanotubes (CNTs) are of great interest for a variety of device applications due to its unique electrical and mechanical properties. One of the potential applications is for a soft/flexible electronics. In this talk, flexible thin film transistors (TFTs), highly sensitive sensors, and foldable electrodes are demonstrated by utilizing metallic and semiconductor behaviors of CNTs and composition materials on a flexible substrate as the electrical components for the future flexible devices. In particular, printing method is discussed for a macroscale flexible electronics that can be targeted to the biologically inspired artificial devices, human interactive devices, and health monitoring wearable devices as examples. Finally, future envision is introduced for the flexible electronics.

I9

Large-scale characterization of carbon nanotube thin-film transistors

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Carbon nanotube thin-film transistors (CNT TFTs) are promising components for various kinds of flexible devices such as rollable displays and wearable healthcare devices. Though great efforts have been made to achieve high-performance CNT TFTs, device-to-device variation in their electrical characteristics is still one of unresolved issues towards their practical applications. In this work, we have investigated electrical performance and characteristic variation of CNT TFTs statistically. High-purity semiconducting single-walled CNTs are used to avoid a formation of short paths of metallic CNTs in a high-density CNT film. The vacuum filtration and film transfer method was adopted, which is considered to be advantageous for relatively uniform and large area film formation on various kinds of substrates. We measured more than 4,000 devices with various number density of CNTs. Although there is a considerable variation in the wafer scale probably due to the film formation process, a quite small variation in on-current (～ 5 %) was obtained in an area of ～ 9 mm^2.

I10

Macro, flexible, and printed electronics based on carbon nanotubes

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Semiconducting single-wall carbon nanotubes have emerged as a promising material for flexible and printed macroelectronics due to their outstanding electrical property, intrinsic mechanical strength, and excellent printability. Nevertheless, there are difficult challenges to realize large-scale integrated circuits and develop a scalable approach for fully-printed high-performance thin-film transistors using carbon nanotubes. Here we report a hybrid integration of p-type carbon nanotube and n-type indiumgalliumzinc-oxide thin-film transistors to achieve large-scale (1,000 transistors for 501-stage ring oscillators) complementary macroelectronic circuits on both rigid and flexible substrates. This approach of hybrid integration allows us to combine the strength of p-type carbonnanotube and n-type indiumgalliumzinc-oxide thin-film transistors, and offers high device yield and low device variation Furthermore, we demonstrate that screen printing, which is a simple, scalable, and cost-effective technique, can be used to produce high-performance flexible thin-film transistors using separated single-wall carbon nanotubes. The resulted nanotube thin-film transistors show excellent electrical performance, outstanding mechanical flexibility and capability to drive organic light-emitting diode. The aforementioned achievements significantly indicate semiconducting single-wall carbon nanotubes renders a promising future for macro, flexible, and printed electronics.

I11

Moldable and flexible double-walled carbon nanotube transparent conductive film and its application for next generation device

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We have synthesized very narrow diameter double-walled carbon nanotube (DWCNT) which has very high purity and electric conductivity by CVD method. By dispersing it to water and coating on plastic substrate with fine coating technology, we have developed DWCNT transparent conductive film (TCF). Our DWCNT TCF has very high transparent conductivity, which are currently among the top in the world. Because of its high tranparency, our DWCNT TCF has been commercialized as upper electrode of e-paper. Great characteristics of our DWCNT TCF are its high stretching and bending durability, and we are trying to apply it for devices on which these features can be utilized. In this presentation, we will introduce prototypes of bendable capacitive touch screen and molded full 3D designed capacitive touch screen and switch. These technologies are expected to be applied for next generation device such as flexible display, 3D designed pointing device and so on.

I12

Flexible films of carbon nanotubes nanocomposites with graphene, nanowires and layered superconductors for functional applications

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Assembly of graphene with carbon nanotubes (CNTs) can yield hybrid materials with new structural characteristics and tailored properties. A single layer CVDgrown graphene and a self-supporting, aligned, multi-walled carbon nanotube (MWNT) sheet were incorporated to produce hybrid films. Using two different assembly arrangements: i) MWNTs on top graphene, and ii) graphene on top of MWNTs, we fabricated MWNT/graphene (MWNT/G) and graphene/MWNT (G/MWNT) hybrid films, respectively. It was observed that, in spite of the same composition, the hybrid films exhibit different optical, electrical and electromechanical properties.

We also have fabricated transparent and conductive free-standing thin film electrodes by adding silver nanowires (AgNWs) to dry-spunMWNTaerogels. ThisAgNW@MWCNT nanocomposite exhibits a decrease in sheet resistance and increase in transmittance simultaneously. Longer and thinner silver nanowires lowered the parallel and perpendicular sheet resistance to RII =25 and RL = 44 Ω/□ respectively with still high transmittances around 90%.. Flexible, weavable and knottable superconducting magnesium diboride nanocomposites with MWCNT yarns have been fabricated that provide attractive gravimetric properties of MgB2@MWCNT as a superconductor, while having a 20 times lower density than for bulk MgB2

C1

Single-carbon-nanotube photonics and optoelectronics

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Single-walled carbon nanotubes have unique optical properties as a result of their one-dimensional structure. Not only do they exhibit strong polarization for both absorption and emission, large exciton binding energies allow for room-temperature excitonic luminescence. Furthermore, their emission is in the telecom-wavelengths and they can be directly synthesized on silicon substrates, providing new opportunities for nanoscale photonics and optoelectronics.

Here we report on the emission properties of devices that utilize individual singlewalled carbon nanotubes. By using specially-designed silicon photonic-crystal nanobeam cavities, efficient coupling can be achieved [1]. More recently, we have found that alternating gate-voltages can generate optical pulse trains from individual nanotubes [2]. These results underscore the distinct characteristics of carbon nanotubes for applications in photonic and optoelectronic devices.

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C2

Mapping charge transport in semiconducting carbon nanotube networks by electroluminescence and raman microscopy

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Charge transport in networks of semiconducting single-walled carbon nanotubes (s-SWNTs) depends on network density, bandgap distribution and alignment. Here, we introduce two techniques to investigate transport in s-SWNT networks: Near-infrared electroluminescence (EL) from ambipolar field-effect transistors (FETs) and in-situ Raman microscopy.

Semiconducting nanotubes are extracted and enriched by dispersion with various polyfluorenes. FETs with these s-SWNTs networks show ambipolar transport with on/off ratios of 10^6, mobilities of 10-50 $cm^2V^{-1}s^{-1}$[1] and near-infrared electrolumi-nescence with narrow peak widths[2]. EL maps/spectra of these networks that differ from corresponding photoluminescence (PL) maps/spectra indicate preferential current paths. The fraction of emission from different s-SWNTs depends on the applied voltages. At high carrier densities red-shifted trion (charged exciton) emission is observed[3].

Further, it is possible to map the carrier distribution within an operating ambipolar s-SWNT transistor by Raman microscopy via the carrier density-dependent G- mode shift. The low density of carriers in the recombination zone compared to the hole and electron accumulation regions within the channel are visualized and corroborate the data obtained by EL and PL mapping[4].

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C3

Lithographically patternable and lightweight CNT-Cu composite interconnects showing longer lifetime and comparable conductivity to pure Cu

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Emerging lithographically processable materials with high conductivity and high stability at high current and high temperature are in demand for high current electronic devices used at high temperature. Here, we will demonstrate that a patterned CNT-Cu composite which exhibits a two times longer lifetime when current is applied at high temperature and comparable conductivity to Cu. In addition, it is patternable on the arbitrary substrates by lithographic processes and electroplating. As we have reported previously, it has 100-times higher ampacity than Cu. We also found that coefficient of thermal expansion (CTE) is approximately 5 ppm/K, which is comparable to that of silicon (3 ppm/K). The comparable CTE between CNT-Cu composite and Si substrate is effective to reduce mechanical strain arising due to the similarity in CTE between the substrate and patterned components during thermal cycling. Therefore, we attribute the longer lifetime to the high ampacity and low mismatch of thermal expansion coefficient of the CNT-Cu composite with the silicon substrate. Highly stable, conductive and lightweight CNT-Cu composite synergizing the advantages of Cu and CNT is promising as future interconnects, enabling highly reliable electronic devices for harsh environment. This presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

CNTFA P1

Controlled synthesis of single-walled carbon nanotubes using sputtered W/Co

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Single-walled carbon nanotubes (SWNTs) have been widely recognized as promising building blocks for nanoscale electronics because of their unique structuredependent electronic properties. However, one of the main obstacles to applications of SWNTs is the controlled synthesis of SWNTs with desired (n, m) structure. Recently, the tungsten-based nano-clusters have been used as catalysts to grow SWNTs with a single chirality of (12, 6), resulting in an abundance higher than 92% [1].

Here, we report an improved density of SWNTs with narrow chirality distribution by using sputtered W/Co. Alcohol catalytic chemical vapor deposition (ACCVD) was conducted for the selective growth of (12, 6) at low temperature, much lower than that of originally reported tungsten-cobalt clusters [1]. High-quality and uniform SWNTs were obtained. Raman spectroscopy with different excitation wavelengths shows narrow (n, m) distribution than that of monometallic cobalt system. The absorption spectroscopy reveals the abundant (12, 6) in the randomly collected samples. Further parametric study of the controlled synthesis of SWNTs will also be presented. The chirality distribution and growth mechanism will be discussed in detail.

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CNTFA P2

Ultrasensitive sandwich-type electrochemical immunosensor based on carboxyl Multiwalled carbon nanotubes decorated dumbbell-like Pd-Ag heterodimers

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Multiwalled carbon nanotubes (MWCNTs) have been explored for potential applications in biological and biomedical fields ever since the discovery of them. The functionalized MWCNTs have attracted broad interest due to their unique properties such as the increasing solubility and dispersion in water. In this work, Carboxylic acid groups (-COOH) are introduced onto the surface of MWCNTs and the MWCNTs-COOH was used to combine with dumbbell-like Pd-Ag heterodimers (Pd-Ag@MWCNTs-COOH). The secondary anti-AFP labeled with Pd-Ag@MWCNTs-COOH nanocomposite is used to develop a sandwich-type electrochemical immunosensor for detection of alpha fetal protein (AFP). The MWCNTs-COOH nanocomposite with large surface area provides more active sites for dumbbell-like Pd-Ag heterodimers whose electrocatalytic properties is excellent to catalyze the hydrolysis of hydrogen peroxide (H2O2). Amination functionalized graphene sheets nanocomposite was used as the sensor platform to combine more primary anti-AFP. And the electrochemical amperometric changes to different concertrations of AFP are achieved after the immunoreaction. Under optimum experimental conditions, the proposed immunosensor exhibits a low detection limit (0.17 pg/mL), a wide linear range (from 0.5 pg/mL to 35 ng/mL) as well as good stability, reproducibility and selectivity.

CNTFA P3

Ultrasensitive electrochemical immunosensor used amination graphene as platform for hepatitis B surface antigen detection

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Graphene sheets (GS), a single layer of sp2-bonded carbon atoms, is a two-dimension honeycomb nanostructure, which has been widely used in infrared-triggered actuators, biomedicine and optoelectronic devices etc. And the chemical functionalization on GS has a wide range of application in immunosensors. The good biological compatibility of amination graphene (NH2-GS) makes it bind antibody and keep the activity of antibody. With high specific surface area and excellent electronic transport ability, NH2-GS could bind a mass of antibodies and achieve good signal of immunosensor. In this paper, we developed an ultrasensitive sandwitch-type electrochemical immunosensor for the detection of Hepatitis B surface antigen (HBsAg). The primary HBsAg-antibody was immobilized onto NH2-GS with the covalent bonding due to the activation of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide/N-hydroxysuccinimide, and the second HBsAg-antibody was bonded to Pt nanoparticles (Pt NPs) decorated amino silanes functionalized montmorillonite (Pt-NH2-MMT) by the Pt NPs and amine groups blinded with each other. Applying the principle of specific binding of antibody and antigen, the current response could direct reflect the concentration of HBsAg in the sample. For HBsAg analysis with the fabricated immunosensor, a wide linear range from 0.5 pg/mL to 20 ng/mL and a low detection limit of 0.16 pg/mL were obtained.

CNTFA P4

Direct growth of sub-nanometer diameter single-walled carbon nanotube films on Si/SiO_2 substrate

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The bandgaps of single walled carbon nanotubes (SWNTs) are reversely proportional to their diameters. Direct growth of small-diameter SWNTs on substrates is very important for applications in electronic and optoelectronic devices. Using alcohol catalytic chemical vapor deposition (ACCVD), we obtained high quality (6,5)-enriched SWNT films by Co and Cu bimetallic catalysts. The chirality distribution is characterized by Raman spectroscopy with different laser excitation and UV-vis-NIR absorption spectroscopy. We also obtained vertically-aligned SWNTs with sub-nanometer average diameter. According to the transmission electron microscopy study, Cu functions as 1) facilitating the catalytic activity at low temperature and 2) anchoring the catalysts on substrate to prevent Co nanoparticles from Ostwald ripening. We expect the high-quality small-diameter SWNT films have great potential for the application of transistors and solar cells.

CNTFA P5

The application of MWCNTs-NH2/PdX (X=Pt, Ni, Co, Cu) nanocages as labels in an ultrasensitive sandwich-type electrochemical immunosensor

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In recent years, carbon nanotubes are promising materials for electrochemical biosensors on account of their high electronic conductivity, great chemical stability, high surface area and extremely high mechanical strength. According to different needs, functionalized carbon nanotubes were introduced to the field of immunoassay. For example, the amino-functionalized multi-walled carbon nanotubes (MWCNTs-NH2) supported PdX (X=Pt, Ni, Co, Cu) nanocages were used as catalytic labels of secondary anti-carcinoembryonic antigen (anti-CEA) for the sandwich-type electro- chemical immunosensor application. PdX (X=Pt, Ni, Co, Cu) nanocages with hollow interiors and porous walls could efficiently enhance electrocatalysis for reduction of H_2O_2. Due to the hydrophilicity of primary amines, MWCNTs-NH2 has better dispersity in water than MWCNTs. Meanwhile, with large specific surface area and amino groups, MWCNTs-NH2 could immobilize a large amount of PdX (X=Pt, Ni, Co, Cu) nanocages by covalent binding between noble metal nanoparticles and amino groups to improve sensitivity and amplify signal of the immunosensor. The sandwich-type immunosensor was fabricated on a glassy carbon electrode covered with 3-aminopropyltriethoxysilane functionalized graphene sheets. Under the optimal conditions, the proposed sensing strategy exhibited a wide linear range (0.001-20 ng/mL), low detection limit (0.2 pg/mL), good precision, acceptable stability and reproducibility, which had a promising application in clinical diagnosis for CEA and enriched electrochemical immunoassays.

CNTFA P6

Addressing commonly overlooked specifications to produce high quality carbon nanotube TCFs

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SingleWalled Carbon Nanotube (SWNT) transparent conductive thin films (TCFs) have been around for many years as an alternative to ITO, however they have not made the breakthrough into full commercial usage. Up until recently it was the transparency and resistivity values of these films that did not meet specification, however a number of different technologies based on carbon nanotubes have emerged to exceed the commonly quoted literature specification of 100 ohms/sq at 90% transparency. However in the drive to reach this point not enough focus has been given to the wider TCF properties of; hardness, adhesion, haze, environmental stability, flexibly and of course cost.

To address the full customer need Linde Nanomaterials has achieved the necessary values for the given specification parameters and here we talk about the specifications, the techniques used to address them and the current result for our SWNT TCFs. Using the ink produced by our unique SEER technology Linde Nanomaterials has produced transparent conductive thin films that can truly be considered as a viable alternative to ITO in current displays and also push forward the quest for fully flexible displays.

CNTFA P7

Improved hole transport layers in perovskite solar cells based on P3HT doped with functionalized carbon nanostructures

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Perovskite solar cells (PSCs) fabricated with two step deposition have been prepared and tested using P3HT as hole transport layer (HTL). P3HT was dissolved in chlorobenzene and blended with single walled carbon nanotubes (SWCNTs) and rGO graphene nanoplatelets (GNPs) bearing on the external surface covalently bound paramethoxyphenyl substituents, aimed at improving their homogeneous mixing with the semiconducting polymer. The SWCNTs and GNPs used for P3HT doping have been functionalized using aryl diazonium chemistry, keeping the amount of functionalities in a range which allows to gain better solubility but do not affect their electronic properties. Caution was taken in order to obtain blends with no insoluble residues, by applying a thorough protocol of sonication/centrifugation steps before spin coating the HTL on top of the hybrid junctions. Different weight percentages of functionalized SWCNTs-GNPs/P3HT were deposited, in order to determine the optimum percentage. Such doping of the P3HT layer resulted in increased efficiencies and prolonged stabilities of the resulting PSCs with respect to devices with undoped P3HT HTLs. The best solar cells showed a power conversion efficiency up to 11.7 %. These promising results prompted us to test the effect of functionalized SWCNTs and GNPs doping on other hole-conductors, such as spiro-OMeTAD.

CNTFA P8

Large area and high adhesion flexible carbon nanotube transparent conducting films fabricated by controllable rod-coating

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Single-walled carbon nanotubes (SWCNTs) were dispersed in water with the help of surfactants to achieve high concentration SWCNT ink. SWCNT transparent conducting films (TCFs) were fabricated by rod-coating using the SWCNT ink. A combination of two surfactants provided optimal rheological behaviour, which produced uniform films by preventing dewetting and rupture of SWCNTs during drying. The combination led to a dramatic increase of shear viscosities but no change of their wettability. The viscosity of SWCNT ink was controlled by the ratio of two surfactants. The addition of binders greatly enhanced the adhesion of SWCNT films to substrate and the cohesion between CNTs, which produced a uniform film of SWCNTs by preventing damage during the post-treatment process. The thickness of SWCNT films is controlled by the amount of SWCNTs in the solution and the diameter of the wire-wound rod used. To test the film adhesion, ScotchTM tape was used to detach some loosely bound SWCNTs. The additive of polyacrylic acid to the SWCNT dispersion improved the film adhesion obviously without decrease its electrical conductivity. The produced uniform SWCNT-TCFs treated by nitric acid have a relatively low sheet resistance at high transmittance. This rod-coating method demonstrates great potential for the scalable fabrication of flexible SWCNT-TCFs.

CNTFA P9

Structured SWNT films as hole transporting layer and electrode for perovskite solar cells

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Low cost, high performance, and stability are being research challenges in the development of organic-inorganic perovskite solar cells. Single-wall carbon nanotubes (SWNTs) are promising materials that can have both metallic and semiconducting properties based on changing diameter and chirality. In this regard, SWNTs were employed as both hole transporting layers and electrodes for $CH_3NH_3PbI_3$ based perovskite solar cells. Different structured SWNT films were prepared seeking the higher power conversion efficiencies (PCEs) mechanism. The flexible, well-structured SWNT directly contacted to the perovskite substrate. The SWNT based perovskite solar cells were fabricated and compared to the common ones that have hole conducting layer and metal electrodes. We believe that the direct contact between SWNTs and perovskite substrate will significantly enhance the charge transport through the solar cell. The possibility of using SWNT films will reduce the energy and cost of fabrication of such promising type of solar cells.

CNTFA P10

Local transport properties in carbon nanotube networks

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Single walled carbon nanotubes (SWCNT) have remarkable electrical, mechanical, optical and chemical properties and have emerged as promising candidates for variety of applications. However, electrical transport through carbon nanotube and bundle contacts and effects of electrostatic and chemical doping to the transport properties are poorly understood. In order to resolve these issues, we have studied highly individualized SWCNTs with mean diameter 1.2 nm by using AFM/STM technique to map the local transport properties of isolated CNT contacts, while characterizing the structural parameters. While bundled tubes have lower contact resistance and gate dependence, we find that junctions made of individual semiconducting and metallic SWCNTs have higher contact resistance. Interestingly, the gating of these contacts substantially modulates drain current.

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CNTFA P11

Single-walled carbon nanotube film based indium-free planar heterojunction perovskite solar cells: investigation of charge selective layers, dopants, and flexible application

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Recent emergence of perovskite solar cells have drawn much attention owing to excellent power conversion efficiency arising from a long exciton diffusion length, high absorption and carrier mobility. Since ITO is indispensible in perovskite solar cells much like in other photovoltaic devices, there are numerous problems such as rising cost and inflexibility. Many organic solar cells researchers have been vigorously working on replacement of ITO by carbon nanotube. Yet, the same application in perovskite solar cells has not been reported to date.

Therefore, in this work, we investi- gated diverse methodologies that can achieve carbon nanotube electrode in indium-free perovskite solar cells. We found that modified PEDOT:PSS function as both electron- blocking layer and dopant analogue to the organic photovoltaics while MoO3 is not compatible which is unique to the perovskite system. We discovered that diluted nitric acid doping with a concentration of 35% serves as the most effective method to enhance optical conductivity of carbon nanotube in a safe manner. A PCE of 6.32% in an ITO-free planar heterojunction perovskite solar cell was recorded when its indium tin oxide based reference gave 9.05%. A further flexible application showed 5.38% on a PET substrate.

CNTFA P12

Large - scale fabrication of transparent conductive metal meshes on rigid and flexible substrates using aby carbon nanotube etching mask

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We report on the experimental realization of using super- aligned carbon nanotubes (SACNTs) as an etching mask in the fabrication of the nanostructured metal meshes. This method can easily be extended to different metals on both rigid and flexible substrates. The as-fabricated metal meshes, including ones made of gold, copper, and aluminum, are suitable for use as transparent conductive layers (TCLs). The metal meshes, which are similar to the SACNT networks in their dimensional features, exhibit compatible performance in terms of optical transmittance and sheet resistance. Moreover, because the metal meshes are fabricated as an integrated material, there is no junction resistance between the interconnected metal nanostructures, which markedly lowers their sheet resistance at high temperature. SACNT networks prepared using a simple drawing and deposition process are proved to be an effective etching mask that can be used to fabricate large-scale TCLs. This approach should be easy to extend to various research fields and has broad prospects in commercial applications.

CNTFA P13

Terahertz sensing and imaging with graphene and carbon nanotube devices

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The advantageous properties of terahertz (THz) waves, such as the important energy spectrum in the meV range, enable various applications of imaging and spectroscopy. However, since the THz region is located between the electronic and photonic bands, even basic components like detector and source have not been fully established, compared to the other frequency regions. The THz wave also has the problem of low imaging resolution, which results from a much longer wavelength than that of the visible light. By employing graphene and carbon nanotube devices, we have developed a new type of THz sensing and imaging devices.We have succeeded in observing THz photoconductivity of graphene, ranging over a wide frequency band of 0.8-33THz. This result demonstrates that the graphene device works as a wide-band, frequencytunable THz detector. By using the graphene THz detector, we have further created a new designed THz imager, in which all the components: an aperture, a probe, and a detector are integrated on one chip. The development of this device has made it possible to perform nanoscale THz imaging and spectroscopy. Finally, other types of THz devices with carbon nanotubes will be also presented.

CNTFA P14

Evaluation of performance uniformity for energy device circuit made from micro-scale CNT supercapacitors

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Electronics have advanced by the miniaturization of components, such as transistors, resistors and inductors, with the exception of Al electrolytic capacitors (AECs) which have remained on the centimeter-scale for the past 50 years. With the advent of novel materials, such as nano-carbons and graphene oxide (GO), approaches have been reported to down-size capacitors to the sub-millimeter scale. Recently, we have developed a method to fabricate CNT micro-supercapacitors ～1/1000-th the size of AECs. However, for this technology to be ultimately attractive and viable industrially, these micro-supercapacitors must demonstrate the ability to operate in arbitrary arrangements to meet the specific demands for any particular device. Therefore, performance uniformity for the individual micro-supercapacitors is required to allow the reliable design of energy circuits.

Here, we have fabricated energy circuits, both in parallel and in series, to evaluate the operation of the entire circuit as well as the uniformity for each individual unit. In this way, we also estimated the performance deviation among capacitors and the operational yield. These important points represent some of the fundamental issues for the industrialization of our device. This presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

CNTFA P15

Demonstration of non-volatile multilevel memory in ambipolar carbon nanotube thin film transistors

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We report that multilevel operation can be implemented by carbon nanotube thin film transistors (CNT-TFTs). We find that three distinct conduction states can be obtained in ambipolar CNT-TFT with bilayer Al_2O_3-epoxy as dielectric to obtain high efficiency ambipolar characteristic.Direct change between any of the three states was demonstrated by selecting appropriate value for the magnitude and duration of each program/erase voltage pulse. The device have low operation voltage of 5V, as well as short duration time of 1 s. The retention time is 2.5×10^4 s. No degradation occurs under endurance measurement. A tradeoff was shown to exist between low voltage and fast switching for a given device.

CNTFA P16

Fabrication and performance of single-walled carbon nanotube thin films with controlled bundle morphology

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We present a novel concept of aerosol synthesis, controlled bundling and deposition of initially individual single-walled carbon nanotubes with invariant length that of 3 microns. The synthesis relies on pre-generated iron catalyst particles via physical evaporation in a nitrogen diluted spark discharge system with geometric mean diameter that of 3 nm (D_g=1.30 nm) and varying number concentrations (N). The floating catalysts are mixed with carbon monoxide (CO) and hydrogen to form SWCNTs in a vertical laminar flow reactor set to 880℃ temperature. With combinations of varying N and the nanotube residence time in the floating state, we control the nanotube bundling after the synthesis process. Based on atomic force microscopy of thermophoretically deposited nanotubes on mica substrates, the morphology of deposited SWCNT varies from predominantly individual (bundle diameter d_b=1.21 nm) to intermediately bundled (d_b=2.41 nm). Correspondingly, we show that the electro-optical performance of non-doped transparent conductive films varies with bundling, with highest performance provided by the smallest bundles (310 Ohms/Square at T=90%) and the lowest performance by the largest (630 Ohms/Square at T=90%).We also discuss the physical processes leading to the observed behavior.

CNTFA P17

Flexible microelectrode based on CNT thin film and its electrochemical sensor applications

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Carbon nanotubes (CNTs) have shown promising properties as electrochemical electrodes such as rapid electron transfer kinetics, wide potential window, and biocompatibility. Flexible devices based on CNTs have been investigated extensively for varieties of applications such as gas sensors, electronics devices, and electrochemical sensors. However, conventional solution-based process to form CNT thin film may degrade the performance and uniformity in electrochemical activity on electrode surface due to contamination associated with dispersal substances. Here, we demonstrate high-performance flexible microelectrodes based on an as-grown CNT thin film for electrochemical sensor applications to detect dopamine, an important neurotransmitter.

CNT microelectrodes were fabricated on a PEN substrate by dry transfer method based on the floating-catalyst CVD and standard microfabrication process. In electrode structure, only CNT surface is exposed to electrolyte and performs electrochemical reaction. To minimize the contamination of CNT surface, CNT surface was covered with an oxide film during fabrication process.

The electrochemical properties of flexible CNT microelectrodes showed high uniform, and high electron transfer rate with the quartile potentials |E3/4 E1/4| ~60 mV, close to ideal value (59 mV). Electrodeposited gold on electrode confirmed the high uniformity in electrochemical activity of CNT surface, especially after an activation process. These CNT microelectrodes also exhibited high sensitivity in detection of dopamine.

CNTFA P18

Sensor properties of backside fluorinated graphene

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The interaction between a graphene surface with polar molecules in a gas phase leads to a change in its electronic state. With adsorption of polar molecules on the surface, the charge transfer occurs from the molecules to the graphene plane. Here we propose a way to create reactive centers by removal of fluorine atoms from the external surface of fluorinated graphene while preserving the backside fluorination. Such partially recovered graphene layers were produced by acting of hydrazine-hydrate vapor on initially non-conducting fluorinated graphite. Reduction degree and sensing properties on ammonia exposure were controlled by measuring the surface conductivity. We show that the adsorption energy of ammonia depends on the graphene recovery, and quantum-chemical calculations relate the dependence with charge distribution induced by the residual fluorine atoms.

CNTFA P19

Full-length re-burning of anode single-walled carbon nanotubes after nanogap formation by electrical breakdown

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Semiconducting single-walled carbon nanotubes (s-SWNTs) are expected to improve both performance and energy efficiency of field effect transistors. Electrical breakdown technique [1] has been often applied to cut metallic (m-) SWNTs to avoid short circuits. After the cutting of SWNTs, nanogaps (~100 nm) are formed and majority of m-SWNTs remains on substrates, which negatively affects high-frequency operation.

Here we report a re-burning phenomenon of the remaining m-SWNTs in full length on anode side after nanogap formation. SWNT arrays grown on crystal quartz substrates were transferred onto the Si/SiO_2 substrates on which metal electrodes were photolithographically defined. SWNT nanogaps were formed by electrical breakdown in dry oxygen. Then, the SWNT arrays were covered with polymethyl methacrylate films and were re-ignited by applying voltage to the nanogaps in wet oxygen. Only anode SWNTs were burned almost in full length [2], probably triggered by field-emittedelectron-induced oxidation with the assistance of water molecules [3]. This phenomenon could be utilized for the fabrication of s-SWNT arrays in large area.

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CNTFA P20

Carbon nanotube feedback-gate field-effect transistor: suppressing current leakage and increasing on/off ratio

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Field-effect transistors (FETs) based on moderate or large diameter carbon nanotubes (CNTs) usually suffer from ambipolar behavior, large off-state current and small current on/off ratio which are highly undesirable for digital electronics. To overcome these problems, a feedback-gate (FBG) FET structure is designed and tested. This FBG FET differs from normal top-gate FET by introducing an extra feedback-gate which is connected directly to the drain electrode of the FET. It is demonstrated that a FBG FET based on a semiconducting CNT with a diameter of 1.5 nm may exhibit low off-state current of about 1E-13, high current on/off ratio of larger than 1E8, negligible drain-induced off-state leakage current and good sub-threshold swing of 75 mV/dec even at large source-drain bias and room temperature. The FBG structure is promising for CNT FETs to meet the standard for low-static-power logic electronics applications, and could also be utilized for building FETs using other small band-gap semiconductors to suppress leakage current.

CNTFA P21

Developing reliable and stable CNT micro-supercapacitors on flexible substrates

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Over the past few years, the development of the electric double-layer capacitor (i.e. supercapacitor) has attracted increased attention due to its high power density, durability and safety compared to batteries. Recently, with the development of novel materials, including carbon nanotubes (CNTs) and graphene oxide, large strides in the improvement of the supercapacitor energy density has been demonstrated. Furthermore, these novel materials have enabled a route toward the miniaturization of capacitors which have remained unchanged in size over the past 50 years. We have recently demonstrated a CNT-micro supercapacitor which has demonstrated both high energy density and high power density while being 1000-times smaller than current aluminum electrolytic capacitors. However, for this technology to reach commercial applications, the individual CNT-micro supercapacitors must demonstrate stable and uniform operation which is largely determined by a stable and uniform production process. Here, we report the development of a stable production process for these CNT-micro supercapacitors on flexible substrates including flexible current collectors. In so doing, we have created a new flexible and durable micro-energy device which widens its potential applications. This presentation is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

CNTFA P22

A census of chirality population in a NIST reference material of single-walled carbon nanotubes

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A reference material is essential to enable and accelerate the commercialization of a new material. The National Institute of Standards and Technology recently released the worlds first reference material (RM) of a single-wall carbon nanotube (SWCNT) dispersion known as RM8281. However, the accompanying User Information doesnt include chirality distribution, which is known as one of the most important structure parameters. Here, we present for the first time a quantitative chirality assessment of the RM8281 by using an enhanced method for absorption spectrum analysis. Our results show that approximately 75 % of SWCNTs in RM8281 have a diameter in the narrow range of 0.7 - 0.9 nm, and 69 % of SWCNTs have a chiral angle from 15° to 30° . Of significance, 25 % of the total RM8281 SWCNT population was found to be the (6,5) species nanotubes. Transmission electron microscopy and electron diffraction techniques were utilized to complete an adequate statistical analysis of chirality distribution in RM8281, giving a satisfactory agreement with the above absorption spectra measurements. More importantly, the independent multiple characterization methods give a full quantitative chirality assessment of the RM8281, which significantly promote the application of the material as a SWCNT reference sample.

CNTFA P23

Single-wall carbon nanotube films with optical and electrophysical properties tunable via time-depended filling of nanotube internal channel with acceptor molecules

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Nowadays films of single-wall carbon nanotubes (SWCNTs) are very promising for application in flexible highly conductive and transparent electronics, light sensitive electronics and nonlinear optics. One of the most important problems is providing a variation of optical, mechanical, electrophysical and chemical properties of this unique material. These properties should be changed in a controllable way.

Here we present a new approach to tune the optical and electrophysical properties of transparent conductive films formed from SWCNTs. A net of SWCNTs grown by an aerosol chemical vapor deposition technique is used as a ground for a gas-phase filling the NT internal channels with strong electron acceptors (iodine or copper chloride). This leads to a remarkable charge transfer from nanotubes to species formed inside them. The approach allows to change step-by-step the Fermi level position, optical transmittance and conductivity of SWNTs. The filling degree is determined by the treatment duration. Thus, this approach provides a p-doping degree variation and the Fermi level shift determined by the treatment time. The effect leads to a smooth changing the optical transmittance and electrical conductivity of SWCNT films. These results are very promising for applications in light-sensitive electronics and nonlinear optics.

CNTFA P24

Phosphorous-doped single-walled carbon nanohorns as supercapacitor electrodes

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Single-walled carbon nanohorns (SWCNHs) can be considered as a promising candidate for supercapacitor electrodes, owing to their highly porous structure and relatively high electrical conductivity. In this study, we report electrochemical behaviors of phosphorous-doped SWCNH electrodes for supercapacitor applications. The phosphorous-doped SWCNHs were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and nitrogen adsorption technique at 77 K. The P2p XPS spectra clearly showed the incorporation of phosphorous atoms in the SWCNH structure after phosphorous-doping treatments. In order to confirm the phosphorous-doping effects, the electrochemical behaviors of the SWCNH supercapacitor electrodes were investigated before and after the phosphorous-doping treatment. Phosphorous-doped SWCNH electrodes exhibited enhanced supercapacitive performance compared to undoped one.

CNTFA P25

An ultrasensitive sandwich-type electrochemical immunosensor for AFP based on cyclodextrin functionalized graphene as platform and X@CuO-MWCNTs (X: Au, Ag, Pd, Pt) as labels

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A novel and ultrasensitive sandwich-type electrochemical immunosensor has been developed for quantitative detection of alpha-fetoprotein (AFP).cyclodextrin functionalized graphene (CD-GS) was used as platform for capturing more primary antibodies owing to its high specific surface, ideal dispersibility and well biocompatibility. Noble metal hybrid multiwalled carbon nanotubes adhered copper oxide (X@CuO-MWCNTs, X: Au, Ag, Pd, Pt) was prepared as labels for multiple amplified signals. This is because noble metal, CuO and multiwalled carbon nanotubes (MWCNTs) can be used as one of catalysts for decomposition of hydrogen peroxide. Synergetic effects of noble metal, CuO and MWCNTs greatly improved the catalytic efficiency and the electrochemical signal output. Under optimal conditions, the fabricated immunosensor exhibited a wide liner range from 1 pg mL-1 to 20 ng mL-1 with a low detection limit of 0.33 pg mL-1 (S/N=3) for AFP. The developed immunosensor showed high selectivity, good reproducibility and accepted stability, which could provide potential applications in clinical monitor of AFP.

CNTFA P26

High purity synthesis of narrow-chirality distributed single-walled carbon nanotube and its growth mechanism by pulse plasma CVD

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Single-walled carbon nanotubes (SWNTs) are potential materials for future high performance opto-electric device application. Since the energy state of SWNTs depends on the chirality, it is important to control the chirality of SWNTs [1-3]. Based on our previous study, we developed novel plasma CVD named pulse plasma CVD, which can grow SWNTs with narrow chirality distribution. To improve the purity of chirality species, it is important to understand the effects of pulse plasma on the growth of SWNTs. In this study, we have investigated the correlation between pulse on/off time parameters and chirality-distribution of SWNTs. It is found that SWNTs chirality distribution is influenced by the balance of pulse effect and Ostwald ripening effect, which is decided by pulse on/off ratio and total process time, respectively. Through the fine tuning of growth conditions by following this growth mechanism, we have succeeded in synthesizing SWNTs with very narrow chirality distribution, where only three chirality species ((6,4), (7,3), (6,5)) are dominant.

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CNTFA P27

Iron-nitrogen-doped nanographene coated carbon nanotubes as oxygen reduction reaction catalyst

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Iron-nitrogen-carbon (Fe-N-C) catalysts have been attracted much attention as alternatives to costly and limited reserves Pt-based catalysts for oxygen reduction reaction (ORR) on cathodes of polymer electrolyte membrane fuel cells. Fe-N-C catalyst possesses ORR active structures that a metal iron atom is coordinated to nitrogen functionalized graphitic carbon. Although numerous studies on development of the Fe-N-C catalysts have been performed, further activation still remains a challenge for a replacement for Pt-based catalysts.

Carbon nanotube has feature of high specific surface area, high electronic conductivity and electrochemical durability, and then has been paid attention as a support material to immobilize ORR catalytic sites. In this study, CNT catalyst wrapped in Fe-N-C nanostructures were fabricated by employing a molecular assembly technique. Iron(II) phthalocyanine (FePc) molecules spontaneously adsorbed on CNT surface by mixing CNT with FePc dispersed solution, and then CNTs wrapped in Fe-N-C nanostructures (Fe-N-C/CNT) were fabricated by pyrolyzing the composite. Rotating disk electrode voltammetry in oxygen saturated 0.5 M sulfuric acid revealed that a half wave potential of Fe-N-C/CNT showed 0.79 V vs. RHE, which is one of the highest ORR activity in previously reported Fe-N-C carbon catalysts. These results indicate that CNT serve as development of CNT based ORR electrocatalyst.

GSS15

K1

Atomic imaging and spectroscopy of low-dimensional materials

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We have been developing the top-level facilities of electron microscopy which enables the atomic resolution analysis of low-dimensional materials. Point defects and edge structures of graphene have been intensively studied with atomic precision in the last decade. The studies of atomic defects and boundaries are of general interest both in the fundamental researches and technological applications of any nanoscale materials. The atomic scale studies can be therefore expanded to the other low-dimensional materials. Here I demonstrate some examples for atomic-scale imaging and spectroscopy of various low-dimensional materials with interrupted periodicities. Active 4|8 defects are most recently found to be responsible for plastic deformation of hexagonal boronnitride (h-BN) layers. Vacancies and edges with radical bonds are also successfully assigned in h-BN. Doping and boundary behaviors of single-layered dichalcogenides (MX2) are also intensively studied. More recently, the impurity atoms such as nitrogen and silicon are proved to affect the properties of graphene.

K2

Advances in raman spectroscopy of graphene and layered Materials

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Raman spectroscopy is an integral part of graphene research [1]. It is used to determine the number and orientation of layers, the quality and types of edges, and the effects of perturbations, such as electric and magnetic fields, strain, doping, disorder and functional groups[2,3]. I will review the state of the art, future directions and open questions in Raman spectroscopy of graphene and related materials, focussing on the effect of disorder[3,4], doping[5,6] and deep UV laser excitation[7]. I will then consider the shear [8] and layer breathing modes(LBMs)[9], due to relative motions of the planes, either perpendicular or parallel to their normal. These modes are present in all layered materials[10,11]. Their detection allows one to directly probe the interlayer interactions [10,11]. They can also be used to determine the elastic constants associated with these displacements: the shear and out-of-plane elastic moduli[12]. This paves the way to the use of Raman spectroscopy to uncover the interface coupling of two-dimensional hybrids and heterostructures[10-12].

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I1

Moiré superlattice

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Recent discovery of atomically thin planar crystals, such as graphene, hBN, and MoS_2, enabled the fabrication of artificial layered-structures. Whenever atomic layers are overlaid in incoherent ways, the moiré interference between the lattices makes a new class of superlattice where the influence of the exceptionally long-period interlayer interaction is crucial to determine its electronic structures. In this talk, I will first discuss the electronic and optical properties of moiré superlattices [1]. I will show that this kind of superlattice is the first example of crystals of which material properties are mainly governed by the moiré interference of atomic arrangement rather than the arrangement itself. Then, I will show that the moiré superlattice affords a unique opportunity to study the fundamental problem on the motions of electrons under the simultaneous influence of a periodic atomic potential and a magnetic field, aka Hofstadters fractal butterfly, in the normally inaccessible regime [2-4].

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I2

Solution processing and device integration of two-dimensional black phosphorus

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Two-dimensional black phosphorus (2D BP) has emerged as a promising candidate for next-generation electronics and optoelectronics. As is common for new materials, much of the early work on 2D BP has focused on measuring and optimizing intrinsic properties on small samples under idealized conditions. However, real-world devices and systems inevitably require large-area samples that are integrated with dielectrics, contacts, and other semiconductors at standard temperature and pressure conditions. These requirements are particularly challenging to realize for 2D BP since its properties are highly sensitive to surface chemistry, defects, and the surrounding environment. This talk will thus explore methods for improving the uniformity of solution-based 2D BP with an eye toward realizing scalable processing of large-area thin-films. Specifically, methods for exfoliating black phosphorus in anhydrous organic solvents will be discussed such that the resulting 2D BP flakes show field-effect transistor mobilities and on/off ratios that are comparable to micromechanically exfoliated flakes. In addition to solution processing, this talk will also report on the integration of 2D BP with dielectrics and other materials. In particular, atomic layer deposition of alumina dielectrics on 2D BP suppresses ambient degradation, thereby preserving electronic properties in field-effect transistors at atmospheric pressure conditions.

I3

Transport studies in black phosphorus field effect transistors

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Ultrathin black phosphorus (BP), or phosphorene is the second known elementary two-dimensional material that can be exfoliated from a bulk van der Waals crystal. Unlike graphene it is a semiconductor with a sizeable band gap that allows both high carrier mobility and large on/off ratios. Its excellent electronic properties make it attractive for applications in transistor, logic, and optoelectronic devices. However, it is also the first widely investigated two dimensional electronic material to undergo degradation upon exposure to ambient air. Therefore a passivation method is required to study the intrinsic material properties, understand how oxidation affects the physical transport properties and to enable future application of phosphorene. I will show that atomically thin graphene and hexagonal boron nitride crystals can be used for passivation of ultrathin black phosphorus.

I4

Heterostructures based on CVD transition metal dichalcogenides

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Transition metal dichalcogenides (TMDs) are attractive for energy and electronic applications. Our recent success in vapor phase growth of TMD monolayer has stimulated the research in growth and applications. I would discuss the synthesis and characterizations of crystalline MoS2 and WSe2 monolayers. These layer materials can be transferred to desired substrates, making them suitable building blocks for constructing multilayer stacks. Both the vertical and lateral heterojunction structures can be grown by CVD methods, where the junction shows unique properties.

I5

Catalytic growth of monolayer graphene on Ge surface

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Large-area graphene has been grown by catalytic chemical vapor deposition (CVD) on various metal substrates. However, the uniform growth of single-crystal graphene over wafer-scale areas remains a challenge toward the commercial realization of graphene-based devices. In this talk, we present the growth of single-crystal monolayer graphene on hydrogen-terminated germanium (Ge) surface. A single-crystal Ge substrate is a promising candidate for the growth of single-crystal graphene, because of (i) its catalytic activity for the catalytic decomposition of the formation of graphitic carbon on the surface; (ii) the extremely low solubility of carbon in Ge even at its melting temperature, enabling growth of complete monolayer graphene; (iii) the anisotropic atomic arrangement of single crystal Ge surface, enabling aligned growth of multiple seeds; (iv) the availability of a large area single-crystal surface via epitaxial Ge growth on Si wafers. We observed that well-defined atomic arrangement on the single crystal Ge surface enabled aligned growth of multiple seeds which can merge to single crystal graphene.

C1

Revealing the mechanical properties of two-dimensional materials by direct in situ transmission electron microscopy

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Two-dimensional (2D) crystals are promising building blocks for flexible electronics, because of their strong in-plane bonding and high flexibility. Therefore, it is important to understand their mechanical properties, especially under bending. We directly investigated the bending behaviors of 2D materials by using the in situ transmission electron microscopy (TEM) method. It was found that the bending mechanisms are closely related to the dimensions. Multilayered boron nitride and graphene ribbons were observed to form localized kinks in the fully reversible bending experiments.1 And the bending behaviors of molybdenum disulphide atomic layers changed from spontaneous rippling (∼5 atomic layers) to homogeneous curving (∼10 layers) and finally to kinking (20 or more layers), depending on the competition of strain energy and interfacial energy.2

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C2

Probing spectroscopic properties of BN and black phosphorous layers

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In this talk, we examine the interplay between structure and spectroscopic properties of both BN and Black Phosphorous (P(black)) mechanically exfoliated layers and how these properties can be further exploited in 2D layered heterostructures. Spectroscopic properties were studied using cathodoluminescence (CL) at 4K, Raman spectroscopy, HRTEM and Electron Energy Loss Spectroscopy (EELS) using a monochromated Libra 200 TEM-STEM at 80 kV.

BN displays original optical properties governed, in the energy range 5.5 – 6 eV, by strong excitonic effects, consisting of D and S lines [1]. From CL experiments, D lines are proved to be due to structural defects and S lines are identified as the intrinsic luminescence of the material [1]. We will show how exfoliated layers could be prepared with no D band and that their S-emission dramatically changes when reducing the number of layers, providing with a signature of the 2D confinement [2]. Low-loss-EELS is an alternative approach to the nature of electronic excitations. One can indeed access to the onset of optical transitions and investigate their angular dependence. We will show that we can probe the whole Brillouin zone of BN layers and represent the plasmon dispersion as a function of the q momentum.

P (black) thin layers have recently raised interest for their original electronic properties. Their study is however very challenging due to its fast degradation under ambient conditions. Thanks to Raman and core-loss EELS spectroscopy, we have shown that this phenomenon is due to a thickness dependant photo-assisted oxidation reaction with absorbed oxygen in water and found appropriate manipulation procedures opening a route to first measurements on pristine layers [3].

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C3

Effective switching of graphene-boron nitride nanotube heterojunctions

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High electron mobility of graphene has enabled their application in high-frequency analogue devices but hindering their use in digital switches. In contrast, the structural analogous, h-BN sheets and BN nanotubes (BNNTs) are insulators. [1] Here we show that graphene-BNNTs heterojunctions are digital switches with a switching ratio of 10^5.

BNNTs are grown on graphene without the use of catalyst by our CVD technique [1]. These graphene-BNNT heterojunctions were characterized for their transport properties at room temperature by four-probe scanning tunneling microscopy (4-probe STM) under real-time monitoring of scanning electron microscopy (SEM) [2]. Current switching was detected either by decreasing the contact distance from the junctions at a fixed biasing, or vice versa. A switching ratio as high as 105 at a turn-on voltage as low as 0.5V were recorded. Simulation by density functional theory (DFT) suggests that mismatch of the density of states (DOS) is responsible for these novel switching behaviors.

Acknowledgement:

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C4

Exploring atomic defects and their dynamic behaviors in monolayer MoS_2 by ADF-STEM

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Defects usually play an important role in tailoring various properties of two-dimensional materials. Molybdenum disulfide (MoS_2) monolayer, a promising two-dimensional semiconductor, may suffer from point defects, leading to large variation of electric and optical properties. Here we present an experiment-theory joint investigation of comprehensive characterization on point defects in MoS_2 monolayers prepared by mechanical exfoliation (ME), physical and chemical vapor deposition (PVD, CVD). Species and concentrations of the defects were systematically identified by aberration-corrected scanning transmission electron microscopy and ab-initio calculation. Exceptionally high defect density close to 3.5×10^{-15} cm^{-2} was found and the dominant category of defects changes from sulfur vacancy in ME and CVD samples to Mo anti-site in PVD samples. Influence of defects on electronic structure, charge carrier mobility and optical absorption was predicted by calculations and observed (confirmed) by photoluminescence experiments. In light of these results, the growth of ultra-high quality MoS_2 monolayers appears a primary task for the community pursuing highperformance electronic devices.

DFT calculations were mainly done by Prof.Wei Ji in Renmin University of China. The work on microscopy were mainly done in the Center for Electron Microscopy of Zhejiang University. We acknowledge financial support from NSFC and MOST.

C5

Optical properties of high-quality WS_2 monolayers grown on graphite

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We report on the growth of high-quality, monolayer WS_2 onto exfoliated graphite by high-temperature chemical vapor deposition (CVD). Monolayer WS_2 single crystals grown presents a uniform, single excitonic photoluminescence peak with a Lorentzian profile and a very small full-width at half maximum of 21 meV at room temperature and 8 meV at 79 K. Furthermore, in these samples, no additional peaks are observed for charged and/or bound excitons, even at low temperature. These optical responses are completely different from the results of previously reported TMDCs obtained by mechanical exfoliation and CVD. Our findings indicate that the combination of high-temperature CVD with cleaved graphite surface is an ideal condition for the growth of high-quality TMDCs, and such samples will be essential for revealing intrinsic physical properties and for future applications.

C6

Substrate effect on photoluminescence properties of tungsten disulfide atomic layers

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Transition metal dichalcogenides (TMDCs) have attracted a great deal of attention because of their unique properties: spin-valley-coupled electronic structure, valley pseudospin degree of freedom, intense photoluminescence and FET operation. The family of TMDCs atomic layers has provided a brand new and widespread platform to investigate physics in two-dimension, leading to the novel application called valleytronics in future. To explore the fascinating possibility of TMDCs, high-quality samples are indispensable. In this work, we have focused on substrates to realize high-quality samples.

WS_2 have been grown by the for the chemical vapor deposition method, where various substrates including SiO_2/Si, sapphire and hexagonal boron nitride (hBN) have been employed. Monolayer WS_2 crystals with triangular shape have successfully been grown onto all substrates used. We have found that intensity and FWHM of PL emission peak strongly depend on the substrates. Monolayer WS_2 on hBN exhibits, in particular, the most intense and sharpest PL emission (FWHM of 22.7 meV). Temperature dependence of PL spectra of WS_2 on hBN is significantly different from WS_2 grown on other substrates, showing new feature at 2.016 eV. The observed unique PL properties of WS_2 on hBN clearly demonstrate the importance of substrate in investigations of physical properties of TMDCs.

C7

Polymer organic-light emitting diodes on high-flatness transparent sheet with graphene films synthesized by plasma treatment

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Because graphene films have one atom-thickness, the morphology of the flatness of the transparent sheet could have a larger influence on the performance for organic light-emitting diode (OLED) devices using graphene films than indium tin oxide (ITO). Therefore, decreasing the surface roughness of the transparent sheet, which results in reducing the possibility of leakage current, is important factor to improve the performance for OLED devices with graphene films. In this study, we have evaluated the polymer OLED devices with graphene films synthesized by plasma treatment on polyethylene terephthalate (PET) sheet and polyethylene naphthalate (PEN) sheet having high flatness. The graphene-based OLED device on the transparent sheet with higher flatness shows high illumination (～8000 cd/m^2 at 15 V) and high current efficiency (6.71 cd/A) at area of 2 mm X 6 mm. The results suggest that the surface roughness of transparent sheet strongly affect the performance for OLED devices with thin transparent electrode such as graphene films.

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C8

Creation of boron-doped graphene by thermal decomposition of B4C thin film on SiC (000-1)

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Graphene, one atomic layer thickness carbon, is a kind of nano-carbon material, and it has good properties, high electrical conductivity, high thermal conductivity, mechanical strength, and so on. Boron doping in graphene is expected as the good technique to modify and improve the electronic properties of graphene. Previously, we have reported epitaxial growth of boron-doped graphene by thermal decomposition of boron carbide (B4C) particles. In this study, we attempted to grow the large-area boron-doped graphene by thermal decomposition of boron carbide thin film grown on the SiC substrate, and investigated the features.

First, the B4C thin films were grown on the C-terminated 6H-SiC (000-1) by heating at 1500 °C in vacuum, together with the B4C powder. Next, we grew graphene by thermal decomposition of the boron carbide thin film, by heating at 1400 °C in vacuum. From the TEM observation, we found that the single-crystal thin film of the boron carbide, whose thickness is approximately 8.3 nm, was grown epitaxially on the SiC substrate over a wide range. After graphene growth, 3～4 graphene layers were observed on the B4C/SiC substrate. As a results of the Hall-effect measurement, the hole conduction was measured, suggesting the presence of doped boron in graphene.

C9

Layer-by-layer oxidation of atomically thin WSe_2: Implications for two-dimensional MOSFETs

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Tunable and uniform oxidation of atomically thin transition metal dichalcogenides is of great importance for electronic applications. Here we demonstrate self-limiting layer-by-layer oxidation of atomically thin WSe_2 through ozone (O_3) exposure at various temperatures. Below 100 °C, the O_3 treatment results in the growth of oxides at the edges and dendritic oxide islands on the surface. With further exposure, the oxides grow laterally and coalesce to each other, ultimately forming a uniform film on top. However, oxidation does not progress to the underlying layers. At 200 °C, the surface layers are oxidized in the layer-by-layer regime, up to trilayers. Using Raman and photoluminescence spectroscopy and x-ray photoelectron spectroscopy, we find that the underlying WSe_2 is mechanically decoupled from the top oxide but strongly hole doped. Transport measurements suggest that the thermally-grown oxides of atomic thicknesses show good insulating properties. These observations have important implications for applications of layered transition metal dichalcogenides in metal-oxide-semiconductor field effect transistors (MOSFETs), in analogy with the silicon-MOSFET.

C10

Gap states analysis in gapped bilayer graphene by conductance method

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The targeted issue for bilayer graphene is low I_{on}/I_{off} at the room temperature, which is explained by the variable range hopping in "gap states". However, as the zero-order approximation, there will be intrinsically no interface states in bilayer graphene because there is no dangling bonds on the basal plane, compared with P_b centers in SiO_2/Si system. The origin for the gap states is still open question. In spite of this, the detailed measurements on D_{it} and time constant for gap states have not been reported yet. One of reasons could be the leakage current through the top gate insulator since robust methodology is not established.

Recently, we demonstrated a considerable suppression of the low-field leakage by applying the high-pressure O_2 annealing to Y_2O_3 top gate insulator. The reliable Y_2O_3 top gate insulator provides the access to the carrier response issue in the largely-opened band gap. In this talk, we focus on the conductance measurements for bilayer graphene to extract D_{it} and time constant. Based on these measurements, two possible origins for the gap states, (i) border traps at the edge of Y_2O_3 and (ii) the local breakdown of A-B stacking in bilayer graphene, are discussed.

C11

Edge-channel interferometer in a graphene quantum Hall pn junction

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We study carrier transport in high-mobility dual-gated h-BN/graphene/h-BN devices fabricated using mechanical exfoliation and dry transfer techniques of atomic layers. The resistance across the npn junctions exhibits an oscillatory behavior in an intermediate magnetic-field range. The resistance oscillation demonstrates a quantum Hall edge-channel interferometer formed in a high-quality graphene pn junction under a high magnetic field. The co-propagating p and n quantum Hall edge channels traveling along the pn interface functions as a built-in Aharanov-Bohm-type interferometer, the interferences in which are sensitive to both the external magnetic field and the carrier concentration. The trajectories of peak and dip in the observed resistance oscillation are well reproduced by our numerical calculation that assumes magnetic flux quantization in the area enclosed by the co-propagating edge channels. Coherent nature of the co-propagating edge channels are confirmed by the checkerboard-like pattern in the dc-bias and magnetic-field dependences of the resistance oscillations.

GSS P1

Preparation of defective graphene sheets using sonoelectrochemical method and their application as electrocatalysts

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A sonoelectrochemical synthetic method is reported for rapidly preparing and dispersing reduced graphene nanosheets (RGNSECM) stabilized in an aqueous electrolyte. The X-ray photoelectron and Raman results demonstrate that the defects on RGNSECM are predominantly physical and not similar to the chemical defects on reduced graphene nanosheets (RGNCM) synthesized via chemical reduction of graphene oxide nanosheets based on Hummers method. The both RGNs were successfully applied as nonenzymatic H_2O_2 sensors and alkaline oxygen reduction reaction (ORR) catalysts. Using electrochemical analysis, a fair comparison of the performances of RGNSECM and RGNCM as H_2O_2 sensors and ORR catalysts has been performed.

GSS P2

Molten glass: an unprecedented solution to uniform monolayer graphene disks and films via direct chemical vapor deposition

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Latest demonstrations in direct CVD growth of graphene on solid dielectrics by us [1] and others [2] mark game-changing breakthroughs to bypass the complex transfer steps. However, such direct synthesis on solid dielectrics possesses severe limitations, e.g., poor quality and uniformity of graphene films. On the other hand, the graphene nucleation and growth on liquid form of substrates (like melted Cu [3]) would surprisingly be better controlled compared to those on solid substrates. In this regard, the use of liquid form of commercial glass would serve as an effective solution for controlling the nucleation and speeding up the growth rate of graphene during direct CVD process.

In the present work, we devise a novel "molten-state" atmospheric pressure CVD route, allowing fast formation of sub-monolayer, uniformly distributed graphene disks (up to ~2 micron) and full monolayer graphene films directly on liquid glasses.

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GSS P3

Gate-controlled photo-oxidation of graphene

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All carbon atoms of graphene belong to its surface, and thus electronic properties of graphene are sensitive to surface chemical modifications. In addition, an external electric field can penetrate into the graphene because the ultrathin body is insufficient to completely screen the field; in the configuration of a field-effect transistor (FET), an electric field from the bottom gate electrode can penetrate to the top surface of graphene. Therefore, the field-effect control of surface chemical reactions is expected to be feasible using the FET configuration.

In this presentation, gate-controlled photo-oxidation of graphene will be introduced [1]. Edge-selective photo-oxidation was observed only with negative gate voltages, and enhanced with the presence of water molecules [2]. The oxidation was found to proceed into the center region, which might enable us to fabricate graphene nanoribbons or nanoconstrictions.

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GSS P4

Plasma-assisted fabrication of monolayer phosphorene and its Raman characterization

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There have been continuous efforts to seek novel functional two-dimensional semiconductors with high performance for future applications in nanoelectronics and optoelectronics. In this work, we introduce a successful experimental approach to fabricate monolayer phosphorene by mechanical cleavage and a subsequent Ar^+ plasma thinning process. The thickness of phosphorene is unambiguously determined by optical contrast spectra combined with atomic force microscopy. Raman spectroscopy is used to characterize the pristine and plasma-treated samples. The Raman frequency of the A_{2g} mode stiffens,and the intensity ratio of A_{2g} to A_{1g} modes shows a monotonic discrete increase with the decrease of phosphorene thickness down to a monolayer. All those phenomena can be used to identify the thickness of this novel two-dimensional semiconductor. This work on monolayer phosphorene fabrication and thickness determination will facilitate future research on phosphorene.

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GSS P5

Large-quantity hierarchical biomorphic graphene gown by chemical vapor deposition

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Mass production of high-quality graphene holds a significant premise for engineering applications such as low-cost and high-performance flexible thin-film electronics, which is commonly integrated into large-area films with a perfect preservation of the parent superior properties. Batch production of graphene micro-flakes was originally realized by chemical reduction of exfoliated graphene oxides (RGO), liquid-phase exfoliation of graphite, etc. However, those scalable routes usually introduce chemically modified groups (or limited crystallinity), as well as uncontrollable layer-thickness and lateral size. Herein, we report a scalable growth of high-quality graphene flakes by chemical vapor deposition (CVD) on naturally abundant substrates of diatomites. Intriguingly, the CVD graphene could rigorously inherit the hierarchical structures of substrates thus following a bio-inspired synthesis mechanism. High quality and controlled thickness of biomorphic graphene have been achieved, which are close to that of planar CVD graphene, and much better than that of RGO. Due to weak interlayer interactions, the 3D biomorphic graphene flakes with could be dispersed rapidly in liquid even after the removal of diatomites. By rod coating and roll-to-roll hot pressing, large-area graphene films have been fabricated as highly conductive and flexible electrodes for optoelectronic applications.

GSS P6

Real-time radiation-mode optical microscopy of chemical vapor deposition growth of graphene on a copper substrate

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Chemical vapor deposition (CVD) on a copper substrate is considered to be the most suitable method to fabricate graphene due to the selectivity of the number of graphene layers and the large area fabrication. The real-time observation is useful to understand the mechanism and control the growth of graphene by CVD. Under the growth condition of graphene on copper by CVD, however, electron microscopes cannot work because the source gases up to atmospheric pressure scatter the electron beam. Here, we report the real-time observation of the CVD growth of graphene on a cupper substrate using a radiation-mode optical microscopy which observes the radiation lights from the materials at high temperatures. The large difference between the radiation intensities of graphene and copper enables us to observe the growing graphene grains responding to the change of the conditions in real-time. The graphene grains are also found to shrink after the shut-off of source gas supply, which is affected by the oxygen partial pressure in the system. On the basis of the real-time observation, we discuss the growth mechanism and a way to optimize the growth conditions of graphene on copper by CVD.

GSS P7

Surface bound graphene molecules: synthesis, electronic structure, excited state dynamics and applications

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Graphene molecules (GMs) are nanographene structures with size of less than five nanometers, typically comprising fewer than 300 carbon atoms. Theory predicts that thanks to the quantum confinement effects GMs should have size-tunable band gap in visible-to-near infrared spectral range. This makes GMs appealing materials for exploitation in optoelectronic applications. However, experimental studies of optical and electronic properties of GMs have been so far limited mainly because of the challenges associated with the preparation of well-defined structures. I will present a new method for a bottom-up preparation of structurally well-defined GMs in-situ, on metal oxide surfaces. This approach reduces the challenges associated with the tendency of GMs to aggregate, facilitates their electronic and optical characterization and provides a convenient path for their integration into devices. I will then present results of our studies of size-dependent electronic structure and excitonic properties of GMs using spectro-electrochemical methods and femtosecond-microsecond transient absorption spectroscopy. Finally, two applications of GMs will be presented: 1) GMs as light-harvesting components in sensitized solar cells 2) GMs as optically active components of electrochromic devices.

GSS P8

High quality graphene synthesis from graphene oxide

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It is important to develop a high through put method for high quality graphene.We have studied about new synthesis methods of graphene from graphene oxide (GO) with Cu single crystals or plasma treatment. We elucidated that high quality graphene is synthesized by only annealing at 1000 ℃ in Ultra high vacuum on Cu single crystals in spite of crystal orientations of Cu. STM images and Raman spectra revealed that high quality graphene with a few defects was synthesized. We also investigated another method with plasma treatment at low temperature (600 ℃) for graphene synthesis from GO. CH_4 and H_2 plasma treatment at 600 ℃ make GO graphene on SiO_2. We succeeded in direct growth of graphene on insulator. Moreover this method has another advantage. We can control the shape and position of graphene by edging of GO in advance. After plasma treatment, the shape of GO is not changed. Therefore we can obtain graphene with the same shape as we fabricated. In this presentation we are going to introduce these methods in detail with the results of STM, Raman spectroscopy and conductivity measurement.

GSS P9

Hexahydroxytriphenylene as a versatile and commercial exfoliant for 2D materials in aqueous and organic solvents through wet and dry processes

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Thin-layer 2D materials, such as graphene, hexagonal boron nitride (h-BN), and molybdenum disulfide (MoS_2), have attracted growing interest due to their unique physical and chemical properties. Since the layers are bound through van der Waals interaction, they have been directly exfoliated from the pristine bulk materials. The most typical way is the ultrasound irradiation in a liquid phase with or without additive. In this paper, we will present a versatile exfoliant, hexahydroxytriphenylene, which exfoliated graphene in aqueous solution as well as a low boiling point organic solvent to give highly concentrated dispersions (as high as 0.19 and 0.13 mg mL^{-1}, respectively). The exfoliation was also successful in the dry process using ball-milling, leading to a few layer graphene with yield more than 80% from pristine graphite. In addition, h-BN, MoS_2 and SWNTs were also exfoliated in aqueous and organic solvents through ultrasound irradiation and ball-milling. Taking versatility, availability and removability into consideration, hexahydroxytriphenylene is considered to be superior to the exfoliants reported so far.

GSS P10

Graphene oxide as a super material

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Graphene oxide (GO) and reduced graphene oxide (rGO) are nontoxic and inexpensive two dimensional (2D) materials, which are stable at room temperature. Since the discovery of their electronic, optical, mechanical, thermal and chemical nature, GO and rGO have been adopted for numerous fascinating applications. In this time, we discuss the possibility of employing GO/rGO as solid electrolyte/proton conductors, ferromagnets, electrodes or electron mediators and as an ingredient of hybrid photocatalysts for water splitting. Nowadays, it is difficult to classify GO/rGO related researches separately. In most cases the functionality and application of rGO is necessarily associated with GO synthesis, its modification and subsequent reduction to rGO. However, the reduction of GO to rGO is the source of various defects, holes, imperfections, semi hydrogenation state and band gap. All these influences affect most of the properties and utility of GO/rGO. Therefore, we will discuss functions with respect to both GO and rGO.

GSS P11

Probing degradation in exfoliated black phosphorus down to the monolayer

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Black phosphorus (P(black)) thin layers have recently raised interest for their semiconducting properties, such as a direct bandgap, tunable from 0.3 to 2 eV with layer thickness, associated to high carrier mobility. As for graphite/graphene, this lamellar crystal of P atoms can be exfoliated down to monolayer 2D-phosphane (also called phosphorene). The realization and the study of P(black) devices appears to be challenging due to the strong reactivity of P(black) thin layers in ambient conditions. We investigated this fast degradation process using in-situ Raman and transmission electron spectroscopies and reported on a thickness dependent reactivity of the layers. Moreover, the degradation process was identified to be due to an ubiquitous photo-induced oxidation of the layers by adsorbed oxygen in water. Using optimum experimental conditions to preserve n-layer 2D-phosphane, we identify oxidation fingerprints in the Raman spectra of exfoliated P(black) and we report on the use of the ratio of intensity of the A1g over A2g modes as an assessment of the crystal quality [1].

[1]Exfoliating black phosphorus down to a monolayer: photo-oxidation and quantum confinement
A. Favron, E. Gaufres, A. Loiseau, R. Martel et al. Nature Materials, (just accepted)

GSS P12

High yield synthesis of densely aligned suspended graphene nanoribbons array by plasma CVD

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Graphene nanoribbons (GNRs) are candidate material for next-generation transistors because of their electrical transport gap. Up to now, we developed a novel plasma CVD method [1] with Ni nanobar for directly fabricating suspended GNRs devices [2]. However, the growth yield of suspended GNRs is low and understanding the growth mechanism is required to solve this problem. In this study, we found that the stability of Ni nanobars can be drastically improved during plasma CVD. Since GNRs nucleate during the cooling process, the Ni nanobar structure has to be maintained even under the high temperature condition (just before cooling) for the growth of suspended GNR. Our experimental results show plasma CVD can improve the thermal stability of Ni nanobar, resulting in the formation of suspended GNR. By following this growth model, precise adjustment of plasma CVD conditions was carried out. As a result, the yield of suspended GNRs growth can be improved (～90%) and the high density GNRs array has been successfully fabricated.

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GSS P13

Growth dynamics of single-layer graphene on epitaxial cu surfaces

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CVD on Cu surface is widely used to grow large-area, single-layer graphene (SLG). Considering relatively low melting temperature of Cu (1083 °C), it is interesting to investigate the growth dynamics of graphene at typical growth temperatures, 1000-1075 °C [1-4], which are close to the Cu melting temperature. As the large single-crystalline graphene domains are grown at high temperatures, it also helps us to develop a method to grow giant graphene domains on Cu surface. Here, we present the systematic study on the domain orientation and structure of the SLG grown on epitaxial Cu(111) surface. When SLG was synthesized at 900～1020 °C, the hexagonal lattice of graphene perfectly followed the underlying Cu(111) lattice, in consistent with our previous work [1-3]. However, when we increased the temperature to 1050 °C, the graphene lattice was rotated by ～3° from the original direction, indicating appearance of a new stable configuration. Higher CVD temperature (1070 °C) resulted in the slightly distorted hexagon orientations due to thermal fluctuation of the Cu(111) lattice.

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[3] J. Phys. Chem. Lett., 3, 219 (2012). [4] Appl. Phys. Exp., 6, 75101 (2013).

GSS P14

Graphene-elastomer thin-film composites

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We present the fabrication and mechanical characterisation of graphene-reinforced elastomer thin-film composites. We focus on water-processable elastomers of two kinds-colloidal latex and polyurethane. Graphene oxide (GO) and reduced graphene oxide (rGO) were used for reinforcement at very low loadings (0.05 - 0.2 wt%). GO was reduced to rGO either ex-situ or in-situ so as to not affect the dispersion stability using non-toxic reducing agents. The elastomers were cast into thin-films (<40 micron thick) by dip-casting. Optical microscopy and raman spectroscopy was used to confirm that the graphene flakes were uniformly and individually dispersed in the elastomer matrix. Mechanical testing was performed according to ASTM standards. The GO and rGO was found to reinforce the elastomers, improving their elastic modulus by up to 50%, without any loss of elasticity. In most cases, the ultimate strain to failure was found to increase by up to 20%. The loading was below the percolation threshold and therefore no electrical conductivity was observed. These graphene reinforced elastomers can be used for a variety of thin-film applications, particularly medical devices such as condoms.

GSS P15

Super-stretchable graphene oxide macroscopic fibers with outstanding knotability fabricated by dry film scrolling

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Graphene oxide (GO) has recently become an attractive building block for fabricating graphene-based functional materials. GO films and fibers have been prepared mainly by vacuum filtration and wet spinning. These materials exhibit relatively high Young's moduli but low toughness and a high tendency to tear or break. Here, we report an alternative method, using bar coating and drying of water/GO dispersions, for preparing large-area GO thin films (e.g., 800-1200 cm^2 or larger) with an outstanding mechanical behavior and excellent tear resistance. These dried films were subsequently scrolled to prepare GO fibers with extremely large elongation to fracture (up to 76%), high toughness (up to 17 J/m^3), and attractive macroscopic properties, such as uniform circular cross section, smooth surface, and great knotability. This method is simple, and after thermal reduction of the GO material, it can render highly electrically conducting graphene-based fibers with values up to 416 S/cm at room temperature. In this context, GO fibers annealed at 2000 °C were also successfully used as electron field emitters operating at low turn on voltages of ca. 0.48 V/μm and high current densities (5.3 A/cm^2). Robust GO fibers and large-area films with fascinating architectures and outstanding mechanical and electrical properties were prepared with bar coating followed by dry film scrolling.

GSS P16

Two-dimensional metallic niobium disulfide (NbS_2): preparation, optical characterizations and transport properties

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Recent finding of high-temperature two dimensional (2D) superconductivity above 100 K opens up a fascinating new research direction towards pursuing high T_c superconductors and understanding the underlying new physics. The extensive study of this new field strongly relies on the synthesis of 2D layered metallic systems. Preparation of 2D metallic systems, however, is not straightforward probably because of the stronger interlayer interaction, which is in stark contrast to the well advanced preparation technique of 2D layered semiconductors. We report here the first successful synthesis of a new 2D metallic transition metal dichalcogenides (TMDs), 3R-NbS_2, which exhibits superconductivity and charge-density-wave (CDW) phases in bulk counterparts, down to the thinnest form (3 layers).

Our as-grown samples were directly synthesized on top of hBN substrates, showing fairly sharp triangular or hexagonal shapes. The Raman bands show systematic shifts depending on the layer numbers while the optical contrasts show strong layer number dependence both of which can be served as reliable signatures for layer number identification. Our transport data demonstrate that 3R-NbS_2 down to the thinnest form still preserve its metallic nature.

GSS P17

Double resonance raman modes in mono- and few-layer MoTe2

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We study the second-order Raman process of mono- and few-layer MoTe2, by combining ab initio density functional perturbation calculations with experimental Raman spectroscopy using 532, 633 and 785 nm excitation lasers. The calculated electronic band structure and the density of states show that the resonance Raman process occurs at the M point in the Brillouin zone, where a strong optical absorption occurs due to a logarithmic Van-Hove singularity of electronic density of states. Double resonance Raman process with inter-valley electron-phonon coupling connects two of the three inequivalent M points in the Brillouin zone, giving rise to second-order Raman peaks due to theMpoint phonons. The calculated frequencies of the second-order Raman spectra agree with the observed laser-energy dependent Raman spectra.

GSS P18

Growth and characterization of W-doped NbS_2 atomic layers

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Atomic-layer transition metal dichalcogenides (TMDCs) are attractive two dimensional materials because of their tunable electronic properties and unique spin-valley physics. To date, very few synthesis studies have been reported for metallic TMDCs such as NbS_2 nanosheets. It is, therefore, still highly desired to prepare high quality, large area metallic TMDC atomic layers for unraveling their unique electronic phases in the two-dimensional limit.
We report the growth and characterization ofW-doped NbS_2 atomic layers. For the crystal growth, stacked WO_3 and Nb films were prepared on various substrates including sapphire and graphite by electron beam deposition. These films were sulfurized by annealing under hydrogen/sulfur/argon atmosphere. We found that the addition of Watoms effectively prompts the growth of Nb-based TMDC crystals. The thickness of such crystals ranges from 4.2 to 70 nm. High-resolution AFM and FFT images reveal the honeycomb lattice of samples with lattice constant of 3.2 Å. These crystals have two characteristic Raman peaks at 360 cm^{-1} and 392 cm^{-1}, which can be assigned to WS_2 E_2g and NbS_2 A_1 modes, respectively. The resistivity of samples is around 10^{-5} ohm/m, which is comparable to that of bulk NbS_2 (∼10^{-6} ohm/m). These results strongly suggest that the present approach provides atomic layer W-doped NbS_2 crystals with metallic properties.

GSS P19

Two-step growth and characterization of WS_2/MoS_2 heterostructures

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The heterostructures of two-dimensional semiconductors have attracted much attention for their potential applications in electronics and optoelectronic. Recently, several groups have reported the vapor-phase growth of lateral and stacked heterostructures based on semiconductor transition metal dichalcogenides (TMDCs) These studies basically use the continuous feeding of two precursors for the growth of two different TMDCs without changing reaction chambers. This process often leads to the alloying of heterojunction interfaces and/or secondary-grown materials because of the contamination of the remaining first precursors in the chambers. To avoid the contamination, it is desired to develop a two-step growth technique of the heterostructures with clean reaction chambers.
Here, we report the two-step growth of WS_2/MoS_2 heterostructures by using such clean environment. First, WS_2 monolayers were formed on a SiO_2/Si substrate by the sulfurization of WO_3 thin films. Then, the samples were put on another quartz tube to avoid the contamination of WO_3 during MoS_2 growth. The MoS_2 atomic layers were grown from sulfur and MoO_3 by chemical vapor deposition. This process leads to the formation of triangle-shaped MoS_2 grains on the WS_2 as shown in the AFM image and Raman spectra. In the poster, the details of sample preparation and characterization will be presented.

GSS P20

Thermoelectric properties of CVD-grown transition metal dichalcogenide monolayers

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Monolayer transition metal dichalcogenides (TMDCs) have attracted a lot of research interests due to their two-dimensional layer structure. Recently, in single-crystal monolayer MoS_2, extremely high Seebeck coefficient (>1 mV/K) was reported, suggesting high thermoelectric efficiency due to the low dimensional system [1, 2, 3]. As a next step, it is necessary to investigate thermoelectric properties of other TMDC monolayers to search better thermoelectric materials. Particularly, for future applications, the large-area polycrystalline samples should be tested. Moreover, because Seebeck coefficient correlates with carrier density strongly, we should control the carrier density of samples to maximize Seebeck coefficient. Therefore, in this research, we clarify the carrier density dependence of Seebeck effect in CVD-grown large-area WSe_2, WS_2 and MoS_2 monolayers. For carrier-density control, we fabricated electric double layer transistors (EDLTs) using ion gel, which is the mixture of ionic liquid and organic polymer. Finally, we successfully accumulated hole and/or electron carriers ($>10^{13}$ cm^{-2}) and obtained relatively high Seebeck coefficient (~0.1 mV/K) for all in monolayer TMDC films.

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GSS P21

Growth and characterization of 1t'-layered transition metal ditelluride single crystals

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Two-dimensional transition metal diclacogenides (MX_2s) are attracting much attention as promising materials for a new generation of optical and electronic devices. Some semiconducting MX_2s are complementary or competitive to graphene because of the existence of a native band gap. Among MX_2s, group-6 transition metal ditellurides having 1T'-layered structures (beta-$MoTe_2$ and WTe_2) are gathering further attention as stable candidates to realize the quantum spin Hall effect device. They are known to have a distorted CdI_2-type unit layer structure with one-dimensional zigzag chains of metal atoms, which differs from the 2H-type trigonal prismatic unit layer structure of MoS_2, WS_2, $MoSe_2$, WSe_2 and alpha-$MoTe_2$. Recently, we have succeeded in growing single crystals of these two 1T'-ditellurides by the chemical vapor transport method using Br_2 as the transport agent. In the presentation, we will report the characterization of their structures and physical properties by the measurement of X-ray diffraction, Raman spectra, X-ray photoelectron spectra, Hall effects and electric conductivities. It has been observed that these ditellurides have higher electric conductivities than 2H-type semiconducting MX_2s, suggesting their semimetallic electronic properties.

GSS P22

Large area synthesis of monolayer tungsten disulfide and its growth kinetics

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Atomic scale two dimensional sheets attract intense attention due to their superior electrical, mechanical, and optical features. Layered transition metal dichalcogenide (TMD) is known as a true two-dimensional (2D) material with excellent semiconducting properties [1]. In spite of its potential, however, various issues still remain for the practical applications of TMD-based optoelectrical devices. In particular, the large area growth, defect free growth, and controllable carrier doping are regarded as crucial issues in their production stage. In this study, we have demonstrated the high quality single crystal growth of WS_2 with relatively large crystal size. Based on the systematic investigations, it was clarified that crystal growth of monolayer WS_2 strongly depends on the growth temperature and diffusion distance from the sulfur source. The high-quality WS_2 with relatively large domain size can be grown only for the specific diffusion distance under the suitable temperature ranges. These systematic investigations also revealed that the growth of WS_2 can be conducted with the balance of growth factor and etching factor.

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GSS P23

Growth and etching of monolayer hexagonal boron nitride

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We report growth of h-BN on Cu surface under low-pressure CVD conditions, the nucleation density of h-BN can be significantly modulated in a large range, resulting in an effective control of h-BN grain sizes. These h-BN grains are single-layered, single crystals with a triangular shape, and the size can reach up to ca. 20um, 45 times larger than that in previously achieved results. We further discovered that h-BN grains can be directly visualized by optical microscopy by oxidizing Cu surface in air. Most importantly, it was found that interfacial properties of transferred h-BN on SiO_2 /Si substrate are critical to the device quality of stacked graphene material. We demonstrated that the contamination on h-BN caused by the traditional poly(methyl methacrylate) (PMMA)-assisted transfer method is responsible for the degradation of graphene device quality, and the oxidation of h-BN film at high temperatures in air can effectively clean monolayer h-BN interface, leading to reliable and much enhanced graphene mobility. Furthermore, we investigated the intrinsic behaviors of CVD grown monolayer h-BN shape evolution and etched h-BN patterns using a CVD grown monolayer h-BN on Cu foil.

GSS P24

Anisotropic dielectric breakdown of hexagonal boron nitride film

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Hexagonal boron nitride (BN) is considered as ideal substrate and gate insulator for graphene devises and other 2D materials. The studies on insulating properties and electrical reliability of BN itself, however, are quite limited. In this study, the anisotropic dielectric breakdown of BN is studied.

Voltage is applied to a relatively thick BN (20-80 nm) through Au/Cr electrodes fabricated by EB lithography. In the case of dielectric breakdown parallel to layers, the current suddenly increases at breakdown voltage in IV measurement, which is very similar to the conventional dielectric breakdown of 3D amorphous oxides. The obtained dielectric field strength (E_{BD}) is ~1 MV/cm. On the other hand, E_{BD} perpendicular to layers is roughly 7 times higher than that parallel to layers. Interestingly, the current gradually increases for more than 10 s during the breakdown. From our previous breakdown experiment using conductive AFM [1], it is expected that this unique behavior is attributed to layer-by-layer breakdown. The difference of E_{BD} in two directions might be related to the anisotropic static dielectric constant.

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[1] Y. Hattori, et al., *ACS nano* 2015 , 9, 916.

GSS P25

Atomically precise semiconductor graphene and hBN interfaces by Ge intercalation

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The integration of graphene and hexagonal boron nitride (*h* BN) into semiconductor technology requires their synthesis on semiconducting surfaces, which is still a challenge due to the low catalytic activity of these substrates in the chemical vapor deposition process. Here we report on the intercalation of monolayer Ge under epitaxial graphene (and *h* BN) on Ni(111). This results in atomically precise interfaces between these 2D materials and Ge with GeC_6 and GeB_3N_3 stoichiometry and sqrt3xsqrt3 reconstruction. Semiconductor interfaces prepared in this way decouple the 2D layer electronically from the substrate and lead to the restoration of the Dirac cone of graphene as well as the unperturbed electronic structure of *h* BN. Photoemission study of alkali-metal doped graphene shows that the intercalated Ge layer prevents charge leakage to the metal substrate, thereby allowing higher doping levels of graphene. This leads to an increase in electron-phonon coupling and thus raises the superconduction transition temperature. Moreover Ge intercalation leads to new adsorbate patterns, as compared to bulk GICs and graphene on metals (i.e. we have found a BaC_8 phase). Together with the application potential of Ge nanostructures this new interface is a path for the integration of graphene and *h* BN into state-of-the-art semiconductor technology.

GSS P26

Interface modifications in epitaxial graphene on SiC (0001)

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To improve the electronic properties of epitaxial graphene on SiC, control of the interface structure is the key to modify coupling of the phonon mode in the epitaxial graphene and the 6 $\sqrt{36}$ $\sqrt{6}$ 3R30o6R30 buffer layer: We found two kinds of interface modification techniques in epitaxial grapheneon S resolution transmission electron microscopy revealed the presence of period ic nitride mono- layer between the 0th carbon layer and the SiC substrate: Due to the nitride interface; the interface carrier scattering was reduced; bunching and playedarole for supplying oxygen atoms as a source into the interface: Due to the intercalationo effect measurement:

GSS P27

Quasi-free-standing graphene formation on SiC (0001) by the post-growth rapid-cooling

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Thermal decomposition of silicon carbide (SiC) (0001) is one of the promising technique for growth of high quality, wafer-scale graphene with a controlled number of layers on the semi-insulating substrate. However, the carrier mobility at room temperature is drastically reduced in comparison to that for free standing graphene. This is due to the existence of buffer layer. In order to improve the electronic properties of graphene on SiC (0001) substrates, the intercalation of atoms such as hydrogen, oxygen, and metals were demonstrated recently. However, to detach a buffer layer by intercalation some problems still remain. Therefore, a new method to detach a buffer layer is required. In this study, we propose a new method to decouple a buffer layer from the SiC substrate by rapid cooling technique. For our experiment, graphene was prepared by heating the 4H-SiC (Cree) substrate at 1550～1560 °C for 5～10 min under atmospheric pressure of Ar flow environment. Following, graphene samples were vacuum sealed (4～510-3Pa); and heated to around 900°C for 30 min and then dropped into liquid nitrogen bath: The result so effect measurement indicated that the buffer layer turned into large area homogenous quasi- free-standing graphene:

GSS P28

Intercalation of copper atoms under graphene film on SiC(0001)

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Graphene has very high carrier mobility and mechanical properties. However, graphene on SiC has lower carrier mobility than the exfoliated graphene because of the carrier scattering by a buffer layer. In this study, we tried to intercalate copper atoms between the buffer layer and the SiC in order to eliminate the effect of the buffer layer.

Graphene was prepared by heating the SiC substrate at 1525 ℃ for 30 min, in Ar 6 atm. Copper nano-particles were deposited on graphene by evaporation method. After that, the substrate was annealed at 600 ° C for 3 hr under Ar flow (2.0 L/min). As a result of the TEM observation, the distance between SiC and graphene became larger than the one of typical graphene on SiC. In addition, we observed the obscure dotted contrast between graphene and SiC. The averaged distance between the dots and the SiC was about 2.7 Å, and this distance was consistent with the theoretical value of the Si-Cu bond. Furthermore, in the Raman spectroscopy, the appearance of the sharp G and 2D peaks and the shift of the 2D peak after annealing also indicate that the buffer layer was converted to graphene by copper intercalation.

GSS P29

Structural and acid-base properties of ion beam damaged substrates and implications for growth of carbon nanotube carpets

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Some applications of carbon nanotube (CNT) carpets require the carpets to be grown directly on specific substrates via CVD. Thus, there is significant interest in understanding the properties of a good catalyst substrate and how to create and maximize these features in inactive substrates. The recent transformation of inactive catalyst substrates to active substrates for CNT carpet growth via ion beam bombardment provides a good model system for this study [1]. The properties of pristine and ion beam damaged crystalline alumina substrates are probed using contact angle measurements [2] and X-ray reflectivity (XRR). The contact angle data have been analyzed using the van Oss-Good-Chaudhury model and the Young-Dupre equation, enabling the determination of the acid-base properties of the substrates. XRR has been used to probe the layer properties (density, thickness, cross-sectional layering, refractive index, and microscopic roughness). The results show interesting correlations between the properties of the catalyst substrate and CNT carpet growth behavior upon Fe deposition. Detailed discussion of the implications of the layer and acid-base properties of the engineered substrates in CNT carpet growth are presented.

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GSS P30

Graphene and single-walled carbon nanotube films for gas sensor applications

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Detection of environmental gases is becoming more and more important for various applications such as global warming, monitoring and control of environmental pollution, advanced diagnostics in medical applications, destruction of the ozone layer, etc. A high sensitivity and selectivity are very important for explosive gas leakage detection and for a real-time detection of toxic or pathogenic gases in industries. Single-walled carbon nanotubes (SWCNTs) and graphene are considered as the most promising materials due to their one atom-thick conjugated structures, a large specific surface area and a high sensitivity.

Thereby, in this work we present a detailed investigation of influence of various gases on the sensory properties of graphene and SWCNT films[1]. The performance of gas sensor was measured by using a relevant apparatus to register a continuous sensor electric resistance variation triggered by an exposure to different gases in air atmosphere at room temperature. We observed different reactions of sensor depending on donor or acceptor mechanism for redistribution of electrons between the gas used and the sensor films.

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GSS P31

Performance of solar cell fabricated with Cs encapsulated semiconducting single-walled carbon nanotube films

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Single-walled carbon nanotubes (SWNTs) are one of the most attractive materials for future high performance solar cells due to their excellent properties. It was also predicted that multiple exciton generation (MEG) can be possible in SWNTs, indicating the efficiency of solar power generation can be drastically improved with SWNTs. For the fabrication of solar cell with SWNTs, it is necessary to establish a controllable doping method. Environmental stability is also another important issue for the practical use of SWNTs in solar cells. In contrast with the p-type transport property of pristine SWNTs, we demonstrated very stable n-type SWNTs-thin film transistors (TFTs) by Cs encapsulation into SWNTs based on a plasma ion irradiation method. In this study, the optoelectrical transport properties were investigated for the controllably Cs doped stable semiconducting SWNTs films. It was found that the clear rectifying drain-source current vs. drain-source voltage characteristics can be observed after the position selective Cs encapsulation into semiconducting SWNTs thin films. Furthermore, a short-circuit current and an open-circuit voltage can be also detected under light illumination using a solar simulator, indicating the solar power generation has been successfully realized by pure junction of p-type and n-type SWNTs films.

GSS P32

Wide angle X-ray and neutron scattering studies of graphene.

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Graphene, due to its nanostructure, proves to be problematic to investigate with diffraction techniques. Small size of coherently scattering regions leads to broader peaks (in reciprocal space) and at some point the line between crystalline and amorphous materials becomes blurred. However if one does not concentrate purely on data in reciprocal space there is more to it than just what one can obtain from the Scherrer equation. By combining analysis of data in real space and computer simulations, more information about the investigated material can be gained. A prerequisite for this is the calculation of one of correlation functions. The one chosen in this study was the Pair Distribution Function, which provides information about atomic distances within the sample. It allows to estimate the size of the investigated system and, along with computer simulations, it gives insight into defects present in the system. Before Molecular Dynamics (MD) simulations were performed, the paracrystalline model was utilized. This rather simple model, can allow to quickly asses dimensions and degrees of disorder within sample. To further evaluate the sample, MD simulations were performed to gain information about presence of physical defects such as mono-vacancies, divacancies and Stone-Thrower-Wales type of defects in the sample.

GSS P33

Fabrication and in-situ TEM characterization of freestanding graphene nanoribbons devices

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Edge-dependent electronic properties of graphene nanoribbons (GNRs) have attracted intensive interests. To fully understand the electronic properties of GNRs, the combination of precise structural characterization and electronic property measurement is essential. For this purpose, a new experimental technique using freestanding GNR devices has been developed, leading to the simultaneous characterization of electronic properties and edge structure of GNRs.

Graphene was first transferred on a Si substrate with an open slit covered by SiO_2 layer. To fabricate a freestanding structure, we first made electronic contacts on isolated graphene by EBL and deposition of Cr/Au, and then SiO_2 membrane underneath the graphene was etched away by buffered hydrogen fluoride acid. The so-prepared freestanding graphene device was assembled to a home-made TEM holder for in-situ characterization. The freestanding graphene was sculpted by a focused electron beam in TEM, purified and narrowed by Joule heating down to several nanometers width. Electronic properties including IV characteristics, differential conductance and transfer curve have been measured using the structure-defined freestanding graphene in TEM. We have observed significant increase in resistance and semiconducting behavior became more prominent with decreasing width of GNR. The details of device preparation and characterization of GNRs devices will be addressed in the presentation.

GSS P34

Applications and preparations of graphene-sandwiched-type environmental cells

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High-resolution transmission electron microscopy (HRTEM) observations provide real-time atomic-level structural information on various materials. HRTEM observation of liquids and solutions　should provide a great impact on physics and chemistry of liquids and solutions. One of the critical issues to realize HRTEM observations of liquids is that samples have to be placed under a high vacuum condition, where the liquid samples are lost spontaneously through vaporization. To overcome this difficulty, we have focused on graphene-sandwiched-type environmental cells for HRTEM observation of liquids and have developed a facile preparation technique to prepare such environmental cells.

High quality graphene was grown on copper foil by using the atmospheric pressure chemical vapor deposition method using methane as the carbon source. The graphene so produced was directly transferred onto a SiN grid. Another graphene was then transferred onto the SiN grid to prepare a suspended bilayer graphene, whose interlayer space can be used to sustain liquids even under vacuum conditions. We expect that our method contribute to obtain brand new insights on various types of liquids including microstructure of liquids, interface between liquids and solids and structure and properties of low-dimensional liquids.

GSS P35

Self-ordered quasi-one dimensional graphene lateral superlattice

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Opening a band gap is essential to the development of graphene electronic devices. Formation of graphene nanoribbons (GNRs) is a promising approach to the band-gap opening in graphene, nevertheless GNR transistors are currently not in practical use, mainly because of the performance degradation due to uncontrollable structures. Here, we report a new approach to graphene band gap engineering, i.e. graphene lateral superlattices (LSLs), in which electronic states are modulated by periodic potentials, indicating ～0.1 eV band gap opening.

Well ordered graphene LSLs are found to be self-assembled on SiC(1-108) facets via surface decomposition of vicinal SiC(0001). SiC(1-108) facets consist of highly ordered pairs of a (0001) terrace and a (1-102) nanofacet with ～2.3 nm periodicity, on which monolayer graphene is corrugated. Combination of such morphological corrugation and one-dimensional potential modulation through the periodic SiC facet/terrace surface induces modification of electronic states in the monolayer graphene at K-points. In transport measurement, the graphene LSL exhibits semiconducting behavior with a band gap of ～0.1 eV, which agrees with the result of DFT calculations. In the presentation, we discuss the details of our results (STM, ARPES, LEED, transport, etc.) as well as the future prospect of our novel approach to graphene band-gap engineering.

GSS P36

Proton conductivities of graphene oxide nanosheets: single, multilayer, and modified nanosheets

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High proton conductivities of multilayer graphene oxide (GO) nanosheets at room temperature are important, because they facilitate the use of graphene oxide as electrolytes in various cells. Herein, we present the proton conductivities of single GO nanosheets and multilayer GO films. The proton conductivity of a single nanosheet was much lower than those of multilayer films, meaning that protons move more easily in the interlayers. Moreover, the conductivity increased with increasing film thickness. Modification of epoxide groups with ethylenediamine leads to decreased proton conductivity, indicating that the hydrated epoxide groups contribute to proton mobility. GO films with sulfuric acid (sGO) had increased proton conductivity under high humidity conditions, and their conductivities were higher than that of Nafion. The high proton conductivity of sGO films is attributed to a large amount of water molecules present in the interlayers. We propose that the methods reported here are applicable to optimize the proton conductivity in other solid electrolytes having nanoscale thickness.

GSS P37

Fermi energy dependence of charge transfer kinetics in molecular adsorption on graphene

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The introduction of guest species to graphene has been extensively studied, since the electronic properties of atomic membrane are easily modulated by the surface adsorption. Hole-doping has been achieved by adsorption of oxygen (O2) as electron accepter, where novel gate-tunable kinetics was observed for the hole injection to graphene. In this study, effect of the adsorption of hydrazine having electron-donating nature on graphene is investigated in terms of the charge transfer kinetics (CT kinetics).

Hydrazine monohydrate (N2H4H2O) was adsorbed with changing EF of graphene by gate voltage to the channel region of graphene field effect transistor prepared by exfoliation on SiO2 substrate, followed by rinsing in extra pure water. Raman spectroscopy was measured with the excitation wavelength of 532 nm in ambient condition as changing N2H4H2O adsorption time.

N2H4H2O adsorption on graphene is found to be chemisorption with the charge transfer interaction, giving electron carrier to graphene. CT kinetics is more rapid in the case of the lower EF of graphene for N2H4H2O, as opposed to the case of O2. This is explained by Electrochemical mechanism for the charge transfer by molecular adsorption on graphene.

GSS P38

Electrochemical properties of perforated graphite

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We developed a method for formation of large vacancy defects (holes) in graphene sheets as the results of graphite oxide heating in concentrated sulphuric acid. The acid acts as a reducing agent and removes part of the oxygenated groups together with carbon atoms. XRD and IR-spectroscopy investigations shoed that reduction degree of graphite oxide and functional composition of the products depend on the temperature and duration of the treatment. It was found that edges of the holes are decorated with hydroxyl, carbonyl, and carboxyl groups and hydrogen. Increase in the temperature promotes formation of carboxyl groups. The influence of oxygenated groups and holes on the supercapacitor performance of reduced graphite oxide samples was checked using cyclic voltammetry measurements. Oxygenated groups provide good wettability of reduced samples and as a consequence high electrochemical performance in the acidic electrolyte. Specific capacitance is contributed by faradaic reactions, polarization at the edges of holes developed in graphene layers, and quick ion diffusion thought the holes.

GSS P39

Study of the effect of H adsorption morphology on the rate of electron transfer in graphene

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The chemical functionalization of pristine graphene sheet by absorbing hydrogen atoms attracts extensive attentions for controlling graphene physical properties.There is also much interest using graphene as an electrode material with widespread application such as, field-effect transistors [1], supercapasitors [2], batteries [3], and solar cells [4]. However, to our knowledge, the fundamental charge transfer rate and its behavior on graphene surfaces are not fully understood.We propose the rule to determine the charge transfer rates from hydrogen to graphene in a wide range of coverage. In our early investigation which is based upon first principle calculation by using Quantum Espresso package, we found the averaged charge transfer value shows roughly a linear behavior from 0.2e for the dilute limit to 0.14e for the half-coverage.We observed that the charge transfer depend on some factors such as supercell size, the location / arrangement of hydrogen atoms, the number of hydrogen, and local surface morphology including buckling and concave-convex deformation.

Reference
[1] B. Li et al., Adv. Mater. 22, 3058 (2010)   [2] Zhang, L. L et al., J. Mater. Chem, 20, 5983-5992 (2010)
[3] Z. J, Wang et al., J.Phys. Chem C, 113, 14071 (2009)   [4] Hsieh, C.T et al., Carbon, 49, 3092-3097 (2011)

GSS P40

Enhanced photocurrent generation in twisted bilayer graphene with van Hove singularity

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Graphene, with ultra-high carrier mobility and short photocarrier lifetime, has shown remarkable potential in ultrafast photodetection [1, 2], though its optical-absorption (~2%) [3] and photoelectric response endure low values. The photo-response efficiency can be improved in a vertical stack of monolayer graphene and other two-dimensional atomic layers[4, 5]. However,the unique photonic and electronic properties of graphene have to compromise with those of the other two-dimensional materials in the hybrid structure, in which the intrinsic advantages of graphene in photodetecion, such as high-speed response, are not guaranteed [5].Here we demonstrate that a twisted bilayer graphene, simple stack of two monolayer graphene with an interlayer twisted angle, leads to a significant light-matter interaction and enhanced photocurrent generation. The photocurrent generated from twisted bilayer graphene was found to be twisted-angle-dependent and enhanced significantly at a matched angle. The twistedangle-dependent enhancement is attributed to the emergence of unique van Hove singularities, which was observed directly by micro-spot angle-resolved photoemission spectroscopy. The twisted bilayer graphene with van Hove singularity with enhanced photoresponse offers new concept in graphene photodetection.

Reference
[1] Nature Nanotechnology, 4, 839-842 (2009) [2] Nature Photonics, 4, 297-301 (2010)
[3] Science, 320, 1308-1308 (2008) [4] Science, 340, 1311-1314 (2013) [5] Nature Nanotechnology, 8, 826-830 (2013)

GSS P41

Chemically modified absorption quenching of graphene

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Although optical properties in graphene are solely defined by the frequency-independent fine structure constant in visible region, some deviations have been observed in infrared region due to Pauli blocking phenomenon. Here, we report a complete absorption quenching in infrared range driven by bis(trifluoromethanesulfon)amine (TFSA), an optically transparent p-type chemical dopant. The Fermi level was downshifted by TFSA to provoke absorption quenching by Pauli blocking phenomenon. The transmission was enhanced in infrared range with increasing doping concentration. The extracted Fermi level shift in doped graphene, which is defined as an absorption onset point, was in congruent with the Schottky barrier height (SBH) extracted from I-V characteristics of graphene/n-Si heterojunction device and X-ray photo-electron spectroscopy. The carrier dynamics of highly doped graphene by TFSA suggests strong carrier scattering reducing the Fermi velocity by three orders of magnitude, reaching 0.35×10^6 m/s. The Fermi level shift is also related to the different substrates which can be understood by dielectric screening.

GSS P42

Electric double layer light-emitting diodes of monolayer WSe_2

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Because of the strong quantum confinement, optical properties of atomically-thin WSe_2 have been attracting interest [1]. Toward their optoelectronic applications, lightemitting devices are significantly important and, recently, light-emitting transistors of WSe_2 monolayers have been reported [2]. However, the remarkable physical phenomena of monolayer WSe_2, such as formation of charged exciton (trion) and large stark effect, have not yet been demonstrated by electrical excitation (electroluminescence, EL) due to lack of carrier density and/or electric field.

Here, we focus on electric double layers owing to their high specific capacitance and internal strong electric field. We propose novel light-emitting device, electric double layer light-emitting diodes fabricated with monolayer WSe_2 and ion gels. In this new device, p-i-n junction is self-assembly formed by applying voltage, leading to obvious EL emission at room temperature. In addition, both high carrier density ($\sim 10^{14}/cm^2$) and strong electric field (>100kV/cm) are realized during light emission, resulting in unique EL spectra which are different from normal photoluminescence spectra and similar to light emission from trions. We will discuss these interesting EL spectra from the aspect of trions and stark effect.

[1] X. Xu, et al., Nat. Phys. 10, 343 (2014). [2] F. Xia, et al., Nat. Photon. 8, 899 (2014).

GSS P43

Exciton many-body effects in transition metal dichalcogenides

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Transition metal dichalcogenides (TMDs) have attracted much attention as novel two-dimensional semiconductors, and are promising candidates for future optoelectric devices [1]. Intriguing many-body effects among optically generated carriers and excitons (bound electron-hole pair) are induced in atomically-thin TMDs. In this study, we studied exciton-exciton interactions in TMDs and their van derWaals hetero structures through photoluminescence (PL) measurements at room temperature.

We observed strong saturation of PL with increasing excitation power in monolayer WSe2 (1L-WSe2). In the time-resolved PL measurement, the short decay components originated from diffusion assisted exciton-exciton annihilation becomes dominant in strong excitation region [2]. We found different feature of exciton many-body effects in 1L-MoS2; the exciton PL intensity is saturated with increasing excitation power, while the trion PL intensity is almost linearly increased. This indicates that trion formation is promoted by Auger photo-carrier generation processes in 1L-MoS2. In the van der Waals hetero structure composed of these monolayeres (1L-MoS2/1LWSe2), the PL saturation behaviour becomes weak owing to the carrier separation. The detailed exciton many-body dynamics in the TMDs will be discussed in the presentation.

[1] K. F. Mak et al., Phys. Rev. Lett. 105, 136805 (2012). [2] S. Mouri et al., Phys. Rev. B 90, 155449 (2014).

GSS P44

Probing edge-activated resonant Raman scattering from mechanically exfoliated 2D MoO_3 nanolayers

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We demonstrated spatially resolved vibrational analysis of mechanically exfoliated single-crystalline MoO_3 nanolayers. Raman scattering from MoO_3 was enhanced predominantly at the outside edges of the nanolayers. The enhanced Raman scattering at the edges was attributed primarily to the enhanced resonant Raman effect caused by a high density of oxygen vacancies localized at the edges. The localized vacancy sites corresponded to a non-stoichiometric phase of MoO_3, which would provide reactive sites with high catalytic activity.

GSS P45

Photoluminescence study for highly-localized impurity state in monolayer tungsten disulfide

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A novel photoluminescence (PL) peak has been observed from a monolayer of transition metal dichalcogenide (TMD), which is known to be an ideal 2D semiconductor. The PL peak appears near the low-energy side of neutral free excitons with very sharp peak width (10 meV) at low temperature (83 K). Systematic temperature-dependent PL measurements reveal that the peak can be explained by bound excitons being trapped by the surface impurities, which results in a highly localized state for the excitons. Since the optically detectable, highly localized impurity state promises to have extensive practical applications for quantum optics, our finding represents an important step in the study of 2D materials for use in quantum computation and information [1].

[1] T. Kato and T. Kaneko, ACS Nano 8, 12777 (2014).

GSS P46

Optical properties of CVD grown large-area WSe2 monolayer under high-density electrochemical carrier doping

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Monolayer transition metal dichalcogenides (TMDCs) are attracting interest due to their direct band gap and strong two-dimensional quantum confinement. Particularly, observation of charged exciton at room temperature in mechanically exfoliated single-crystal samples is one of the solid evidences of confinement effect in TMDC monolayers and opens a new route to functional devices [1]. For future applications, we need to shift samples from micrometers-scale single crystals to centimeters-scale polycrystalline films [2]. In this research, we investigated quantum confinement effect and formation of charged exciton in CVD-grown large-area WSe_2 monolayers under high-density carrier doping.
Here, we fabricated electric double layer transistors (EDLTs) using the ion gel, which is the mixture of ionic liquid and organic polymer.We successfully accumulated both hole and electron carriers, resulting in highest carrier density of $2\times10^{20}/cm^3$. Finally, we measured the carrier density dependence of photoluminescence (PL) spectra. Interestingly, compared to single-crystal samples, it is not simply explained by exciton and charged exciton. However, PL spectra at highest carrier density suggest the formation of charged exciton in large-area samples, indicating strong quantum confinement effect.

[1] S. Mouri, K.Matsuda et al., Nano Lett, 13, 5944(2013)
[2] J. K. Huang, T. Takenobu et al., ACS Nano. 8, 923(2014)

GSS P47

Control of optoelectrical property of few-layer tungsten diselenide with mild O2 plasma treatment

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Atomically-thin two-dimensional (2D) sheets attract intense attention for their superior electrical and optical features. Transition metal dichalcogenide (TMD) is known as a 2D material with excellent semiconducting properties. Monolayer TMD has strong Photoluminescence (PL) intensity for its direct band gap [1]. Although multi-layer (25 layers) TMD doesnt show bright PL because of its indirect band structure, its carrier mobility is higher than that of monolayer one. For the fabrication of high performance optoelectrical device, it is required to combine these optical and electrical properties of mono- and multi-layer TMD, respectively.
In this study, we investigated the electrical and optical properties of few-layer tungsten diselenide (WSe_2) before and after mild plasma treatment [2,3]. We found that mild O_2 plasma treatment can drastically enhance PL intensity of WSe_2, whereas the initial electrical properties of WSe_2 can be maintained even after the mild plasma treatment. This result indicates the mild O_2 plasma treatment can fabricate functionalized TMD including better optoelectrical features.

[1] T. Kato and T. Kaneko, ACS Nano 8 , 12777 (2014).
[2] T. Kato, L. Jiao, X. Wang, H. Wang, X. Li, L. Zhang, R. Hatakeyama, and H. Dai, Small 7 , 574 (2011).
[3] T. Kato and R. Hatakeyama, Nature Nanotechnology 7 , 651 (2012).

GSS P48

PN-type photodiodes of large-area WSe_2 monolayer thin films

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Monolayer transition metal dichalcogenides (TMDCs) are promising materials for optical sensing applications owing to pronounced surface effects because of very high surface-to-volume ratios and Debye lengths comparable to their feature sizes. Although many excellent photodetectors with high photoresponsivity and light power conversion have already been fabricated, chemically formed PN-type photodetectors have not yet been performed due to lack of doping methodology. Here, we report the optoelectronic properties of large-area WSe_2 thin film PN photodiodes formed by freezing-while-gating technique, which is firstly demonstrated by Zhang et al.[1] Large-area WSe_2 thin film was prepared by chemical vapor deposition [2] and PN junctions were electrochemically formed by ion gels. Finally, these PN junctions were stabilized by freezing of biased ion gels. We successfully observed photo-current under monochromized light (730nm) and investigated internal quantum efficiency of 1.35 %. This would open the route for the application of WSe_2 thin films as PN-type photoelectrical devices.

[1] Y. J. Zhang et. al., Science 344 , 725 (2014).
[2] J.-K. Huang T. Takenobu et. al., ACS Nano 8 (1), 923 (2014).

GSS P49

Quantum correction to conductance in graphene antidot lattices

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Antidot lattice (AL) is a two-dimensional conductor with regular holes. We have observed Altshuler-Aronov-Spivak (AAS) and Aharonov-Bohm (AB) type and oscillations in triangular AL of monolayer graphene. Near zero magnetic field, negative magnetoresistance coexisted with AAS oscillations which has a period of half quantum flux ($h/2e$). In higher magnetic field, the period altered to (h/e). The latter oscillation was AB-type oscillation due to orbital quantization rather than pure AB oscillation due to interference of electrons. These features appeared in both an electron and a hole regime, but became less pronounced as the gate voltage approached a charge neutrality point. The phase of the AAS oscillations was the same as that originating from weak localization mechanism rather than anti-weak localization. This indicated that system was influenced by frequent inter-valley scattering.

GSS P50

Josephson effect at NbSe$_2$/NbSe$_2$ vdW junction

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We demonstrate that the vdW junction between two superconductors can be used to construct a Josephson junction. Layered dichalcogenide superconductor NbSe$_2$ is mechanically exfoliated, and vdW contact between freshly cleaved surfaces has been built by using dry transfer technique. Atomically flat vdW interface free from oxidation and inter-diffusion has been achieved by eliminating all heat treatment during junction preparation. Current-voltage characteristic shows a flow of zero bias current together with current hysteresis; thus suggesting the flow of Josephson current in vdW junction. The fabricated vdW junction revealed resistance-area product RA =16 Ohm-cm^2 and large Josephson critical current density of 6600 A/cm^2. These values are comparable to modern Josephson junctions used for single flux quantum circuits; revealing that the vdW interface is highly transparent to the phase coherent transport of supercurrent. By applying magnetic field parallel to the junction, the periodic modulation of the Josephson current (Fraunhofer pattern) is observed. Furthermore, the product between normal-state resistance and critical current $R_N I_c$ reaches the value of 1.04 mV; this is close to the maximum value expected from the Ambegaokar-Baratoff theory (1.14 meV). These results indicate that high quality vdW Josephson junction has been fabricated in vdW interface.

GSS P51

Quantum hall effect in slightly twisted bilayer graphene

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We report on magnetotransport measurements in high-quality twisted bilayer graphene with small twist angles fabricated by using the mechanical exfoliation and drytransfer technique of graphene and hexagonal boron nitride (h-BN). In small magnetic fields B, we observed quantum Hall effects at Landau level (LL) filling factors $\nu = 8n + 4$, where n is an integer, indicating the formation of eightfold degenerate LLs. When B was increased, the quantum Hall sequence was changed as $\nu = 4n$, indicating the eightfold to fourfold transition of LL degeneracies. The B dependence of the energy gaps extracted by Arrhenius plot were in qualitative agreement with the continuum theory, and showed that the transition of LL degeneracies took place at the van Hove singularity point $E_ntextrm{VHS}$. In high B, full lifting of spin and valley degeneracies of LLs were observed, and the tilted B studies showed that quantum Hall states at $\nu = 4n + 2$ were due to spin splitting. In addition, the fractional quantum Hall effects with odd denominators were observed. These observations show that twisted bilayer graphene with small twist angles constitute a new type of two-dimensional electron systems that differed both from monolayer and Bernal stacked bilayer graphene.

GSS P52

Layer-by-layer transport measurements on Bi atomic layers

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Thin film growth of Bi and related compounds has been attracted much attention because of their exotic properties originating in the large spin-orbit interaction of Bi. Growth of its simple substance in the initial stage is known to result in formation of a thin-film phase accompanied with a modified black-phosphorus structure [1], which can be regarded as a variety of atomic layers. In this work, Bi growth on Si(111)-7x7 has been performed in a multi-probe VT-STM system, which provides wide-ranging opportunity of kinetic control and in-situ transport measurement during the thin film growth. By tuning the kinetic condition of the growth, it becomes possible to grow the thin-film phase uniformly covering the substrate in layer-by-layer mode. In-situ transport measurement has been performed during the layer-by-layer growth of the Bi thin-film phase, distinguishing the conductivity of each growth unit. It oscillates with a period of 2 ML, which reflects the atomic structure of the thin-film phase.

[1] Nagao et al., Phys. Rev. Lett. 93, 105501 (2004).

GSS P53

1/f-Noise in suspended bilayer graphene

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Flicker noise, a.k.a. 1/f noise, is typically a low frequency nuisance, but it can also cause problems at higher frequencies due to upconversion, and even lead to degradation of future high frequency graphene devices. It was shown by Lin et. al. that 1/f noise is reduced in bilayer graphene due to its band structure that leads to effective screening of charge fluctuations [1].We have studied suspended bilayer graphene where one can expect even lower intrinsic 1/f noise levels [2]. Our samples were high quality sheets suspended on top of LOR-resist, and current annealed to obtain residue-free graphene. The measurements were carried out at cryogenic temperatures using a voltage bias scheme while measuring the low frequency current fluctuations. Near the Dirac point, we indeed find a noise level that is record low compared with all results on graphene bi- and monolayers.

The low intrinsic 1/f noise level suggests suspended bilayer graphene to form a good platform for gas sensing. Our measured data demonstrate a detectable change when the sample is exposed to 0.1 mBar of air.

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[2] M. Kumar, A. Laitinen, D. Cox, and P. Hakonen, submitted to APL

GSS P54

Cooper pair splitting by means of graphene quantum dots

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Split Cooper pairs form a natural source for entangled electrons, which is a basic element for solid-state quantum information. Quantum entanglement has successfully been utilized in optics, while progress in electronic systems has been modest. A Cooper pair, split out from a superconductor into two different terminals, will form a non-local, entangled spin pair [1,2]. We report experiments on a superconductor-graphene double quantum dot (QD) system, in which we observe Cooper pair splitting (CPS) up to a CPS efficiency of ~10% [3]. Compared to Cooper pair splitters using nanowires, we could tune independently the energy levels and the bias of the two graphene QDs. For the first time, the levels of the two QDs were tuned to be asymmetric or symmetric with respect to Fermi level in the superconductor, which led to predominance of CPS or elastic co-tunneling as predicted by current theories. The realization of CPS in graphene creates possibilities for this material in future quantum information processing.

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[2] P. Recher, E. Sukhorukov, and D. Loss, Phys. Rev. B 63 (2001) 165314.
[3] Z. Tan, et al., Phys. Rev. Lett. 114, 096602 (2015).

GSS P55

Charge fluctuation forces in capacitive nanoribbon systems

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Forces may be induced by fluctuations of any thermodynamic parameter. The most well known fluctuation induced force is the Van-derWaals/Casimir force, which is due to dipolar fluctuations. A less studied force is the force due to monopolar charge fluctuations, which are related to the capacitance of the system. This talk will focus on monopolar charge fluctuation forces in solid state nanodevices. In particular the force is calculated for a parallel plate system[1] involving both a graphitic nanostructure and a metal plate. Both the classical and quantum mechanical effects will be discussed. This force will be shown to be comparable or greater than the Van-der Waals/Casimir force[2,3] in systems with reduced dimensionality, such as ones involving graphitic nanostructures.

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[3] D. Drosdoff and L. M. Woods, PRL 112, 025501(2014).

GSS P56

Origin of magnetism in graphene: theoretical perspective

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Introduction of magnetism in graphene in terms of defects has been gaining interest in recent times, owing to their application possibilities towards spin transport and sensor devices. The basic idea of this magnetism lies in Liebs theorem for bipartite lattice, which says: the inequality between two sublattice points, A and B introduces net magnetic moment. Being a bipartite lattice, this theorem is valid in case of graphene as well. The graphene unitcell consists of two sublattice points, A and B that prefer opposite spin occupancies, making the over all net magnetization zero. Therefore, it is expected that, the vacancy defects can introduce inequality between A and B, making the two-dimensional graphene magnetic. The formation of zigzag edges, a defect, introduced by finite termination of graphene along a certain crystallographic direction can also introduce net magnetization. We observe that, hole doping can make the zigzag edge ribbons magnetic and metallic. Moreover, in presence of enhanced correlation, the magnetic excitations become more facile. The magnetism in graphene can also arise from the grain boundaries, formed during chemical vapor deposition of graphene. These magnetic grain boundaries can induce asymmetric spin conduction behavior, which can be exploited for sensor and spin-filtering applications.

GSS P57

Strong exchange scatterings of low-energy quasi-particles at the Dirac point by the zero mode of graphene

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At the Dirac point, we have a limited number of low-lying quasi-particle modes. When a topological zero mode appears in addition, we have several characteristic two-body interactions. Using DFT basis functions, we have derived an effective Hamiltonian of the hydrogenated graphene vacancy, V_{111}.[1] The model involves an on-site Coulomb correlation term U and an isotropic two-body magnetic scattering term J. The anti-ferromagnetic exchange interaction does not come from orbital hybridization between the zero mode and the Dirac mode, because they are eigen modes of the effective one-body Hamiltonian and thus no hybridization exists. Our derivation of the exchange scatterings is based on a newly developed density functional theory for the strongly correlated electron systems. The super exchange mechanism coming from the combined two-body correlated-hopping and exchange-hopping terms gives the effective exchange scattering of $J_{super} \sim O$ (0.1eV). We discuss implication of the strong exchange scatterings among the low-lying Dirac modes correlated with the localized topological zero mode. Keyword: Graphene, Kondo effect, Hydrogen, Topological zero mode

[1] N. Morishita, et al. arXiv:1412.8589.

GSS P58

Monolayer MX (M=Ga, In; X=S, Se, Te) as promising substrates for germanene electronic devices: density functional calculations

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Germanene, a new member of the Dirac materials family, has the largest intrinsic carrier mobility and the largest spin-orbit coupling effect in theory compared to graphene and silicene. Regretfully, just like silicene, it can only be synthesized with high quality on metal substrates and suffer from deformation on many common oxides in addition to its insufficient intrinsic band gap. On the other hand, electronic devices require semiconducting or insulating substrates to reduce leakage currents, as well as an adequate gap size in the channel material. In this study, by using the ab initio density functional theory, the stability and electronic structure of germanene on semiconducting monolayer GaS, GaSe, GaTe and InSe are investigated. Our results suggest that these monolayers are promising as substrates for germanene devices. Germanene preserves its low-buckled honeycomb structure on all the studied substrates like the free-standing situation. Moreover, germanene is neutrally semiconducting on monolayer GaTe and InSe, preserving its Dirac-cone-like band structure with a bandgap of around 0.14～0.16 eV (estimated with the HSE functional) at the Dirac point. The effective masses of germanene remain as small as 0.05～0.06 m 0, and the estimated carrier mobility is up to 2.2×10^5 $cm^2V^{-1}s^{-1}$.

GSS P59

Edge effect on vacancy state in semi-infinite graphene

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Vacancies are point lattice defects that naturally occur in graphene during growth. They can drastically modify the electronic properties of graphene at both low and high energies. A single vacancy could produce a strong resonance at exactly zero energy. The wave function of this resonant state was shown to be un- normalizable. However, all existing studies ignore edge effects, which must be present in reality.

In our recent study [Hai-Yao Deng and Katsunori Wakabayashi, Phys. Rev. B 90, 115413 (2014)], we employed Greens function method and analytically showed that the presence of edge could critically alter the properties of or even completely obliterate the resonant state, depending on the shape of the edge. In case of an armchair edge, we found that the resonant state wave function decays much faster and then becomes normalizable. This is due to the intervalley interference caused by the edge. However, when a zigzag edge is present, the resonant state disappears, because of the so-called edge states that are localized on the edge. These results reveal close interplay between vacancies and edges in graphene systems.

GSS P60

Topological phases in multi-orbital honeycomb lattice

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Silicene,Germanene and Stanene, the counterpart of graphene for silicon, germanium and tin, with low buckled honeycomb geometry, have specific electronic nature. Due to their large spin-orbit coupling, quantum spin hall effect can be observed in an experimentally possible temperature regime, so that they are expected as candidates of two-dimensional topological insulators. In our studies, we consider their edge states by using the multi-orbital Hamiltonian, in comparison with those for the single-orbital Hamiltonian. We show the importance of multi-orbital degrees of freedom for the edge state. We also investigate hydrogen termination electronic states in the novel two-dimensional materials.

[1] C.-C. Liu,H. Jiang, and Y. Yao, Phys. Rev. B 84, 195430 (2011)

[2] Y. Xu, B. Yan, H.-J. Zhang, J.Wang, G. Xu, P. Tang,W. Duan, and S.-C. Zhang, Phys. Rev. Lett. 111, 136804 (2013)

CNBMT15

K1

Biomaterial applications and safety of carbon nanotubes

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There is increasing interest in the unique biological and medical properties of carbon nanotubes (CNTs), and it is expected that biomaterials incorporating CNTs will be developed for clinical use. There has been a great deal of progress in improving the various properties of CNTs for use in biomaterials and for promotion of tissue regeneration as scaffold materials. However, many of these studies have not shown clinical success because the safety of CNTs has not yet been confirmed. Of course, the concerns regarding the safety of CNT inhalation are completely different from those associated with CNT implants present in the human body for a long time. Therefore, safety tests of CNTs and their composites used as implantation materials in the body must be performed, including monitoring of inflammatory reactions, acute cytotoxicity, irritation, sensitization, chronic toxicity, carcinogenicity, and so on. However, further research and development in this area will lead to the production of superior CNTs for application as biomaterials, which will be of great benefit to large numbers of patients in the near future.

K2

Photothermal therapy with single-walled carbon nanotubes to treat cancer metastasis

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Single-walled carbon nanotubes (SWNTs) have been extensively explored for applications in biomedicine including biomedical imaging, drug delivery, and cancer therapy. In our recent studies, it was uncovered that multi-modal imaging guided photothermal therapy with SWNTs afforded effective destruction of primary tumors together with cancer cells in sentinel lymph nodes, resulting in remarkably prolonged mouse survival compared to mice treated by elimination of only the primary tumor by either surgery or conventional photothermal therapy. Our next study further evidenced that photothermal ablation of primary tumors with SWNTs was able to trigger significant adaptive immune responses, which were not observed if tumors were removed by surgical resection. Such a treatment in combination with anti-CTLA-4 antibody therapy is able to prevent the development of tumor metastasis, a major cause of cancer death.

Refereces
1, Liang C et al. Adv. Mater. 26, 5646-5652 (2014)
2, Wang C et al. Adv. Mater. 26, 8154-8162 (2014)

I1

Safety evaluation of fullerene and development of new drugs containing fullerene derivatives

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Introduction: Our company has sought to identify compounds with strong antioxidant activity for cosmetic use. Thus, we have developed water-soluble fullerene as an ingredient for cosmetics. Furthermore, we are developing novel drugs using fullerene and its derivatives. In this symposium, I will present data regarding the safety of fullerene in cosmetics and topical products, and the efficacy of fullerene-containing cosmetics. Finally, I will introduce our studies seeking to develop new drugs containing fullerene derivatives.

Safety evaluation: The fullerene used in cosmetics was evaluated by all safety tests for application as an additive in quasi-drugs. We demonstrated that fullerene did not induce toxicity, irritation, or chromosomal aberration.

Antioxidant activity: Skin photoaging is caused by reactive oxygen species (ROS), which are generated by ultraviolet rays hitting the skin. Fullerene prevents photoaging by preventing skin ROS generation.

Possibility of innovative drug development: Because fullerene has superior antioxidant ability, it may represent a novel therapeutic for oxidative stress-associated diseases. Our group has undertaken studies to develop innovative drugs for oxidative stress-associated diseases using fullerene derivatives.

I2

Fullerene as a new cosmeceutical: From nanotechnology to cosmetic nanomedicine

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Because fullerene is a potent radical scavenger, it is expected to function as a therapeutic reagent for oxidative stress-induced diseases including alterations of skin as the outermost organ. Then, we examined various possibilities of fullerene as a new cosmeceutical. Since oxidative stress plays a major role in acne formation, we studied effectiveness of fullerene gel for acne vulgaris. An open trial using a 1% fullerene gel showed that inflammatory acne lesions significantly decreased at 4 and 8 weeks. Experimentally,polyvinylpyrrolidone-fullerene inhibited sebum production from hamster sebocytes, suggesting the anti-acne activity through sebum suppression. Next, we examined effect of topical fullerene on the conspicuous facial pores and found that 1% fullerene lotion applied on the face twice a day for 8 weeks significantly decreased the conspicuous pores. Further, experimentally fullerene significantly suppressed UVB-induced PGE2 production from the reconstructed human epidermis. Since PGE2 is an important mediator for melanogenesis, which can cause conspicuous pores, this suppression of PGE2 is a possible pathway for the cosmetic effect on the conspicuous pores. Besides, 1% fullerene lotion accelerated male hair growth based on a placebocontrolled study. Together, fullerene expectedly exerts a variety of cosmeceutical activities.

I3

Compared environmental impact of different carbon nanoparticles

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Because of their exceptional properties and use in numerous industrial applications, carbon nanoparticles are widely used and ultimately expected to get into the environment. This work deals with the ecotoxicological assessment of different carbon nanoparticles (CNPs) in the aquatic compartment by comparing the effects of different nanocarbons: Carbon Nanotubes (CNTs: double-walled, multiwalled), few-layer graphene (FLG), nanodiamonds (ND) and carbon black (CB), using the ISO 21427-1 biotoxicity assay on Xenopus laevis larvae.
Three different endpoints were carried out at 12 days of exposure: (i) acute toxicity (mortality), (ii) chronic toxicity (growth inhibition) and (ii) genetic toxicity (micronucleus assay). Beside toxicity bioassays, a complete characterization of nanocarbons was undertaken.
Neither mortality nor genotoxicity was observed regardless of the type of nanocarbon. Only growth inhibition was observed and depended on the nature of the nanocarbon. Growth inhibition expressed using three different metrics (mg/L; number of particles/L and surface area in m2) showed that the toxicity of the investigated nanocarbons seems to depend mainly on the total surface area of the nanoparticles. Furthermore, we hypothesize that toxicity observed in larvae exposed to high concentrations of nanocarbons would be limited to physical effects (gill clogging and/or abrasive effects and or nutrients deprivation).

I4

Biosensors based on graphene oxide for drug screening

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For the development of practically useful bioanalytical systems in biomedical applications, one should be able to understand and fully utilize chemical/physical properties to detect molecular changes during certain biochemical transformations in a biological system. New bioanalytical platforms should overcome limitations of conventional assay methodsdetection limits, cost issues, labors, efficiencies, quantitativeness, reproducibility, etc. In this talk, I will introduce recent studies which harness graphene derivatives for developing bioanalytical platforms to quantitatively analyze various enzyme activities and biomarkers including helicase and microRNA. The systems rely on attractive interaction between graphene oxide and nucleic acids and fluorescence quenching by graphene oxide. Quantitative microRNA sensing was successfully demonstrated in living cells. Recently, we employed one of the graphene-based bioassay systems to anti-viral drug screening and identified potent hit compounds to treat hepatitis C. This study shows that a new nanobiotechnology can be routinely implemented in drug discovery with high-throughput capability, providing many advantages over conventional methods. In addition, Ill briefly introduce our efforts towards development of mesoporous nanomaterials that are practically useful in biomedical applications, for example, intracellular delivery of DNA and proteins for the development of biopharmaceuticals.

I5

Photothermal conversion of functional nanocarbons for biotechnological applications

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Nanocarbons, such as carbon nanotubes and carbon nanohorns, are materials of interest in many fields of science and technology because of their remarkable chemicophysical properties. In particular, nanocarbons possess extraordinary photothermal energy conversion efficiency and high absorption cross sections in a wide wavelength range. In this presentation, this powerful photothermal conversion property of nanocarbons for nanobiotechnology will be presented with the examples of several applications.

I6

Magnetic manipulation, imaging and therapy using carbon nanotube/metallic nanoparticle hybrids

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Carbon-based nanomaterials are considered unique materials for many applications in different fields including bio- and nanomedicine. These types of carbon forms are offering the possibility of original chemical functionalization and design of complex multifunctional systems that allow further their exploitation in therapy, imaging and diagnosis.

In this presentation, I will describe the chemical approaches to functionalize multiwalled carbon nanotubes with appropriate functional groups, therapeutic molecules and metallic nanoparticles in view of their potential biomedical applications in therapy and imaging (i.e. MRI) (Lamanna, G et. Nanoscale 2013, 5, 4412; Liu, X et al. ACS Nano 2014, 8, 11290). In particular, I will present our recent results on the decoration of carbon nanotubes and the filling of their inner space with iron/cobalt nanoparticles. The final hybrids are endowed of magnetic properties that allow their remote manipulation in vitro and in vivo to under the application of an external magnetic field. I will also describe the photothermal characteristics of these hybrids that can be exploited in anticancer therapy.

C1 **CNBMT P1**

Carbon nanotubes-polymer electrospun nanofibers as biocompatible scaffolds for neuronal cells differentiation

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Carbon nanotubes (CNTs) are attractive candidates for the development of scaffolds able to support neuronal growth and development thanks to their ability to conduct electrical stimuli, to interface with cells and to mimic the neural environment.We recently proposed for tissue engineering purposes a freestanding nanocomposite scaffold that combines the conductive and topographical features of functionalized multi wall carbon nanotubes (MWCNTs) with the biocompatible and mechanical properties of a polylactide matrix (PLLA). The functionalization of MWCNTs, necessary for their proper compatibilization into the polymeric matrix, has been achived through the addition of diazonium salts. We will present here in addition a novel morphology for the neuritogenetic nanocomposite substrate, based on electrospun nanofibers deposited onto a glass substrate. This particular morphology is characterized by an extremely high surface to volume ratio and its porosity allows better mimicking of the extracellular matrix in which neurons normally grow in physiological conditions. Details on the preparation and characterization of such nanofibers will be given, together with preliminary evidences of polarized neurite outgrowth along the scaffold nanofibrous topography and peripheral blood stem cells selective differentiation into neurons.

C2 **CNBMT P7**

Carbon nanohorns boost alkaline phosphotase activity in co-culture of macrophages and mesenchymal stem cells

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Carbon nanohorns (CNHs) consist of a rolled graphene structure with a coneshaped tips, which are currently developed for biological applications. Previously, we have reported that CNHs promote rat calvarial bone formation in 2 weeks, when many macrophages were observed around CNHs. We hypothesized that CNHs stimulate the macrophages to produce some growth factor promoted osteogenesis, and the osteoblast close to CNHs differentiate to form new bone. Here we show that alkaline phosphotase activity dramatically increased in the presence of CNHs during a 7 days co-culture of human monocyte derived macrophages and human mesenchymal stem cells. CNHs were observed in the lysosomes of macrophages more than in mesenchymal stem cells after 24 hours co-culturing. Oncostatin M (OSM) from activated macrophages has been reported to induce osteoblast differentiation and matrix mineralization through STAT3. The amount of OSM in the supernatant cultured with CNHs was much more than those without CNHs. These results demonstrate that the macrophages engulfed CNHs thus accelerating the differentiation of mesenchymal stem cells into the osteoblasts via OSM.

C3 **CNBMT P5**

Biodegradation of carbon nanohorns in macrophage cells

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With the rapid development in the medical application of carbon nanomaterials such as carbon nanohorns (CNHs), carbon nanotubes, and graphene based nanomaterials, understanding the long-term fate, health impact, excretion, and degradation of these materials have become crucial. Here, the in vitro biodegradation of CNHs was determined using a non-cellular enzymatic oxidation method and two types of macrophage cell lines. Approximately 60% of the CNHs were degraded within 24 h in a phosphate buffer solution containing myeloperoxidase. Furthermore, approximately 30% of the CNHs were degraded by both RAW 264.7 and THP-1 macrophage cells within 9 days. Inflammation markers such as pro-inflammatory cytokines interleukin 6 and tumor necrosis factor alpha; were not induced by exposure to CNHs. However, reactive oxygen species were generated by the macrophage cells after uptake of CNHs, suggesting that these species were actively involved in the degradation of the nanomaterials rather than in an inflammatory pathway induction.

C4 **CNBMT P14**

Synthesis of polyglycerol-functionalized graphene and SWNTs, and their application to carrier of a photosensitizer in photodynamic therapy

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For biomedical in vivo applications of nanocarbons as drug carriers, they have to be dispersed well in a physiological environment. Recently, we have found that polyglycerol (PG) grafted onto diamond and iron oxide nanoperticles, and afforded very good hydrophilicity and biocompatibility. In this study, we applied this methodology to synthesize PG functionalized graphene (G-PG) and SWNTs (SWNT-PG), and employed them for photodynamic therapy (PDT) after a photosensitizer was loaded on their hydrophobic surface.

Since we exfoliated graphene in water from graphite under sonication in the presence of hydroxytriphenylene, the resulting graphene was functioned with PG after removal most of the exfoliant. A photosensitizer, chlorin e6 (Ce6), was loaded on the hydrophobic surface of G-PG through hydrophobic interaction. The obtained G-PGCe6 exhibited good aqueous dispersibility. After incubating HeLa cells in the presence of G-PG-Ce6 under light irradiation, the G-PG-Ce6 complex showed remarkable PDT effect as compared to Ce6 itself. In the case of SWNTs, they were functionalized with PG after cutting and Ce6 was loaded on them. The resulting SWNT-PG-Ce6 also exhibited similar photodynamic activity.

C5 **CNBMT P12**

Application of oxygen-doped carbon nanotubes as imaging probes and fluorescent labels

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Optical imaging using near-infrared (NIR) fluorescence is a new imaging modality that has recently emerged in the fields of biology and medicine. Especially, above 1300 nm, tissue autofluorescence is much low and the fluorescence of molecular probes escapes from the light absorption of water. Single-walled carbon nanotubes (CNTs) show fluorescence in the wavelength region of 1000-1400 nm. Recently, it is reported that stable covalently oxygen-doped CNTs, prepared by exposure to ozone and then light, showed extreme enhancement in fluorescent efficiency as compared to the pristine CNTs.

Here, we report the synthesis method of a new oxygen-doped CNTs in bulk. The oxygen-doped (6, 5) CNTs show NIR fluorescence at a much longer wavelength than that of the oxygen-doped CNTs reported previously, which is just advantageous for NIR imaging (∼1280 nm). Immunoassay and gastrointestinal contrast imaging using the CNTs as the NIR fluorescent labels and imaging agents, respectively, are demonstrated.

C6 **CNBMT P11**

Highly ordered one-dimensional fullerene crystals for concurrent control of macroscopic cellular orientation and differentiation towards large-scale tissue engineering

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One of the most important factors in tissue engineering is a cell scaffold. Cell scaffolds must be biocompatible and must also promote adhesion, growth, and differentiation of cells with concurrent control of their morphology. Here, we show that cell scaffolds composed of highly aligned microscale fullerene-crystals, also known as fullerene whiskers (FWs), can be used to control cell morphology, orientation and differentiation. These cell scaffolds were prepared in a single step using the Langmuir-Blodgett (LB) approach. The aligned FWs cause elongation of deposited myoblast cells and induce cell differentiation to muscle cells. Our aligned FW substrate is made by a facile method of the LB approach, and hence our substrate is a promising alternative to other recently reported cell scaffolds for tissue engineering.

C7 **CNBMT P2**

Fingerprinting in vivo protein corona-carbon nanohorn interaction

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Carbon nanomaterials are useful in various applications ranging from biologics to optics. Single-wall carbon nanohorns (CNHs) are nanostructured spherical aggregates of graphitic tubes with uniform sizes of about 100 nm, thereby being dispersed in physiological solutions easily. They possess high potential in medical uses (drug delivery, diagnostic imaging, photothermal therapy). However, at present there are several technical barriers that must be understood and overcome. These problems include CNH surface opsonization, nanoparticle uptake and retention in reticuloendothelial organs, and the long-term fate and toxicity. For the CNHs to serve as an efficient therapeutic agent and their increased projected usage in medicine, the biocompatibility, blood halflife, biodegradation and excretion of these materials has attracted increasing interest. Differently surface functionalized CNHs (bare and lipid-pegylated) were prepared and were exposed to mice through intravenous injection. The protein coronas formed due to the exposure were fingerprinted. The study will be followed by analyzing the effect of protein corona decorated CNHs presentation at cellular and organ level interactions in vivo. Analyzing the protein corona fingerprints caused by plasma-nanoparticle interactions would provide towards the understanding of pathophysiology of CNHs and the development of new CNHs based theranostics.

C8 **CNBMT P6**

Carbon nanomaterials negatively affect cell viability and gene expression

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Carbon nanomaterials (CNMs), which include carbon nanotubes (CNTs) and their derivatives have diverse technological and biomedical applications. The potential toxicity of CNMs to cells and tissues has become an important emerging question in nanotechnology. To assess the toxicity of CNTs and fullerenol C60(OH)24, we in the present work used the budding yeast Saccharomyces cerevisiae, one of the simplest eukaryotic organisms that share fundamental aspects of eukaryotic cell biology. We found that treatment with CNMs, regardless of their physical shape, negatively affected the growth rates, end-point cell densities and doubling times of CNMs-exposed yeast cells when compared to unexposed cells. To investigate potential mechanisms behind the CNMs-induced growth defects, we performed RNA-Seq dependent transcriptional analysis and constructed global gene expression profiles of fullerenol C60(OH)24- and CNT-treated cells. When compared to nontreated control cells, CNP-treated cells displayed differential expression of genes whose functions are implicated in membrane transporters and stress response, although differentially expressed genes were not consistent between CNT- and fullerenol C60(OH)24-treated groups, leading to our conclusion that CNMs could serve as environmental toxic factors to eukaryotic cells.

C9 **CNBMT P13**

Bio-mimetic membranes and bio-functionalization of graphene by dip-pen nanolithography

Aravind Vijayaraghavan[1], Michael Hirtz[2], Andrea Verre[1],
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The integration and patterning of biomolecules and biomimetic membranes on graphene has significant implications in biosensing, drug delivery and toxicology. We demonstrate the assembly of biomolecules on graphene and graphene oxide using dippen nanolithography (DPN), a direct-write technique with sub-100 nm resolution. In the case of non-covalent assembly, self-assembled biotinated lipid membranes can be assembled on graphene. For the covalent case, the graphene is functionalised with biotin using click-chemistry under the dip-pen tip. In either case, the biotin functional groups remains active towards streptavidin binding. The functionalization, spreading and binding is imaged using AFM in liquid and air. We also show that there is charge transfer interaction between the biomolecules and graphene, through fluorescence quenching, Raman spectroscopy and electronic transport measurements. We demonstrate how this fabrication can be scaled up using multi-pen DPN, using up to 64 tips in parallel, covering large areas. Finally, we demonstrate how membrane proteins can be incorporated into the lipid membranes, and their subsequent binding to analytes.

Hirtz, M.; Oikonomou, A.; Georgiou, T.; Fuchs, H.; Vijayaraghavan, A.; Multiplexed biomimetic lipid membranes on graphene by dip-pen nanolithography. Nature Communications, 2013, 4, 2591(1-8).

CNBMT P1 ※Please refer to **C1**

CNBMT P2 ※Please refer to **C7**

CNBMT P3

Release mechanism of cisplatin from carbon nanotube capped by magnetic nanoparticles. a molecular dynamics study

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The release dynamics of cisplatin from the interior of the carbon nanotube is studied using molecular dynamics simulations. The nanotube is initially capped by magnetic nanoparticles which, upon exposure to an external magnetic field, detach from the nanotube tips and the initially encapsulated cisplatin molecules leave the nanotube interior according to the diffusion mechanism. Diffusivities of cisplatin in bulk water and inside the nanotube were determined by analysing the mean square displacements and they take the values 2.1×10－5cm2s－1 and 0.6－0.9 × 10－5cm2s－1, respectively, at 310K. The release of cisplatin was found to be anactivated process with the activation barrier ～25 kJ mol-1 in an ideal model. Simulations predict that, for the studied ideal architecture, the release completes in a few milliseconds. A simple analytic equation was derived by assuming that the release proceeds according to the activated one-dimensional diffusion. That equation perfectly fits the simulation results as well as some experimental data.

CNBMT P4

BN nanoparticles with developed surface as anticancer drug delivery system

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The present study is focused on the development of spherical BN nanoparticles (BNNPs) with petal-like surface structure, which are able to absorb a large amount of antitumor drug, and their utilization for killing tumor cells. The BNNPs, 100-200 nm in diameter, were obtained by chemical vapor deposition. The morphology of synthesized products and their chemical composition were studied using X-ray diffraction, scanning and transmission electron microscopy, energy-dispersive X-ray spectroscopy, and Fourier-transform infrared spectroscopy. Particle agglomerates were dispersed using ultrasonic treatment in distilled water. Particle size distribution was estimated using dynamic light scattering method. BNNPs were further saturated with doxorubicin (DOX) either by sonication of BNNPs in the DOX solution, or by their continuous mixing in DOX solution using a magnetic stirrer. The DOX release from BNNPs was studied by fluorescence spectroscopy. The BNNPs immersed in distilled water showed stable binding with DOX molecules over a week. Triple washing out had no effect on subsequent DOX release, indicating good DOX association with the BNNPs. The laser confocal scanning microscopy showed that the BNNPs loaded with DOX penetrated into the neoplastic IAR-6-1 cells, after which the DOX release into cytoplasm and the cell nucleus resulted in cell death.

CNBMT P5 ※Please refer to **C3**

CNBMT P6 ※Please refer to **C8**

CNBMT P7 ※Please refer to **C2**

CNBMT P8

A reduction of rat research activity in the open field test caused by carbon nanotubes

N. V. Sayapina[1], T. A. Batalova[1], V. V. Chaika[2], V. L. Kuznetsov[3], D. V. Krasnikov[3], K. S. Golokhvast[2]

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For the first time the influence of MWCNT on functioning of higher nervous activity of mammals was observed. Wistar rats were fed (in forage) multi-walled carbon nanotubes (MWCNTs; d∼9 nm, w(metals)< 2 % wt.; S(BET)=300 m2/g; aggregate size 0.005-0.1 mm) in a dosage of 500 mg/kg per day for 3 or 10 days.

MWCNTs were shown to have a considerable negative impact on research activity and anxiety of laboratory rats. Anxiety level of rats being fed MWCNTs started to grow as early as on the 3rd day and almost doubled after 10 days of exposure. Also MWCNTs decrease locomotor activity level by a factor of 2 after 3 days and by a factor of 4 after 10 days of exposure.

We assume that MWCNT may impact indirectly on the emotional status and central nervous system functioning via development of the inflammatory processes in body of rat. MWCNT pathogenicity can be caused by their structure (fibrous morphology and small size) via direct damage of cells as well as by impurities (Fe, Co, Al) and their high surface area which can block enzymes or other species.

This study was supported by Scientific Fund of Far Eastern Federal University (13-06-0318-m_a).

CNBMT P9

Lysosomal membrane permeabilization induced by carbon nanohorn in macrophage and cell apoptosis mechanism

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Eijiro Miyako[1], Sumio Iijima[2], Masako Yudasaka[3]

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Practical uses of nancarbons in various fields are rapidly extending, where concerns about their toxicity are emerging. The nanocarbons are engulfed by macrophages in the body, staying in the body for a long time. To discuss the long term toxicity, understanding their interaction with the macrophages in the subcellular level is important. Thus, we studied cell death mechanism of macrophage (RAW 264.7) caused by single-walled carbon nanohorns (CNH). CNH has low toxicity; therefore, toxicity mechanism was studied at high cellular uptake condition. It was found that CNHs were accumulated in lysosomes, which induced lysosome membrane permeabilization and cathepsin release from lysosome, resulting in the mitochondrial dysfunction. The mitochondrial dysfunction further induced the ROS generation and caspase activation, leading to the cell apoptosis. Despite these seemingly adverse phenomena, RAW264.7 cells did not secrete inflammatory cytokines. Namely, the high uptake of CNHs induced the cell death, but it may not cause adverse responses in the other cells. This may suggest that even though the CNHs accumulated in the macrophages in the body for a long time, the long-term toxicity could be low.

References:
[1] Tahara et al. Biomaterials, 2012, 33: 2762-2769.
[2] Yang et al. Toxicology and Applied Pharmacology, 2014, 280:117-126. Contact: m-yudasaka@aist.go.jp

CNBMT P10

The effect of carbon nanotube blocks on bone regeneration

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Masanori Okamoto[1], Yuki Usui[5], Hiroyuki Kato[1]

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Because of their biocompatibility and bone formation-promoting effect, Multi-Walled Carbon nanotubes (MWCNTs) are promised to be material of the devices used in medical surgeries. The purpose of this study is to evaluate the bone regenerating ability of the MWCNT solidified by compression (p-MWCNT block) in vivo and in vitro.

We implanted rhBMP-2/p-MWCNT block composites in the dorsal musculature of ddy mice. 3 weeks later, they showed ectopic bone formation as well as controls in micro-CT and histlogical examination. We also observed the osteoconduction of p-MWCNT blocks by implanting them into the mice calvarial critical size bone defect and check the degree of bone repair with micro-CT and histlogical examination at 12 and 24 weeks after implantation. At the in vitro experiment, we confirmed the cell proriferation and differentiation ability on the blocks with culturing MC3T3-E1 cells on the blocks.

P-MWCNT blocks acted well as scaffold of bone regeneration because of their high biocompatibility and pores of suitable size for bone ingrowth. In future, as well as further validate the impact on the bone forming ability of p-MWCNT block, it seems that there is a value to proceed with further investigation targeting the application as a scaffold material.

CNBMT P11 ※**Please refer to** **C6**

CNBMT P12 ※**Please refer to** **C5**

CNBMT P13 ※**Please refer to** **C9**

CNBMT P14 ※**Please refer to** **C4**

Seventeenth International Conference on the Science and Application of Nanotubes

University of Vienna, Austria
7–13 August 2016

Local organizing committee

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Program

	Saturday 27-Jun	Sunday 28-Jun		Monday 29-Jun	Tuesday 30-Jun	Wednesday 1-Jul	Thursday 2-Jul	Friday 3-Jul
8:15				Registration				
8:30		Registration			Registration	Registration	Registration	Registration
8:45				Opening				
9:00		Satellite Symposia CCTN15 MSIN15 CNTFA15 GSS15 CNBMT15		Keynote 1 Sumio Iijima	Keynote 2 Michael S. Arnold	Keynote 3 Roman Fasel	Keynote 4 Esko I. Kauppinen	Keynote 5 David Tománek
9:15								
9:30								
9:45				Invite 1 Xiangfeng Duan	Invite 3 Mark C. Hersam	Invite 6 Yan Li	Invite 9 Matteo Pasquali	Invite 10 Achim Hartschuh
10:00								
10:15				Poster Talk 1 Susumu Okada	Poster Talk 3 Ado Jorio de Vasconcelos	Invite 7 Jeffrey Blackburn	Poster Talk 5 Annick Loiseau	Coffee Break
10:30								
10:45				Poster 1 and Coffee break	Poster 3 and Coffee break	Coffee Break	Poster 5 and Coffee break	Invite 11 R. Bruce Weisman
11:00								
11:15						Invite 8 Lian-Mao Peng		Invite 12 Thomas Pichler
11:30								
11:45						Tsuyohiko Fujigaya		Lei Shi
12:00						Kazuhiro Yanagi		Poster Summary & Poster Award Younghee Lee
12:15						Yang Wei		
12:30						Felix Pyatkov		Conference Summary Mildred S. Dresselhaus
12:45				Lunch	Lunch	Lunch	Lunch	
13:00								AD for NT16 Paola Ayala
13:15								Closing
13:30							Special Panel "Application of CNT" Younghee Lee Morinobu Endo Shoushan Fan Esko I. Kauppinen Otto Zhou Motoo Yumura Seunghyun Baik	
13:45								
14:00			Registration	Tobias Hertel	Invite 4 Erik C. Neyts	Excursion & Banquet		
14:15				Navaneetha Krishnan Subbaiyan				
14:30				Invite 2 Yoshihiro Iwasa	Invite 5 Vasili Perebeinos			
14:45								
15:00			Tutorial 1 Mildred S. Dresselhaus	Shinichiro Mouri	Annick Loiseau			
15:15				Zheng Liu	Jin Zhang			
15:30				Miho Fujihara	Yoshikazu Homma		Yuan Chen	
15:45				Aravind Vijayaraghavan	Xiao Wang		Susumu Katagiri	
16:00			Tutorial 2 Hiromichi Kataura	Poster Talk 2 Yan Li	Poster Talk 4 Sofie Cambré		Poster Talk 6 Seunghyun Baik	
16:15								
16:30				Poster 2 and Coffee break	Poster 4 and Coffee break		Poster 6 and Coffee break	
16:45								
17:00	Registration		Registration					
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