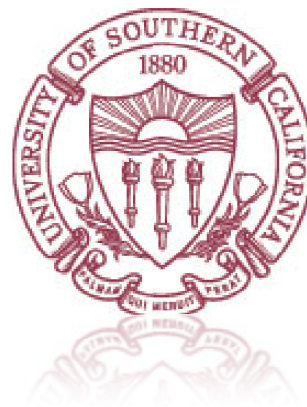


The logo for the Fifteenth International Conference on the Science and Applications of Nanotubes (N14). It features the letters 'N14' in a stylized, bold, red font. The 'N' is composed of two thick, curved lines. The '14' is also in red, with the '1' being a simple vertical bar and the '4' having a distinctive shape. The logo is set against a background of a yellow honeycomb or hexagonal grid pattern.

**Fifteenth International
Conference on the
Science and Applications
of Nanotubes**

2-6 June 2014

University of Southern California

Los Angeles, California, USA



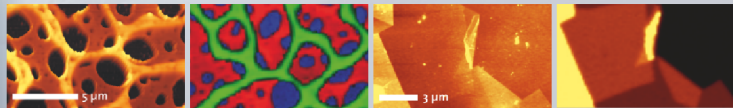
NT14 Program Schedule

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday							
	June 1	June 2	June 3	June 4	June 5	June 6	June 7							
9:00	Satellite Symposia CCTN14, MSIN14, CNTFA14	Shoushan Fan	Kenji Hata	Ming Zheng	Young Hee Lee	Feng Wang	Satellite Symposia GSS14							
9:15														
9:30		Florian Banhart	Alexander Hoegele	Giorgia Pastorin	H.Kataura	Yutaka Ohno								
9:45														
10:00		R. Saito	Artyukhov	R. Zhang	S.Maruyama	M. Picher								
10:15														
10:30		Nasibulin	H. Hasdeo	Goltapehei	R. Krupke	Xi Ling								
10:45														
10:45		Poster 1+2 Summary	Poster 3+4 Summary	Poster 5+6 Summary	Sofie Cambre	F. Papadim.								
11:00														
11:15		Poster Session 1 and Exhibition	Poster Session 3 and Exhibition	Poster Session 5 and Exhibition	K. Otsuka	Summary and Poster								
11:30														
11:45		Poster Session 1 and Exhibition	Poster Session 3 and Exhibition	Poster Session 5 and Exhibition	H. Wang	NT15 Preview								
12:00														
12:15		Poster Session 1 and Exhibition	Poster Session 3 and Exhibition	Poster Session 5 and Exhibition	H. Jiang	Closing								
12:30														
12:30		Poster Session 1 and Exhibition	Poster Session 3 and Exhibition	Poster Session 5 and Exhibition	A. Loiseau	Lunch								
12:45														
13:00	Lunch	Lunch	Lunch	Excursion and Banquet	Lunch									
13:15														
13:30	Stephen Purcell	O. T. Gul	Jerry Tersoff		Excursion and Banquet									
13:45														
14:00	Nikolaev	X. Wei	Laurent Cognet			Excursion and Banquet								
14:15														
14:30	J. Campo	Sakurai	T.Maruyama				Excursion and Banquet							
14:45														
15:00	J. Yang	B. H. Son	T.Maruyama					Excursion and Banquet						
15:15														
15:30	Poster Session 2 and Exhibition	Poster Session 4 and Exhibition	Poster Session 6 and Exhibition						Excursion and Banquet					
15:45														
16:00	Poster Session 2 and Exhibition	Poster Session 4 and Exhibition	Poster Session 6 and Exhibition							Excursion and Banquet				
16:15														
16:30	Poster Session 2 and Exhibition	Poster Session 4 and Exhibition	Poster Session 6 and Exhibition								Excursion and Banquet			
16:45														
17:00	G. Soavi	T. Susi	J. S. Lauret									Excursion and Banquet		
17:15														
17:30	Mikito Koshino	Alan Windle	Yuichiro Kato	Excursion and Banquet										
17:45														
18:00-20:00	Welcome Reception													

Keynote Talk	Poster summary
Invited Talk	Poster Session
Contributed Talk	Satellite Symposium

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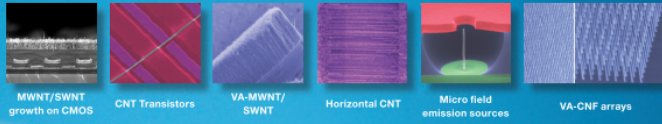


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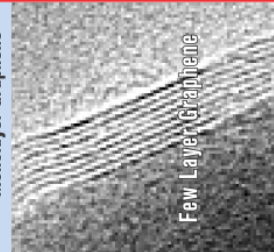
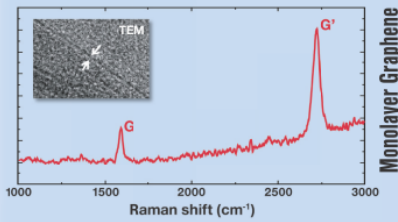
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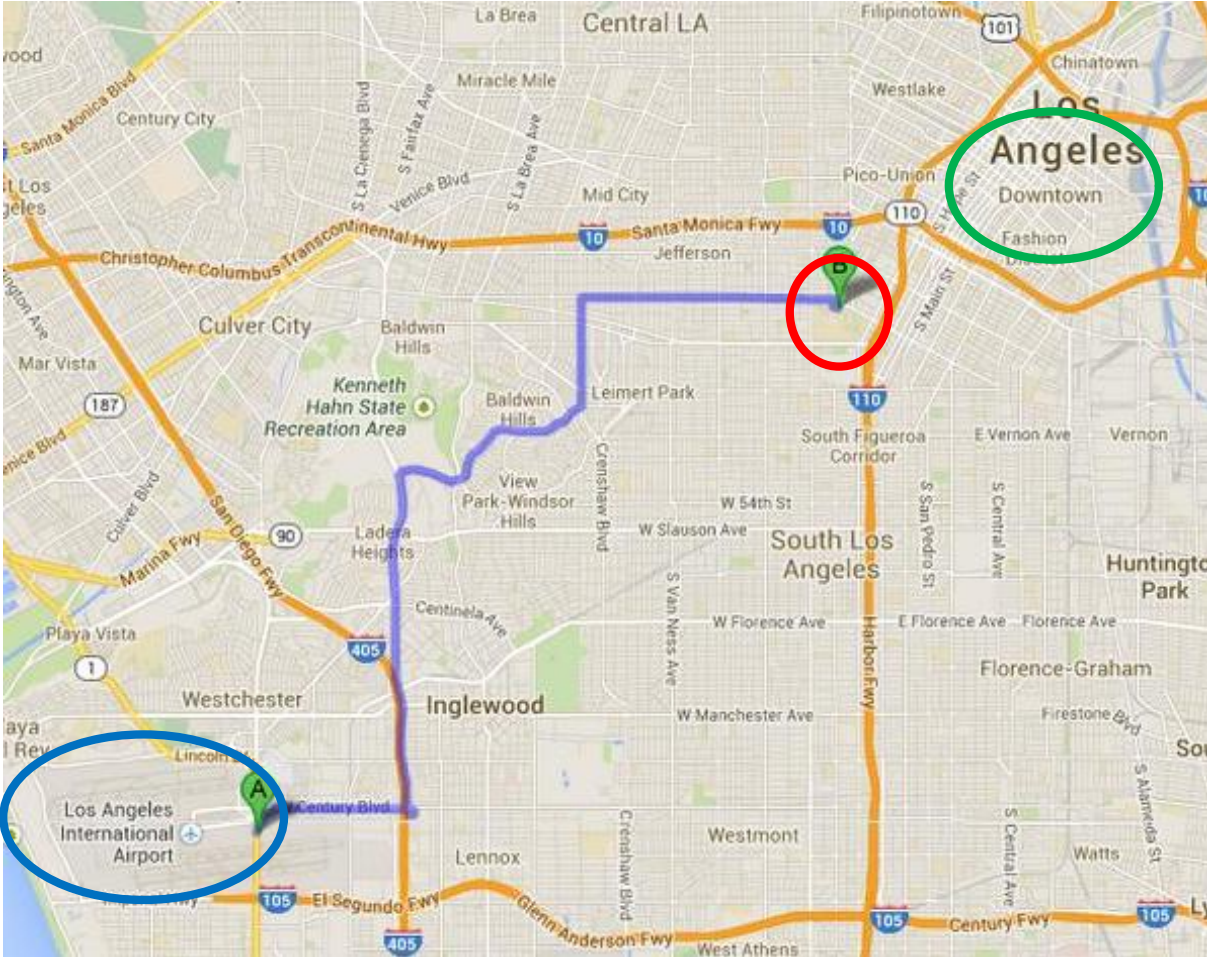


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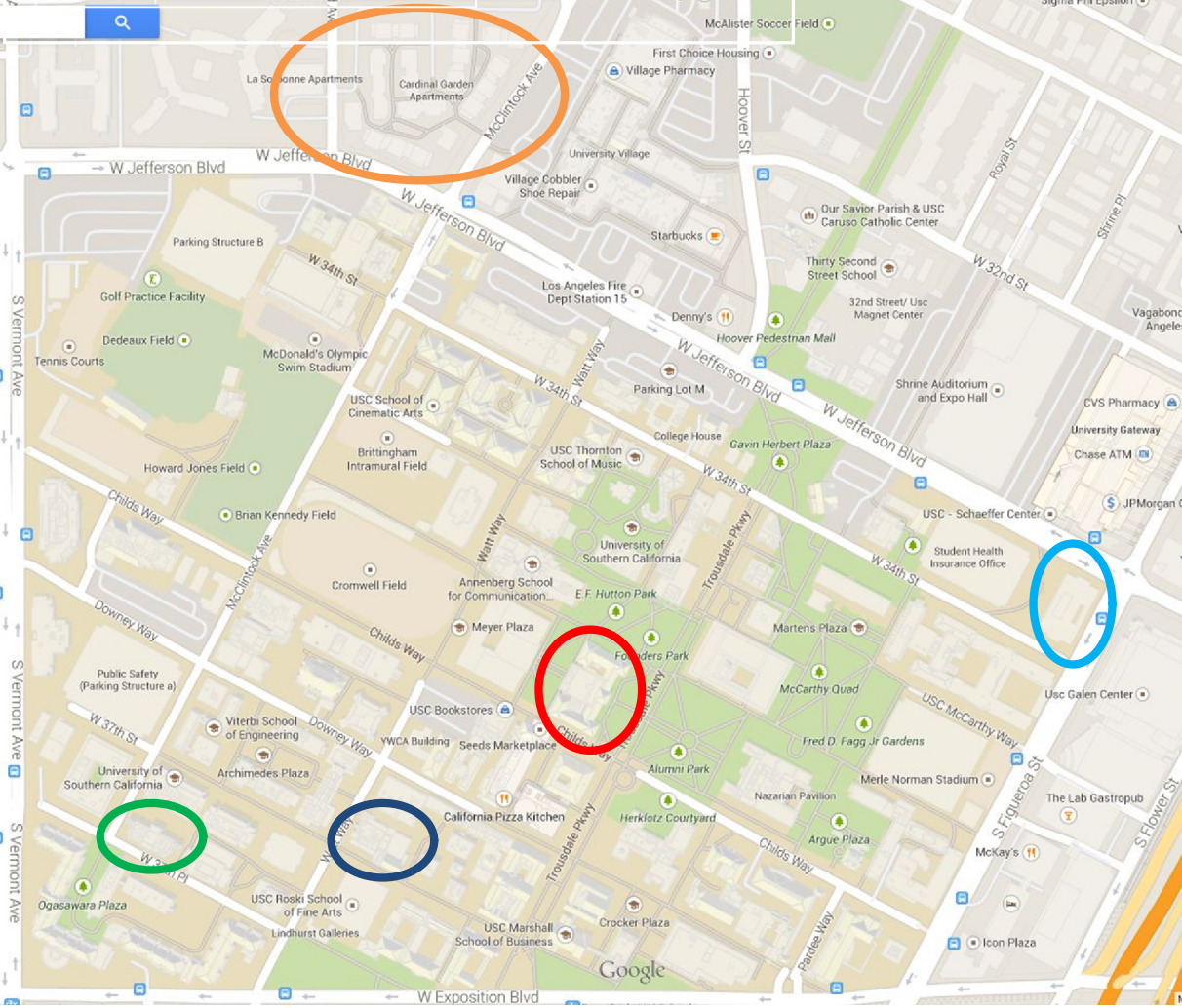


University of Southern California

Downtown Los Angeles

Los Angeles International Airport (LAX)

USC Campus Map



Bovard Auditorium (ADM)
3551 Trousdale Parkway

Cardinal Gardens (CAR)
3131 McClintock Avenue

Davidson Conference Center (DCC)
3415 South Figueroa Street

Stauffer Science Lecture Hall (SLH 100, SLH102)
831 Bloom Walk

Hughes Aircraft Electrical Engineering Center (EEB 132)
3740 McClintock Ave.

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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).

Monday

Carbon Nanotubes: From Basic Research to Commercialization

Shoushan Fan

Department of Physics & Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing, Beijing, China
fss-dmp@mail.tsinghua.edu.cn

Carbon nanotube (CNT) is a promising nanomaterial for real applications due to its excellent mechanical, electrical, and thermal properties. The real products of CNT are expected after long time intensive research efforts on it. In this talk, I will present our research works on CNTs in the past two decades, including studies on the growth mechanism, controllable synthesis, physical properties, and real applications of CNTs. In particular, I will show that a unique macroscopic form of CNTs, the super-aligned CNTs, can bridge the gap between nano-world and macro-world and lead CNTs into real applications.^[1-7] Many real applications, such as field and thermionic emission electron sources,^[8-12] high strength CNT yarns,^[2,6,7] electrodes for batteries and supercapacitors,^[13-17] loudspeakers,^[18,19] displays,^[20-22] SERS substrate,^[23] IR detector^[24] etc. have been demonstrated. Real products of CNT TEM grids^[25,26] and CNT touch panels^[4] have already been commercialized. More products based on super-aligned CNTs are expected to go to the market in the near future.^[27]

- [1]. K. L. Jiang, Q. Q. Li, S. S. Fan, *Nature* 2002, 419, 801
- [2]. X. B. Zhang, K. L. Jiang, et al. *Adv. Mater.* 2006, 18, 1505
- [3]. K. Liu, et al. *Nano Lett.* 2008, 8, 700
- [4]. C. Feng, K. Liu, et al. *Adv. Funct. Mater.* 2010, 20, 885
- [5]. K. Liu, Y. H. Sun et al. *Adv. Funct. Mater.* 2011, 21, 2721
- [6]. K. Liu, Y. H. Sun, et al. *Nanotechnology* 2010, 21, 045708
- [7]. K. Liu, Y. H. Sun, et al. *ACS Nano* 2010, 4, 5827
- [8]. Y. Wei, et al. *Appl. Phys. Lett.* 2006, 89, 063101
- [9]. P. Liu, Y. Wei, K. L. Jiang et al. *Phys. Rev. B.* 2006, 73, 235412
- [10]. Y. Wei, K. L. Jiang, X. F. Feng, P. Liu, L. Liang, S. S. Fan, *Phys. Rev. B.* 2007, 76, 045423
- [11]. Y. Wei, K. L. Jiang, L. Liang, Z. Chen, S. S. Fan, *Nano Lett.* 2007, 7, 3792
- [12]. L. Xiao, et al. *Appl. Phys. Lett.* 2008, 92, 153108
- [13]. H. X. Zhang, C. Feng, et al. *Adv. Mater.* 2009, 21, 2299
- [14]. R. F. Zhou, et al. *Nanotechnology* 2010, 21, 345701
- [15]. S. Luo, et al. *Adv. Mater.* 2012, 24, 2294
- [16]. Y. Wu, et al. *Nano Lett.* 2013, 13, 818
- [17]. K. Wang, et al. *Adv. Funct. Mater.* 2013, 23, 846
- [18]. L. Xiao et al., *Nano Lett.* 2008, 8, 4539
- [19]. L. Xiao et al., *J. Appl. Phys.* 2011, 110, 084311
- [20]. P. Liu, et al. *Adv. Mater.* 2009, 21, 3563.
- [21]. P. Liu, et al. *Nano Lett.* 2012, 12, 2391
- [22]. Y. Wei, et al. *Nano Lett.* 2012, 12, 2548

- [23]. Y. H. Sun, et al. Nano Lett. 2010, 10, 1747.
[24]. L. Xiao et al., Nanotechnology, 2011, 22, 025502.
[25]. L. N. Zhang, et al. Nano Lett. 2008, 8, 2564.
[26]. L. N. Zhang, et al. Nanotechnology, 2011, 22,385704
[27]. K. L. Jiang, et al. Adv Mater. 2011, 23, 1154.

I1

Atomic Carbon Chains: A Perfectly One-Dimensional Carbon Phase Beyond Nanotubes

F. Banhart, O. Cretu, A. La Torre, A. Botello-Mendez, J. -C Charlier

Institut de Physique et Chimie des Matériaux, University of Strasbourg, Strasbourg, Alsace, France

Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Louvain, Walloon Brabant, Belgium

florian.banhart@ipcms.u-strasbg.fr

Carbon chains can be considered as sp^1 -hybridized strings of carbon atoms of monoatomic thickness, constituting the logical one-dimensional phase of carbon. They have been proposed since a long time until they were observed by electron microscopy. Recent experiments show that, by using a measuring system with an STM tip in a TEM specimen stage, carbon chains can not only be made but also characterized (O. Cretu et al., Nano Lett. 13, 3487 (2013)). By passing a current through the chains, their electrical properties have been measured for the first time. The chains are obtained by unraveling carbon atoms from nanotubes or graphene ribbons while an electrical current flowed through the tubes or ribbons and, successively, through the chain. The electrical conductivity of the chains was found to be much lower than predicted for ideal chains. First-principles calculations show that strain in the chains determines the conductivity in a decisive way. Indeed, carbon chains are always under varying non-zero strain that transforms their atomic structure from cumulene (double bonds throughout the chain) to polyene (alternating single/triple bonds), thus inducing a tunable band gap. New experiments show the bonding characteristics at contacts between metals and carbon chains as well as characteristic current-voltage curves, depending on the type of contact. The experiments show a perspective toward the synthesis of carbon chains and their application as the smallest possible interconnects or even as one-dimensional semiconducting devices.

Coherent phonon spectra of G band in single wall carbon nanotubes

Ahmad R. T. Nugraha, Eddwi H. Hasdeo, Riichiro Saito

Department of Physics, Tohoku University, Sendai, Miyagi, Japan

rsaito@flex.phys.tohoku.ac.jp

In ultrafast (femtosecond) pump-probe spectroscopy, coherent phonons have been known to be observed in terms of oscillations of the change in optical constants (e.g. reflectivity and transmittance) as a function of delay time between pump and probe pulses, in which these oscillations are directly related to the modulations of absorption coefficient. For a single wall carbon nanotube (SWNT), Fourier power spectra of the differential reflectivity or transmittance as a function of phonon frequency show several peaks that correspond to the SWNT's coherent phonon modes, such as the radial breathing mode (RBM), G band, and even acoustic modes.^[1,2] In the case of RBM, oscillations of optical constants are already understood as a result of a diameter-dependent band gap.^[3,4] However, this mechanism cannot be used for the other phonon modes. In particular, if we consider the same mechanism for the G-band, it was previously predicted that the modulations of absorption coefficient due to G-band phonons are about 1000 times smaller than those caused by the RBM.^[5] However, recent experiments showed that the coherent G-band signal is comparable to, and almost on the same order as, the RBM signal.^[6]

In this work, we present an origin of the strong coherent G-band signal. Instead of the energy gap modulations as in the RBM, here we expect that the modulations of electron-photon interaction as a function of time should be relevant to the coherent G-band intensity. We also compare the coherent G-band intensity with the other coherent phonon modes in a specified SWNT chirality. We expect that there might be a common origin of the coherent phonon spectral line shapes of any materials due to changes of phase in the coherent oscillations. This theory could be a significant progress for understanding a general and systematic behavior of coherent phonons.

[1]. A. Gambetta et al., Nat. Phys. 2, 515-520 (2006)

[2]. Y.-S. Lim, A. R. T. Nugraha, et al., Nano Lett. (2014), in press. DOI: 10.1021/nl404536b

[3]. A. R. T. Nugraha et al., Phys. Rev. B 84, 174302 (2011)

[4]. A. R. T. Nugraha et al., Phys. Rev. B 88, 075440 (2013)

[5]. G. D. Sanders et al., Phys. Rev. B 79, 205434 (2009)

[6]. J.-H. Kim et al, Phys. Rev. B 86, 161415 (2012)

Single-Walled Carbon Nanotube Networks for Ethanol Vapor Sensing Application

Albert Nasibulin, Ilya Anoshkin, Prasantha Mudimela, Maoshuai He, Vladimir Ermolov, Oleg Tolochko, Esko Kauppinen

Dept. Applied Physics, Aalto University, Espoo, Uusimaa, Finland

Nokia Research Center, Nokia, Espoo, Uusimaa, Finland

Institute of Materials and Technologies, Saint-Petersburg Polytechnic State University, Saint-Petersburg, Russia, Russian Federation

Dept. Applied Physics, Aalto University, Espoo, Uusimaa, Finland

albert.nasibulin@aalto.fi

Networks of pristine high quality single walled carbon nanotubes (SWNTs), the SWNTs after Ar-plasma treatment (from 2 to 12 min) and carbon nanobuds (CNBs) have been tested for ethanol vapor sensing. It was found that the pristine high quality SWNTs do not exhibit any ethanol sensitivity, while the defect introduction in the tubes results in the appearance of the ethanol sensitivity. The CNB network showed the ethanol sensitivity without plasma treatment. Both CNB and low defective (after 3 min treatment) SWNT networks exhibit significant drift in the resistance baseline, while heavily plasma-treated (9 min) SWNTs exhibited high ethanol vapor sensitivity without the baseline change. The mechanisms of the ethanol sensitivity and stability after the plasma irradiation are attributed to the formation of sensitive dangling bonds in the SWNTs and formation of defect channels facilitating an access of the ethanol vapor to all parts of the bundled nanotubes.

Posters 1+2 Summary (David Tomanek)

Poster Session 1 and Exhibition

Giant Currents and Temperatures for Coulomb Blockade during Field Emission from Single Wall Carbon Nanotubes

S. Perisanu, A. Pascale-Hamri, A. Derouet, C. Journet, P. Vincent, A. Ayari, S. T. Purcell

Institut Lumière Matière, Université Claude Bernard Lyon 1 and CNRS, Villeurbanne, Lyon,
Francea6@b2.com

The Coulomb Blockade (CB) has been and continues to be studied intensively for its interest in fundamental physics and technology. Two important limitations of CB devices are low operating currents, now reported up to ~ 100 nA, and poor room temperature performance. The later has been improved over the years by fabricating ever smaller structures, in particular when the Coulomb island is a Single Wall Carbon Nanotube (SWCNT). We present here well-defined Coulomb staircases (CS), using an original Field Emission (FE) experiment on several individual in-situ grown SWCNT cantilevers. Additional individual electrons on the SWCNTs were detected in FE currents and mechanical resonance eigenfrequencies. Results quantitatively agree with CB FE theory developed by Raichev. A unique in-situ shortening technique was applied nine times to one SWCNT to increase progressively the oscillations periods from 5.5 V to 80V, the temperature for observable CS to 1100 K and the currents to 1.8 μ A, all the largest values found in the literature (to the best of our knowledge). This process led to the brightest electron source reported (9×10^{11} A/(str.m².V)).

CT3

Automated Carbon Nanotube Synthesis by Water-assisted CVD

Pavel Nikolaev, Daylond Hooper, Benji Maruyama

UES Inc., Dayton, OH, United States

*Materials and Manufacturing Directorate, RXAS, Air Force Research Laboratory, WPAFB, OH,
United States*

pavel.nikolaev.ctr@us.af.mil

Among many techniques of carbon nanotube (CNT) synthesis available today, chemical vapor deposition (CVD) is the most popular by far due to low cost, ease of set-up, and wide range of nanotube morphologies that can be produced. The throughput of a typical research CVD system, however, is limited to a few runs per day due to time necessary for heating, conditioning, growing, and cooling steps. This makes it difficult and time-consuming to explore the multi-dimensional experimental parameter space that includes temperature, pressure, feedstock composition; catalyst and catalyst support composition. The Adaptive Rapid Experimentation and in-situ Spectroscopy (ARES) CVD system described in this contribution makes over 100 CVD experiments possible in a single day in fully automatic mode, with pre-programmed growth recipes and without user intervention. CNTs are grown in a miniature cold wall CVD reactor, with the same laser used for both thermal activation of the growth process and Raman excitation. Raman spectra are acquired in real time, enabling in-situ analysis of growth kinetics and nanotube characteristics. Further linear regression modeling allowed mapping regions of selectivity towards SWNT and MWNT growth in the complex parameter space of the water-assisted CVD synthesis. This is the first demonstration of automated experimentation combined with regression analysis applied to the CNT synthesis by CVD. This development of the automated rapid serial experimentation is a significant progress towards an autonomous closed-loop learning system: a Robot Scientist.

Giant Nonlinear Optical Response from Dye-filled Carbon Nanotube Hybrids

Jochen Campo, Sofie Cambré, Charlie Beirnaert, Christof C. Verlackt, Wim Wenseleers

Physics Department, University of Antwerp, Wilrijk, Antwerp, Belgium
Jochen.Campo@uantwerp.be

Asymmetric dipolar molecules, acting as electric ‘rectifiers’ with a large second-order nonlinear optical (NLO) response (first hyperpolarisability β), find applications in ultrafast electro-optic switches for optical telecommunication networks and wavelength conversion of lasers.^[1] In 3D bulk systems, however, such dipolar molecules tend to align in a pairwise anti-parallel way, thus cancelling each other’s directional properties, such as the NLO response. Parallel alignment is traditionally achieved by electric field poling in a polymer matrix, but long term stability of this alignment remains problematic.

Here we show that by encapsulating such elongated dipolar molecules in the 1D internal channel of single-wall carbon nanotubes (SWCNTs), Coulomb interactions naturally favor a polar head-to-tail alignment of the molecular dipoles, leading to a cooperative enhancement of their second-order NLO responses. This principle is demonstrated for a prototypical dipolar molecule encapsulated in various SWCNT samples. The encapsulation is evidenced by extensive wavelength-dependent fluorescence-excitation^[2] and resonance Raman^[3] experiments on bile-salt solubilized^[4] dye-filled SWCNTs, revealing the effect of encapsulation on the vibrational and electronic properties of the SWCNTs and the encapsulated molecules. Wavelength-dependent hyper-Rayleigh scattering^[5,6] (i.e. second harmonic light scattering) experiments effectively show that these organic-SWCNT nanohybrids possess giant NLO responses ($\beta = 68800 \times 10^{-30}$ esu at resonance; $\beta_0 = 9770 \times 10^{-30}$ esu in the static limit; corresponding to ~ 70 identically aligned chromophores, depending on the SWCNT diameter range). Their equally giant dipole moment and size promises a good and stable alignment of the nanohybrids in a polymer film, which opens up an entirely new route to the rational design of solution-processible yet stable NLO materials.

[1]. E. Goovaerts et al. In Handbook of advanced electronic and photonic Materials and Devices, Vol. 9: Nonlinear optical materials, Academic Press, San Diego, 127-191 (2001)

[2]. S. Cambré et al., ACS nano 6, 2649 (2012)

[3]. W. Wenseleers et al., Adv. Mater. 19, 2274 (2007)

[4]. W. Wenseleers et al., Adv. Funct. Mater. 14, 1105 (2004)

[5]. J. Campo et al., Optics Express 17, 4587 (2009)

[6]. J. Campo et al., J. Phys. Chem. Lett. 3, 2248 (2012)

Radial Deformation of Single-Walled Carbon Nanotubes on Quartz Substrates and the Resultant Anomalous Diameter-Dependent Reaction Selectivity

Juan Yang, Yu Liu, Daqi Zhang, Xiao Wang, Yan Li

College of Chemistry and Molecular Engineering, Peking University, Beijing, Beijing, China
yang_juan@pku.edu.cn

Owing to the unique conjugated structure, chemical reaction selectivity of single-walled carbon nanotubes (SWNTs) has attracted great attentions. By utilizing the radial deformation of SWNTs caused by the strong interactions with the quartz lattice, we achieve an anomalous diameter-dependent reaction selectivity of quartz lattice-oriented SWNTs in treatment with iodine vapor, which is distinctly different from the widely reported and well accepted higher reaction activity in small-diameter tubes over the large ones. The radial deformation of SWNTs on quartz substrate is verified by detailed Raman spectra and mappings in both G band and RBM. Due to the strong interaction between SWNTs and the quartz lattice, large-diameter tubes present larger degree of radial deformation and more delocalized partial electrons are distributed at certain sidewall sites with high local curvature. It is thus easier for the carbon-carbon bonds at those high curvature sites on large-diameter tubes to break down upon reaction. This anomalous reaction activity offers a novel approach for selective removal of small-bandgap large-diameter tubes.

Poster Sesssion 2 + Exhibition

Ultrafast charge photogeneration and dynamics in semiconducting carbon nanotubes

Giancarlo Soavi, Francesco Scotognella, Daniele Viola, Timo Hefner, Tobias Hertel, Giulio Cerullo, Guglielmo Lanzani

Dipartimento di Fisica, Politecnico di Milano, Milano, Lombardia, Italy
Dept. of Chemistry and Pharmacy, Inst. for Physical and Theoretical Chemistry, University of Würzburg, Würzburg, Bavaria, Germany

Dipartimento di Fisica, Politecnico di Milano, Milano, Lombardia, Italy
Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Milano, Lombardia, Italy
giancarlo.soavi@polimi.it

Single-walled carbon nanotubes (SWNTs) are excellent model systems for the study of photoexcitation dynamics in one-dimensional (1D) quantum confined systems. Theory predicts that Wannier-Mott excitons are the elementary photoexcitations in SWNTs, due to the strong Coulomb interaction caused by the weak screening. Such excitons have peculiar 1D characteristics, such as extraordinary large binding energies, large size and 1D transport. Experimental observations, such as the measured binding energy, typically 0.1-1 eV, and the electron-hole correlation length, in the 1-10 nm domain confirm theoretical predictions. The exciton model alone, however, fails to capture the whole dynamics following photoexcitation, and many other photoexcited species have crowded the complex scenario of SWNTs' optical response, ranging from triplets to bi-excitons and trions. Experiments based on photocurrent, transient absorption and THz spectroscopy also point out a non-negligible photogeneration of free charge-carriers. This is in contrast with the excitonic model and the reduced Sommerfeld factor that predicts that excitons should be the only species generated upon photoexcitation. Attempts to solve this discrepancy proposed non-linear processes, such as exciton-exciton annihilation, as a mechanism of charge-carrier photogeneration. However, there is solid experimental evidence that charge-carrier photogeneration is linear with the pump fluence.

Here we apply broadband ultrafast transient absorption spectroscopy to the semiconducting (6,5) SWNT and show that charge-carriers can be identified by their effect on excitonic resonances, in particular the large Stark shift that they induce on high-energy, easily polarizable excitons (S_{22} and S_{33}). Having identified the Stark shift as a good spectroscopic fingerprint for charge-carriers, we are able to study their dynamics in a nearly ideal 1D system. We find that a fraction of the absorbed photons generates geminate charge-carrier pairs within our temporal resolution (≈ 50 fs), which then recombine on the picosecond timescale following the characteristic kinetic law of random walk in 1D. Our analysis starts from the observation that the first derivative of the ground state absorption spectrum, i.e. a photoinduced red shift of the excitonic transition, can reproduce many of the features observed in the differential transmission ($\Delta T/T$) spectra of semiconducting SWNTs. This effect can be ascribed to different physical mechanisms, such as

bi-excitons or trions formation, thermal effects or Stark effect. Here we unambiguously demonstrate that this derivative shape is indeed due to strong local electric field induced by photogenerated charge-carriers, which shifts the electronic transitions by Stark effect. In particular, we show that the energy shift is stronger for excitons with lower binding energy, as for S_{33} with respect to S_{11} , as expected for the Stark effect. This suggests that the higher energy S_{33} exciton is ideally suited for directly probing charge-carriers in SWNTs and can be exploited to further analyze the charge photogeneration process and to study charge-carrier dynamics in one dimension. Our data show that the free charge-carriers are generated within 50 fs. The temporal evolution of the S_{33} pump-probe dynamics is very accurately reproduced by a power law $\sim t^{-0.5}$. A monomolecular power law decay is the predicted dynamics for geminate recombination of free particles after random walk in an infinite one-dimensional chain. A more detailed modelling of the geminate recombination process indicates that the initial distance between the geminate e-h pair is of the same order of magnitude of the exciton correlation length, thus suggesting that charge-carriers arise from instantaneous linear exciton dissociation.

Our results shed new light onto the charge photogeneration mechanism in SWNTs, suggesting that the nascent exciton dissociates spontaneously, perhaps in presence of extrinsic screening of the Coulomb attraction, possibly due to water or other ambient contamination.

Electronic properties in moiré superlattice in rotationally stacked atomic layers

Mikito Koshino, Pilkyung Moon

Department of Physics, Tohoku University, Sendai, Miyagi, Japan
School of Computational Sciences, Korean Institute for Advanced Study, Dongdaemun-gu, Seoul,
Korea, Republic Of
(koshino@cmpt.phys.tohoku.ac.jp)

We report recent theoretical studies on the electronic properties of rotationally stacked atomic layer systems, including graphene-graphene bilayer, and graphene-hBN (hexagonal boron nitride) composite bilayer. The misoriented atomic structure gives rise to a moiré superlattice structure with a long spatial period, and it strongly modifies the band structure in the low-energy region. We develop an effective continuum model based the tight-binding Hamiltonian, which correctly describes the electronic structure of moiré superlattice.^[1] In a magnetic field, the coexistence of the moiré pattern and the Landau quantization causes the fractal energy spectrum so-called Hofstadter's butterfly. We calculate the spectral evolution as a function of magnetic field, and demonstrate that the quantized Hall conductivity changes in a complicated manner in changing Fermi energy and the magnetic field amplitude.^[2] We also calculate the optical absorption in the fractal band regime, and find that the absorption spectrum and the optical selection rule exhibit recursive self-similar structure as well, reflecting the fractal nature of the energy spectrum.^[3]

[1]. P. Moon and M. Koshino, Phys. Rev. B 87, 205404 (2013)

[2]. P. Moon and M. Koshino, Phys. Rev. B 85, 195458 (2012)

[3]. P. Moon and M. Koshino, Phys. Rev. B 88, 241412(R) (2013)

Poster Session 1

T1

Coherent phonon spectra of G band in single wall carbon nanotubes

Ahmad R. T. Nugraha, Eddwi H. Hasdeo, Riichiro Saito

Department of Physics, Tohoku University, Sendai, Miyagi
Japanrsaito@flex.phys.tohoku.ac.jp

In ultrafast (femtosecond) pump-probe spectroscopy, coherent phonons have been known to be observed in terms of oscillations of the change in optical constants (e.g. reflectivity and transmittance) as a function of delay time between pump and probe pulses, in which these oscillations are directly related to the modulations of absorption coefficient. For a single wall carbon nanotube (SWNT), Fourier power spectra of the differential reflectivity or transmittance as a function of phonon frequency show several peaks that correspond to the SWNT's coherent phonon modes, such as the radial breathing mode (RBM), G band, and even acoustic modes.^[1,2] In the case of RBM, oscillations of optical constants are already understood as a result of a diameter-dependent band gap.^[3,4] However, this mechanism cannot be used for the other phonon modes. In particular, if we consider the same mechanism for the G-band, it was previously predicted that the modulations of absorption coefficient due to G-band phonons are about 1000 times smaller than those caused by the RBM.^[5] However, recent experiments showed that the coherent G-band signal is comparable to, and almost on the same order as, the RBM signal.^[6]

In this work, we present an origin of the strong coherent G-band signal. Instead of the energy gap modulations as in the RBM, here we expect that the modulations of electron-photon interaction as a function of time should be relevant to the coherent G-band intensity. We also compare the coherent G-band intensity with the other coherent phonon modes in a specified SWNT chirality. We expect that there might be a common origin of the coherent phonon spectral line shapes of any materials due to changes of phase in the coherent oscillations. This theory could be a significant progress for understanding a general and systematic behavior of coherent phonons.

- [1]. A. Gambetta et al., Nat. Phys. 2, 515-520 (2006)
- [2]. Y.-S. Lim, A. R. T. Nugraha, et al., Nano Lett. (2014), in press. DOI: 10.1021/nl404536b
- [3]. A. R. T. Nugraha et al., Phys. Rev. B 84, 174302 (2011)
- [4]. A. R. T. Nugraha et al., Phys. Rev. B 88, 075440 (2013)
- [5]. G. D. Sanders et al., Phys. Rev. B 79, 205434 (2009)
- [6]. J.-H. Kim et al, Phys. Rev. B 86, 161415 (2012)

Quantum interference effect in Raman spectra of metallic nanotubes

Eddwi H. Hasdeo, Ahmad R. T. Nugraha, Mildred S. Dresselhaus, Riichiro Saito

Department of Physics, Tohoku University, Sendai, Miyagi, Japan

Department of Physics, MIT, Cambridge, MA, United States

Department of Physics, Tohoku University, Sendai, Miyagi, Japan

hasdeo@flex.phys.tohoku.ac.jp

In graphene and metallic single wall carbon nanotubes (m-SWNTs), the existence of gapless linear energy bands (Dirac cones) modify the G band (in-plane optical phonon modes) 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 the G phonon and an electron-hole pair in the linear energy band.^[1] The other phenomenon is the asymmetric spectral shape of the G band, also known as Breit-Wigner-Fano (BWF) line shape, which long been observed in m-SWNTs^[2] and recently observed in graphene.^[3] However, the origin of this BWF lineshape asymmetry remains a question. In this presentation, the origin of BWF line shape is explained by means of quantum interference of phonon G band spectra and electronic Raman spectra (ERS).^[4] The ERS are electronic spectra whose origin comes from an electron-hole pair excitation in the vicinity of the Dirac cone.^[5]

In this work, we calculated the exciton-exciton interaction between a photo-excited exciton and an exciton in the linear band of a m-SWNT which is relevant to the ERS. We calculated ERS spectra as a function of laser excitation energy and we reproduced the experimental BWF spectral shape for all laser excitation energies. The Coulomb potential, generally, gives a maximum value at momentum transfer $q=0$ but surprisingly, we found that the direct Coulomb interaction between the two excitons vanishes at $q=0$. The absence of the direct Coulomb interaction is due to the symmetry of the two sub-lattices of SWNTs unit cell. Using the same method, we extend the story in graphene and reproduce the experimental result of the G band asymmetry as a function of Fermi energy. We also predict that the radial breathing phonon mode (RBM) spectra in m-SWNTs exhibit the opposite BWF asymmetry to that of the G band, by showing the laser energy dependence of RBM spectra.

[1]. "Raman spectroscopy in graphene related systems", A. Jorio et al, Wiley (2011)

[2]. S. D. M. Brown et al., Phys. Rev. B 63, 155414, (2001)

[3]. D. Yoon et al., Carbon, 61, 373-378, (2013)

[4]. E. H. Hasdeo et al. Phys. Rev. B 88, 115107, (2013)

[5]. H. Farhat et al., Phys. Rev. Lett. 107, 157401 (2011)

T3

Spontaneous formation of O₈ clusters and chains within nanostructures

Daniel Vasconcelos Pazzini Massote, Mário Sérgio Mazzoni

Physics Department, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil

massote@fisica.ufmg.br

We perform first principles calculations based on the density functional theory to show that the building blocks of the oxygen ϵ -high pressure solid phase spontaneously form when oxygen molecules are enclosed within fullerenes and small diameter nanotubes. We observe that the stability increases with the enclosure diameter. The building blocks consist in O₈ clusters, which are able to self-assemble into periodic arrays inside nanotubes. Such chains are semiconductors when isolated or when encapsulated in boron nitride nanotubes, and become doped when confined in carbon materials. In the same way as we observe a magnetic collapse in oxygen ϵ solid phase, these O₈ clusters maintain this property when encapsulated. Molecular dynamics simulations confirm the formation and stability of the clusters and chains in ambient conditions.

Wave propagation along coplanar transmission line covered with inkjet printed multi-walled carbon nanotubes network

Ibtissem Oueriemi¹, Jean-Pierre Raskin, Fethi Choubani, Védi Dupont, Véronique Lardot, Isabelle Huynen

*ICTEAM-ELEN, Université catholique de Louvain, Louvain-la-Neuve, Brabant-wallon, Belgium
Innov'Com Lab, Higher school of Communications of Tunis, El Ghazala, Ariana, Tunisia
Belgium Ceramics Research Center, université de Mons, Mons, Brabant-wallon, Belgium
ICTEAM-ELEN, Université catholique de Louvain, Louvain-la-Neuve, Brabant-wallon, Belgium
ibtissem.oueriemi@gmail.com*

The trend of device minimization in size, weight and cost for use in commercial wireless communication systems has resulted in an increasing demand for highly integrated system-on-chip solutions. To shrink the size of interconnections and passive devices, many researchers have proposed the use of slow-wave propagation mode in order to reduce the effective electrical wavelength of the RF signals.^[1]

On the other hand, carbon nanotubes (CNTs) are emerging as novel nanomaterial for a large variety of applications, particularly as electronic material owing to their amazing mechanical, thermal and unique electrical properties.^[2] Thin films of CNTs networks/arrays, a planar topology is usually preferred, with in view the application to CNT-based interconnects and carbon-based circuits.^[3] The use of CNTs network could bring solutions to reduce the size of microwaves circuits in addition to the benefit of short-time and low-cost fabrication using inkjet printing. Furthermore, this technique gives the possibility to readily control the pattern geometry, location, film thickness, and uniformity of the films.

In this present study, we aim at investigating the mode propagation when multi-walled carbon nanotubes (MWCNTs) ink is used to print films on coplanar waveguides (CPWs) lying on glass substrate. The extracted line characteristics from measured S-parameters offer an accurate analysis of the propagation mechanism, revealing the existence of a slow-wave mode regime. A good master of this property is appropriate for exploiting the slow-wave phenomenon in order to scale down the size of passive integrated structures. Thus, the impact of geometry and the number of alternate deposited CNTs networks are experimentally tested.

[1]. R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett., 60, p. 2204, 1992

[2]. J. Sor, Y. Qian, and T. Itoh, IEEE Trans. Microwave Theory Techn., vol. 49, pp. 2336-2341, Dec. 2001

[3]. M. A. El Sabbagh, Proceedings of IEEE International Symposium on Electromagnetic Compatibility (EMC), pp. 841-846, July 2010

Phase diagram of Ni-C nanoparticles from computer simulation

Yann Magnin

CINaM TSN, CNRS, Marseille, Bouche du Rhône, France
magnin@cinam.univ-mrs.fr

Carbon nanotube synthesis critically depends on the chemical and physical states of the catalyst particle from which they grow. In the typical temperature range (600-1000 °C) of SWNT synthesis, pure isolated Ni nanoparticles are solid although atomic diffusion can lead to significant shape changes. Under growth conditions, these nanoparticles are exposed to reactive carbon. Depending on temperature, carbon chemical potential and nanoparticle size, carbon can either 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] we try and calculate size dependent liquid/solid phase diagrams for Ni-C alloys. We thus extend our previous calculations^[2,3] and rationalize our findings using suitable order parameters, as proposed by Steinhardt et al.^[4]

[1]. H. Amara et al., Phys. Rev. B 79, 014109 (2009)

[2]. M. Diarra et al., Phys. Stat. Sol. B 249, 12, 2629–2634 (2012)

[3]. M. Diarra et al., Phys. Rev. Lett. 109, 185501 (2012)

[4]. P. Steinhardt, D. Nelson, and M. Ronchetti, “Bond-orientational order in liquids and glasses,” Phys. Rev. B, 28, 2, 784–805 (1983)

Is exciton BEC possible in individual carbon nanotubes? A theoretical prospective

Igor Bondarev

Math and Physics, North Carolina Central University, Durham, NC, United States
ibondarev@nccu.edu

I will tell about one interesting possibility that we have lately theoretically demonstrated to exist for the 1D exciton Bose-Einstein condensation (BEC) phenomenon in individual small-diameter ($\sim 1-2$ nm) semiconducting carbon nanotubes (CNs).^[1] This originates from the strong coupling of excitons and low-energy inter-band plasmons enabled via the quantum confined Stark effect by using an external electrostatic field applied perpendicular to the CN axis. The perpendicular electrostatic field mixes excitons and inter-band plasmons of the same band,^[2] to result in strongly coupled hybridized excitations-exciton-plasmons in one individual CN.^[3] Such hybridized excitations are strongly correlated collective Bose-type quasi-particles and, therefore, could likely be condensed under appropriately created external conditions — in spite of the well-known statements of the BEC impossibility in ideal 1D/2D systems^[4] and experimental evidence reported earlier for no exciton BEC effect in CNs.^[5] Possibilities for achieving BEC in 1D/2D systems are theoretically demonstrated earlier in the presence of an extra confinement potential.^[6] The correlated exciton-plasmon system in a CN presents such a special case. The effect requires fields ~ 1 V/nm and temperatures below 100 K that are experimentally accessible.^[7] The effect offers a testing ground for fundamentals of 1D condensed matter physics and opens up perspectives to develop a tunable highly coherent polarized light source with CNs.

This research is supported by the US Department of Energy (DE-SC0007117).

- [1]. I.V. Bondarev and A.V. Meliksetyan, Phys. Rev. B 89, 045414 (2014)
- [2]. I.V. Bondarev, L.M. Woods, and K. Tatur, Phys. Rev. B 80, 085407 (2009)
- [3]. I.V. Bondarev, Phys. Rev. B 85, 035448 (2012)
- [4]. R.P. Feynman, Statistical Mechanics (W.A. Benjamin, Inc., Massachusetts, 1972)
- [5]. Y. Murakami and J. Kono, Phys. Rev. Lett. 102, 037401 (2009)
- [6]. V. Bagnato and D. Kleppner, Phys. Rev. A 44, 7439 (1991)
- [7]. Y. Zhang, et al., Nature 459, 820 (2009)

The influence of the curvature of surface and π electrons on adsorption of nanocarbons

Takumi Araki, Syogo Tejima, Shatoshi Nakamura, Hisashi Nakamura, David Tomanek,
Morinobe Endo

*Division of Computational Science and Technology, Research Organization for Information
Science & Technology, Shinagawa, Tokyo, Japan*

*Physics and Astronomy, Michigan State University, East Lansing, Michigan, United States
Factory of Engineering, Shinsyu University, Wakasato, Nagano, Japan*

araki@rist.or.jp

Nano carbons structures as CNTs, graphenes, fullerene, Mackay crystal and their composite have been attracting scientists and engineers to finding of novel functional materials for water technology and electronics.

We have investigated the adsorption of nanocarbons as adsorbent with varying their surface curvature at adsorption point by use of ab initio simulation. The adsorption of CNTs, fullerene, graphene and Mackay crystals, has been simulated for Cesium, Cs, as adsorbate. The results show commonly that π -electron extending beyond the surface of carbons plays important role for catching the valence 6s electron of alkali metal Cs. The valence 6s electron of Cs flows into nanocarbon's π orbitals. It helps for nanocarbons to adsorb Cs stably by the charge transfer interaction. The surface curvature of the adsorption point clearly influences on the adsorption strength. The adsorption becomes more stable if curvature radius of CNTs increases. For the negative Gaussian curvature of Mackay crystals, the adsorption is enhanced around octagonal rings among the hexagons. This result points out that such a sophisticated configuration by the spread of π electrons contributes to the adsorption strength. The feature is useful for nanocarbon filter or film in novel water technology or future carbon electronic materials.

Detection mechanisms in carbon-nanotube-based molecular sensors

Yan Li, Miroslav Hodak, J. Bernholc

Center for High Performance Simulation and Department of Physics, North Carolina State University, Raleigh, NC, United States

yli26@ncsu.edu

Carbon Nanotubes (CNTs) are highly promising for chemical and biological sensing applications, owing to their high chemical and mechanical stabilities, high surface areas and unique electronic properties. We report the results of theoretical studies of detection mechanisms of both pristine and receptor-functionalized CNTs. The calculations use density functional theory (DFT) combined with Keldysh non-equilibrium Green's function (NEGF) method to examine changes in conductance and current due to attachment of analyte molecules. These include ammonia, nitrogen dioxide, glucose and ethylene. For nitrogen dioxide, which chemisorbs on the CNT, we show that the attachment produces significant differences in both transmission and Current-Voltage (I-V) curve. For ammonia, we find that it can be either physisorbed or chemisorbed depending on its position relative to the metallic leads. The chemisorbed case shows detectable differences in transmission and I-V curves. For glucose detection, we investigate the sensing mechanism of CNTs functionalized with pyrene-1-boronic acid. Glucose attachment results in formation of an anion complex, which decreases conductivity through the CNT. For ethylene detection, the sensing mechanism of CNT functionalized with a copper(I)-based receptor is investigated. We find that ethylene binding to the receptor results in detectable changes in both conductance and current. For all cases, the calculated changes in conductance and current are consistent with experiments.^[1-4]

- [1]. J. Kong, N. Franklin, C. Zhou, M. Chapline, S. Peng, K. Cho, and H. Dai, *Science* 287, 622 (2000)
- [2]. N. Peng, Q. Zhang, C. L. Chow, O. K. Tan, and N. Marzari, *Nano Lett.* 9, 1626 (2009)
- [3]. M. B. Lerner, N. Kybert, R. Mendoza, R. Villechenon, M. A. B. Lopez, and A. T. C. Johnson, *Appl. Phys. Lett.* 102, 183113 (2013)
- [4]. B. Esser, J. M. Schnorr, and T. M. Swager, *Angew. Chem. Int. Ed.* 51, 5752 (2012)

Focusing of low energy electrons by Carbon Nanotubes

Samuel A. Hevia, Rodrigo Segura, Patricio Häberle

Departamento de Física, Pontificia Universidad Católica de Chile, Santiago, Región Metropolitana, Chile

Departamento de Química, Universidad de Valparaíso, Valparaíso, V Región, Chile
Departamento de Física, Universidad Técnica Federico Santa María, Valparaíso, V Región, Chile

patricio.haberle@usm.cl

The trajectories of low kinetic energy electrons, in the range of a few eV, are strongly modified by the interaction with the polarization charges they induce on a surface. We show how this effect is relevant in inverse photoemission spectroscopy (IPS) data analysis from carbon nanotubes (CNTs). IPS from CNTs exhibit two main resonances, located around 2.5 eV and 12.5 eV above the Fermi level. The intensity of the first resonance is dependent on the average tube diameter and the second one has a distinctive spectral shape, which can be related to the graphitization level of the CNTs' external walls.

In order to analyze the origin of these resonances, a phenomenological reconstruction of an IPS spectrum from a CNTs' array was performed. This reconstruction successfully reproduces the spectral shape of the 12.5 eV resonance. However, the intensity is lower than the actual measurements in the initial energy range of the spectrum. The analysis of these results, using graphite's electronic band structure, suggests the additional intensity required to reproduce the experimental data, could have its origin in an electronic focusing mechanism, induced by the CNTs' image charge potential. Calculations of the electronic trajectories close to the tubes show this focusing effect is significant for both low energy electrons and small diameter tubes.

Theoretical Limits to Suspended Graphene Varactors and Tunneling Relays

Mohamed AbdelGhany, Monorina Mukhopadhyay, Thomas Szkopek

*Electrical and Computer Engineering Department, McGill University, Montreal, Quebec,
Canada*

mohamed.abdelghany@mail.mcgill.ca

The high yield strength, low flexural rigidity and low mass density of suspended graphene membranes are potentially promising for nanoelectromechanics applications. We have explored the theoretical limits to graphene varactor and tunneling relay performance. The suspended graphene varactor, where capacitance is tuned by electrostatic actuation of membrane deflection, provides a capacitor tuning range of ~76%, with a membrane pull-in voltage V_p as low as ~1V. An intrinsic electrical quality factor as high as 200 is predicted at 1 GHz for these devices [M. AbdelGhany et al. Appl. Phys. Lett. 101, 153102 (2012)]. Nonlinear currents arising from capacitance modulation under sinusoidal drive are predicted to appear at odd harmonics, with amplitude proportional to $(V_{ac}/V_p)^{(5/3)}$. We have also considered the theory of the tunneling relay, where the electrostatic actuation of a graphene membrane is combined with the exponential dependence of tunneling current through a vacuum gap. Sub-threshold swings as steep as 10 mV/decade are predicted, breaking the thermionic limit of 60 mV/decade at room temperature [M. AbdelGhany et al. Appl. Phys. Lett. 104, 013509 (2014)]. The predicted performance suggests that a significant reduction in dynamic energy consumption over conventional field effect transistors is physically achievable. We will report on our recent experimental progress towards realizing graphene nanoelectromechanical devices with large area graphene.

Electronic properties of bilayer β -graphyne

Mónica Pacheco, Alejandro León

Departamento de Física, Universidad Santa María, Valparaíso, V Región, Chile
Facultad de Ingeniería, Universidad Diego Portales, Santiago, RM
Chilemonica.pacheco@usm.cl

Among the large variety of carbon allotropes there are some graphene-like structures which can be constructed by replacing some bonds $=C=C=$ in graphene by acetylenic linkages $-C\equiv C-$, called graphynes (GYs),^[1] or by diacetylenic linkages $-C\equiv C-C\equiv C-$, called graphdiynes (GDYs)^[2]. These non-natural carbon allotropes include both, sp^2 - and sp^1 -hybridized carbon atoms. After the theoretical prediction of these flat structures, with exceptional electronic, thermal and mechanical properties, several experimental studies have been performed to achieve their large-scale synthesis.^[3] Due to their intrinsic semiconducting properties, GYs and GDYs have been proposed as promising candidates in many electronic and photoelectronic applications and also with potential applications as membranes to separate molecules, hydrogen storage media, and anode materials in lithium-ion batteries.^[4,5]

According to first-principles electronic structure calculations^[6] some particular types of graphynes-like networks also possess Dirac cones as the case of graphene. One of these structure, β -graphyne, has a Dirac cone not located at the K and K' points of the Brillouin zone, but on lines between the high symmetry Γ and M points. In this work we show a theoretical study based on DFT of the electronic properties of bilayers of β -graphyne, for different stacking configurations. Our results show that the bilayer is semimetal or semiconductor, depending on the staking mode. The system changes from a metal, for A-A stacking, to a semiconductor with a small gap of 0.15 eV, for A-B stacking, being this most stable configuration according to the study of total energy and stability.

By applying an electric field perpendicular to the layers, the gap of the semiconductor can be closed and a metallic state is obtained. This behavior is contrary to that reported for the case of α -graphyne^[7] for which the semi-metallic systems become semiconductor with a gap that increases with the field intensity.

- [1]. R H Baughman, H Eckhardt, M Kertesz, J Chem Phys, 87 (1987) 6687
- [2]. M. M. Haley, S. C. Brand and J. J. Pak, Angew. Chem., Int. Ed. Engl., 36 (1997) 836
- [3]. G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, Chem. Commun., 46 (2010) 3256
- [4]. A L Ivanovskii, Progress in Solid State Chemistry 41 (2013) 1
- [5]. Q Tang, Z Zhou, Z Chen, Nanoscale, 5 (2013) 4541
- [6]. D Malko, C Neiss, F Vines, A Gorling, Phys. Rev. Lett., 108 (2012) 086804
- [7]. O. Leenaerts, B. Partoens, and F. M. Peeters, Applied Physics Letters 103, 013105 (2013)

Computational Modeling of Channel Length Modulation in Carbon Nanotube Field Effect Transistors

Adam W. Bushmaker, Moh R. Amer, Stephen B. Cronin

Physical Science Laboratories, The Aerospace Corporation, El Segundo, CA, United States

Electrical Engineering, University of Southern California, Los Angeles, CA, United States

abushmaker@gmail.com

Single walled carbon nanotube (CNT) field effect transistors (FETs) are unique devices because of their intrinsically one-dimensional transport, tunable band gap, and high mobility. They also offer potential performance advantages such as high-linearity in analog RF amplifiers, high surface-to-volume ratio, which is useful for chemical sensors, high frequency mechanical oscillations for RF NEMs devices, and high cutoff frequencies in the THz region. Several research groups have used theoretical and computational methods to analyze electrical transport in CNT FETs, and there are several software tools available for this. Studies have focused on improving numerical methods or modeling for process and circuit design, or specific aspects of transport in CNT FETs, such as multiband effects, carrier velocity saturation, Schottky barrier effects, and electron-phonon scattering. The vast majority of these studies and tools, however, assume a uniform voltage, resistance, and Fermi energy along the length of the CNT. This assumption is not valid because the gate, source and drain capacitances vary spatially, which requires a spatial solution of Poisson's equation. Also, this assumption precludes modeling of pinch-off and channel length modulation, effects that strongly influence electrical transport in FET devices. Here we report computational modeling and characterization of quasi-ballistic electrical transport in semiconducting carbon nanotube field effect transistors, and fit experimental electrical transport data from both suspended and on-substrate single-walled carbon nanotube transistors fabricated using chemical vapor deposition. Numerical modeling is performed using finite element methods within the Landauer framework while explicitly including spatial inhomogeneity by calculating the voltage, resistance and Fermi energy at discrete points along the CNT channel. These spatial variations play an important role in several high voltage effects that are important in the quasi-ballistic transport regime where most present day devices operate. We show the relationship between device geometry and pinch-off, current saturation, and channel length modulation in the quantum capacitance regime, and discuss computational modeling issues. This model can be used for extraction of device properties from experimental data and as a design tool for device processing optimization and CNT based circuitry. Such analysis is urgently needed in order to gain a more complete understanding of CNT FET operation.

Ab initio molecular dynamics study of bond dissociation mechanism of ethanol during carbon nanotube growth via CVD process

Tomoya Oguri, Kohei Shimamura, Yasushi Shibuta, Fuyuki Shimojo, Shu Yamaguchi

Department of Materials Engineering, The University of Tokyo, Tokyo, Japan

Department of Physics, Kumamoto University, Kumamoto, Kumamoto, Japan

Department of Materials Engineering, The University of Tokyo, Tokyo, Japan

Department of Physics, Kumamoto University, Kumamoto, Kumamoto, Japan

Department of Materials Engineering, The University of Tokyo, Tokyo, Japan

shibuta@material.t.u-tokyo.ac.jp

The growth mechanism of carbon nanotubes and graphenes has been widely discussed their discovery. At present, most of the computational studies focusing on the growth process of these materials starts using isolated carbon atoms and therefore ignores the initial dissociation process.^[1] Under such circumstance, we have investigated the dissociation of carbon source molecules on the flat and curved metal surfaces by ab initio molecular dynamics (MD) simulation to discuss the initial stage of formation process.^[2-4] Especially, dissociation of ethanol on a nickel cluster has been closely investigated.^[3,4] From our latest simulation,^[4] it is confirmed that C–C bonds in only CH_xCO fragments are dissociated on the nickel cluster, whereas there is no preferential structure among the fragments for C–O bond dissociation. The dissociation preference is not correlated with the bond dissociation energy of corresponding bonds in freestanding molecules but is correlated with the energy difference between fragment molecules before and after dissociation on the nickel surface. In the presentation, our recent results will be introduced with relevant calculation results on this matter.

[1]. Y. Shibuta, *Diamond and related Materials*, 20 (2011) 334

[2]. Y. Shibuta, R. Arfin, K. Shimamura, T. Oguri, F. Shimojo, S. Yamaguchi, *Chem. Phys. Lett.*, 565 (2013) 92

[3]. T. Oguri, K. Shimamura, Y. Shibuta, F. Shimojo, S. Yamaguchi, *J. Phys. Chem. C*, 117 (2013) 9983

[4]. T. Oguri, K. Shimamura, Y. Shibuta, F. Shimojo, S. Yamaguchi, *Chem. Phys. Lett.* 595-596 (2014) 185

Origins of carbon nanotube helicity and preference for (n, n–1) tubes

Vasilii I. Artyukhov, Evgeni S. Penev, Boris I. Yakobson

Department of Materials Science and NanoEngineering, Rice University, Houston, Texas, United States

artyukhov@rice.edu

The future fate of many practical applications of carbon nanotubes hangs on the capability to selectively produce CNT with required chirality. Despite all the progress in exploration of CNT nucleation and growth, the understanding of the origins of nanotube chirality is still missing. Thermodynamically, the energetics of CNT–catalyst interface^[1] appear to favor achiral armchair or zigzag CNT, and although the structures of CNT caps differ for different tubes, there is no additional “intrinsic” bias from cap energetics^[2] that could favor other chiralities. Yet neither achiral type is frequently produced in CVD growth. Simple arguments based on the screw dislocation model^[3] outline an explanation of the overall trend towards larger chiral angles. But a more in-depth look at the experimental results finds crucial “fine details” that seemingly contradict expectations, e.g., the almost complete absence of purely armchair CNT. To resolve these issues, we’ve developed a comprehensive theory of CNT nucleation and growth (with termination easily added to the picture) that includes the different factors shaping the chirality distribution of CNT yield, including nanotube–catalyst interface^[1], the energetic landscape of CNT caps,^[2] and growth kinetics,^[3] building upon our “nanoreactor” framework developed for graphene synthesis.^[4] Our study reveals how the aggregate state of the catalyst particle can substantially alter the equations governing nucleation and growth rate, in such a way that jointly they provide a CNT type distribution that is sharply peaked at the minimally chiral CNT types, thus explaining the abundance of near-armchair tubes such as (6, 5) in recent experimental studies (e.g.,^[5]) yet little or no pure armchair.

[1]. Y. Liu, A. Dobrinsky, B. I. Yakobson, *Phys. Rev. Lett.* 105, 235502 (2010)

[2]. E. S. Penev, V. I. Artyukhov, and B. I. Yakobson, *ACS Nano* 8, 1899 (2014)

[3]. F. Ding, A. R. Harutyunyan, B. I. Yakobson, *Proc. Natl. Acad. Sci. U.S.A.* 106, 2506 (2009)

[4]. V. I. Artyukhov, Y. Liu, B. I. Yakobson, *Proc. Natl. Acad. Sci. U.S.A.* 109, 15136 (2012)

[5]. M. He, et al., *Sci. Rep.* 3, 1406 (2013)

SWCNT Growth from Organic Precursors Without a Catalyst: Possibilities and Limitations Revealed by Theoretical Simulations

Hai-Bei Li, Alister J. Page, Stephan Irle, Keiji Morokuma

Department of applied chemistry, School of Ocean, Shandong University, Weihai, Shandong, China

Discipline of Chemistry, School of Environmental and Life Sciences, The University of Newcastle, Callaghan, NSW, Australia

WPI-Institute of Transformative Bio-Molecules and Department of Chemistry, Nagoya University, Nagoya, Nagoya, Japan

Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Kyoto, Japan

lihaibei@sdu.edu.cn

Our recent simulations of catalyst-free, chirality-controlled growth from cycloparaphenylene (CPP) precursors are presented. We will show that different chemical routes for chirality-controlled growth exist, and depend on the nature of the growth agent. We demonstrate this phenomenon using acetylene (C_2H_2) and the ethynyl radical (C_2H) as growth agents, at temperatures ranging from 300 to 800 K. In the case of the ethynyl radical, we observe a strong dependence of the SWCNT growth rate on the chiral angle. This is consistent with a previously proposed screw-dislocation-like model of transition metal-catalyzed SWCNT growth. However, the absence of a catalyst in this case indicates that the SWCNT growth rate is an intrinsic property of the SWCNT edge itself. Additionally, the ability of a SWCNT to avoid defect formation during growth is also an intrinsic quality of the SWCNT edge, one that is maximized at lower temperatures. However, using the ethynyl radical as the growth agent, the SWCNT diameter does not influence the growth rate; acetylene-based growth is, on the other hand, strongly diameter-dependent. We therefore predict the existence of a maximum local growth rate for a particular (n,m) SWCNT at a given acetylene/ethynyl ratio.

Spontaneous origami in multi-phase 2D phosphorus

Zhen Zhu, Jie Guan, David Tomanek

Physics and Astronomy, Michigan State University, East Lansing, MI, United States
zhuzhen@msu.edu

Similar to graphitic carbon, phosphorus monolayers, dubbed phosphorene,^[1] can be exfoliated from layered [black phosphorus](http://nanotube.msu.edu/IPS14/#intro). Phosphorene is a p-type semiconductor with a significant band gap. It is stable, flexible, and displays a high carrier mobility,^[1] suggesting its potential use in 2D electronics. Most interesting, based on ab initio density functional calculations, we found that phosphorus can form four different 2D structural phases that are almost equally stable and may be inter-connected. Connection of two planar phases resembles a sharp origami-style fold, displayed in Fig. 1. This fold occurs naturally in this multi-phase system, whereas in single-phase systems like graphene it requires the presence of defect lines or lines of adsorbed atoms. We also find the possibility of moving this fold by structural transformation from one allotrope to another, with an unusually low activation barrier of <0.5 eV per bond. Since the electronic properties of multi-phase phosphorene may also be tuned by in-layer strain, including a semiconductor-to-metal transition, we postulate that origami-style folded phosphorene should display an unprecedented richness in its electronic behavior.

[1]. H. Liu et al. ACS Nano 8 (2014)

[2]. Z. Zhu and D. Tomanek, Phys. Rev. Lett. (2014)

Polygonal nanotubes of multi-phase layered phosphorus

Jie Guan, Zhen Zhu, David Tomanek

Physics Department, Michigan State University, East Lansing, Michigan, United States
guanjie@msu.edu

Similar to graphite, black phosphorus is a layered structure that can be exfoliated to monolayers dubbed phosphorene^[1]. Similar to carbon nanotubes, which are related to few-layer graphene, we propose the existence of phosphorus nanotubes formed of phosphorene. Different from graphite, besides the black allotrope, layered phosphorus has three stable structural phases, called blue-P^[2], γ -P and δ -P, which can be connected naturally. The fact that connected structures do not lie in a plane allows us to design nanotubes by connecting laterally nanoribbons of different phases. Unlike single-phase nanotubes consisting of a layer rolled up to a cylinder, multi-phase phosphorene nanotubes will have a polygonal cross-section, as shown in Fig. 1. Both single-wall and multi-wall phosphorene nanotubes may be constructed in this way. The availability of more than one structural phase offers much larger structural richness than the carbon counterpart with one single phase. Consequently, we find that the electronic properties of phosphorene nanotubes depend not only on the chiral vector that defines the edge structure, but also the presence of the individual phosphorene phases. In analogy to the successful synthesis of carbon nanotubes by ball milling of graphite, we believe that phosphorene nanotubes may be formed in the same way in an inert atmosphere.

[1]. H. Liu et al. ACS Nano 8 (2014)

[2]. Z. Zhu and D. Tomanek, Phys. Rev. Lett. (2014)

Adsorption of NH₃ and BH₃ on the Surface of Boron Nitride Nanotubes – A DFT Study

Rajashabala Sundaram, Tapas Kar

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah, United States
rajashabala@yahoo.com

Adsorption of NH₃ and BH₃ on the surface of different boron nitride single-wall nanotubes (BNNTs) have been investigated using density functional theory (DFT-B3LYP). The optimized geometries and density difference plots are obtained using 6-31+G* basis set and the characterization techniques such as Infra-red (IR) studies, X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance studies (NMR) were determined using 6-31G* basis functions. Adsorption sites and chemisorption energies of NH₃ and BH₃ on the BNNTs surface depends on the chirality of BNNT. Electron deficient BH₃ forms stronger chemisorbed complex than NH₃. As expected, about 0.3e charge is transferred from NH₃ to BN nanotube and it is confirmed by the density difference plot. However, electron density gain or loss by BNNT depends on the structure of BH₃-BNNT complexes. Major changes in B(1s) and N(1s) binding energies and chemical shifts of 11B and 15N are found at the vicinity of adsorption sites, and these theoretical results may be useful in characterizing such complexes experimentally.

Poster Session 2

C1

Giant nonlinear optical response from dye-filled carbon nanotube hybrids

Jochen Campo, Sofie Cambré, Charlie Beirnaert, Christof C. Verlaeckt, Wim Wenseleers
Physics Department, University of Antwerp, Wilrijk, Antwerp, Belgium
Jochen.Campo@uantwerp.be

Asymmetric dipolar molecules, acting as electric ‘rectifiers’ with a large second-order nonlinear optical (NLO) response (first hyperpolarisability β), find applications in ultrafast electro-optic switches for optical telecommunication networks and wavelength conversion of lasers.^[1] In 3D bulk systems, however, such dipolar molecules tend to align in a pairwise anti-parallel way, thus cancelling each other’s directional properties, such as the NLO response. Parallel alignment is traditionally achieved by electric field poling in a polymer matrix, but long term stability of this alignment remains problematic.

Here we show that by encapsulating such elongated dipolar molecules in the 1D internal channel of single-wall carbon nanotubes (SWCNTs), Coulomb interactions naturally favor a polar head-to-tail alignment of the molecular dipoles, leading to a cooperative enhancement of their second-order NLO responses. This principle is demonstrated for a prototypical dipolar molecule encapsulated in various SWCNT samples. The encapsulation is evidenced by extensive wavelength-dependent fluorescence-excitation^[2] and resonance Raman^[3] experiments on bile-salt solubilized^[4] dye-filled SWCNTs, revealing the effect of encapsulation on the vibrational and electronic properties of the SWCNTs and the encapsulated molecules. Wavelength-dependent hyper-Rayleigh scattering^[5,6] (i.e. second harmonic light scattering) experiments effectively show that these organic-SWCNT nanohybrids possess giant NLO responses ($\beta = 68800 \times 10^{-30}$ esu at resonance; $\beta_0 = 9770 \times 10^{-30}$ esu in the static limit; corresponding to ~ 70 identically aligned chromophores, depending on the SWCNT diameter range). Their equally giant dipole moment and size promises a good and stable alignment of the nanohybrids in a polymer film, which opens up an entirely new route to the rational design of solution-processible yet stable NLO materials.

[1]. E. Goovaerts et al. In Handbook of advanced electronic and photonic Materials and Devices, Vol. 9: Nonlinear optical materials, Academic Press, San Diego, 127-191 (2001)

[2]. S. Cambré et al., ACS nano 6, 2649 (2012)

[3]. W. Wenseleers et al., Adv. Mater. 19, 2274 (2007)

[4]. W. Wenseleers et al., Adv. Funct. Mater. 14, 1105 (2004)

[5]. J. Campo et al., Optics Express 17, 4587 (2009)

[6]. J. Campo et al., J. Phys. Chem. Lett. 3, 2248 (2012)

S-SWNT interaction with microring resonators

Adrien Noury, Xavier Le Roux, Laurent Vivien, Nicolas Izard

Institut d'Electronique Fondamentale, CNRS UMR 8622, Orsay, Université Paris Sud, France
adrien.noury@u-psud.fr

Semiconducting Single Wall Carbon Nanotubes (s-SWNT) are a promising material for silicon photonics, due to their ability to emit, modulate and detect light. Indeed, Silicon is an indirect bandgap material, unable to efficiently emit photons, thus light emitters are strongly desirable for optical devices on silicon.

Recent work showed integrability of s-SWNT on silicon waveguide, either coupling nanotubes photoluminescence (PL) ^[1] or thermal emission ^[2] with the optical mode of the waveguide. In order to enhance interaction of s-SWNT with the silicon photonics device, the use of microcavities was proposed.^[3,4,5] The main drawback of these cavities designs is the difficulty to efficiently couple them with access waveguides in order to build realistic devices.

We propose the use of silicon microring resonator covered with s-SWNT to address this issue. Microrings are fabricated by e-beam lithography and covered with PFO-extracted s-SWNT. Nanotubes' PL interacts with the microcavity mode, leading to very narrow emission peaks, with quality factors as high as 4000.^[6] Both far-field emission and integrated PL are studied, and we show that mainly photons coupled to the microcavity mode are observed at the waveguide output, with well-defined polarization.

This is the first demonstration of cavity-enhanced PL coupled to a silicon waveguide, which is an important milestone in the area of 'Carbon Nanotube Photonics', and for future realistic applications using this nanomaterial.

- [1]. E. Gauffrès, N. Izard, A. Noury, X. Le Roux, G. Rasigade, A. Beck and L. Vivien, ACS Nano, 6 (2012) 3813
- [2]. S. Khasminkaya, F. Pyatkov, B. S. Flavel, W. H. Pernice and Ralph Krupke, Advanced Materials (2014), just accepted
- [3]. R. Watahiki, T. Shimada, P. Zhao, S. Chiashi, S. Iwamoto, Y. Arakawa, S. Maruyama and Y. K. Kato, Appl. Phys. Lett. 101, 141124 (2012)
- [4]. H. Sumikura, E. Kuramochi, H. Taniyama and M. Notomi, Appl. Phys. Lett. 102, 231110 (2013)
- [5]. S. Imamura, R. Watahiki, R. Miura, T. Shimada and Y. K. Kato, Appl. Phys. Lett. 102, 161102 (2013)
- [6]. A. Noury, X. Le Roux, L. Vivien, N. Izard, submitted

Carbon nanotube integration strategies with silicon photonics

Adrien Noury, Miguel Diez-Garcia, Xavier Le Roux, Laurent Vivien, Damien Querlioz,
Nicolas Izard

Institut d'Electronique Fondamentale, CNRS-UMR 8622, Univ. Paris-Sud, Orsay, 91405, France
nicolas.izard@u-psud.fr

Semiconducting carbon nanotubes (s-SWNT) constitute a fascinating material, with unique optical properties due to their unidimensionality. They have the ability to emit, modulate and detect light in the wavelength range of silicon transparency which make them an emerging material for nanophotonics. Indeed, the indirect band-gap of silicon prevents efficient light emission at these wavelengths, and s-SWNT are envisioned as an active material in silicon photonics technology.

We have developed several years ago an efficient method to selectively extract s-SWNT displaying strong optical properties.^[1,2] It is therefore particularly attractive to couple s-SWNT with optical resonators. Previous results make use of photonic crystal cavities^[3] or silicon microdisk resonators^[4] but the lack of access waveguides make these designs poorly adapted for silicon photonics. On the other hand, we recently proposed the use of silicon microring resonators to address this issue.^[5]

These different approaches all struggle with the difficulty to integrate 1D nanomaterials such as carbon nanotubes with planar, silicon based, photonic devices. Here, we discuss about strategies to efficiently couple s-SWNT PL with silicon waveguides, using either strip or slot waveguides, and their efficient integration within a photodetector. Additionally, residual metallic nanotubes strongly affect the performance of the structures. We present Monte Carlo simulations and their analysis which allow us estimating acceptable proportions of metallic nanotubes for our applications. All these results allow us advancing the credibility of nanotubes as an active material for silicon photonics.

[1]. N. Izard et al., Appl. Phys. Lett., 92, 243112 (2008)

[2]. E. Gauffrès et al., Appl. Phys. Lett., 96, 231105 (2010)

[3]. R. Watahiki et al., Appl. Phys. Lett., 101, 141124 (2012)

[4]. S. Imamura et al., Appl. Phys. Lett., 102, 161102 (2013)

[5]. A. Noury et al., submitted

Radial Deformation of Single-Walled Carbon Nanotubes on Quartz Substrates and the Resultant Anomalous Diameter-Dependent Reaction Selectivity

Juan Yang, Yu Liu, Daqi Zhang, Xiao Wang, Yan Li

College of Chemistry and Molecular Engineering, Peking University, Beijing, Beijing, China
yang_juan@pku.edu.cn

Owing to the unique conjugated structure, chemical reaction selectivity of single-walled carbon nanotubes (SWNTs) has attracted great attentions. By utilizing the radial deformation of SWNTs caused by the strong interactions with the quartz lattice, we achieve an anomalous diameter-dependent reaction selectivity of quartz lattice-oriented SWNTs in treatment with iodine vapor, which is distinctly different from the widely reported and well accepted higher reaction activity in small-diameter tubes over the large ones. The radial deformation of SWNTs on quartz substrate is verified by detailed Raman spectra and mappings in both G band and RBM. Due to the strong interaction between SWNTs and the quartz lattice, large-diameter tubes present larger degree of radial deformation and more delocalized partial electrons are distributed at certain sidewall sites with high local curvature. It is thus easier for the carbon-carbon bonds at those high curvature sites on large-diameter tubes to break down upon reaction. This anomalous reaction activity offers a novel approach for selective removal of small-bandgap large-diameter tubes.

Optical Properties of Single Chirality (5,4) SWCNTs

Xiaojun Wei, Yasuhiro Ito, Takuya Hirakawa, Atsushi Hirano, Shunjiro Fujii, Yuhei Miyauchi, Kazunari Matsuda, Takeshi Tanaka, Hiromichi Kataura

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

Institute of Advanced Energy, Kyoto University, Uji, Kyoto, Japan

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

gi.weixiaojun@aist.go.jp

Although more than 20 years have passed after the discovery of single-wall carbon nanotubes (SWCNTs), still we don't know well about their detailed structures due to lack of the single-crystal of SWCNT that enables us to analyze its precise structure. Because current SWCNT products are mostly composed of various structures, structure sorting of SWCNTs is necessary for the single crystal growth.

Previously, Liu et al. succeeded to separate 13 kinds of single chirality SWCNTs using multicolumn gel chromatography method.^[1] In this work, we have improved the method and optimized it for thin SWCNTs. Here (5,4) SWCNTs, which have the smaller diameter than C60 are successfully separated for the first time. In the Raman spectrum, single radial breathing mode peak at 373 cm^{-1} and highly softened TO phonon peak at 1497 cm^{-1} were observed. Interestingly, some bright photoluminescence (PL) peaks corresponding to the oxygen doped SWCNTs^[2] were observed probably due to high chemical reactivity of highly curved side wall. Moreover, higher order excitations corresponding to E_{33} and E_{44} of (5,4) SWCNTs were clearly observed in an excitation spectrum using CCD detector. Good agreement between the excitation spectrum and the absorption spectrum indicates successful separation of high purity (5,4).

[1]. H. Liu et al. Nat. Commun. 2, 309 (2011)

[2]. Y. Miyauchi et al., Nat. Photonics 7, 715 (2013)

Strained graphene nanoribbons and hexagonal quantum rings under external magnetic fluxes

Daiara Faria, Andrea Latgé, Nancy Sandler

Departamento de Física, Instituto de Física, Niteroi, Rio de Janeiro, Brazil

Departamento de Física, Instituto de Física, Niteroi, Rio de Janeiro, Brazil

Department of Physics and Astronomy, Physics Institute, Athens, Ohio, United States

andrea.latge@gmail.com

The coupling between geometrical and electronic properties is a promising avenue to engineer conduction features in graphene. External magnetic fields and electronic confinement added to strain effects allow a rich interplay of different transport mechanisms with potential device applications. In particular, we explored the transport properties of graphene nanoribbons and hexagonal zigzag quantum rings coupled to left and right leads given by semi-infinite zigzag nanoribbons. Electronic density of states and conductance are obtained using the tight-binding approximation and following the Green's function formalism and real space renormalization techniques. We investigate the individual sublattice contributions to the local density of states that should be individually scanned by a STM image.^[1] The electronic mapping shows regions exhibiting trigonal structure even in the absence of buckling or taking into account staggered potentials.

The localization effects on the physical responses of the ring were considered as a consequence of the finite-size confinement of the central part of the nanostructure and due to the applied magnetic field and the presence of tension giving origin to pseudofields. When the magnetic flux is considered, the conductance results exhibit clear Fano-like resonances. The peculiar null conductance states are pinned at the same energy values independently of the magnetic field intensity. We highlight that strain also promotes a change in the energy values at which the conductance is fully suppressed. The results suggest that the nanoring may be used as a dispositive in which the conductance patterns provide a simple way of measuring the strain strength when compared to the unstrained situation.

[1]. T. Mashoff et al., Nano Lett. 10, 461 (2010)

Ultrafast charge photogeneration and dynamics in semiconducting carbon nanotubes

Giancarlo Soavi, Francesco Scotognella, Daniele Viola, Timo Hefner, Tobias Hertel, Giulio Cerullo, Guglielmo Lanzani

Dipartimento di Fisica, Politecnico di Milano, Milano, Lombardia, Italy
Dept. of Chemistry and Pharmacy, Inst. for Physical and Theoretical Chemistry, University of Würzburg, Würzburg, Bavaria, Germany

Dipartimento di Fisica, Politecnico di Milano, Milano, Lombardia, Italy
Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Milano, Lombardia, Italy
giancarlo.soavi@polimi.it

Single-walled carbon nanotubes (SWNTs) are excellent model systems for the study of photoexcitation dynamics in one-dimensional (1D) quantum confined systems. Theory predicts that Wannier-Mott excitons are the elementary photoexcitations in SWNTs, due to the strong Coulomb interaction caused by the weak screening. Such excitons have peculiar 1D characteristics, such as extraordinary large binding energies, large size and 1D transport. Experimental observations, such as the measured binding energy, typically 0.1-1 eV, and the electron-hole correlation length, in the 1-10 nm domain confirm theoretical predictions. The exciton model alone, however, fails to capture the whole dynamics following photoexcitation, and many other photoexcited species have crowded the complex scenario of SWNTs' optical response, ranging from triplets to bi-excitons and trions. Experiments based on photocurrent, transient absorption and THz spectroscopy also point out a non-negligible photogeneration of free charge-carriers. This is in contrast with the excitonic model and the reduced Sommerfeld factor that predicts that excitons should be the only species generated upon photoexcitation. Attempts to solve this discrepancy proposed non-linear processes, such as exciton-exciton annihilation, as a mechanism of charge-carrier photogeneration. However, there is solid experimental evidence that charge-carrier photogeneration is linear with the pump fluence.

Here we apply broadband ultrafast transient absorption spectroscopy to the semiconducting (6,5) SWNT and show that charge-carriers can be identified by their effect on excitonic resonances, in particular the large Stark shift that they induce on high-energy, easily polarizable excitons (S_{22} and S_{33}). Having identified the Stark shift as a good spectroscopic fingerprint for charge-carriers, we are able to study their dynamics in a nearly ideal 1D system. We find that a fraction of the absorbed photons generates geminate charge-carrier pairs within our temporal resolution (≈ 50 fs), which then recombine on the picosecond timescale following the characteristic kinetic law of random walk in 1D. Our analysis starts from the observation that the first derivative of the ground state absorption spectrum, i.e. a photoinduced red shift of the excitonic transition, can reproduce many of the features observed in the differential transmission ($\Delta T/T$) spectra of semiconducting SWNTs. This effect can be ascribed to different physical mechanisms, such as

bi-excitons or trions formation, thermal effects or Stark effect. Here we unambiguously demonstrate that this derivative shape is indeed due to strong local electric field induced by photogenerated charge-carriers, which shifts the electronic transitions by Stark effect. In particular, we show that the energy shift is stronger for excitons with lower binding energy, as for S_{33} with respect to S_{11} , as expected for the Stark effect. This suggests that the higher energy S_{33} exciton is ideally suited for directly probing charge-carriers in SWNTs and can be exploited to further analyze the charge photogeneration process and to study charge-carrier dynamics in one dimension. Our data show that the free charge-carriers are generated within 50 fs. The temporal evolution of the S_{33} pump-probe dynamics is very accurately reproduced by a power law $\sim t^{-0.5}$. A monomolecular power law decay is the predicted dynamics for geminate recombination of free particles after random walk in an infinite one-dimensional chain. A more detailed modelling of the geminate recombination process indicates that the initial distance between the geminate e-h pair is of the same order of magnitude of the exciton correlation length, thus suggesting that charge-carriers arise from instantaneous linear exciton dissociation.

Our results shed new light onto the charge photogeneration mechanism in SWNTs, suggesting that the nascent exciton dissociates spontaneously, perhaps in presence of extrinsic screening of the Coulomb attraction, possibly due to water or other ambient contamination.

In-situ Observation on Wetting Behavior of Ionic Liquid on a Carbon Nanotube

Konan Imadate, Kaori Hirahara

Mechanical Engineering, Osaka University, Suita, Osaka, Japan

ikonan425@gmail.com

Wettability of materials is generally determined by the balance of interface tensions acting at air-liquid, liquid-solid, solid-air boundaries, but it is also well known that nanometer-scale morphologies of solid surface often affects to the wetting. It is therefore interesting question how a carbon nanotube (CNT) wet by liquid, since it has extremely high curvature surface due to their cylindrical shapes with nanometer scale diameters. In this study, we report unique wetting behavior on a single CNT investigated by in-situ electron microscopy. Ionic liquid was employed as a liquid in the present experiment, since it is rather stable in vacuo due to extremely small evaporation pressure. A single CNT was operated to fix to the tip of cantilever probe by using a manipulator in scanning electron microscope (SEM) or transmission electron microscope (TEM). Tip of the CNT is then approached to the surface of ionic liquid, and we recorded the series of TEM or SEM images as movies when the CNT tip is touched to the liquid surface. As the result, meniscus formed at the contact region, besides a thin film with 3nm thickness simultaneously formed to cover entire the CNT. The contact angle measured at the meniscus was almost zero. These results indicate that CNT shows autophobic wetting, although macroscale droplet on a plane graphite surface shows about 25° contact angle. In addition, attractive wetting force was measured on the basis of Wilhelmy method for individual CNTs with 5~15 nm diameters. We found that the measured values tended to be greater than calculated ones using Wilhelmy equation representing the correlation of the force, tube diameter and surface tension. Instead, fitted curve to the experimental data showed an increment in an effective diameter of cylindrical sample. The corrected value was 2.84 nm, which is consistent to the thickness of liquid film formed on CNT. Accordingly, the wetting behavior observed in the present study can be explained by considering that the liquid film acts as a part of a solid cylinder, which suggests a possibility that liquid molecules are rather strongly constrained on the CNT surface.

Photoconductivity spectroscopy of individual suspended carbon nanotubes

Takushi Uda, Yusuke Kumamoto, Masahiro Yoshida, Akihiro Ishii, Yuichiro K. Kato

Institute of Engineering Innovation, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
takushi@katogp.t.u-tokyo.ac.jp

To investigate photoconductivity of chirality-identified carbon nanotubes, we have fabricated field-effect transistors with individual air-suspended nanotubes.^[1] Trenches are etched into SiO₂/Si substrates, and Pt/Ti are deposited on both sides of the trenches. By ethanol chemical vapor deposition, carbon nanotubes are grown over the trenches. We have also constructed a system which can simultaneously measure photocurrent and photoluminescence excitation spectra.^[2] Nanotubes are excited with a wavelength-tunable continuous wave Ti:sapphire laser, and photoluminescence is detected by an InGaAs photodiode array attached to a spectrometer. Photoluminescence imaging and excitation spectroscopy allows us to locate the nanotubes and identify their chirality. For photocurrent microscopy, excitation laser is modulated by an optical chopper and a lock-in amplifier is used for detection.

Work supported by KAKENHI, The Canon Foundation, The Asahi Glass Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The devices were fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

[1]. S. Yasukochi, T. Murai, S. Moritsubo, T. Shimada, S. Chiashi, S. Maruyama, and Y. K. Kato, Phys. Rev. B 84, 121409 (2011)

[2]. Y. Kumamoto, M. Yoshida, A. Ishii, A. Yokoyama, T. Shimada, and Y. K. Kato, Phys. Rev. Lett. 112, 117401 (2014)

In-plane Conduction of Dense Carbon Nanotube Forest formed on Silicon Carbide

Masafumi Inaba, Chih-Yu Lee, Kazuma Suzuki, Megumi Shibuya, Miho Myodo, Atsushi Hiraiwa, Wataru Norimatsu, Michiko Kusunoki, Hiroshi Kawarada

Graduate School of Advanced Science and Engineering, Waseda University, Shinjuku, Tokyo, Japan

EcoTopia Science Institute, Nagoya University, Nagoya, Aichi, Japan

Graduate School of Advanced Science and Engineering, Waseda University, Shinjuku, Tokyo, Japan

inaba-ma@ruri.waseda.jp

Dense Carbon nanotube forest formed by silicon carbide surface decomposition method (CNTs on SiC) consists of nearly ideally close-packed CNTs.^[1] Generally, CNT conducts in its on-axis direction, yet such highly dense CNT forest may cause high in-plane direction conductivity. In addition, CNTs on SiC do not have entangled or wavy part, it is useful to investigate in-plane conductivity of dense CNT forest. Here we report on the in-plane conductivity evaluation of CNT forest formed on SiC.

On-axis C-face (000-1) of semi-insulating SiC substrates ($< 10^{-8}$ S/cm) were annealed at 1500~1600 °C in vacuum ($\sim 10^{-3}$ Pa). The in-plane conductivity was measured by van der Pauw method in room temperature in air. There are four parts which may contribute to CNTs on SiC in-plane conductivity, CNT caps, CNT bulk, CNT/SiC interface, and SiC bulk. To determine which part(s) is/are dominant in conduction, CNT lengths were varied by controlling decomposition time, which changes CNT bulk conductivity. To confirm which of the other parts conduct, we conducted two approaches, CNT forest removing by acid mixture, CNT cap removing by H₂O₂ mild oxidation.^[2]

As a result, in-plane CNT bulk (cylindrical part) conductivity was estimated to be ~ 50 S/cm. The SiC bulk conduction is negligible, since the conductance of initial SiC substrate is extremely low as $\sim 10^{-9}$ S. The CNT/SiC interface conductivity was also sufficiently small. The sheet conductivity of CNT caps as $\sim 7 \times 10^{-4}$ S/sq.

[1]. M. Kusunoki et al., Appl. Phys. Lett. 77 (2000) 531

[2]. R. Marega et al., Carbon 47 (2009) 675

Testing the pseudospin conjecture in carbon nanotubes: transport measurement to determine the scattering strength of charged impurity as a function of chirality

Ryuichi Tsuchikawa, Daniel Heligman, Zhengyi Zhang, James Hone, Eduardo Mucciolo, Masahiro Ishigami

*Department of Physics, University of Central Florida, Orlando, Florida, United States
Department of Mechanical Engineering, Columbia University, New York, New York, United States*

Department of Physics, University of Central Florida, Orlando, Florida, United States
ryuichi@t@gmail.com

Metallic carbon nanotubes are predicted to be resilient to scattering by charged impurities while semiconducting carbon nanotubes are susceptible to the same impurities as a result of the pseudospin degree of freedom. However, such pseudospin conjecture has never been tested directly. We have measured the resistivity of nanotubes as a function of the density of charged impurities and determined their scattering cross section as a function of chirality to test this conjecture. We find that the charged impurities affect transport properties of both metallic and semiconducting nanotubes. We will discuss the implication of our results on the pseudospin conjecture.

Nucleation of Graphene and its Conversion to Single Walled Carbon Nanotube revealed

Matthieu C Picher, Pin Ann Lin, Jose Sahrma, Perla B Balbuena, Renu Sharma

Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, United States

Department of Chemical Engineering, Texas A&M University, College Station, TX, United States

Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, United States

matthieu.picher@nist.gov

During catalytic chemical vapor deposition, the chirality of single wall carbon nanotubes is determined when the growing graphene nucleus wraps around the catalyst and converts into a tubular structure. Elucidating this critical process is required to develop deterministic bottom-up strategies aiming at better chiral distribution control. Direct observations of carbon nanotube growth, and theoretical modeling and simulations of the nucleation have been published but experimental atomic-resolution evidence of single-walled carbon nanotube nucleation has, until now, eluded us.

The main challenge is that nucleation involves a few atoms only and a short time scale, thus requiring a combination of high spatial and temporal resolution for direct observation. Here, we overcome the temporal resolution constraint by reducing the growth rate in order to match the temporal resolution of our recording medium. We employ an environmental scanning transmission electron (E-STEM), equipped with an image corrector and a digital video recording system, to follow SWCNT growth using Co-Mo/MgO catalyst and acetylene (C₂H₂) as a carbon source (see Methods). We present atomic-resolution movies that reveal the nucleation of graphene on cobalt carbide nanoparticles followed by its transformation to a single-walled carbon nanotube. We find that the surface termination of the faceted catalyst nanoparticles regulates the nucleation of the graphene sheet and its conversion into a nanotube. Additional density functional theory calculations show that the disparity in adhesion energies for graphene to different catalyst surfaces is critical for nanotube formation: strong work of adhesion provides anchoring planes for the tube rim to attach, while weak work of adhesion promotes the lift-off of the nanotube cap.

Chirality dependence of the absorption cross-section of carbon nanotubes

Fabien Vialla, Cyrielle Roquelet, Géraud Delport, Silvia Morim Santos, Benjamin Langlois, Christophe Voisin, Jean-Sébastien Lauret

LPA, ENS, Paris, France

Aimé Cotton Laboratory, ENS Cachan, CNRS, Paris Sud university, Orsay, France

LPA, ENS, Paris, France

Aimé Cotton Laboratory, ENS Cachan, CNRS, Paris Sud university, France

jean-sebastien.lauret@lac.u-psud.fr

On one hand, the synthesis methods of carbon nanotubes produce heterogeneous samples with broad distribution of (n, m) species. On the other hand, absorption spectroscopy is a common and easy tool used to determine concentrations thanks to the molar extinction coefficient. This method is however very difficult to implement for the nanotubes case. In fact it relies on the knowledge of the variation of the nanotube absorption cross-section as a function of the chiral indices. Some theoretical studies pointed a possibly strong variation of this absorption cross-section with diameter, the chiral angle and the family type (n-m mod 3).^[1] On the experimental point of view, some measurements of the absolute absorption cross-section through single nanotube spectroscopy was reported for the (6, 5) and (18, 5) species,^[2, 3] and very recently on few chiral species through short-wave IR fluorescence microscopy.^[4]

Here, we report on a new experimental method to scale the (n, m)-dependence of the absorption cross section of single wall carbon nanotubes.^[5] Porphyrin molecules stacked on the wall of the nanotubes provide an original way to achieve efficient and uniform photo-excitation of the whole set of chiral species present in the sample,^[6] which allows to reveal intrinsic properties of the nanotubes. We show that the absorption varies by up to a factor of 3 for zigzag nanotubes of opposite family type. Finally, we propose a phenomenological formula to evaluate quantitatively the absorption cross section of small diameter carbon nanotubes as a function of their chiral indices.^[5]

- [1]. Y. Oyama et al., Carbon 44, 873 (2006) ; E. Malic et al., Phys. Rev. B 74, 195431 (2006)
- [2]. S. Berciaud et al., Phys. Rev. Lett. 101, 077402 (2008)
- [3]. D. Christofilos et al., Chem. Phys. Lett. 3, 1176 (2012)
- [4]. J.K. Streit et al, Nano Letters 14, 1530 (2014)
- [5]. F. Vialla et al, Phys. Rev. Lett. 111, 137402 (2013)
- [6]. C. Roquelet et al., Appl. Phys. Lett. 97, 141918 (2010)

C14

Electron temperature dependence of the strength of the electron-phonon coupling in double wall carbon nanotubes

Ioannis Chatzakis

*Electrical Engineering-Electrophysics, University of Southern California, Los Angeles, CA,
United States*
chatzaki@usc.edu

We applied Time-Resolved Two-Photon Photoemission spectroscopy to probe the electron-phonon (e-ph) coupling strength in double-wall carbon nanotubes. The e-ph energy transfer rate $G(T_e, T_l)$ from the electronic system to the lattice depends linearly on the electron (T_e) and lattice (T_l) temperatures for $T_e > \Theta_{\text{Debye}}$. Moreover, we numerically solved the Two-Temperature Model. We found: (i) a T_e decay with a 3.5 ps time constant and no significant change in T_l ; (ii) an e-ph coupling factor of $2 \times 10^{16} \text{ W/cm}^{-3}$; (iii) a mass-enhancement parameter, λ , of $(5.4 \pm 0.9) \times 10^{-4}$; and (iv) a decay time of the electron energy density to the lattice of 1.34 ± 0.85 ps.

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

Identifying dopants and catalytically active sites in nitrogen-doped carbon nanotubes

Toma Susi, Yann Tison, Jérôme Lagoute, Divya Srivastava, Maryam Borghei, Esko I. Kauppinen, Kari Laasonen, Paola Ayala

Faculty of Physics, University of Vienna, Vienna, -, Austria
LPQM, Université Paris Diderot-Paris 7, Paris, -, France
Department of Chemistry, Aalto University, Espoo, -, Finland
Department of Applied Physics, Aalto University, Espoo, -, Finland
Department of Chemistry, Aalto University, Espoo, -, Finland
Faculty of Physics, University of Vienna, Vienna, -, Austria
toma.susi@univie.ac.at

Doping carbon nanotubes and graphene with atoms such as nitrogen (N) has long been pursued as means to controlling their electronic and chemical properties. Exciting recent applications such as electrocatalysis have spurred increasing interest in doped carbon materials. However, the local atomic structure of the dopant sites, and which of those are catalytically active, remains a crucial unsolved problem. We have been synthesizing nitrogen-doped single-walled carbon nanotubes (N-SWCNTs) using a floating catalyst chemical vapor deposition method,^[1] which allows the material to be directly deposited on various substrates and characterized by a variety of microscopic and spectroscopic means.

Previously, we investigated the electron beam stability of doped nanocarbons by atomic resolution imaging and first principles molecular dynamics.^[2] More recently, we have studied the atomic and electronic structure of N-SWCNTs by scanning tunneling microscopy and spectroscopy supported by electronic structure calculations.^[3] Spectroscopic measurements on semiconducting nanotubes revealed that these local structures can induce either extended shallow levels or more localized deep levels. In a metallic tube, a single doping site associated with a gap donor state was observed at an energy close to that of the first Van Hove singularity. Our theoretical analysis shows that this feature correspond to a substitutional nitrogen atom, identified for the first time in carbon nanotubes.

We also studied the adsorption and dissociation of oxygen on three nitrogen-doped nanocarbon systems: graphene, single-walled and double-walled carbon nanotubes using density functional theory calculations.^[4] The adsorption and dissociation energies were determined for both pristine and N-SWCNTs of different diameters with various N configurations in order to elucidate the effect of diameter and dopant type. We observed that higher nitrogen concentrations greatly reduce the energy barrier for graphitic nitrogen. Our results contribute towards a better understanding of the catalytic reaction mechanism for nitrogen-doped carbon nanomaterials.

[1]. T. Susi et al., Chem. Mater. 23 (2011) 2201

- [2]. T. Susi et al., ACS Nano 6 (2012) 8837
[3]. Y. Tison et al., ACS Nano 7 (2013) 7219
[4]. D. Srivastava et al., RSC Adv., accepted (2014), DOI: 10.1039/C3RA47784C

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Observation of Upconversion Photoluminescence from Carbon Nanotubes

Yuhei Miyauchi, Naoto Akizuki, Shinichiro Mouri, Kazunari Matsuda

Graduate School of Science, Nagoya University, Chikusa, Nagoya, Japan
Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, Japan
miyauchi@iae.kyoto-u.ac.jp

Photoluminescence (PL) properties of single-walled carbon nanotubes (SWNTs) have been intensively studied over the past decade because of their potential applications in optoelectronics and bioimaging, as well as for exploring fundamental exciton physics in one-dimensional electronic systems.^[1, 2] Here, we report a novel optical phenomenon in SWNTs: PL emission by excitation with lower energy photons than those of the emission, which is known as upconversion PL (UCPL). UCPL has been attracting much interest related to optical manipulation of phonons in solid, high efficiency solar cells, and bioimaging. Our findings will thus provide a new dimension for optical applications of SWNTs.

The SWNTs were dispersed with 0.2 wt% SDBS in D₂O. PL spectra of SWNTs around (6,5) E₁₁ exciton peak were observed under excitation with higher (2.18 eV, normal PL) and lower (1.13 eV, UCPL) energy photons than (6, 5) E₁₁ exciton energy (1.26 eV). We observed distinct peaks at the photon energy close to (6, 5) E₁₁ in the both PL spectra. The UCPL intensity exhibited weak sublinear dependence on the excitation density; this result rules out the possibility that the observed UCPL originates from a two photon excitation process that should show a quadratic dependence. On the basis of the observations of temperature and excitation photon energy dependence, the UCPL is attributed to the excitation processes mediated by large energy optical phonons in SWNTs. We will discuss the detailed mechanism of the UCPL, and the further enhancement of the UCPL intensity by introducing lower energy local states^[2] in SWNTs.

[1]. Y. Miyauchi, J. Mater. Chem. C 1, 6499 (2013)

[2]. Y. Miyauchi, M. Iwamura, S. Mouri, T. Kawazoe, M. Ohtsu, and K. Matsuda, Nature Photon. 7, 715 (2013)

Tensile Strength of CNT Fibres: Characteristic Length, Stress Transfer and other Impact Factors

Thurid Susanne Gspann, Nicola Montinaro, Alan Hardwick Windle

*Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire,
United Kingdom*
tsg28@cam.ac.uk

The initial strength hype over carbon nanotubes arose from predictions of the strength of individual graphene layers, encouraged by measurements of individual MWCNTs and SWCNT bundles in AFM.^[1,2] However, while the scientists were professionally explicit as to what they had measured, the publicity assumed that these figures could also be readily realized in materials made from these components. It's against a background of this overselling that we examine the gradual improvement in strength of macroscopically useful materials. Yarn-like fibres composed of carbon nanotubes made by the direct spinning process^[2] have been used as the subject of this study. There have been occasional observations of strengths greater than 5 N/tex,^[3] which have served to maintain the enthusiasm for on-going developments. Here, we will re-examine those high strength reports in the context of the response of nanotubes aggregates to applied tensile stress.

- [1]. M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, R. S. Ruoff, *Science* 287, p.637 (2000)
- [2]. M.-F. Yu, B. S. Files, S. Arepalli, R. S. Ruoff, *Phys. Rev. Lett.* 84, p.5552 (2000)
- [3]. Y.-L. Li, I. A. Kinloch, A. H. Windle *Science* 304 p.276 (2004)
- [4]. K. Koziol, J. Vilatela, A. Moisala, M. Motta, P. Cunniff, M. Sennett, A. Windle, *Science* 318, p.1892 (2007)

Experimentally Determined Electronic States of Oxygen-doped Single-walled Carbon Nanotubes

Tomonari Shiraishi, Naoto Akizuki, Yuhei Miyauchi, Kazunari Matsuda, Naotoshi Nakashima

Kyushu University, Department of Applied Chemistry, Graduate School of Engineering, Fukuoka, Fukuoka, Japan

Kyoto University, Institute of Advanced Energy, Uji, Kyoto, Japan

Kyushu University, Department of Applied Chemistry, Graduate School of Engineering, Fukuoka, Fukuoka, Japan

t.shiraishi@mail.cstm.kyushu-u.ac.jp

Oxygen-doped SWNTs provide new photoluminescence (PL) bands with extraordinary exciton brightening. However, the detailed electronic structure of the oxygen-derived local states has not yet been revealed. We have reported that the electronic potentials of the SWNTs can be determined using an in-situ PL spectroelectrochemical method.^[1-3] Here, we applied this method to determine the precise electronic potentials of the oxygen-doped SWNTs and found that the doping caused change in the oxidation and reduction potentials of the oxygen-doped SWNTs.

[1]. N. Nakashima et al. *Angew. Chem. Int. Ed.* 48, 7655 (2009)

[2]. N. Nakashima et al. *J. Am. Chem. Soc.* 132, 13072 (2010)

[3]. N. Nakashima et al. *Scientific Reports*, 3, 2959 (2013)

Imaging ultrafast carrier transport in carbon nanotube and nanowire transistors using femtosecond photocurrent microscopy

Byung Hee Son, Jae Ku Park, Yeong Hwan Ahn

Department of Physics and Department of Energy Systems Research, Ajou University, Suwon, Gyeonggi, Korea, Republic Of
ahny@ajou.ac.kr

We visualize ultrafast carrier dynamics in one-dimensional nanoscale devices such as carbon nanotube and silicon nanowire transistors by using combined, scanning photocurrent microscopy^[1] and time-resolved pump-probe techniques. Spatio-temporal image is particularly useful for investigating the transit times of carriers (which range 1–100 ps) that are photo-generated near one of metallic electrode and subsequently transported toward the opposite electrode through drift and diffusion processes. The carrier dynamics have been studied for various working conditions such as source-drain and gate bias voltages. In particular, the average carrier velocities extracted from the transit times increase for larger gate-bias, which is in accordance with the increased field strength at the Schottky barrier located near metal contacts. Our work will post an important step forward understating ultrafast dynamics in various low-dimensional nanoscale devices and developing future high-speed electronic devices.

[1]. Y. H. Ahn et al., “Photocurrent Imaging of p-n Junctions in Ambipolar Carbon Nanotube Transistors” *Nano Lett.* 7, 3320 (2007)

Determining the Progression of CNT Sheet Deformation with Wide Angle X-Ray Diffraction

Joe Severino, Jenn-Ming Yang, Larry Carlson

Materials Science and Engineering, University of California Los Angeles, Los Angeles, California, United States

Institute for Technology Advancement, University of California Los Angeles, Los Angeles, California, United States

jseverino@ucla.edu

Individual carbon nanotubes have extraordinary strength and stiffness; however, after two decades of intensive research we are still unable to effectively use those properties in macroscopic structures. Various methods have been tried to alleviate defects that lead to diminished performance with the goal of producing high strength sheets, yarns or ribbons that can be applied to common polymer matrix composites. The inability to translate the properties of nanotubes demonstrates a lack of understanding about the deformation mechanics of carbon nanotube assemblies. In this work, we investigate the mechanics of carbon nanotube assemblies by evaluating the structural rearrangement that occurs during tensile deformation. Two-dimensional wide angle x-ray diffraction (2D-WAXRD) is used to characterize CNT alignment and a methodology is developed to interpret the diffraction data, thereby making it simpler to quantify alignment. Additionally, field emission SEM imaging is used to qualitatively monitor the alignment of CNTs for structural features that directly affect deformation. Orientation of the sheet specimens is found to play a role in the strength, modulus, and elongation to failure. This effect is examined by 2D-WAXRD to establish a relationship between structural rearrangement and mechanical properties. With a better understanding of the deformation mechanisms within CNT assemblies, it is possible to design processes to achieve fully aligned CNT assemblies that finally utilize the exceptional strength and modulus of individual carbon nanotubes.

Exciton diffusion and related decay processes in individual air-suspended carbon nanotubes

Akihiro Ishii, Masahiro Yoshida, Yuichiro K. Kato

Institute of Engineering Innovation, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
akihiro@katogp.t.u-tokyo.ac.jp

We investigate exciton diffusion, end quenching, and exciton-exciton annihilation processes in individual air-suspended carbon nanotubes by photoluminescence microscopy.^[1] We have performed excitation spectroscopy on thousands of nanotubes to identify their chiralities and filter out bundles. In such a large dataset, we observe slightly redshifted satellite peaks which suggest the existence of single chirality bundles. Intrinsic exciton diffusion lengths for six different chiralities are obtained by analyzing the length dependence of emission intensity with a random walk theory.^[2,3] We also estimate absorption cross sections by comparing the power dependence with Monte Carlo simulations, and inspired by the agreement, we have obtained an analytical expression that reflects the one-dimensional nature of exciton diffusion.

Work supported by KAKENHI, SCOPE, The Canon Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. A. I. is supported by a JSPS Research Fellowship.

[1]. A. Ishii, M. Yoshida, Y. K. Kato, manuscript in preparation

[2]. S. Moritsubo, T. Murai, T. Shimada, Y. Murakami, S. Chiashi, S. Maruyama, Y. K. Kato, Phys. Rev. Lett. 104, 247402 (2010)

[3]. M. D. Anderson, Y.-F. Xiao, J. M. Fraser, Phys. Rev. B 88, 045420 (2013)

Spontaneous Exciton Dissociation and Stark Effect in Carbon Nanotubes

Masahiro Yoshida, Yusuke Kumamoto, Akihiro Ishii, Akio Yokoyama, Takashi Shimada, Yuichiro K. Kato

Institute of Engineering Innovation, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
yoshida@katogp.t.u-tokyo.ac.jp

Under an application of longitudinal electric fields, we have performed simultaneous photoluminescence and photocurrent measurements on individual single-walled carbon nanotubes. We observe nonzero photoconductivity at small fields, indicating that the injected excitons are spontaneously dissociating into free electron-hole pairs.^[1] By modeling the excitation power and voltage dependences of emission intensity and photocurrent, we find that a significant fraction of excitons are dissociating before recombination. We are also able to estimate the absorption cross section and the oscillator strength from the same model. The field-induced redshifts do not depend on excitation power or energy, ruling out effects from heating or relaxation pathways. As the shifts scale quadratically with electric fields, we attribute them to Stark effect.^[2] These results show the potential for controlling excitons in individual nanotubes using external electric fields.

Work supported by KAKENHI, SCOPE, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The samples are fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

[1]. Y. Kumamoto, M. Yoshida, A. Ishii, A. Yokoyama, T. Shimada, and Y. K. Kato, Phys. Rev. Lett. 112, 117401 (2014)

[2]. M. Yoshida, Y. Kumamoto, A. Ishii, A. Yokoyama, and Y. K. Kato, manuscript in preparation

Optoelectronics with Metallic Carbon Nanotube pn-Devices

Moh Amer, Shun-Wen Chang, Rohan Dhall, Jing Qiu, Steve Cronin

Ming hsieh department of electrical engineering, University of Southern California, Los Angeles, CA, United States
mohammra@usc.edu

Conventional optical photodetectors are based on semiconductors with relatively large band gaps. However, recent measurements of quasi-metallic nanotubes have shown band gaps on the order of 10-100meV, where optoelectronic devices are still severely lacking. For nanoscale devices with ballistic transport, not much is known about the depletion fields and their associated separation of photo-induced carriers, which is central to optoelectronic device operation. Here, we introduce the electronic and optoelectronic properties of quasi-metallic nanotube pn-devices, which have smaller band gaps than most known bulk semiconductors. These carbon nanotube-based devices deviate from conventional bulk semiconductor device behavior due to their low dimensional nature. We observe rectifying behavior based on band-to-band tunneling of ballistic carriers instead of ideal diode behavior, as limited by the diffusive transport of carriers. We observe substantial photocurrents at room temperature, suggesting that these quasi-metallic pn-devices may have a broader impact in optoelectronic devices operating at room temperature. A new technique based on photocurrent spectroscopy is presented to identify the unique chirality of nanotubes in a functional device. This chirality information is crucial in obtaining a theoretical understanding of the underlying device physics that depends sensitively on nanotube chirality, as is the case for quasi-metallic nanotube devices. A detailed model is developed to fit the observed I-V characteristics, which enables us to verify the band gap from these measurements as well as the dimensions of the insulating tunneling barrier region.^[1]

[1]. M. R. Amer, S.-W. Chang, R. Dhall, J. Qiu, and S. B. Cronin, "Zener Tunneling and Photocurrent Generation in Quasi-Metallic Carbon Nanotube pn-Devices," *Nano Letters*, vol. 13, pp. 5129-5134, 2013

Double-resonance Raman scattering of iTO and LA phonons in carbon nanotubes

Christoph Tyborski, Felix Herziger, Janina Maultzsch

Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Berlin, Germany

Christoph.Tyborski@physik.tu-berlin.de

We present resonance Raman measurements of single-wall carbon nanotubes in the spectral region of 1950 cm^{-1} and 2450 cm^{-1} . We analysed a HiPCO sample using laser excitation energies between 1.58 eV and 2.73 eV, focussing on the combinational modes of iTO (in-plane transverse optical) and LA (longitudinal acoustic) derived phonon bands. Both peaks can be explained by double-resonance Raman scattering. The Raman band around 2450 cm^{-1} is an intervalley scattering process between two inequivalent \mathbf{K} points, whereas the other Raman band originates from an intravalley process around a single \mathbf{K} point.

We find a multippeak structure for the intravalley iTOLA mode that can be explained by the large variety of different carbon nanotubes probed. Using a geometric model, we calculate the resonant wave vector for the intervalley iTOLA of the four lowest optical transitions for all carbon nanotubes with diameters between 0.5 nm and 2.5 nm. Hence we can derive the appropriate energies of the combinational Raman bands as well as explain our experimental findings.

Single-wall carbon nanotube films filled with acceptor molecules for transparent electrodes

Elena D. Obraztsova, Alexander A. Tonkikh, Pavel V. Fedotov, Ekaterina A. Obraztsova, Viktor I. Tsebro, Alexander A. Dolgoborodov, Albert G. Nasibulin, Esko I. Kauppinen, Andrei L. Chuvilin

Natural Sciences Center, A.M. Prokhorov General Physics Institute, RAS, Moscow, Russian Federation

Theory Department, Lebedev Physical Institute, RAS, Moscow, Russian Federation
Department of Applied Physics, Aalto University School of Science, Espoo, Finland
Electron Microscopy Laboratory, CIC nanoGUNE Consolider, San Sebastian, Spain
elobr@kapella.gpi.ru

In this work we propose a new approach for modification of optical and electronic properties of thin (thinner than 100 nm) films of single-wall carbon nanotubes (SWNTs) via their gas phase filling with different acceptor molecules (iodine^[1], CuCl^[2]). The modified films can serve as efficient transparent electrodes with parameters comparable with those of indium tin oxide (ITO) films.

We have realized a gas phase filling of aerosol-grown SWNT films with two types of acceptors – iodine and CuCl. HRTEM measurements have revealed well-ordered one-dimensional crystals inside nanotubes. With both fillers the optical transparency of SWNT films remained higher than 90%. The optical absorption bands, corresponding to E₁₁ transition (for iodine) and both E₁₁ and E₂₂ transitions (for CuCl) have been suppressed. This happened due to a Fermi level shift into the valence band. The filled SWNT films have demonstrated a drop of electrical resistance of one order of magnitude (down to 70 Ohm/square).

The work was supported by RFBR grants 13-02-01354, 14-02-31818, 14-02-31829, RAS research programs, projects IRSES-295241 and MK-6201.2014.2

[1]. A.A. Tonkikh, E.D. Obraztsova, et al., *Physica Status Solidi B* 249 (2012) 2454

[2]. P.V. Fedotov, A.A. Tonkikh, et al., *Physica Status Solidi* (2014) (submitted)

Electron Tomography for Quantitative 3-Dimensional Characterization of Carbon Nanotube Composites

Bharath Natarajan, Thomas Lam, Noa Lachman, Brian L Wardle, Renu Sharma, James Alexander Liddle

Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, United States
Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, MA, United States
Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, United States
bharath.natarajan@nist.gov

A variety of carbon nano-additives are being integrated into industrial composites, yielding bulk materials with enhanced structural and electrical properties. This enhancement is determined by the meso and nanoscale arrangement of the incorporated filler species. A quantitative understanding of the spatial arrangement of these fillers is, therefore, required to establish structure property relationships for materials design and optimization. Here we demonstrate the use of advanced electron microscopic techniques (energy-filtered transmission electron microscopy, tomography) in extracting high-resolution 3-dimensional microstructural information from high volume fraction aligned carbon nanotube (CNT)-polymer composites.^[1-3]

High-quality, electron-transparent samples were prepared from these composite materials using a focused ion beam. A tilt series of energy-filtered images (optimized for contrast) was collected. An image stack of the 3D volume was reconstructed from the tilt series using the Simultaneous Iterative Reconstruction Technique (SIRT). The stack was then segmented using a novel image-processing algorithm, developed in-house. This algorithm results in time savings on the order of a few hours as compared to traditional manual segmentation, thereby enabling high-throughput tomography of low contrast CNT-Polymer composites. The segmented images were further converted to high resolution (z-depth Resolution: 1.5 nm, 10% of average NT diameter and inter-NT spacing) 3D visualizations of the nanotube morphology within the matrix. The visualizations thus obtained were imported into MATLAB as voxel volumes to obtain NT packing fractions. These volumes can additionally be used to extract other dispersion metrics or be employed in finite element models to quantitatively understand the role of the microstructure on continuum scale composite properties.

The details of the image acquisition, processing, reconstruction and microstructural quantification methodologies will be presented in conjunction with tomography results from varied NT loading systems.

- [1]. Wardle, Brian L., et al. "Fabrication and Characterization of Ultrahigh-Volume-Fraction Aligned Carbon Nanotube–Polymer Composites." *Advanced Materials* 20.14 (2008): 2707-2714
- [2]. Marconnet, Amy M., et al. "Thermal conduction in aligned carbon nanotube–polymer nanocomposites with high packing density." *ACS nano* 5.6 (2011): 4818-4825
- [3]. Cebeci, Hülya, et al. "Multifunctional properties of high volume fraction aligned carbon nanotube polymer composites with controlled morphology." *Composites Science and Technology* 69.15 (2009): 2649-2656

SWNT vs MWNT. Comparative study of electrical properties in composites and transparent films

Mikhail Pedtechenskiy, Alexander Bezrodny, Nina Krechetova, Vladimir Saik, Yuri Varlamov

R&D, OCSiAl Group, Novosibirsk, Russian Federation
bezrodny.ae@ocsial.com

For novel applications of carbon nanotubes, their quality and properties are crucial. In our study, we have compared the influence of SWNT and MWNT added in small amounts into some epoxy compounds on the electrical conductivity, with the commercially available SWNT produced by OCSiAl (“Tuball” ®) being used. SWNT were used as produced without further purification. The “as-produced” material contained less than 10% of inorganic impurities and more than 75% of SWNT. Concentration of SWNT as low as 0.0001% was enough to obtain the conductivity well above percolation threshold (10^{-6} S/cm). The same conductivity could be obtained by the use of MWNT at much higher concentrations, above 0.01%.

It is well known that CNT can be used to produce conductive coating on the surface of polymer film. The properties of such conductive films depend on the quality of CNT used. We have prepared conductive films on the PET surface by the use of spray coating. The film made of SWNT had the resistance about 110 Om/sq., while transmittance was above 90% at 550 nm. We compared it to the film made of commercially available MWNTs. Its resistance was from 10 to 100 times higher at about the same transmittance. The superior characteristics of the conductive films made of SWNT “Tuball” make them useful for such applications as touch screens, solar cells and smart windows.

Slip inhibition between graphenes by de-fluorination of fluorinated multi-walled carbon nanotubes

Hikaru Nishizaka, Yoshinori Sato, Kazutaka Hirano, Tatsuhiro Yabune, Kenichi Motomiya, Kazuyuki Tohji

Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi, Japan
Research and development department, Stella Chemifa Corporation, Izumiootsu, Osaka, Japan
Graduate School of Environmental Studies, Tohoku University, Sendai, Miyagi, Japan
nishizaka@s.tohoku.ac.jp

Carbon nanotubes (CNTs) are the strongest and stiffest materials in terms of tensile strength and elastic modulus. However, the mechanical properties of macroscale CNT materials still fail to match the mechanical properties of their constituent CNTs. Especially, a significant mechanical weakness of macroscale multi-walled carbon nanotube (MWCNT) materials is an interfacial slip between graphenes within a MWCNT or between adjacent MWCNTs. The graphene of MWCNTs consists of sp²-hybridized carbon atoms bound by covalent bonds. In contrast, adjacent graphenes interact through van der Waals forces in the case of the contact point between neighboring MWCNTs and the interlayer of MWCNTs. Therefore, the interfacial slips between adjacent nanotubes^[1] and between graphenes of MWCNTs^[2] reduce the mechanical properties of the macroscale materials. In order to form covalent bonds between the contacting or overlapping graphenes, the generation of sp³-hybridized carbon atoms at the points is needed.

Fluorination of carbon atoms in carbon materials with sp²-hybridized orbitals changes the hybridization of carbon atoms to sp³-hybridize orbitals.^[3] In this study, we performed de-fluorination of fluorinated MWCNT fibers to form connections between the overlapping graphenes through dangling bonds from sp³-hybridized carbon atoms. Scanning electron microscopy and transmission electron microscopy observations of the tip of the fractured de-fluorinated MWCNT fibers after tensile tests revealed that all layers in each MWCNT were broken and the interfacial slip of graphenes was inhibited by de-fluorination. However, the tensile strength of de-fluorinated MWCNT fibers was lower than that of as-prepared MWCNT fibers before fluorination. We conclude that the poor tensile strength of de-fluorinated MWCNT fibers resulted because fluorination and de-fluorination destroyed the graphenes of their constituent MWCNTs.

[1]. Kis et al., *Nature Mater.*, 2004, 3, 153-157

[2]. Peng et al., *Nature Nanotech.*, 2008, 3, 626-631

[3]. Nair et al., *Small*, 2010, 6, 2877-2884

Microsecond-Resolution Single-Molecule Dynamic Sensing

Maxim V. Akhterov, Yongki Choi, Patrick C. Sims, Tivoli J. Olsen, Mariam Iftikhar, Kaitlin Pugliese, O. Tolga Gul, Brad L. Corso, Gregory A. Weiss, Philip G. Collins

Dept. of Physics and Astronomy, Univ. of California Irvine, Irvine, CA, United States

Dept. of Chemistry, Univ. of California Irvine, Irvine, CA, United States

Dept. of Physics and Astronomy, Univ. of California Irvine, Irvine, CA, United States

Dept. of Chemistry, Univ. of California Irvine, Irvine, CA, United States

Dept. of Physics and Astronomy, Univ. of California Irvine, Irvine, CA, United States

akhterov@uci.edu

Single-molecule chemistry can be monitored using optical fluorescence, mechanical forces, or electronic conduction. Of these three, electronic solid state devices offer a straightforward solution to the fundamental bandwidth limitations of the optical and mechanical techniques. Furthermore, single-walled carbon nanotube (SWNT) field effect transistors (FETs) offer ideal properties for this application since they combine high bandwidth and excellent sensitivity with a nanoscale active area that is ideal for single-molecule biofunctionalization. Recent work has shown that it is straightforward to label a SWNT-FET with a single molecule and then study that molecule's dynamic interactions with surrounding analytes ^[1].

Here, we extend this principle of single-molecule sensing to a temporal resolution of 2 μ s, exceeding the bandwidth of fluorescence- and force-based transduction by nearly one-hundred fold. At the microsecond scale, SWNT-FETs report protein transitions and motions that have remained hidden to other techniques. For example, applying the technique to the enzymatic activity of T4 lysozyme has resolved a broad distribution of motions in the range of 1 to 200 μ s – too fast to be observed by FRET but too slow for NMR or molecular dynamics modeling. Statistical analysis of thousands of events reveals the characteristic timescales and energy landscape of these motions and the biochemistry that drives them. The technique is easily generalized to other proteins to generate similar “fingerprints” of biochemical activity.

[1]. Y. Choi et al., *Science* 335 319 (2012). Y. Choi et al., *Nano Lett.* 13 625 (2013). T. J. Olsen, et. al., *JACS* 135 7855 (2013). P.C. Sims, et. al., *JACS* 135 7861 (2013)

Highly thermal conductive CNT/carbon fiber/polymer Composite for thermal interface material

Seisuke Ata, Ayumi Nishizawa, Takeo Yamada, Kenji Hata

NTCR, AIST, Tsukuba, Ibaraki, Japan

ata-s@aist.go.jp

In 2004, we developed the super-growth chemical vapor deposition technique to synthesis high-purity, long and exclusively single walled CNTs. The growth efficiency of this technique is superior to other SWNT enabling industrial mass production (in ton-scale), an aspect which will soon become reality. Furthermore, the single wall carbon nanotubes synthesized using this technique (SG-SWNT) exhibits several unique properties such as high aspect ratio, high surface area, high purity and good dispersibility, making them one of the best available conductive fillers for the development of composites. These properties were utilized for the development of a highly conductive rubber-like composite by mixing long single wall-nanotubes (SWNTs), an ionic liquid, and a fluoridated co-polymer.

We investigate the various factors critical for achieving SG-SWNT/polymer with superior electrical and mechanical properties, such as dispersion method, evaluation of CNT in solution (for process control), compounding. These investigations have culminated in the development of SG-SWNT/polymer composite with excellent electrical and thermal conductivity, high durability and environmental resistance. I would be introducing some of our recent results and achievements in this area, during the course of my presentation. Recently, efficient thermal transfer from devices is important issue for high many fields, such as supercomputer, automobile and space craft. In general, high thermal materials are hard and high density. However, to decrease the thermal resistance, soft and high thermal conductive materials are required.

In this presentation, we propose the high thermal conductive CNT/carbon fiber/polymer composite. Thermal conductivity of our composite is about 100 W/mK, this value is almost same as that of iron or brass. This high thermal conductivity is achieved by increasing of thermal transfer efficiency between carbon fiber with CNTs.

Photocurrent microscopy reveals chiral index fingerprint and thermoelectric power of CNT FETs

Lee Aspirtarte, Tristan Deborde, Tal Sharf, Joshua Kevek, Ethan Minot

Physics, Oregon State University, Corvallis, Oregon, United States
aspirtarte@gmail.com

We have performed scanning photocurrent microscopy and spectrally-resolved photoconductivity measurements of field-effect transistors (FETs) made from individual suspended carbon nanotubes (CNTs). Photoconductivity peaks associated with individual CNTs are referenced against existing Rayleigh scattering measurements to uniquely identify chiral indices. There is a close agreement between our assigned exciton resonances and the previously published exciton resonances. We further investigate the spatial-dependence, polarization-dependence, and gate-dependence of photocurrent and photovoltage in these devices. While previous studies of surface-bound CNT FET devices have identified the photovoltaic effect as the primary mechanism of photocurrent generation, our measurements show that photothermoelectric phenomena play a critical role in the optoelectronic properties of suspended CNT FETs. We have quantified the photothermoelectric mechanisms and identified regimes where they overwhelm the photovoltaic mechanism.

Electronic Dissipation in Single-Walled Carbon Nanotubes Imaged by Kelvin Probe Force Microscopy

Elliot J Fuller, Deng Pan, Philip G Collins

Dept. of Physics & Astronomy, University of California at Irvine, Irvine, CA, United States
efuller@uci.edu

Electronic dissipation in single-walled carbon nanotubes (SWNTs) has been studied extensively due to their outstanding electrical properties. However, the precise role of defects, disorder and chirality in electronic scattering remain largely unknown due to the lack of experimental methods that effectively distinguish these effects. Here, we demonstrate Kelvin Probe Force Microscopy (KPFM) as a quantitative tool for studying electronic scattering in active SWNT field effect transistors. KPFM has a unique advantage of directly imaging dissipative electrostatic gradients along a SWNT. The electrostatic potential profile of a device can be used, for example, to distinguish between pristine SWNTs and those containing a single point defect.

For pristine SWNTs, we observe a uniform potential gradient that directly determines the inelastic mean free path λ as a function of bias and can distinguish contact resistance from homogeneous inelastic scattering. At 185 K, we observe λ decreasing from nearly 1 μm at low bias to 100 nm at high bias. Fitting λ to established models determines the roles of surface plasmon-polariton scattering in one limit and optical phonon emission at the other. We find the optical phonon mean free path for spontaneous emission to be 62 ± 20 nm at 300 K, nearly 50 nm longer than observed in previous experimental studies.

In contrast to the pristine case, SWNTs with point defects exhibit a sharp potential step at a defect site. The resistance of a defect is then directly determined by the magnitude of the potential step. The shape of the potential step reveals the defect's scattering potential and propensity for trapping charges. The combination of KPFM and two-terminal transport data are well fit to a one-dimensional Frenkel-Poole model of conduction.

Distinguishing individual and ensemble carbon nanotubes by Raman spectroscopy

Asmus Vierck, Emanuele Poliani, Florentina Gannott, Manuel Schweiger, Jana Zaumseil, Janina Maultzsch

Institute for solid state physics, TU Berlin, Berlin, Berlin, Germany
Nanomaterials for Optoelectronics Group, Institute of Polymer Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Bavaria, Germany
Institute for solid state physics, TU Berlin, Berlin, Berlin, Germany
avierck@physik.tu-berlin.de

Raman spectroscopy on single-walled carbon nanotubes (SWCNTs) is one of the most powerful methods to analyse their structural, optical, and electronic properties. While Raman studies are usually performed on mixed SWCNT ensembles, it is essential to investigate the inherently distinct Raman signal of the underlying individual tubes.

Using isopropanol as a precursor, our samples were grown from patterned iron catalyst particles by CVD in a tube furnace system. Using ST-cut quartz as a substrate, we obtain perfectly aligned, mostly individual tubes, as confirmed by Raman spectroscopy, AFM and SEM imaging.

We present Raman spectra acquired under different excitation wavelengths from many individual SWCNTs and compare them to those of SWCNTs in areas with higher density that interact with each other. We assess the inherent variation of the acquired Raman signal along individual tubes statistically and discuss whether the Raman spectra from nanotube ensembles can be modelled by a superposition of individual SWCNT spectra. We show the importance of our findings when e.g. using the Raman intensities of D and G modes for the determination of defect concentration or their position and lineshape for deducing the metallic / semiconducting content of the sample.

Using Image force microscopy to visualize optical absorption in individual single walled carbon nanotubes

Derek Nowak, William Morrison, Jonah Shaver, Sang-Hyun Oh, Sung Park

R&D, Molecular Vista Inc., San Jose, CA, United States

Department of Electrical and Computer Engineering, University of Minnesota, Twin Cities, Minneapolis, MN, United States

R&D, Molecular Vista Inc., San Jose, CA, United States

derek@molecularvista.com

Image Force Microscopy detects near-field resonant optical scattering by measuring the dipole-dipole force interaction through the use of an SPM tip.^[1] This technique provides exceptional spatial resolution, circumventing the traditional difficulties with far-field optical detection, where the weak scattered light collection efficiencies and background signal levels affect measurements from small target volumes. To demonstrate the image force technique, samples of HiPco single-walled carbon nanotubes was used. The nanotubes were dispersed in sodium deoxycholate using standard sonication and ultracentrifugation techniques, resulting in a concentrated suspension with sharp absorption and strong photoluminescence features.^[2,3] Single nanotubes were imaged by wide-field micro-photoluminescence in dilute conditions in solution and spin coated on mica substrates. Spectra of single nanotubes were obtained to verify sample quality and tube individualization. These samples were then studied using simultaneous image force, topography, and confocal/tip-enhanced photoluminescence in our near-field scanning probe system.

[1]. I. Rajapaksa, K. Uenal, and H. Kumar Wickramasinghe, Appl. Phys. Lett. (2010) 97, 073121 (dx.doi.org/10.1063/1.3480608)

[2]. W. Wenseleers et al., Adv. Funct. Mater. 2004, 14, p 1105 (dx.doi.org/10.1002/adfm.200400130)

[3]. J. Fagan et al., Adv. Mater. 2014 in press (dx.doi.org/10.1002/adma.201304873)

Tuesday

K2

Milestones in Synthesis, Dispersion, and Applications that Realized Single-walled Carbon Nanotubes Industrialization

Kenji Hata

Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST) and TASC: Technology Research Association for Single Wall Carbon Nanotubes , Higashi Tsukuba, Ibaraki, Japan
kenji-hata@aist.go.jp

After two decades of extensive research, single-walled carbon nanotubes (SWNT) are going to be industrialized at last. By the time of the conference, Nippon-Zeon will have announced that they will launch the first commercial SWNT production plant based on the super-growth technology in 2015. Concurrently, a couple of applications such as SWNT super-capacitors and composites would hit the market. To realize this, not only the development of mass production technique was necessary but also new concepts in CNT dispersion were crucial to keep the length of the long SWNTs and development of new application were required. Indeed, I envision that the “first” SWNT industrial applications are going to be very different from what we researchers had thought CNT would be useful for. In this talk I will present milestones, new concepts, new directions and aspects in synthesis, dispersion and applications of long SWNTs that have led to industrialization.

Cryogenic Optical Spectroscopy of Carbon Nanotubes

Alexander Högele, Matthias S. Hofmann, Jan T. Glückert, Jonathan Noé, Alexander Kneer

*Fakultät für Physik and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität
München, München, Bavaria, Germany*
alexander.hoegele@lmu.de

Semiconducting single-wall carbon nanotubes exhibit excitonic optical transitions ^[1] with applications ranging from biomedical markers ^[2] to light harvesting devices ^[3]. Strong optical resonances also provide an intriguing interface between photon and spin ^[4] or phonon ^[5] degrees of freedom in carbon nanotube quantum devices. In this context, we will discuss recent progress in cryogenic optical spectroscopy of individual carbon nanotubes with signatures of exciton localization ^[6] and narrow spectral emission ^[7]. These results, combined with stable trion emission from carrier-doped tubes ^[8], clearly motivate further studies of quantum effects in carbon nanotubes by optical means.

- [1]. S.M. Bachilo et al, Science 298, 2361 (2002); F. Wang et al, Science 308, 838 (2005).
- [2]. Z. Liu et al, Nano Research 2, 85 (2009).
- [3]. D.J. Bindl, N.S. Safron, and M.S. Arnold, ACS Nano 4, 5657 (2010).
- [4]. C. Galland and A. Imamoglu, Phys. Rev. Lett. 101, 157404 (2008).
- [5]. I. Wilson-Rae et al, New Journal of Physics 14, 115003 (2012).
- [6]. A. Högele et al, Phys. Rev. Lett. 100, 217401 (2008); W. Walden-Newman et al, Nano Letters 12, 1934 (2012); Y. Miyauchi et al, Nature Photonics 7, 715 (2013).
- [7]. M. S. Hofmann et al, Nature Nanotechnology 8, 502 (2013); I. Sarpkaya et al, Nature Communications 4, 2152 (2013).
- [8]. R. Matsunaga, K. Matsuda and Y. Kanemitsu, Phys. Rev. Lett. 106, 037404 (2011).

CT7

Origins of carbon nanotube helicity and preference for (n, n–1) tubes

Vasilii I. Artyukhov, Evgeni S. Penev, Boris I. Yakobson

Department of Materials Science and NanoEngineering, Rice University, Houston, Texas, United States
artyukhov@rice.edu

The future fate of many practical applications of carbon nanotubes hangs on the capability to selectively produce CNT with required chirality. Despite all the progress in exploration of CNT nucleation and growth, the understanding of the origins of nanotube chirality is still missing. Thermodynamically, the energetics of CNT–catalyst interface ^[1] appear to favor achiral armchair or zigzag CNT, and although the structures of CNT caps differ for different tubes, there is no additional “intrinsic” bias from cap energetics ^[2] that could favor other chiralities. Yet neither achiral type is frequently produced in CVD growth. Simple arguments based on the screw dislocation model ^[3] outline an explanation of the overall trend towards larger chiral angles. But a more in-depth look at the experimental results finds crucial “fine details” that seemingly contradict expectations, e.g., the almost complete absence of purely armchair CNT. To resolve these issues, we’ve developed a comprehensive theory of CNT nucleation and growth (with termination easily added to the picture) that includes the different factors shaping the chirality distribution of CNT yield, including nanotube–catalyst interface ^[1], the energetic landscape of CNT caps ^[2], and growth kinetics ^[3], building upon our “nanoreactor” framework developed for graphene synthesis ^[4]. Our study reveals how the aggregate state of the catalyst particle can substantially alter the equations governing nucleation and growth rate, in such a way that jointly they provide a CNT type distribution that is sharply peaked at the minimally chiral CNT types, thus explaining the abundance of near-armchair tubes such as (6, 5) in recent experimental studies (e.g., [5]) yet little or no pure armchair.

[1]. Y. Liu, A. Dobrinsky, B. I. Yakobson, *Phys. Rev. Lett.* 105, 235502 (2010).

[2]. E. S. Penev, V. I. Artyukhov, and B. I. Yakobson, *ACS Nano* 8, 1899 (2014).

[3]. F. Ding, A. R. Harutyunyan, B. I. Yakobson, *Proc. Natl. Acad. Sci. U.S.A.* 106, 2506 (2009).

[4]. V. I. Artyukhov, Y. Liu, B. I. Yakobson, *Proc. Natl. Acad. Sci. U.S.A.* 109, 15136 (2012).

[5]. M. He, et al., *Sci. Rep.* 3, 1406 (2013).

Quantum interference effect in Raman spectra of metallic nanotubes

Eddwi H. Hasdeo, Ahmad R. T. Nugraha, Mildred S. Dresselhaus, Riichiro Saito

Department of Physics, Tohoku University, Sendai, Miyagi, Japan

Department of Physics, MIT, Cambridge, MA, United States

Department of Physics, Tohoku University, Sendai, Miyagi, Japan

hasdeo@flex.phys.tohoku.ac.jp

In graphene and metallic single wall carbon nanotubes (m-SWNTs), the existence of gapless linear energy bands (Dirac cones) modify the G band (in-plane optical phonon modes) 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 the G phonon and an electron-hole pair in the linear energy band^[1]. The other phenomenon is the asymmetric spectral shape of the G band, also known as Breit-Wigner-Fano (BWF) line shape, which long been observed in m-SWNTs^[2] and recently observed in graphene^[3]. However, the origin of this BWF lineshape asymmetry remains a question. In this presentation, the origin of BWF line shape is explained by means of quantum interference of phonon G band spectra and electronic Raman spectra (ERS)^[4]. The ERS are electronic spectra whose origin comes from an electron-hole pair excitation in the vicinity of the Dirac cone^[5].

In this work, we calculated the exciton-exciton interaction between a photo-excited exciton and an exciton in the linear band of a m-SWNT which is relevant to the ERS. We calculated ERS spectra as a function of laser excitation energy and we reproduced the experimental BWF spectral shape for all laser excitation energies. The Coulomb potential, generally, gives a maximum value at momentum transfer $q=0$ but surprisingly, we found that the direct Coulomb interaction between the two excitons vanishes at $q=0$. The absence of the direct Coulomb interaction is due to the symmetry of the two sub-lattices of SWNTs unit cell. Using the same method, we extend the story in graphene and reproduce the experimental result of the G band asymmetry as a function of Fermi energy. We also predict that the radial breathing phonon mode (RBM) spectra in m-SWNTs exhibit the opposite BWF asymmetry to that of the G band, by showing the laser energy dependence of RBM spectra.

[1] “Raman spectroscopy in graphene related systems”, A. Jorio et al, Wiley (2011)

[2] S. D. M. Brown et al., Phys. Rev. B 63, 155414, (2001)

[3] D. Yoon et al., Carbon, 61, 373-378, (2013)

[4] E. H. Hasdeo et al. Phys. Rev. B 88, 115107, (2013).

[5] H. Farhat et al., Phys. Rev. Lett. 107, 157401 (2011).

Poster Sessions 3 + 4 Summary (Annick Loiseau)

Poster Session 3 and Exhibition

Using Nanotube Transistors for Single-Molecule Studies of DNA Polymerase I

O. Tolga Gul, Yongki Choi, Kaitlin Pugliese, Brad L. Corso, Gregory A. Weiss, Philip G. Collins

Physics and Astronomy, University of California, Irvine, Irvine, CA, United States

Chemistry, University of California, Irvine, Irvine, CA, United States

ostogu@gmail.com

DNA polymerases are critical enzymes for DNA replication, and because of their complex catalytic cycle they are excellent targets for investigation by single-molecule experimental techniques. Recently, we studied the Klenow fragment (KF) of DNA polymerase I using a label-free, electronic technique involving single KF molecules attached to carbon nanotube transistors^[1]. The nanotube sensitivity allowed a single KF molecule to be monitored over long durations as it processed thousands of template strands. Processivity of up to 42 nucleotide bases was directly observed, and statistical analysis of the recordings determined key kinetic parameters for the enzyme's open and closed conformations. Subsequently, we have used the same technique to compare the incorporation of canonical nucleotides to analogs like α -thio-dNTPs, 2-thio-dTTP or dCTP, and 6-chloro-dGTP. The analogs had almost no effect on the closed conformation, during which the nucleotide is incorporated. Instead the entire effect of the analogs was during the open conformation. The thiolated and chlorinated analogs appear to interfere with KF's recognition and binding, two key steps that determine its ensemble turnover rate.

[1]. T. J. Olsen, et. al., JACS 135, 7855 (2013).

Optoelectronic Properties and Electromechanical Resonance Behavior in Individual Suspended Carbon Nanotube pn-Junctions and Devices

Steve Cronin

*Department of Electrical Engineering, University of Southern California, Los Angeles, CA,
United States*
scronin@usc.edu

In carbon nanotubes pn-junctions, we observe Zener tunneling behavior and photocurrent generation in quasi-metallic nanotubes^[1], which have smaller band gaps than most known bulk semiconductors. These carbon nanotube-based devices deviate from conventional bulk semiconductor device behavior due to their low dimensional nature. We observe rectifying behavior based on Zener tunneling of ballistic carriers instead of ideal diode behavior, as limited by the diffusive transport of carriers. We observe substantial photocurrents at room temperature, suggesting that these quasi-metallic pn-devices may have a broader impact in optoelectronic devices. We also explore the role of weak clamping forces, typically assumed to be infinite, in the electromechanical resonance behavior of these suspended carbon nanotubes.^[2] Due to these forces, we observe a hysteretic clamping and unclamping of the nanotube device that results in a discrete drop in the mechanical resonance frequency on the order of 5–20 MHz, when the temperature is cycled between 340 and 375 K. This instability in the resonant frequency results from the nanotube unpinning from the electrode/trench sidewall where it is bound weakly by van der Waals forces. Interestingly, this unpinning does not affect the Q-factor of the resonance, since the clamping is still governed by van der Waals forces above and below the unpinning. For a 1 μm device, the drop observed in resonance frequency corresponds to a change in nanotube length of approximately 50–65 nm. On the basis of these findings, we introduce a new model, which includes a finite tension around zero gate voltage due to van der Waals forces and shows better agreement with the experimental data than the perfect clamping model. From the gate dependence of the mechanical resonance frequency, we extract the van der Waals clamping force to be 1.8 pN. The mechanical resonance frequency exhibits a striking temperature dependence below 200 K attributed to a temperature-dependent slack arising from the competition between the van der Waals force and the thermal fluctuations in the suspended nanotube.

[1]. Amer, M.R., S.-W. Chang, R. Dhall, J. Qiu and S. Cronin, Zener Tunneling and Photocurrent Generation in Quasi-Metallic Carbon Nanotube pn-Devices, Nano Letters, DOI: 10.1021/nl402334e (2013).

[2]. Mehmet Aykol, Bingya Hou, Rohan Dhall, Shun-Wen Chang, William Branham, Jing Qiu, and Stephen Cronin, Clamping Instability and van der Waals Forces in Carbon Nanotube Mechanical Resonators, Nano Letters, DOI: 10.1021/nl500096p (2014).

Optical Properties of Single Chirality (5, 4) SWCNTs

Xiaojun Wei, Yasuhiro Ito, Takuya Hirakawa, Atsushi Hirano, Shunjiro Fujii, Yuhei Miyauchi, Kazunari Matsuda, Takeshi Tanaka, Hiromichi Kataura

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan
Institute of Advanced Energy, Kyoto University, Uji, Kyoto, Japan
Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan
gi.weixiaojun@aist.go.jp

Although more than 20 years have passed after the discovery of single-wall carbon nanotubes (SWCNTs), still we don't know well about their detailed structures due to lack of the single-crystal of SWCNT that enables us to analyze its precise structure. Because current SWCNT products are mostly composed of various structures, structure sorting of SWCNTs is necessary for the single crystal growth.

Previously, Liu et al. succeeded to separate 13 kinds of single chirality SWCNTs using multicolumn gel chromatography method ^[1]. In this work, we have improved the method and optimized it for thin SWCNTs. Here (5, 4) SWCNTs, which have the smaller diameter than C60 are successfully separated for the first time. In the Raman spectrum, single radial breathing mode peak at 373 cm^{-1} and highly softened TO phonon peak at 1497 cm^{-1} were observed. Interestingly, some bright photoluminescence (PL) peaks corresponding to the oxygen doped SWCNTs ^[2] were observed probably due to high chemical reactivity of highly curved side wall. Moreover, higher order excitations corresponding to E_{33} and E_{44} of (5,4) SWCNTs were clearly observed in an excitation spectrum using CCD detector. Good agreement between the excitation spectrum and the absorption spectrum indicates successful separation of high purity (5,4).

[1]. H. Liu et al. Nat. Commun. 2, 309 (2011).

[2]. Y. Miyauchi et al., Nat. Photonics 7, 715 (2013).

Catalyst control for the selective growth of Semiconductor Single-Walled Carbon Nanotubes

Shunsuke Sakurai, Maho Yamada, Hiroko Nakamura, Don N Futaba, Kenji Hata

*Nanotube Research Center, National Institute of Advanced Industrial Science and Technology,
Tsukuba, Ibaraki, Japan*
shunsuke-sakurai@aist.go.jp

Novel method to synthesize the single-walled carbon nanotube (SWNT) of semiconductor-type is reported. Selective synthesis of semiconductor-SWNT was realized by exposing the iron catalyst into the gas ambient containing small amount of H₂O just before SWNT growth. Raman spectra (laser wavelength: 532, 633, 780 nm) from the as-grown SWNT films has suggested the preferential growth of semiconducting SWNTs with small diameter of 0.8-1.1 nm range. Importantly, high selectivity was only achieved when the yield of CNT was low, suggesting the selective growth can be achieved by adjusting the catalyst activity. High performance of field-effect transistor (FET) device was performed by using as-grown CNT film as channel of FET, where high on/off ratio (> 10,000) and mobility (c.a. 10 cm²/Vs) at a relatively short channel length (5 μm). These characteristics shows that the approach of selective growth can greatly contribute to the widespread electronics application, such as flexible electronics device. To achieve high growth selectivity, and high performance of FET, fine control on catalyst size distribution, furnace ambient, and gas flow in the heating zone is required. Details are presented in this paper.

Imaging ultrafast carrier transport in carbon nanotube and nanowire transistors using femtosecond photocurrent microscopy

Byung Hee Son, Jae Ku Park, Yeong Hwan Ahn

Department of Physics and Department of Energy Systems Research, Ajou University, Suwon, Gyeonggi, Korea, Republic Of
ahny@ajou.ac.kr

We visualize ultrafast carrier dynamics in one-dimensional nanoscale devices such as carbon nanotube and silicon nanowire transistors by using combined, scanning photocurrent microscopy^[1] and time-resolved pump-probe techniques. Spatio-temporal image is particularly useful for investigating the transit times of carriers (which range 1–100 ps) that are photo-generated near one of metallic electrode and subsequently transported toward the opposite electrode through drift and diffusion processes. The carrier dynamics have been studied for various working conditions such as source-drain and gate bias voltages. In particular, the average carrier velocities extracted from the transit times increase for larger gate-bias, which is in accordance with the increased field strength at the Schottky barrier located near metal contacts. Our work will post an important step forward understating ultrafast dynamics in various low-dimensional nanoscale devices and developing future high-speed electronic devices.

[1] Y. H. Ahn et al., “Photocurrent Imaging of p-n Junctions in Ambipolar Carbon Nanotube Transistors” *Nano Lett.* 7, 3320 (2007).

Poster Session 4 and Exhibition

Identifying dopants and catalytically active sites in nitrogen-doped carbon nanotubes

Toma Susi, Yann Tison, Jérôme Lagoute, Divya Srivastava, Maryam Borghei, Esko I. Kauppinen, Kari Laasonen, Paola Ayala

Faculty of Physics, University of Vienna, Vienna, Austria
LPQM, Université Paris Diderot-Paris 7, Paris, France
Department of Chemistry, Aalto University, Espoo, Finland
Department of Applied Physics, Aalto University, Espoo, Finland
Department of Chemistry, Aalto University, Espoo, Finland
Faculty of Physics, University of Vienna, Vienna, Austria
toma.susi@univie.ac.at

Doping carbon nanotubes and graphene with atoms such as nitrogen (N) has long been pursued as means to controlling their electronic and chemical properties. Exciting recent applications such as electrocatalysis have spurred increasing interest in doped carbon materials. However, the local atomic structure of the dopant sites, and which of those are catalytically active, remains a crucial unsolved problem. We have been synthesizing nitrogen-doped single-walled carbon nanotubes (N-SWCNTs) using a floating catalyst chemical vapor deposition method ^[1], which allows the material to be directly deposited on various substrates and characterized by a variety of microscopic and spectroscopic means.

Previously, we investigated the electron beam stability of doped nanocarbons by atomic resolution imaging and first principles molecular dynamics ^[2]. More recently, we have studied the atomic and electronic structure of N-SWCNTs by scanning tunneling microscopy and spectroscopy supported by electronic structure calculations ^[3]. Spectroscopic measurements on semiconducting nanotubes revealed that these local structures can induce either extended shallow levels or more localized deep levels. In a metallic tube, a single doping site associated with a gap donor state was observed at an energy close to that of the first Van Hove singularity. Our theoretical analysis shows that this feature correspond to a substitutional nitrogen atom, identified for the first time in carbon nanotubes.

We also studied the adsorption and dissociation of oxygen on three nitrogen-doped nanocarbon systems: graphene, single-walled and double-walled carbon nanotubes using density functional theory calculations ^[4]. The adsorption and dissociation energies were determined for both pristine and N-SWCNTs of different diameters with various N configurations in order to elucidate the effect of diameter and dopant type. We observed that higher nitrogen concentrations greatly reduce the energy barrier for graphitic nitrogen. Our results contribute towards a better understanding of the catalytic reaction mechanism for nitrogen-doped carbon nanomaterials.

[1] T. Susi et al., Chem. Mater. 23 (2011) 2201

- [2] T. Susi et al., ACS Nano 6 (2012) 8837
- [3] Y. Tison et al., ACS Nano 7 (2013) 7219
- [4] D. Srivastava et al., RSC Adv., accepted (2014), DOI: 10.1039/C3RA47784C

A decade of Carbon Nanotube Fibres: projections for the future

Alan Windle

Department of Materials Science, University of Cambridge, Cambridge, CB3 0FS, United Kingdom

ahw1@cam.ac.uk

The embodiment of aligned carbon nanotubes as a fibre represents one of the most straightforward molecule to material routes, preserving uniaxial symmetry across the size scales. In the mechanical, electrical and thermal sense, it is the axial properties of the nanotubes which promise so much, and a fibre is where axial properties are the most important. In reviewing the past decade, focus will be on: coagulation spinning, where the product is a CNT/polymer composite; spinning from vertical arrays of nanotubes grown from a substrate; spinning from a solution, possibly a lyotropic solution, of carbon nanotubes in a solvent, and spinning directly from the CVD reactor zone where the nanotubes are grown from a floating catalyst. The first issue to be addressed concerns not only the current state of these processes, but also their rate of advancement, particularly with regard to scale-up activities in the commercial domain.

Future projections will focus on the further realization of the exotic properties of individual nanotubes, with a focus on questions such as: Can CNT fibre strength and stiffness be further enhanced without sacrificing the toughness and general robustness of the CNT fibres? Is the theoretical prediction of ballistic electrical conductivity a pipe dream and what might we have to do in terms of structure control to even approach it. How can the excellent axial thermal conductivity of CNT fibres be exploited in a way which might be useful? and...

Might CNT fibres replace conventional high performance material in composites, would there be any advantages and what could be the time scale.

Poster Session 3

S1

Single-walled carbon nanotube ink for large area transparent conducting films by rod-coating method

Yan Meng, Xiao-Bing Xu, Hu Li, Yan Wang, Er-Xiong Ding, Ze-Chen Zhang, Hong-Zhang Geng

School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin, Tianjin, China

genghz@tjpu.edu.cn

High concentration SWCNT ink was obtained by dispersing single-walled carbon nanotubes (SWCNTs) in water with the help of a combination of surfactants. SWCNT transparent conducting films (TCFs) were fabricated by rod-coating using the SWCNT ink. The 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 thickness of SWCNT films could be easily varied by controlling both the concentration of SWCNT ink and the size of the wire-wound rod. The TCFs were characterized using scanning electron microscope, transmission electron microscope, and Raman spectroscopy. The produced uniform SWCNT-TCFs treated by nitric acid have a relatively low sheet resistance with high transmittance. The performance has a wide range of applied interest for touch screen and flexible electronics.

A simple method for purifying metallic impurities from Multi-walled Carbon Nanotubes by Chloroform Treatment

Chang Jin Lim, Naesung Lee, Jeung Choon Goak, Elsy Agustina

Nano engineering, Sejong univeristy, Seoul, South Korea, Korea, Republic Of
changjinlim@naver.com

INTRODUCTION

Carbon nanotubes (CNTs) renowned of their excellent properties, such as mechanical strength, chemical stability, as well as the high thermal and electrical conductivity, have encouraged the researches to actively evolve the application of CNTs in various industries.^[1] However, the as-prepared CNTs are generally accompanied by carbonaceous or metallic impurities due to the utilization of metallic catalyst during the synthesis process.

Despite of the easily removed carbonaceous impurities, the encapsulated metallic impurities are chemically and thermally stable which prevent their removal due to the exposing difficulties. In comparison to single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) have less carbonaceous impurities, whilst on the other hand have more hardly removed metallic impurities.

The metallic impurities of MWCNT are serious impediments of the higher value-added applications (ex: lithium-ion batteries, high voltage cable) due to decrement of thermal stability, electrical and magnetic properties. Therefore, metal impurities should be removed, in which an effective purification technology is needed.^[2]

Up to now, various CNT purification methods have been developed such as liquid phase oxidation by strong acid^[3], microwave-assisted-method^[4], or vacuum-high temperature treatment^[5]. In this study, we developed an effective purification method in terms of time, cost and environmental friendly for overcoming problems of conventional methods.

MATERIALS AND METHODS

Material

MWCNT used in this study was synthesized by chemical vapor deposition method using iron (Fe) and cobalt (Co) catalyst on alumina (Al_2O_3) support from JEIO.

Chloroform is anhydrous from SigmaAldrich.

Method

CNT was placed in a glass tube located in the vertical-furnace at the nitrogen atmosphere and heated from room temperature to 500~900°C. When each of set temperatures is reached, chloroform carried by nitrogen gas was injected for one hour by 100mL/min flow rate allowing the reaction to take place. After 1 hour purification at the assigned temperature, furnace was cooled down to room temperature at the nitrogen atmosphere.

Nitrogen as the common industrially carrier gas was used to vaporize chloroform reagent which then injected to pass through the CNTs. Without strong acid or complex treatment, metal impurities can be easily removed by this purification method. It is noteworthy that a simple cold trap can be applied to secure the by-product of reaction, such as the excessive chloroform and hydrochloric acid, preventing the hazardous chemical to escape. Purification occurs via chloroform decomposition to generate HCl gas and Cl radical which react with the metallic impurities in CNT. At the high temperature applied, metal chlorides in gaseous state (FeCl_3 , CoCl_2 , AlCl_3) were produced and directly emitted through exit hood.

RESULTS AND DISCUSSION

According to the analysis of ICP-AES for the purified CNT, concentration of metallic impurities decreases linearly along with the increment of the reaction temperature from 500 to 800°C while above 800°C, effect is saturated. Unpurified CNT contained 14,670 ppm of metallic impurities (Fe, Co, Al) and reduced to 535ppm after purification achieving 96.4% elimination.

EDX spectra indicate the change of surface state of the sample after treatment with chloroform. The contents of aluminium, iron, cobalt and oxygen is decreased while that of chlorine increased. Chlorine radical can be attached to the end of CNTs forming functional group chlorine containing instead of oxygen containing.

Raman spectroscopy shows that the crystalline quality is preserved or improved slightly during chloroform treatment.

CONCLUSIONS

In this work, chloroform treatment is proposed to eliminate metal impurities and advanced some properties such as thermal stability, crystalline quality. This system was optimized at 800°C for 1 h, where the purification efficiency is ~96.4%, producing MWCNTs as pure as 99.95% (metallic impurities ~ 524 ppm). During purification, chlorine is functionalized to the surface of CNT, it changes surface properties of CNT. This can be detected by EDX On the Raman analysis, at a higher purification temperature, IG/ID was slightly improved, indicating that CNTs became more highly crystalline. On the TGA analysis, at a higher purification temperature, the oxidation temperature became higher, probably because a larger amount of metallic impurities were removed at a higher temperature. This purification process is simple, environmentally friendly, and cheap, so that our method is expected to be applied to preparation of highly pure MWCNTs for Li-ion batteries, supercapacitors, HV cables, etc.

REFERENCES

- [1]. V.N. Popov, "Carbon nanotubes: properties and application," *Materials Science and Engineering*, vol.43, pp.61-102, 2004
- [2]. P.X. Hou, C. Liu and H.M. Cheng, "Purification of carbon nanotubes," *Carbon*, 2008, 46(15), 2003-2025
- [3]. Hu H, Zhao B, Itkis ME, Haddon RC, "Nitric acid purification of single-walled carbon nanotubes" *J Phys Chem B* 2003;107(50):13838-42
- [4]. K. Mackenzie, O. Dunens, A.T. Harris, "A review of carbon nanotube purification by microwave assisted acid digestion" *Separation and purification Technology*, 2009; 209-222
- [5]. W. Huang, Y. Wang, G. Luo, F. Wei "99.9% purity multi-walled carbon nanotubes by vacuum high-temperature annealing" 2003; *Carbon* 41 : 2585-2590

S3

Substituent Effect of Small Aromatic Solubilizers on Selective Separation of Single-Walled Carbon Nanotubes

Masashi Fukuzawa, Fumiyuki Toshimitsu, Yuichi Kato, Naotoshi Nakashima

Dept. of Applied Chemistry, Kyushu University, Fukuoka, Fukuoka, Japan
m.fukuzawa@mail.cstm.kyushu-u.ac.jp

Single-walled carbon nanotubes (SWNTs) are classified into metallic- or semiconducting-SWNTs according to their chirality. They are produced as a mixture of various chiralities. It would be a great break through to develop an efficient method of extracting specific chiralities of the SWNTs.

We previously revealed that the flavin with alkyl chains can selectively solubilize/extract semiconducting-SWNTs. Here we report a substituent effect of the flavin on the selective separation of the SWNTs by changing alkyl chains. The effects were investigated by several spectroscopies, which revealed the supramolecular interactions of flavins are important.

S4

Structure separation of metallic SWCNTs using gel column chromatography

Takeshi Tanaka, Yasuko Urabe, Takuya Hirakawa, Hiromichi Kataura

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
tanaka-t@aist.go.jp

As-produced single-wall carbon nanotubes (SWCNTs) always contain various structures (chiralities). Recently we reported single chirality separation of semiconducting (S-) SWCNTs using gel column chromatography^[1,2]. In this separation, metallic (M-) SWCNTs were not adsorb to the gel and not separated from each other. Here we report chirality separation of M-SWCNTs. Proceeding chirality separation of M-SWCNTs, M/S separation of HiPco-SWCNTs was conducted. The separated M-SWCNTs mixture was concentrated and applied to 60 cm long column packed with Sephacryl S-200 gel equilibrated with 0.3% SDS. After flowing 0.3% SDS, the concentration of elution solution changed to 0.4%, 0.5% SDS and 2% sodium cholate. From the optical adsorption spectra of eluted fractions, clear difference of adsorption peaks was observed, indicating chirality separation of M-SWCNTs. The early and late eluted fractions tended to contain M-SWCNTs with optical absorption peaks of longer and shorter wavelengths, respectively. Detailed analyses containing the result of Raman spectroscopy will be presented.

[1]. H. Liu et al., Nature Commun., 2011, 2, 309.

[2]. H. Liu et al., Nano Lett., 2013, 13, 1996.

S5

Full-length selective removal of metallic single-walled carbon nanotubes by organic film-assisted electrical breakdown

Keigo Otsuka, Taiki Inoue, Shohei Chiashi, Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
otsuka@photon.t.u-tokyo.ac.jp

Horizontal arrays of semiconducting (s-) single walled carbon nanotubes (SWNTs) grown on crystal quartz substrates have potential for the use in field effect transistor channels, especially for the SWNT-based large-scale integrated circuits. However metallic (m-) SWNTs simultaneously grown in the SWNT arrays are one of the major obstacles to the realization of high-performance devices. Although many researchers have been tackling on this problem, satisfying the required purity of s-SWNTs and purification scalability is still of great difficulty.

Here we present an organic film-assisted electrical breakdown method, which creates the horizontal arrays of pure s-SWNTs by removing full length of metallic SWNTs. SWNT arrays grown on quartz substrates were transferred onto Si/SiO₂ substrates for control of the electrical conductivity of s-SWNTs. Ti/Pd electrodes were patterned for voltage application on the SWNT arrays in their axial direction, followed by organic film deposition on the SWNT arrays. Performing electrical breakdown on the SWNT arrays embedded in the films resulted in over 100 times as long removal of m-SWNTs as conventional electrical breakdown technique. Remaining s-SWNT arrays after the breakdown can be used for the fabrication of the SWNT-based integrated circuits.

Effect of Temperature on The Selection of Semiconducting Single Walled Carbon Nanotubes using Poly(3-dodecylthiophene-2,5-diyl)

Widianta Gomulya, Jorge Mario Salazar Rios, Vladimir Derenskyi, Stefan Jung, Satria Zulkarnaen Bisri, Sybille Allard, Ullrich Scherf, Maria Antonietta Loi

Physics, Zernike Institute for Advanced Materials, University of Groningen, Groningen, Groningen, Netherlands

Chemistry, Institute for Polymer Technology, Wuppertal University, Wuppertal, North Rhine-Westphalia, Germany
w.gomulya@rug.nl

Polymer wrapped single-walled carbon nanotube (SWNT) has been demonstrated to be a very efficient technique to obtain high purity semiconducting SWNT. To obtain not only the high quality but also high concentration of SWNTs, a careful control of the physical parameter during the selection process is indispensable. Here, we report on the investigation of the influence of temperature on the selective dispersion of SWNT by Poly(3-dodecylthiophene-2,5-diyl) (P3DDT) wrapping. The interaction mechanism between the polymer chains and the semiconducting SWNTs are studied by controlling the temperature before, during, and after the selection process. Optical absorption and photoluminescence measurements are used to study the degree of interaction between the polymer in different aggregation forms and the carbon nanotubes. Better SWNTs individualization is achieved when the polymer is completely solubilized before the sonication process. The highest concentration of SWNT in the dispersion is obtained when the sonication is performed at low temperature. The high quality of the sample obtained with fully solubilized polymer is confirmed by the fabrication of field effect transistors, which demonstrate higher on-current and higher carrier mobility (up to 1.5 times) than those fabricated from SWNT solutions wrapped with polymer solubilized at low temperature.

S7

The effect of DNA adsorption on optical transition in mono-dispersed single-walled carbon nanotube

Masahiro Ito, Yusuke Ito, Daisuke Nii, Hiroki Kato, Kazuo Umemura, Yoshikazu Homma

Department of physics, Tokyo University of Science, Shinjuku, Tokyo, Japan

m-ito@rs.tus.ac.jp

Single-walled carbon nanotubes (SWNTs) are solubilized and functionalized by means of DNA adsorption onto the surface^[1,2]. The hybridization of DNA and SWNT (DNA-SWNT) is expected to have applications in chemical and biochemical fields. As a result of DNA-SWNT dispersed in solution, photoluminescence (PL) can be observed from SWNTs. PL from an SWNT is sensitive to the surrounding environment, and should reflect the impact of adsorbed DNA on SWNT. However PL from DNA-SWNT ensemble makes spectrum analysis difficult. Recently, we revealed that PL could be obtained even from DNA-SWNT attaching to a substrate under the dry condition^[3]. In this study, we investigated the intrinsic effect of single stranded DNA (ssDNA) and double stranded DNA (dsDNA) adsorption on the optical transition in mono-dispersed DNA-SWNTs under the dry condition.

The DNA-SWNT solution was diluted low enough with pure water. We obtained PL spectra from individual DNA-SWNTs on the substrate. We compared PL spectra from the same chirality SWNT under five different conditions: SWNT suspended between micro structures in air, ssDNA-SWNT in solution, ssDNA-SWNT under the dry condition, dsDNA-SWNT in solution and dsDNA-SWNT under the dry condition. The optical transition wavelength showed clear red shifts in the order, suspended SWNT, ssDNA-SWNT and dsDNA-SWNT. Furthermore, the emission wavelength from ssDNA-SWNT was different between under the wet and dry condition, while the emission wavelength of dsDNA-SWNT was retained the same. The present results imply that excitonic transition is sensitively influenced by the local environment on the SWNT surface, such as the molecular configuration and density.

[1]. N. Nakashima et al.: Chem. Lett. 32, 456 (2003)

[2]. M. Zheng et al.: Nature Mater. 2, 338 (2003)

[3]. M. Ito et al.: Appl. Phys. Lett. 104, 043102 (2014)

S8

Thermodynamics of Quasi-Epitaxial Assembly of FMN around various (n,m)-SWNTs

Fotios Papadimitrakopoulos, Roholah Sharifi, Milinda Samaraweera, José A. Gascón

Chemistry, Institute of Materials Science, Storrs, CT, United States

papadim@ims.uconn.edu

The helical assembly of self-organized flavin mononucleotide (FMN) around single-walled carbon nanotubes (SWNTs) presents among the highest organization order in nanotube surfactants. In this contribution, we quantitatively analyze and model for the first time the cooperative hydrogen bonding of adjacent flavin moieties as well as the concentric π - π interactions between the isoalloxazine moieties and the underlying graphene lattice as a function of (n,m)-SWNT chirality. For this we use dissociation thermodynamics of FMN-wrapped (n,m)-SWNTs dispersed in both H₂O and D₂O as a function of FMN concentration. The binding strength of these FMN assemblies has been assessed in terms of ΔH , ΔS and ΔG . Atomistic molecular simulations were used to modeled these data and link their dependence in terms of nanotube diameter (d_t) the chiral angle (ϕ). The findings of this study provide the first quantitative proof of the quasi-epitaxial assembly of FMN around various (n,m)-SWNTs. This study demonstrates the architectural fidelity of FMN-wrapped SWNTs that closely emulates the dissociation mechanics of double-stranded DNA in its aqueous solutions.

S9

In situ characterization of DGU separation by full 2D fluorescence-excitation and resonant Raman spectroscopy in the centrifuge tube

Sofie Cambré, Pieter Muyshondt, Remi Federicci, Wim Wenseleers

Physics department, University of Antwerp, Antwerp, Antwerp, Belgium

Wim.Wenseleers@uantwerp.be

Density gradient ultracentrifugation (DGU) is one of the most promising techniques for chirality sorting of carbon nanotubes (CNTs),^[1] but the separation mechanisms are not quite fully understood, as they depend on the subtle differences in surfactant coating and filling^[2,3] of CNTs. Proper characterization of composition and filling requires dedicated spectroscopic techniques, not available in analytical centrifuges. We present ultrasensitive setups capable of recording full 2D IR fluorescence-excitation maps and high resolution resonant Raman spectra at various laser wavelengths, in situ in the centrifuge tube as a function of position (density) immediately after DGU separation. Applied to isopycnic DGU, this yields far more precise information on the density of surfactant coated SWNTs as a function of their diameter and chiral structure, than achievable by studying extracted aliquots. This in turn yields useful information on the diameter-dependent surfactant coating, which is also crucial to the understanding of other separation methods, such as aqueous two-phase extraction^[4,5]. The variation in surfactant stacking explains for instance the long standing paradox that sodium cholate would provide a better diameter sorting, while the extremely similar deoxycholate is the more efficient surfactant for solubilizing the nanotubes.

[1]. M.S. Arnold, A.A. Green, et al., *Nature Nanotechnol.* 1, 60 (2006)

[2]. W. Wenseleers, S. Cambré, et al., *Adv. Mater.* 19, 2274 (2007)

[3]. S. Cambré and W. Wenseleers, *Angew. Chem.* 50, 2764 (2011)

[4]. C.Y. Khripin, J.A. Fagan, M. Zheng, *J. Am. Chem. Soc.* 135, 6822 (2013)

[5]. N.K. Subbaiyan, S. Cambré, et al., *ACS Nano* 8, 1619 (2014)

The functionalization of multi-walled carbon nanotubes and carbon materials for application in gas separation and gas sensors

John A. A. Gibson, Andrei V. Gromov, Ben Hunter, Stefano Brandani, Eleanor E. B. Campbell

*School of Engineering and School of Chemistry, University of Edinburgh, Edinburgh, Scotland,
United Kingdom*

A.Gibson@ed.ac.uk

Multi-walled carbon nanotubes (MWCNTs) can be functionalized to enhance their mechanical, electrical and thermal properties for a given application. Functionalized MWCNTs have potential applications ranging from gas sensors to catalysis.

Amine moieties were grafted to the surface of the MWCNTs by both a one-step and two-step functionalization process. In the one-step process lithium, ethylene diamine (EDA) and MWCNTs were reacted to directly graft EDA to the surface. In the two step process, the nanotubes were first oxidised by a variety of techniques, including air plasma and reaction with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$. Second, the oxygen groups formed on the surface were used to covalently graft derivatives of polyethylenimine to the surface. The extent and success of the functionalization was studied by IR, XPS, laser ablation mass spectrometry and gas adsorption analysis.

Amino functionalized carbon nanotubes and carbon materials have potential application in carbon capture, through the adsorption based gas separation of CO_2 from the flu gas of fossil fuelled powered power stations. The basic amino group provides chemisorption-based selectivity for the slightly acidic CO_2 gas with respect to the non-acidic components of the flue gas mixture. The CO_2 uptake of the adsorbents was investigated by thermal gravimetric analysis and by the zero length column experiment. The effect of the different weight loadings of amine, on porous activated carbon, on the available pore volume, surface area and the change in the pore size distribution was investigated by nitrogen adsorption analysis. An increase in the CO_2 capacity was observed with the introduction of amine groups. The heat of adsorption was investigated in an attempt to understand the extent and mechanism of the chemisorption.

To investigate the electrical properties of the functionalized MWCNTs, thin films, or bucky papers, were prepared. The sheet resistivity of the various functionalised films was measured by the van der Pauw method under various gas atmospheres, (N_2 , O_2 and CO_2). We report a change in the sheet resistivity on exposure to the different atmospheres.

S11

Single chirality desorption of single-wall carbon nanotubes using mixed surfactant gel chromatography

Yohei Yomogida, Mayumi Tsuzuki, Atsushi Hirano, Shunjiro Fujii, Takeshi Tanaka, Hiromichi Kataura

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan
y-yomogida@aist.go.jp

Previously, we reported a multicolumn gel chromatography method that can separate single chirality single-wall carbon nanotubes (SWCNTs), where a chirality selective adsorption of SWCNT to the gel was utilized ^[1]. In this study, we have improved the elution process of a single column chromatography and have demonstrated a single chirality separation using chirality selective desorption of SWCNTs.

We used aqueous solution of mixed surfactants, sodium dodecyl sulfate (SDS) and sodium deoxycholate (DOC) for the chirality selective elution. Precisely controlled DOC concentration enabled chirality selective elution and high-purity (6,5) and (7,6) SWCNTs were obtained from a tiny amount of HiPco solution that was not sufficient for the multicolumn method. The chirality distribution of each fraction was analyzed in detail using optical absorption and photoluminescence (PL) spectra. Results suggest the desorption process is highly diameter selective probably due to diameter selective DOC adsorption to SWCNTs. Because this separation is based on a quite simple adsorption chromatography, this method can be easily applicable to a large scale separation of single-chirality SWCNTs.

[1]. H. Liu et al. Nat. Commun. 2, 309 (2011).

S12

Chirality sorting of SWCNTs using gradient elution in gel column chromatography

Hiromichi Kataura, Mayumi Tsuzuki, Takeshi Tanaka

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

h-kataura@aist.go.jp

Because single-wall carbon nanotube (SWCNT) has three different C-C bonds due to its tiny cylindrical structure, to know the precise structure of SWCNT is very important for understanding its physical properties. For this purpose, large scale separation of single-chirality SWCNT is one of the most important research targets, which enables growing a single crystal for X-ray diffraction measurement. Previously, we reported that diameter selective desorption of SWCNTs was possible using different concentration of sodium deoxycholate (DOC) in the gel column chromatography^[1]. In this work, we have extended this method into mixed surfactant system and tried a gradient elution for DOC concentration using a high performance liquid chromatography (HPLC). In this system, we can get UV-VIS-NIR absorption spectra in situ, which showed clear chirality sorting for HiPco SWCNTs. Because "overloading effect" is not necessary in this method, this is more effective for large scale separation of single-chirality SWCNTs than the multicolumn method that we reported previously^[2].

This work was partly supported by JSPS KAKENHI No. 25220602.

[1]. Huaping Liu et al. J. Phys. Chem. C 114 (2010) 9270.

[2]. Huaping Liu et al., Nat. Commun. 2 (2011) 309.

Poster Session 4

M1

Designer stabilizer for preparation of pristine graphene/polysiloxane films and networks

Dorsa Parviz, Ziniu Yu, Ronald Hedden, Micah J. Green

Chemical Engineering, Texas Tech University, Lubbock, Texas, United States
dorsa.parviz@ttu.edu

A designer polysiloxane-based stabilizer for graphene was used as the polymer matrix to prepare a highly conductive polymer film. To synthesize the stabilizer, 1-ethynylpyrene was grafted to the backbone of a poly (dimethylsiloxane)-co-(methylhydrosiloxane) random copolymer by Pt-catalyzed hydrosilylation with a SiH:ethynyl ratio of 1.0:1.3. Graphene was stabilized in chloroform through the π - π interactions with the pyrene groups of the resulting copolymer. A graphene/polymer film was cast from the dispersion in chloroform. SEM and TEM images confirmed the homogeneous distribution of the graphene sheets in the film. The conductivity of this film with 4 wt% loading of graphene was measured to be 220 S/m, the first case of a melt-processable, conductive graphene/polymer film reported in the literature. When the ratio of SiH:ethynyl was changed to 1.7:1.0, the copolymer self-crosslinked at 110 °C and resulted in a direct production of a conductive graphene/silicon elastomeric composite. The crosslinking reaction was observed by FT-IR spectroscopy and the network formation was confirmed by swelling and extraction of the product.

M2

High-performance carbon nanotubes reinforced aluminum matrix composites fabricated by friction stir processing and rolling

Z. Y. Ma

Institute of Metal Research, Shenyang National Laboratory for Materials Science, Shenyang, Liaoning, China
zyrna@imr.ac.cn

Aluminum matrix composites with significantly enhanced mechanical and physical properties are expected by using the carbon nanotube (CNT) as the reinforcement, due to its good mechanical properties (extremely high strength ~30 GPa, modulus ~ 1 TPa) as well as good electrical and thermal conductivity. However, it is a challenging task to individually disperse CNTs into the metal matrix due to the entangling or bundling of CNTs resulting from large aspect ratio and the strong Vander force. The CNT clusters in the CNTs reinforced metal matrix (CNT/metal) composites would reduce either mechanical or physical properties of the resultant composites. Individual dispersion of CNTs, relatively long CNT length and good CNT-metal interface bonding are the keys to obtain high-performance CNT/metal matrix composites.

In this work, 1.5-4.5vol.% CNTs reinforced 2009Al (CNT/2009Al) composites were fabricated by means of friction stir processing (FSP) technique and subsequent rolling, and subjected to detailed microstructural investigation and property evaluation. Firstly, the CNT/2009Al composites were fabricated by multi-pass FSP. Microstructural observations indicated that the CNTs were uniformly and randomly dispersed in the aluminum matrix after 3-pass FSP. The CNTs were cut shorter as the FSP pass increased and it was found that the reciprocal of CNT length exhibited a linear relationship with the number of FSP passes. The grains of the matrix were significantly refined due to the effective pinning of CNTs on the growth of recrystallized grains, and the grain size tended to stable after 3-pass FSP. The maximum strength of the composites was obtained with 3-pass FSP. This is attributed to the combined effect of CNT cluster reduction, grain refinement and CNT shortening.

Secondly, in order to align CNTs in the aluminum matrix, the FSP CNT/2009Al composites with randomly arranged CNTs were subjected to hot-rolling with a reduction of 80%. Microstructural observations indicated that CNTs were directionally aligned along the rolling direction in the composites after hot-rolling. The tube structure of the CNTs was retained and the CNT-Al interface was well bonded without pores after FSP and rolling. As a result, both the strength and modulus of the composites were significantly enhanced compared to the 2009Al and increased with increasing the CNT volume fraction. In particular, 3vol.% CNT/2009Al composite exhibited an ultimate tensile strength of 600 MPa and elongation of 10%, much higher than the corresponding values for CNT/Al composites fabricated by other processes.

M3

Pristine Graphene/Polymer Hydrogel and Aerogel Structures

Fahmida Irin, Sriya Das, Francis O. Atore, Micah J. Green

Department of Chemical Engineering, Texas Tech University, Lubbock, Texas, United States
fahmida.irin@ttu.edu

Graphene-polymer hydrogels and aerogels hold interest for both fundamental studies of graphene-polymer interactions as well as the production of nano-enhanced polymeric materials. Flexible, compressible, and self-healing pristine graphene/polymer hydrogels were synthesized via in-situ polymerization of the monomer in the polymer-stabilized graphene dispersion. The graphene sheets act as physical cross-linkers and permit gelation without the presence of any chemical cross-linker. Rheological measurements indicate that these physically cross-linked gels have higher storage modulus and toughness compared to the chemically cross-linked baseline. These gels are turned into conductive aerogels (or cryogels) by critical point drying or freeze drying. The aim is to create percolating composites with ultralow filler content by utilizing aerogels or cryogels as a conductive template. This is done by backfilling and polymerizing epoxy resin into the scaffold. The infusion of the resin does not disrupt the monolithic structure or conductive network. Three different aerogel systems (inorganic, organic and polymer aerogel) are investigated with both graphene and carbon nanotubes loading, with successful percolation in each case. A percolation threshold as low as 0.012 vol. % is obtained for graphene loaded organic aerogel/epoxy composite. This is the lowest reported threshold of any graphene based nanocomposites.

M4

Large Area Electrospinning of Carbon Nanotubes for Advanced Composite Materials

Simon George King, Vlad Stolojan, Andrew J Goodwin, S Ravi P Silva

Advanced Technology Institute, University of Surrey, Guildford, Surrey, United Kingdom
Advanced Materials, Thomas Swan & Co. Ltd., Consett, County Durham, United Kingdom
s.g.king@surrey.ac.uk

With rising fuel costs, the demand for increased efficiency has led to the need for developing further advanced materials, which can deliver increased strength and reduced weight at the same time. Due to the low-weight, high-strength properties, and having the ability to take on multi-roles, such as charge storage, composite materials are increasingly becoming the material of choice in modern applications. In order to develop composite materials to meet the modern demands for applications, electrospinning was employed to produce arrays of highly-aligned SWCNTs. These nanotube arrays were seen to increase the properties drastically in a poly(ethylene oxide) (PEO) composite material, leading to an increase of tensile strength and ductility by a factor of 3 and the Young's modulus by a factor of 4. In addition to this a large area electrospinning rig was then designed and built, producing the World's first large area sheets of aligned carbon nanotubes.

M5

Preparation of Graphene wrapped LiFePO₄/C nanocomposites by Mild Solution Synthesis for Lithium Ion Batteries

Muchun Liu, Yan Zhao, Yan Wang, Yuexin Duan

School of Materials Science and Engineering, Beihang University, Beijing, Beijing, China
santo.alchemist@gmail.com

To reduce the reaction time, electrical energy consumption, and free from high reaction pressure as well as unsafe condition, we reported an easy and efficient method for synthesis of LiFePO₄/C/graphene. The cathode composite material was in situ fabricated in open system using microwave-assisted solvent treatment. The carbon-coated LiFePO₄ nanoparticles were 20-40 nm in size, and well dispersed on the surface of graphene, which helped limit the size of nanocrystals as well as facilitate the coating process. The microstructure and morphology of LiFePO₄/C/graphene were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, field emission scanning electron microscopy, and transmission electron microscopy. The composite material could deliver a capacity of 157 mAh g⁻¹ (theoretical

specific value is 170 mAh g⁻¹) at 0.1C discharge rate and show a decay rate no more than 1% within 15 cycles.

M6

Porous Micro-spherical LiFePO₄/Graphene Nanocomposites with High Tap Density for High-performance Li-Ion Battery Cathode Materials

Sen Gao, Wei Wei, Lin Guo

School of Chemistry and Environment, Beihang University, Beijing, Beijing, China
gaosen900626@gmail.com

Due to many appealing features, such as long cycle life, high theoretical capacity (170 mAhg⁻¹), low cost, and environmental friendliness, LiFePO₄ (LFP) has been considered as a promising cathode candidate for the next generation of LIBs. Yet the intrinsically low electronic conductivity, sluggish Li⁺ transport and low tap density degrade the rate performance and energy density of LFP, and thus limit its further applications. As reported, uniform micro-sized spherical particles exhibit higher tap density, while suffering problems of both poor ionic and electronic conductivity. To solve the problems above, we developed a simple hydrothermal method followed by a high temperature chemical lithiation process to design and synthesize porous micro-spherical LFP/graphene nanocomposites (LFP/GNs). The nanocomposites are consisted of uniform LFP microspheres (~3 μm) with most of their primary particles (~100 nm) sandwiched between layers of graphene nanosheets. Mesopores (~25 nm) are widely existed in the microspheres. These structural features promise the LiFePO₄/graphene nanocomposites with high tap density (1.56 g/cm³), good electronic conductivity and fast Li-ion diffusion rate. When studied as cathode material for Li-ion batteries, the nanocomposites show excellent high rate property. At 20 °C, the nanocomposites display high capacity of 118.2 mAh/g. Since the synthetic method is simple and easily to be scaled up, it is reasonable to claim that the as-designed LiFePO₄/graphene nanocomposites are promising cathode materials for the next generation Li-ion batteries.

M7

Epoxy composites with aligned assemblies of carbon nanotubes and high-performance carbon nanotubes fibres

Anastasiia Mikhalchan, Alan Windle

Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom
am2264@cam.ac.uk

Amongst the different forms of carbon materials, assemblies of aligned carbon nanotubes in the form of sheets or mats, yarns and fibres are particularly fascinating and promising materials, enabling the translation of the superior axial properties of carbon nanotubes into the functionality of polymeric composites.

This report, as a part of ongoing research, will provide perspectives of the utilization of carbon nanotubes fibres, synthesized by the direct single-step spinning process, in epoxy composites using a conventional impregnation technique.

Peculiarities of carbon nanotubes mats and fibres will be linked with practical issues for nanocomposites development and their characteristics. The mechanical and thermal properties will be discussed in terms of interaction mechanisms and compared those from composites filled with conventional PAN- and pitch-based carbon fibres.

M8

Preparation of Single-Walled Carbon Nanotube/Ultrathin Cross-Linked Polymer Hybrids for Biomedical Applications and their Functionalization

Yusuke Tsutsumi, Tsuyohiko Fujigaya, Naotoshi Nakashima
Dept. of Applied Chemistry, Kyushu University, Fukuoka, Fukuoka, Japan
y.tsutsumi@mail.cstm.kyushu-u.ac.jp

Polymer hybrids with single-walled carbon nanotubes (SWNTs) are attracting increasing attention in biological applications due to their unique thermal, physical and optical properties. We developed a novel method to prepare SWNTs/ultrathin cross-linked polymer hybrids by the polymerization in the interior of surfactant micelle encapsulating around SWNTs. Here N-isopropylacrylamide was used as a monomer. This method provides the highly stable composite materials in aqueous solution upon heating, freeze-drying and the addition of a large amount of

surfactant. This method also enables further functionalization to the composite materials by the utilizing a variety of monomers in cross-linked polymer around SWNT surfaces ^[1].

[1]. Y. Tsutsumi, T. Fujigaya, N. Nakashima, RSC. Adv., 2014, 4, 6318.

M9

Backside fluorine-functionalized graphene for gas detection

Mikhail Katkov, Vitaliy Sysoev, Artem Guselnikov, Lyubov Bulusheva, Alexander Okotrub

*Functional materials, Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk,
Novosibirsk region, Russian Federation*
katkovmi@gmail.com

Graphene is a remarkable material due to its excellent mechanical strength and ultrafast electron transport. It has the best surface to volume ratio as a fact of its 2D nature, which implies that every atom can be considered as a surface one. These features make graphene attractive for use as a sensing material. A way to enhance the sensing properties of graphene is to create reactive centers on the surface by functionalizing graphene layers. We investigate sensing properties of reduced graphene fluoride C₂F revealed on ammonia exposure. The degree of the C₂F surface reduction was controlled by measuring the conductivity and evaluated by XPS analysis. We demonstrate the influence of the reduction degree on the sensor response supported by calculations done within the framework of a quantum-chemical approach.

We showed a possibility of detecting certain types of molecules in a gas phase and measuring their concentrations due to different responses of individual sensors to the molecules with different chemical structures. The sensor responses to electron donor (ammonia) and acceptor (nitrogen oxide) molecules have opposite signs and different response characteristic times.

M10

Large Area Graphene Ion Sensitive Field Effect Transistors with Tantalum Pentoxide Sensing Layers for pH Measurement

Ibrahim Fakh, Shadi Sabri, Farzaneh Mahvash Mohammadi, Mohamed Siaj, Thomas Szkopek

Electrical Engineering, McGill University, Montreal, Quebec, Canada
Chemistry, UQAM, Montreal, Quebec, Canada
ibrahim.fakh@mail.mcgill.ca

We have fabricated and characterized large area graphene ion sensitive field effect transistors (ISFETs) using different pH buffer solutions. We use resistive and capacitive measurement of graphene's Fermi level versus changes in pH. Bare graphene devices are insensitive to changes in

pH due to the absence of surface sites available to participate in the protonation and deprotonation process necessary for pH sensing. Deposition of a thin layer of Ta₂O₅ by atomic layer deposition increases the density of surface sites, enhancing the buffering capacity of the sensing surface layer, thus increasing the sensitivity of graphene based ISFETs. We have achieved a linear pH sensitivity up to 32.5 mV/pH and we interpret our results using the Bergveld ISFET model. Device response is stable over ~ two weeks. We will report our recent work towards reaching the Nernstian limit of 60 mV/pH sensitivity.

M11

Impedance Spectroscopy of Epoxy Matrix Nanocomposites Reinforced with Graphene Nanoplatelets

Sergio Henrique Pezzin, Renata Hack, Daniela Becker, Airtton Ramos

Materials Science and Engineering Program, Center of Technological Sciences, Dept. Chemistry, Santa Catarina State University - UDESC, Joinville, Santa Catarina, Brazil
shpezzin@gmail.com

Impedance spectroscopy measurements have been carried out to evaluate the dispersion of graphene nanoplatelets in epoxy systems, and the effect on the bulk electrical conductivity and other dielectric properties. Graphene nanoplatelets (GP), produced from natural graphite by a modified Hummers method followed by chemical reduction, have been dispersed in epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), by sonication, with or without the help of a solvent (tetrahydrofuran). The nanocomposites of epoxy matrix (DGEBA) reinforced with GP have been prepared in concentrations of GP up to 2.00 wt% by in situ polymerization and molded by casting directly on disposable measurement cells. The results obtained for cured nanocomposites show an increase on the conductivity with the current frequency, consistent with dielectric materials that present dipolar relaxation. Epoxy/GP nanocomposites show a behavior of imperfect dielectric materials, with conductivity increasing with frequency. It was also observed that using a solvent to help dispersion of GP into the epoxy resin can significantly influence the electrical properties of the nanocomposites. No electric percolation has been observed for nanocomposites with less than 1 wt% of GP. The specimens containing 0.75 and 1.00 wt% of GP presented bulk conductivity in the order of 10⁻⁹ to 10⁻⁸ S/m, while for 2.00 wt% the conductivity goes to over 10⁻⁴ S/m, indicating dielectrical percolation. For this nanocomposite, two different behaviors can be observed. At relatively low frequencies (102 to 105 Hz) the conductivity increases monotonically with the frequency, while at higher frequencies (over 1 MHz) the conductivity increases abruptly, indicating interfacial polarization and percolation networks. It can be concluded that the conductivities of these specimens are due to conduction currents caused by percolating paths, which are independent of the frequency, and interfacial polarization, dependent of the frequency, but with lower amplitude interference.

M12

Preparation and characterization of epoxy/graphene nanocomposite

Guangfen Li, Shaolei Liang

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, School of Material Science and Technology, Tianjin Polytechnic University, Tianjin, Tianjin, China

School of Material Science and Technology, Tianjin Polytechnic University, Tianjin, Tianjin, China

liguangfen@tjpu.edu.cn

In the Study, graphene was first chemically modified with poly(sodium-p-styrenesulfonate) (PSS) and then mixed with epoxy resin to produce epoxy/graphene nanocomposite. The morphology, mechanical, electrical and thermal properties of the graphene nanocomposite were characterized by different methods, such as SEM, XRD, TGA etc.. The results show that the PSS modified graphene can easily disperse in epoxy materials and thus leads to an enhanced mechanical properties. The tensile strength also shows an increase with the addition of PSS-Graphene content.

M13

Bulk Direct Band Gap MoS₂ by Plasma Induced Layer Decoupling

Rohan Dhall, Matthew Mecklenburg, Zhen Li, Cameron Moore, Stephen Cronin

*Ming Hsieh Department of Electrical Engineering, University of Southern California,
Los Angeles, CA, United States
Center for Electron Microscopy and Microanalysis, University of Southern California,
Los Angeles, CA, United States
Research Division, XEI Scientific, Redwood City, CA, United States
rdhall@usc.edu*

We report a robust method for engineering the optical and electronic properties of few layer MoS₂ based on a low energy oxygen plasma treatment. Gas phase treatment of MoS₂ with oxygen radicals generated in an upstream N₂-O₂ plasma is shown to enhance the photoluminescence (PL) of few layer, mechanically exfoliated MoS₂ flakes by up to 20 times, without reducing the layer thickness of the material. In addition to removing surface contaminants, the plasma treatment enables partial intercalation of the interlayer spaces in few layer MoS₂, thereby decoupling the electronic states in the individual layers, and causing an indirect to direct band gap transition. We study the effect of this soft oxygen plasma treatment on the MoS₂ layer thickness using atomic force microscopy (AFM) and Raman spectroscopy. Shifts in the plasmon peak in the electron energy loss spectra (EELS) indicate that the oxygen plasma process is accompanied by an increase in the density of valence electrons in the MoS₂, due to the introduction of electron donor atomic species interspersed between the individual MoS₂ layers. With optimized plasma treatment parameters, we observed enhanced PL signals for 32 out of 35 few layer MoS₂ flakes tested, indicating this method is robust and scalable.

M14

Covalent and non-covalent functionalization of graphene by dip-pen nanolithography

Aravind Vijayaraghavan, Michael Hirtz, Antonios Oikonomou

School of Materials, The University of Manchester, Manchester, Greater Manchester, United Kingdom
Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Baden-württemberg, Germany
aravind@mancheser.ac.uk

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 dip-pen nanolithography, 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.

Graphenylene-based nanotubes

Andrew T. Koch, Saloome Motavas, Harrison D. E. Fan, Amir H. Khoshaman, George Sawatzky, Alireza Nojeh

Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada

Physics, University of British Columbia, Vancouver, British Columbia, Canada
akoch@ece.ubc.ca

The electronic properties of a new type of carbon nanotube based on the graphenylene motif were investigated using density functional and tight-binding methods. The structure of a graphenylene nanotube consists of six-membered as well as four-membered rings of sp² carbon atoms, with localized pi bonds fixed around the six-membered rings. As a result, these nanotubes exhibit three distinct bond lengths between carbon atoms. They also possess unique dodecagonal pores with ~5.4 Å diameter. Analogous to conventional graphene-based carbon nanotubes, a two-dimensional graphenylene sheet can be “rolled” into a seamless cylinder in armchair, zigzag, or chiral orientations. The resulting nanotube can be described using the familiar (n,m) nomenclature. Density functional theory-based calculations predict zigzag graphenylene nanotubes to be small bandgap semiconductors, with an increasing bandgap as the diameter decreases. Similar to traditional carbon nanotubes, zigzag graphenylene nanotubes with indices mod(n-m,3)=0 exhibit a smaller bandgap than other zigzag graphenylene nanotubes with comparable diameters. Interestingly, density functional calculations predict metallic behavior for armchair graphenylene nanotubes with small diameters (< 13 Å), and semiconducting behavior with a small bandgap for armchair graphenylene nanotubes with larger diameters.

References:

- [1] J. M. Soler et al. J. Phys.: Condens. Matter 14 2745 (2002)
- [2] D. Porezag, T. Frauenheim, T. K. Kohler, G. Seifert, R. Kaschner, Phys. Rev. B 51, 12947–12957 (1995)
- [3] G. Brunetto et al. J. Phys. Chem. C, 116, 12810-12813 (2012)
- [4] Q. Song et al. J. Mater. Chem. C, 1, 38 (2013)

M16

Carbon Nanospheres/Silicon/Alumina Hollow Structure as Anode for Lithium-Ion Batteries

Bing Li, Young Hee Lee

Department of Energy Science, CINAP, IBS, Suwon, Gyeonggi-do, Korea, Republic Of
libingwp@gmail.com

Silicon is regarded as one of the most promising anode materials for next generation lithium-ion batteries due to its high theoretical capacity. However, poor capacity retention induced by pulverization of silicon and high irreversible capacity resulting from unstable solid-electrolyte interphase (SEI) formation during cycling hinder its practical applications. In this report, a carbon nanospheres/silicon/alumina (CNS/Si/Al₂O₃) hollow structure is fabricated to overcome the above issues. CNS thin film substrate is fabricated by the electrophoretic deposition technique, and amorphous silicon and a thin layer of Al₂O₃ are then deposited. The CNS/Si/Al₂O₃ hollow structure not only provides a conductive CNS 3D substrate, but also accommodates large silicon volume expansion due to the existence of void space provided by CNSs. Moreover, the electrochemical performance is further improved owing to the thin and stable SEI enabled by Al₂O₃ layer and the efficient transport of electrons and lithium ions capacitated by the surface-to-surface contact mode. The electrode exhibits high specific capacity and remarkable capacity retention simultaneously: 1560 mAh/g after 100 cycles at current density of 1 A/g with retention of 84.8% and an average decay rate of 0.16 % per cycle. The superior battery properties are confirmed by cyclic voltammetry and impedance measurement furthermore.

M17

2-D Solid State Hydrogen Molecules in Layered Structure Potassium Intercalated GO

Tae Hoon Lee, Young Hee Lee

Department of Energy Science, IBS Center for Integrated Nanostructure Physics, Institute for Basic Science, Sungkyunkwan University, Suwon, Gyeonggi-do, Korea, Republic Of
Department of Physics, IBS Center for Integrated Nanostructure Physics, Institute for Basic Science, Sungkyunkwan University, Suwon, Gyeonggi-do, Korea, Republic Of
hooni0629@skku.edu

Due to limited fossil fuels and carbon dioxide emission, we need to research green energy fuels for automobiles. There is promising unlimited resources known as, hydrogen, has high specific energy compared with petroleum, and also the combustion of product in Hydrogen Fuel Cell Vehicle (HFCV) is water vapor. However, there is drawback storage the hydrogen in high pressure owing to latent explosion hazards. Therefore, we study hydrogen storage in layered structure potassium intercalated graphite oxide (GO) at low pressure and room temperature to meet the practical application. The storage capacity of hydrogen was determined by quadruple quartz crystal microbalance (QCM) and BET measurement. The hydrogen storage with potassium intercalated GO reached ~ 2 wt % at 5 atm and 300 K from QCM. BET total surface area ($110 \text{ m}^2 \text{ g}^{-1}$), micropore volume (0.03 mL g^{-1}), and mesopore volume (0.4 mL g^{-1}) were confirmed in the bulk state of material. Our potassium intercalated porous graphite oxide has possibility for promising hydrogen storage to meet the U.S Department of Energy target.

Chemical Route for Graphite Nanoplatelets

Yvonne Demkiw, Kati Gharagozloo-Hubmann, Stepahnie Reich

Institut of Experimentalphysics, Freie Universität Berlin, Berlin, Berlin, Germany

yvonne.demkiw@fu-berlin.de

Since graphene shows promising properties, researchers have explored intensively different routes for its mass production in order to make it for application fields available. Two most feasible methods for preparation of graphene are chemical vapor deposition (CVD) and “hummer oxidation reaction”. While CVD method delivers direct graphene with large lateral size and good qualities for optical and electrical applications, the graphene oxides from the oxidation routs have be reduced first. The non-attached graphene layers in liquid needs to be stabilized by chemicals in order to prevent restacking again into non-crystalline graphite. Although the oxidation and the reduction steps both works well, the quality of the product suffers due to the aggressive reactants.

An alternative approaches is the intercalation reaction of graphite with electron donators or acceptors. In case of the graphite intercalation with electron donators like alkaline metals, the alkaline metal transfers electrons into graphite. Due to the negative charge became the layer distances larger and the separation of graphene from the stack is relieved. By this method we could obtain single graphene layers and also tiny graphene multi layers. However in solution graphene layers are instable and restack into multi layers or fold into crumpled graphene. By chemical stabilization the restacking of multi layers were prevented. The results were verified by Raman and AFM measurements.

M19

Carbon nanotube/polyaniline nanocomposites applied as gas sensor device for NH₃

Marcelo Eising, Carlos Eduardo Cava, Rodrigo V. Salvatierra, Aldo J.G. Zarbin,
Lucimara S. Roman

PIPE, UFPR - Federal University of Paraná, Curitiba, Paraná, Brazil
Material Science, UTFPR - Technological Federal University of Paraná, Londrina, Paraná,
Brazil

Chemistry, UFPR - Federal University of Paraná, Curitiba, Paraná, Brazil

Physics, UFPR - Federal University of Paraná, Curitiba, Paraná, Brazil

carloscava@utfpr.edu.br

In this work we study the characteristics of gas sensors devices based on carbon nanotube/polyaniline (CNT/PANI) nanocomposites. The sensor device is based on an active layer film of CNT/PANI with primary doping using H₂SO₄ and applied to detect some kind of acid vapor, and another secondary doping using camphorsulfonic acid and m-cresol, applied to organic vapor detection, by self-assembled method, deposited on a chromium/gold (Cr/Au) interdigitated electrode, achieved by common photolithography. Keeping constant the amount of CNT and varying the amount of aniline at the polymerization. A total of four ratios were synthesized, each proportion doped in three different ways. Morphological analyzes (SEM and AFM) indicated the film formation, the increase of the irregularities and roughness with the increasing amount of PANI in the composite. Electrical analyzes of devices based on these composites showed a high sensitivity (values up to 418.50±43.50%), low response times (minimum values of 75.00±15.50 s) and low recovery times (minimum values of 378.50±24.50 s) to 1,000 PPM of ammonia in air.

Acknowledgments: This work was supported by CNPq, CAPES, Fundação Araucária - PR and INCT- Nanomateriais de Carbono.

Near-band edge optical properties of h-BN: from bulk to nanolayers and nanotubes

Aurélie Pierret, Léonard Schué, Frédéric Fossard, Simona Moldovan, Ovidiu Ersen, François Ducastelle, Julien Barjon, Annick Loiseau

LEM, ONERA-CNRS, Chatillon, France, France

IPCMS, CNRS - Université de Strasbourg, Strasbourg, France, France

LEM, ONERA-CNRS, Chatillon, France, France

GEMAC, Université Versailles St Quentin - CNRS, Versailles, France, France

LEM, ONERA-CNRS, Chatillon, France, France

loiseau@onera.fr

h-BN is a wide band gap semiconductor (6.4 eV), which can be synthesized, as graphite, its carbon analog, as bulk crystallites, nanotubes and layers. These structures meet a growing interest for deep UV LED and graphene engineering. In this talk, we will review the interplay between the structure, defects and luminescence properties of different BN structures and how these properties can be further exploited for their characterization. To this aim, we carry out optical and structural characterizations by combining Photoluminescence (PL), cathodoluminescence (CL) measurements at 4K in the UV range (up to 7eV) using dedicated experimental sets-up ^[1, 2] and TEM analyses using HRTEM, diffraction contrast imaging, electron tomography and Energy Loss spectroscopy (EELS).

We first examined properties of high quality single crystals ^[3], and have shown that their optical properties are governed, in the energy range 5.5 – 6 eV, by strong excitonic effects ^[1, 4], which have been confirmed by reliable theoretical calculations ^[5, 6]. Near band edge luminescence consists of two series of lines called S and D ^[2, 4]. PLE experiments indicate that binding energy of S excitons is equal to 370 meV, whereas the gap is measured to be equal to 6.4 eV ^[7]. Furthermore S excitons are found to be self-trapped, due to a Jahn-Teller effect ^[3, 7]. Thanks to the imaging capability of the CL, emission related to D lines, is found to be localized on defects, such as grain boundaries or stacking faults. In defect free areas, D lines completely vanish and S lines only are observed. D/S ratio can therefore be used as a qualification parameter of the defect densities present in the material ^[1]. This procedure has been applied to understand the first luminescence studies of few layers individual BN flakes obtained by mechanical exfoliation ^[1] and has revealed that the luminescence is significantly perturbed by the exfoliation process.

Second, we have studied multi wall nanotubes made of typically 10 to 20 layers ^[8]. CL images reveal that the luminescence in the 5.5 – 6eV energy range is strongly inhomogenous and oscillating. Thanks to a deep investigation combining different TEM techniques, we have shown that the tubes display a complex twisted faceted structure and that the twist period is correlated with the luminescence oscillations. Furthermore, we could show that excitons, responsible for the spectacular localization of the luminescence, are trapped to specific defects, twisted along with the faceting structure.

Finally, low-loss EELS providing an alternative approach to the nature of electronic excitations^[9], we will show how it is an efficient tool to investigate the local structure and optical properties with an energy resolution below 100meV of different BN layers and nanotubes.

Acknowledgements: The research leading to these results has received funding from the European Union Seventh Framework Programme under grant agreement n°604391 Graphene Flagship. D. Golberg, T. Taniguchi and K. Watanabe from NIMS, Japan, are warmly acknowledged for providing samples (Nanotubes and HPHT single crystals).

- [1] P. Jaffrennou et al., Phys. Rev. B 77 (2008) 235422
- [2] A. Pierret et al., Phys. Rev. B 89 (2014) 035414
- [3] Y. Kubota et al., Science 317, (2007) 932
- [4] K. Watanabe et al., Phys. Rev. B 79 (2009) 193104
- [5] B. Arnaud, et al. Phys. Rev. Lett. 96 (2006) 026402
- [6] C.-H. Park et al., Phys. Rev Lett. 96 126105 (2006).
- [7] L. Museur et al., Phys. Stat. Sol. rrl, 5 (2011) 414
- [8] C. Tang et al., Chem. Commun. 12 (2002) 1290
- [9] R. Arenal et al., Phys. Rev. Lett. 95 (2005) 127601

2-D hybrids of graphene and single-walled carbon nanotube

Rui Wang, Yaqiong Xu

Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, United States

Department of Electrical Engineering, Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, United States

rui.wang.1@vanderbilt.edu

Graphene and single-walled carbon nanotube have shown superior potential in nanoelectronics due to their excellent thermal, mechanical, electronic and optical properties. A simple method has been developed to fabricate ultra-thin graphene/single-walled carbon nanotube hybrids through chemical vapor deposition. Unlike large-area single-layer chemical vapor deposition graphene, these novel hybrids can float on the surface of water during transfer process without such polymer like PMMA as a support membrane. This 2-D material possesses good electrical conductivity and optoelectronic properties via scanning photocurrent measurement. The network in photocurrent response reflects the junction area of graphene and single-walled carbon nanotubes, which is also observed by transmission electron microscope. The introduction of single-walled carbon nanotube network into graphene plane can alter graphene morphology in 2-D, which develops promising graphene structure for future application in energy storage and optoelectronics.

Electrical properties and crystallization behavior of poly(ethylene terephthalate)/multiwall carbon nanotube nanocomposites

Changkun Ding, Keyan Liu, Xiuping Xin, Bowen Cheng

School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin, Tianjin, China

dingchangkun@tjpu.edu.cn

Nanostructuring of polymers has opened up new perspectives for multi-functional materials ^[1-3]. In this paper we report on the poly(ethylene terephthalate) (PET) based nanocomposites prepared with four different types of multi-walled carbon nanotubes (MWNT) through a coagulation method. The electrical conductivity study demonstrates that MWNT of 30-50 nm diameter possess the best electrical conductivity. The composites of 1 wt% MWNT in PET had a electrical resistance of 109 Ω . The morphology of nanocomposites was characterized using scanning electronic microscopy (SEM). A coating on MWNT by PET chains was observed by comparison of micrographs of raw MWNT, and this coating was considered as evidence of interfacial interaction between MWNT and PET chains. The MWNT of 8 nm diameter possess the best interfacial interaction. Crystallization behavior of PET nanocomposites was studied by differential scanning calorimetry (DSC). The very small amount of MWNT displayed a great nucleating effect on the PET crystallization. The crystallization temperature was improved for around 40 °C by using only 0.1 wt % MWNT owing to MWNT decreased chain mobility of PET. The thermal stability of PET nanocomposites was improved by adding MWNT as well.

[1] Lee H. J., Oh S. J., Choi J.Y., et al. Chem. Mater. 2005, 17, 5057-5064.

[2] Tzavalas S., Drakonakis V., Mouzakis D. E., et al. Macromolecules 2006, 39, 9150-9156.

[3] Grady B. P. Macromol. Rapid Commun. 2010, 31, 247-257.

Raman Enhancement Effect on Two-dimensional Layered Materials: graphene, h-BN and MoS₂

Xi Ling, Wenjing Fang, YI-Hsien Lee, Paulo Araujo, Xu Zhang, Joaquin Rodriguez-Nieva, Yuxuan Lin, Jin Zhang, Jing Kong, Mildred Dresselhaus

Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, United States

Material Sciences and Engineering, National Tsing-Hua University, Hsinchu, Taiwan, Taiwan, Province Of China

Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL, United States

Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, United States

College of Chemistry and Molecular Engineering, Peking University, Beijing, Beijing,

United States

xiling@mit.edu

Realizing Raman enhancement on a flat surface has become increasingly attractive after the discovery of graphene enhanced Raman scattering (GERS). Two-dimensional (2D) layered materials, exhibiting a flat surface without dangling bonds, were thought to be strong candidates for both fundamental studies of this Raman enhancement effect and its extension to meet practical applications requirements. Here, we study the Raman enhancement effect on graphene, hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS₂), by using the copper phthalocyanine (CuPc) molecule as a probe. This molecule can sit on these layered materials in a face-on configuration. However, it is found that the Raman enhancement effect, which is observable on graphene, hBN and MoS₂, has different enhancement factors for the different vibrational modes of CuPc, depending strongly on the surfaces. Higher frequency phonon modes of CuPc (such as those at 1342, 1452, 1531 cm⁻¹) are enhanced more strongly on graphene than that on h-BN, while the lower frequency phonon modes of CuPc (such as those at 682, 749, 1142, 1185 cm⁻¹) are enhanced more strongly on h-BN than that on graphene. MoS₂ demonstrated the weakest Raman enhancement effect as a substrate among these three 2D materials. These differences are attributed to the different enhancement mechanisms related to the different electronic properties and chemical bonds exhibited by the three substrates: (1) graphene is zero-gap semiconductor and has a non-polar C-C bond, which induces charge transfer (2) h-BN is insulating and has a strong B-N bond, while (3) MoS₂ is semiconducting with the sulfur atoms on the surface and has a polar covalent bond (Mo-S) with the polarity in the vertical direction to the surface. Therefore, the different Raman enhancement mechanisms differ for each material: (1) charge transfer may occur for graphene ; (2) strong dipole-dipole coupling may occur for h-BN and (3) both charge transfer and dipole-dipole coupling may occur, although weaker in magnitude, for MoS₂. Consequently, this work studied the origin of the Raman enhancement (specifically, chemical enhancement), and identifies h-BN and MoS₂ as two different types of 2D materials with potential for use as Raman enhancement substrates.

Polystyrene - Poly(3-thiophene acetic acid)/MWCNT Composite Fibers by Electrospinning for Actuator Devices

Cristal Martínez Ibañez, Juan Carlos García-Gallegos, José Jarib Alcaraz, Humberto Terrones, André Galembeck, Celso P. de Melo, Fernando J. Rodríguez-Macías, Yadira I. Vega-Cantú

Department of Fundamental Chemistry, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil

Department of Physics, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil
Department of Physics, Pennsylvania State University, State College, Pennsylvania, United States

Department of Fundamental Chemistry, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil

Department of Physics, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil
Department of Fundamental Chemistry, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil

yadira@inct-inami.com.br

Carbon nanostructures such as multiwalled carbon nanotubes (MWCNT) improve the electrical and mechanical performance of actuators of poly(3-thiophene acetic acid) (PTAA) composites. In this work, an electrospinning (ES) process was used to produce very thin (sub-micrometer) fibers of polystyrene (PS) on a conical-collector-system electrode, as a support. These non-woven fiber fabrics were then covered with PTAA composites by casting, and used as an electromechanical actuator, electrospun films of mixtures of PS-PTAA-MWCNT were also produced for comparison. The PTAA composites were obtained by functionalizing MWCNT with hydroxylated thiophene linker (thiophene-3-ethanol) (th-MWCNT) ^[1] for a better interaction with PTAA, followed by in situ polymerization of 3-thiophene acetic acid ^[2]. The reaction was carried out under nitrogen, with a 4:1 mole ratio of FeCl₃ to thiophene monomer. The response of actuators was evaluated as function of content of th-MWCNTs (~1, ~3, and ~5 wt. %) in composites. The composite fibers were characterized electrically (DC and AC measurements) to study percolation threshold of fillers and dielectric changes due to th-MWCNTs filler and conducting polymer load as function of content of PS.

[1]Harel, Y., Azoubel, S., Magdassi, S., et al., J Colloid Interface Sci 2013; 390(1): 62-9.

[2]Royappa, A.T. and Rubner, M.F., Langmuir 1992; 8(12): 3168-3177.

Effect of Different Carbon Nanostructures as Reinforcements on the Performance of Polyaniline Actuators

Juan Carlos Garcia-Gallegos, Ignacio Martin-Gullon, Juan A. Conesa, Yadira I. Vega-Cantu,
Fernando J. Rodriguez-Macias

*Departamento de Quimica Fundamental, Universidade Federal de Pernambuco, Recife,
Pernambuco, Brazil*

Chemical Engineering Department, University of Alicante, Alicante, Alicante, Spain
*Departamento de Quimica Fundamental, Universidade Federal de Pernambuco, Recife,
Pernambuco, Brazil*

dr.fernandojrm@gmail.com

Four nanostructured carbon materials (multi-walled carbon nanotubes, MWCNT; nitrogen-doped MWCNT, CN_x; helicoidal-ribbon carbon nanofibers, HR-CNF; and graphene oxide platelets, GO, from CNF) were used to reinforce polyaniline (PAni) in electromechanical bilayer bending actuators. These devices are based on the macroscopic expansion/contraction of PAni by reversible redox processes. Films of PAni-nanocarbon composite, processed with N-methylpyrrolidone (NMP), attached to a cellophane film were tested in a liquid electrolyte cell system. Experimental design was used to select type of nanocarbon filler and composite loadings that showed a good balance of electromechanical properties. Raman spectroscopy suggests good interaction between PAni and the nanocarbon fillers. Electron microscopy showed best nanofiller dispersion for graphene oxide, followed by MWCNT. CN_x composites showed dispersion problems and thus poorer performance. MWCNT composite actuators had a better combination of bending angle, bending velocity and maximum working cycles (measured considering nanofiller loading and applied voltage), with GO the second best in regards to working cycles.

Supercompressible Porous Foam Network made of Single-Walled Carbon Nanotubes coated with Graphene

Youngseok Oh, Kyu-Hun Kim, Mohammad F. Islam

*Composites Research Center, Korea Institute of Material Science, Changwon, Gyeongnam,
Korea, Republic Of*

*Department of Material Science and Engineering, Carnegie Mellon University, Pittsburgh, PA,
United States*

youngsoh@kims.re.kr

Lightweight, cellular solids or foams with elasticity and resilience even under large cyclic strain have been considered attractive materials for use as dampers, thermal cloaks, heat sinks, electrochemical electrodes, and sieves. Single-walled carbon nanotubes (SWCNTs) have excellent mechanical, electrical, thermal properties including high aspect ratio (>1,000). The combination of the properties enables the nanotubes to use in building multifunctional lightweight foams. However the pristine carbon nanotube foams are physically fragile and undergo significant plastic deformation due to the weak van der Waals attractive force between the nanotubes when they are subjected to large cyclic compressive strain.

Here we will show the fabrication of SWCNT based foam networks and their mechanical improvement by coating graphene nanoplates around CNT-CNT junctions ^[1]. We have first produced individually dispersed SWCNTs in water using an anionic surfactant, sodium dodecyl benzene sulfonate (NaDDBS). We have then created aqueous elastic gels from these SWCNT dispersions to fabricate ultra-light-weight, electrically conducting and thermally insulating but mechanically fragile three-dimensional SWCNT foams. The introduction of the graphene layers on the nanotubes has been achieved via polyacrylonitrile (PAN) coating followed by the pyrolysis process at 1050 °C in Ar. The graphene-coated aerogel exhibits no change in mechanical properties after more than 1×10^6 compressive cycles, and its original shape can be recovered quickly after compression release. Moreover, the graphene coating does not affect the structural integrity or the compressibility and porosity of the nanotube network. The coating also increases Young's modulus and energy storage modulus by a factor of ~6, and the loss modulus by a factor of ~3.

M27

Scalable synthesis of hierarchically structured carbon nanotube-graphene fibers for capacitive energy storage

Yuan Chen, Dingshan Yu

*School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore,
Singapore, Singapore*
chenyuan@ntu.edu.sg

Micro-supercapacitors are promising energy storage devices that can complement or even replace batteries in miniaturized portable electronics and microelectromechanical systems. Their major limitation, however, is the low volumetric energy density when compared to batteries. In this work, we describe a hierarchically structured carbon microfibre made of an interconnected network of aligned single-walled carbon nanotubes with interposed nitrogen-doped reduced graphene oxide sheets. The nanomaterials form mesoporous structures of large specific surface area ($396 \text{ m}^2 \text{ g}^{-1}$) and high electrical conductivity (102 S cm^{-1}). We develop a scalable method to continuously produce the fibres using a silica capillary column functioning as a hydrothermal microreactor. The resultant fibres show a specific volumetric capacity as high as 305 F cm^{-3} in sulphuric acid (measured at 73.5 mA cm^{-3} in a three-electrode cell) or 300 F cm^{-3} in polyvinyl alcohol (PVA)/ H_3PO_4 electrolyte (measured at 26.7 mA cm^{-3} in a two-electrode cell). The full micro-supercapacitor with PVA/ H_3PO_4 gel electrolyte, free from binder, current collector and separator, has a volumetric energy density of $\sim 6.3 \text{ mWh cm}^{-3}$ a value comparable to that of 4V-500 Ah thin-film lithium batteries while maintaining a power density more than two-order of magnitude higher than that of batteries and a long cycle life. To demonstrate that our fibre-based, all-solid-state micro-supercapacitors can be easily integrated into miniaturized flexible devices; we used them to power a UV photo-detector and a light-emitting diode.

Reference: Nature Nanotechnology, 2014, accepted

Preparation of highly active nitrogen-doped few-layer graphene/carbon nanotube composite electrocatalyst for oxygen reduction reaction in alkaline media

Sander Ratso, Ivar Kruusenberg, Merilin Vikkisk, Eugene Shulga, Urmas Joost, Ilmar Kink, Tanja Kallio, Kaido Tammeveski

Institute of Chemistry, University of Tartu, Tartu, Tartumaa, Estonia
Institute of Physics, University of Tartu, Tartu, Tartumaa, Estonia
School of Chemical Technology, Aalto University, Espoo, Espoo, Finland
elrenuir1@gmail.com

We report the synthesis and electrochemical investigation of nitrogen-doped few-layer graphene/multi-walled carbon nanotube (FLG/MWCNT) composite catalyst for oxygen reduction reaction in alkaline media. In search for the best electrode material, composites were prepared from two different nitrogen precursors with addition of acid-treated MWCNTs and graphene oxide (GO) to increase conductivity and surface area. The composite materials were prepared by single step process by pyrolyzing in flowing argon atmosphere at 800 °C. The N-doped composite catalyst samples were characterized by scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy, the latter method revealed successful nitrogen doping. The oxygen reduction reaction (ORR) was studied in 0.1 M KOH on glassy carbon electrodes modified with N-doped FLG/MWCNT electrocatalysts employing the rotating disk electrode (RDE) method. The RDE results indicated that these metal-free nitrogen-doped nanocarbon catalysts possess remarkable electrocatalytic activity towards the ORR in alkaline media similar to that of commercial Pt/C catalyst. The results obtained in this work are particularly important for the development of non-Pt cathode catalysts for alkaline membrane fuel cells.

Reference

S. Ratso, I. Kruusenberg, M. Vikkisk, U. Joost, E. Shulga, I. Kink, T. Kallio, K. Tammeveski, *Carbon* 73 (2014) 361-370.

M29

Photoluminescence study of tungsten disulfide grain boundaries

Toshiaki Kato, Toshiro Kaneko

Department of Electronic Engineering, Tohoku University, Sendai, Miyagi, Japan

kato12@ecei.tohoku.ac.jp

Novel photoluminescence (PL) peak has been observed at the grain boundary of tungsten disulfide known as one of the true two dimensional (2D) semiconductor materials. Detailed atomic force microscopy and PL intensity mapping measurements show the novel peak appears only from the grain boundary region. Temperature dependent PL measurements also revealed that the novel peak can be divided into two types (type 1 and type 2) as a difference of peak energy and these can be assigned as peak of neutral excitons weakly and strongly bounded at the grain boundaries, respectively. This finding is important for the future optoelectrical applications of 2D atomic sheet with grain boundary engineering, which is one of the geometrical standpoints of 2D atomic sheet materials.

Transition metal dichalcogenide film transistors

Taishi Takenobu

Department of Applied Physics, Waseda university, Shinjyuku, Tokyo, Japan
takenobu@waseda.jp

Recently, TMDC monolayers, such as MoS₂, MoSe₂ and WSe₂, have attracted considerable interest because of its high carrier mobility, mechanical strength, large intrinsic bandgap and optical properties. Here, we demonstrate the fabrication of CVD-growth MoS₂ thin-film transistors (TFTs) using ion gel as elastic gate dielectrics^[1,2]. Because these transistors revealed good performance (mobility of 12.5 cm²/Vs and On/Off ratio of 100,000), we transferred MoS₂ films on flexible plastic substrates and realized excellent flexibility down to a curvature radius of 0.75 mm^[1,2]. We also fabricated MoS₂ transistors on stretchable rubber substrates and achieved high stretchability under 5% channel strain without significant degradation of the carrier mobility and on/off current ratio, which might be owing to a relaxation of ripples^[1,3]. As the next step, we challenged to expand material variation and successfully fabricated high-performance CVD-growth WSe₂ transistors (mobility of 90 cm²/Vs and On/Off ratio of 10,000,000) and simple resistor-loaded inverters^[4].

1. J. Pu, L.-J.Li and T. Takenobu, *Phys. Chem. Chem. Phys.*, 10.1039/C3CP55270E (2014).
2. J. Pu, Y. Yomogida, K.-K.Liu, L.-J.Li, Y. Iwasa, and T. Takenobu, *Nano Letters*, 12, 4013-4017, (2012).
3. J. Pu, Y. Zhang, Y. Wada, J. T.-W. Wang, L.-J.Li, Y. Iwasa, and T. Takenobu, *Appl. Phys. Lett.*, 103, 23505 (2013).
4. J.-K. Huang, J. Pu, C.-L.Hsu, M.-H.Chiu, Z.-Y.Juang, Y.-H.Chang, W.-H.Chang, Y. Iwasa, T. Takenobu, and L.-J. Li, *ACS Nano*, 8, 923-930 (2014).

Growth and functionalization of layered transition metal dichalcogenides by controllable mild plasma treatment

Tomoyuki Takahashi, Toshiaki Kato, Toshiro Kaneko

Department of Electronic Engineering, Tohoku University, Sendai, Miyagi, Japan
takahashi13@ecei.tohoku.ac.jp

Layered transition metal dichalcogenide (TMD) is known as a true two-dimensional (2D) material with excellent semiconducting properties. In spite of its potential, however, there are still remained lots of issues 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 MoS₂ and WS₂. The effects of catalysts and growth conditions on the structure of MoS₂ and WS₂ were also investigated. Furthermore, mild plasma treatment ^[1,2] was also carried out aiming for the controllable functionalization of these TMDs.

[1] T. Kato, L. Jiao, X. Wang, H. Wang, X. Li, L. Zhang, R. Hatakeyama, and H. Dai, *Small*, 7 (2011) 574.

[2] T. Kato and R. Hatakeyama, *Nat. Nanotechnol.*, 7 (2012) 651.

Copper-coated Nanotubes at the Single Nanotube Scale

Deng Pan, Brad L. Corso, Osman Tolga Gul, Philip G. Collins

Department of Physics and Astronomy, University of California Irvine, Irvine, California, United States

dengp@uci.edu

High conductivity and high ampacity are both essential specifications for next-generation solid-state electronics. Recently, Subramaniam et. al. reported remarkable increases in copper conductivity and ampacity using a bulk composite of copper and carbon nanotubes (CNTs).^[1] Here, we describe similar measurements performed with a model system composed of individual single-walled or multiwalled CNTs. Cu electrodeposition on single CNTs is straightforward in bulk, but smooth challenging to control at the nanometer-scale. Cu coated single CNTs with ratios as low as 10:1 have been electrically tested as a function of film thickness and device temperature. We have not yet observed the same conductance improvement as Subramaniam et. al. reported, but we obtain similar temperature coefficients, which indicates that the CNT core plays roles in dissipation and thermal equilibration.

[1] C. Subramaniam et. al., Nat. Comm. 4 (2013)

Lysosomal membrane permeabilization induced by carbon nanohorns caused reactive oxygen species generation and apoptosis in RAW264.7 cell

Mei Yang, Minfang Zhang, Yoshio Tahara, Sumio Iijima, Masako Yudasaka

*Nanotube Research Center, National Institute of Advanced Industrial Science and Technology,
Tsukuba, Ibaraki, Japan*

*Department of Material Science and Engineering, Meijo University, Nagoya, Aichi, Japan
Nanotube Research Center, National Institute of Advanced Industrial Science and Technology,
Tsukuba, Ibaraki, Japan
m-yudasaka@aist.go.jp*

Carbon nanomaterials have offered a wide range of potential applications including biomedicine and nanotechnology. In the meantime, public concern on their environmental and health effects is growing rapidly. Many adverse effects such as inflammatory response, oxidative stress, and thrombus induction have been reported in vitro and in vivo studies. Recent studies showed that carbon nanomaterials induced cell apoptosis, and reactive oxygen species (ROS) generation was considered as the main adverse effect, but the details are still unclear.

In this study, we investigated the cell death mechanism of macrophage (RAW264.7) induced by excess uptake of oxidized carbon nanohorns (CNH). We found that neither the mitochondria nor oxidase systems were directly involved in the CNH-related ROS production and provided another ROS generation process induced by carbon nanohorns. The overload of CNHLaox in lysosomes induced lysosomal membrane permeabilization (LMP) ^[1], leading to the cathepsins (lysosomal enzyme) release, and the cathepsin caused ROS generation. Both cathepsin and ROS induced mitochondrial dysfunction, subsequently, the caspases activation and the cell apoptosis. Our studies clarified the macrophage apoptotic pathway induced by nanocarbons, provided some clues about how nanocarbons induce the ROS production and indicated LMP are the initial effectors for nanocarbon-related cell death. This work may complement the understanding of toxicology mechanism of nanocarbons.

[1] Y. Tahara et al. Biomaterials, Biomaterials 33 (2012) 2762e2769

Effects of plasma on growth of suspended graphene nanoribbon from nickel nanobar under rapid heating plasma CVD

Hiroo Suzuki, Toshiaki Kato, Toshiro Kaneko

Department of Electronic Engineering, Tohoku University, Sendai, Miyagi, Japan
suzuki12@ecei.tohoku.ac.jp

Graphene nanoribbons combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. Although nanoribbons can be made in a variety of ways, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. Plasma chemical vapor deposition (CVD) is known as fruitful method for the structural-controlled growth and damage-free functionalization of nano carbon materials such as carbon nanotubes [1] and graphene [2,3]. We have developed a new, simple, scalable method based on the advanced plasma CVD method for directly fabricating narrow (~23 nm) suspended graphene nanoribbon devices with a clear transport gap (58.5 meV) and a high on/off ratio (>10000) [4]. Since the establishment of our novel graphene nanoribbon fabrication method, direct conversion of a Ni nanobar to the graphene nanoribbon is now possible. The growth mechanism of graphene nanoribbon, however, is not well understood, which is important for the stable fabrication of graphene nanoribbon devices. We investigate the growth mechanism of graphene nanoribbon by comparing evaporation rate of nickel between plasma and thermal CVD. It is found that the evaporation rate of nickel is low in plasma CVD compared with that of thermal CVD. This should relate with the difference of carbon concentration in nickel. In plasma CVD, large amount of hydrocarbons can be supplied to nickel due to high rate dissociation of carbon source gas. From this result, we can give a model which reveals that the graphene nanoribbon can be grown by plasma CVD.

[1] T. Kato and R. Hatakeyama, ACS Nano, 4 (2010) 7395.

[2] T. Kato and R. Hatakeyama, ACS Nano, 6 (2012) 8508.

[3] H. Suzuki, T. Kato, and T. Kaneko, Plasma Fusion Research, in press (2014).

[4] T. Kato and R. Hatakeyama, Nature Nanotechnology, 7 (2012) 651.

Industrialization of Boron Nitride Nanotubes: From Synthesis to Applications

Keun Su Kim, Michael Jakubinek, Amy Hrdina, Yadienka Martinez-Rubi, Behnam Ashrafi, Mark Plunkett, Shuqiong Lin, Stephane Denommee, Christopher Kingston, Benoit Simard

*Emerging Technologies Division, National Research Council Canada, Ottawa, Ontario, Canada
Aerospace, National Research Council Canada, Montreal, Quebec, Canada*

*Emerging Technologies Division, National Research Council Canada, Ottawa, Ontario, Canada
christopher.kingston@nrc-cnrc.gc.ca*

Boron nitride nanotubes (BNNTs) exhibit a range of properties that are as impressive as those of carbon nanotubes (CNTs), including comparable mechanical properties and thermal conductivity, but with substantially higher thermal stability and, unlike CNTs, polarizability, wide band gap, and transparency in the visible region ^[1]. These characteristics make BNNTs attractive for the development of high-performance light-weight engineering materials, with potential to impact a range of sectors such as aerospace and armor materials, including for reinforced transparent armor. Historically, very low production volume has prevented the science and technology of BNNTs from evolving at even a fraction of the pace of CNTs, especially in areas such as reinforced composites where substantial quantities are required even for R&D activities. The National Research Council Canada (NRC) has recently addressed this limitation through the development of an industrially scalable plasma process for BNNT production from pure hexagonal boron nitride ^[2,3]. The method produces few-walled, highly crystalline small-diameter, BNNTs (~5 nm diameter) at a rate of ~20 g/hr, which is 100 times previous literature reports for structurally similar BNNTs ^[4] (or close to 20 times rates reported for larger diameter BNNTs. E.g., ^[5]), and with demonstrated single-run yields approaching 200 g. A cost-effective, scalable purification protocol also has been developed and the purified material is highly stable in air to at least 900 °C. This world-leading production capacity enables, in some cases for the first time in the history of BNNTs, development of large-scale BNNT applications including for polymer, ceramic and metal composites, BNNT sheets and coatings, and BNNT fibers. A range of initial examples will be presented including non-woven BNNT sheets up to 30 cm x 100 cm showing excellent flame resistance, polymer composites based on both impregnated sheets and dispersed BNNTs, and ceramic composites. These findings represent a major advance towards the exploitation of BNNTs in real-world applications.

1. Pakdel, C. Zhi, Y. Bando, D. Golberg. Low-dimensional boron nitride nanomaterials. *Materials Today* 15(6), 246-265 (2012).
2. K.S. Kim, C. Kingston, B. Simard. Boron nitride nanotubes and process for production thereof. US#61/813,324(2013).
3. K.S. Kim, C.T. Kingston, A. Hrdina, M.B. Jakubinek, J. Guan, M. Plunkett, B. Simard. Hydrogen-catalyzed, pilot-scale production of boron nitride nanotubes and their macroscopic assemblies. Submitted 2014.

4. Huang, Y.; Lin, J.; Tang, C.; Bando, Y.; Zhi, C.; Zhai, T.; Dierre, B.; Sekiguchi, T.; Golberg D., Bulk Synthesis, Growth Mechanism and Properties of Highly Pure Ultrafine Boron Nitride Nanotubes with Diameters of Sub-10 nm. *Nanotechnology* 21, 145602 (2011).
5. C. Zhi, Y. Bando, C. Tang, S. Honda, H. Kuwahara, D. Golberg. Boron nitride nanotubes/polystyrene composites. *Journal of Materials Research* 21, 2794-2800 (2006).

Synthesis, Raman Spectroscopy Studies and Photoluminescence Edge Enhancement on Monolayered WS₂

Humberto R Gutierrez, Nestor Perea-Lopez, Ana Laura Elias, Ayse Berkdemir, Andres R. Botello Mendez, Ruitao Lv, Vincent H. Crespi, Florentino Lopez-Urias, Jean-Christophe Charlier, Humberto Terrones, Mauricio Terrones

*Department of Physics & Astronomy, University of Louisville, Louisville, KY, United States
Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA, United States*

Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCL), Louvain la neuve, Louvain la neuve, Belgium

*School of Materials Science & Engineering, Tsinghua University, Beijing, Beijing, China
Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA, United States*

Advanced Materials Department, IPICYT, San Luis Potosi, SLP, Mexico

Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCL), Louvain la neuve, Louvain la neuve, Belgium

Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY, United States

Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA, United States

aue4@psu.edu

Here we describe the direct synthesis of WS₂ monolayers with triangular morphologies and strong room-temperature photoluminescence (PL)^[1]. The Raman response as well as the luminescence as a function of the number of S–W–S layers is also reported. The PL weakens with increasing number of layers due to a transition from direct band gap in a monolayer to indirect gap in multilayers. The edges of WS₂ monolayers exhibit PL signals with extraordinary intensity, around 25 times stronger than that at the platelet's center. Moreover, the Raman scattering of single- and few-layered WS₂ is studied as a function of the number of S-W-S layers and the excitation wavelength in the visible range (488, 514 and 647 nm)^[2]. For single-layer WS₂, the 514.5 nm laser excitation generates a second-order Raman resonance involving the longitudinal acoustic mode (LA(M)). This resonance results from a coupling between the electronic band structure and lattice vibrations. First-principles calculations were used to determine the electronic and phonon band structures of single-layer and bulk WS₂. The reduced intensity of the 2LA mode was then computed, as a function of the laser wavelength, from the fourth-order Fermi golden rule. Our observations establish an unambiguous and nondestructive Raman fingerprint for identifying single- and few-layered WS₂ films.

[1] H. R. Gutiérrez, et al., Nano Lett. 13, 3447–3454 (2013).

[2] A. Berkdemir, H. R. Gutiérrez, et al., Sci. Rep. 3:1755, DOI: 10.1038/srep01755 (2013).

M37

Thermodynamically favorable dissolution of graphene via intercalation of graphite

P.L.Cullen, D.J.Buckley, C.A.Howard, S.A.Hodge, M.S.P.Shaffer, N.T.Skipper
London Centre for Nanotechnology, University College London, London, South Kensington, U.K.
patrick.cullen.10@ucl.ac.uk

There is great interest in graphene production/manipulation via liquid-phase routes which can be used for the scalable production of functional films and composites. However all reported methods of top down production have thus far relied on chemical functionalization, ultrasonication, stirring or centrifugation. In this study, graphene has been exfoliated from potassium-ammonia graphite intercalation compounds spontaneously in NMP without the need for agitation or chemical modification of any kind.

Wednesday

K3

Carbon Nanotube Sorting via Molecular Interactions in Liquid Phases

Ming Zheng

*Materials Science and Engineering Division, National Institute of Standards and Technology,
Gaithersburg, Maryland, United States*

ming.zheng@nist.gov

Chirality control is one of the most challenging problems in the carbon nanotube field. Over a decade ago, we and others began to explore separation of single-wall carbon nanotubes by exploiting chirality-dependent molecular interactions in liquid phases. By now, efforts from many groups around the world have resulted in a number of effective ways to achieve metal/semiconductor separation and single-chirality purification, enabling fundamental studies and application development. In this presentation, I will review various separation methods developed so far, discuss common physical mechanism underlying these methods, and highlight a polymer-based liquid two-phase extract method we have recently reported (J. Am. Chem. Soc. 2013, 135, p6822; Adv. Mat. 2014, DOI: 10.1002/adma.201304873). I will give examples to illustrate the versatility of the new method, and provide an outlook for its future development to enable carbon nanotube-based applications.

Strategic Functionalization of Nanomaterials for Potential Biomedical Applications

Giorgia Pastorin

Department of Pharmacy, National University of Singapore, Singapore, Singapore, Singapore
phapg@nus.edu.sg

Recent advances in nanomaterials have led to several opportunities in biomedical research. The current and most promising applications of these nanomaterials include, but are not limited to, drug delivery and tissue repair. Indeed, drug delivery systems represent one of the most interesting results deriving from the development of advanced materials, among which carbon nanotubes (CNTs) seem to embody an intriguing option; this is due to some favorable attributes including CNTs' unique shape, which promotes cellular uptake, and large aspect-ratio that facilitates functionalization of bioactive molecules on their surface ^[1,2].

In our group we have investigated several strategies for the incorporation of different drug molecules both via covalent linkage ^[2] and via encapsulation in form of "nano-bottles" ^[3-5]. The efficacy of drugs released from our drug delivery systems was improved in vitro in comparison with the free drug, probably due to remarkable mitochondrial injury, as demonstrated by the decrease in mitochondrial membrane potential resulting from accumulation of CNT-drug constructs at the mitochondrial level. Conversely, empty carriers neither reduced cell viability significantly nor incurred mitochondrial damage.

Also, we have demonstrated that carbon-based materials might provide a promising biocompatible scaffold in tissue engineering, since they do not hamper the proliferation of human mesenchymal stem cells (hMSCs) and accelerate their specific differentiation into bone cells ^[6,7]. Interestingly, cell differentiation occurred even in the absence of additional biochemical inducing agents, as evidenced by multiple independent criteria at the transcriptional, protein expression and functional levels ^[6]. Since the differentiation rate is comparable to the one achieved with currently used growth factors, these results pave the way for the potential use of these nanomaterials for stem cell research.

References

- [1] B.S. Woong et al. *Adv. Drug Deliv.Rev.* 2013, 65, 1964.
- [2] G. Pastorin et al. *Chem. Commun.* 2006, 21, 1182.
- [3] Zhao C. et al. *Biotechnol. Adv.* 2013, 31, 654.
- [4] W. Wu et al. *Angew.Chem. Int. Ed.*, 2005, 44, 6358.
- [5] R. Yupeng and G. Pastorin. *Adv.Mater.* 2008, 20, 2031.
- [6] J. Li et al. *Chem. Sci.* 2012, 3, 2083.
- [7] S. L. Yoong et al. *Biomaterials*, 2014, 35, 748.
- [8] T. R. Nayak et al. *ACS Nano*.2010, 4, 7717.
- [9] T. R. Nayak et al. *ACS Nano*.2011, 5, 4670.

Macroscale Superlubricity in Centimeters Long Perfect Double-walled Carbon Nanotubes under Ambient Conditions

Rufan Zhang, Zhiyuan Ning, Yingying Ning, Quanshui Zheng, Qing Chen, Huanhuan Xie, Qiang Zhang, Weizhong Qian, Fei Wei

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, Beijing, China
Key Laboratory for the Physics & Chemistry of Nanodevices, Peking, Beijing, Beijing, China
Center for Nano and Micro Mechanics, Tsinghua University, Beijing, Beijing, China
Key Laboratory for the Physics & Chemistry of Nanodevices, Tsinghua, Beijing, Beijing, China
Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, Beijing, China
zhangrufan4201@163.com

Friction and wear are two main causes for mechanical energy dissipation and component failure, especially in micro/nano-mechanical systems with large surface-to-volume ratio. The past decade has witnessed increasing research interest in superlubricity, a phenomenon where the friction almost vanishes between two incommensurate solid surfaces, which is also called structural superlubricity. However, all experimental structural superlubricity was obtained on micro/nano-scale and mostly under high vacuum. Multi-walled carbon nanotubes (MWCNTs), composed of coaxial cylindrical graphene layers with a high aspect-ratio, are ideal candidates to study superlubricity. The MWCNT shells can slide or rotate with respect to each other. Due to the difficulty in nano-manipulation, there are only a few experimental reports on the sliding or rotational behavior of MWCNT shells in the past two decades. The measured intershell friction was much higher than the theoretical values due to the presence of defects or deformations in MWCNTs. Besides, the manipulation of individual CNTs is also a challenge because of their nanosized diameters.

Here we show that macroscale superlubricity can be realized in centimeters long double-walled carbon nanotubes (DWCNTs) under ambient conditions. Centimeters long inner shells could be continuously pulled out from DWCNTs. The intershell friction was lower than 1 nN and independent of the DWCNT length. The shear strength of the DWCNTs is only several Pascals, four orders of magnitude lower than the lowest reported value. The perfect structure of the ultralong DWCNTs used in our experiments is essential to the macroscale superlubricity. The macroscale superlubricity in DWCNTs can be understood in view of the absence of either defects or large axial curvatures in the as-employed DWCNTs and the length-independent variation of the vdW interaction between CNT shells during the pull-out process. The observation of superlubricity in ultralong DWCNTs is a promising result for many practical applications, such as ultrasensitive sensors, fine positioning devices, gyroscopes, fast switches and more.

On the Nitrogen Doping Mechanism in Small Diameter Single Walled Carbon Nanotubes; Impact on Electronic Properties and Growth Selectivity

HamidReza Barzegar Goltapehei, Eduardo Gracia-Espino, Tiva Sharifi, Florian Nitze, Thomas Wagberg

Physics, Umea University, Umea, Vasterbotten, Sweden

Department of Chemical and Biological Engineering, Chalmers University of Technology, Gothenburg, Gothenburg, Sweden

Physics, Umea University, Umea, Vasterbotten, Sweden

hamid.barzear@physics.umu.se

Despite numerous studies on nitrogen doped single walled carbon nanotubes (SWCNTs), the structural conformation and stability of nitrogen functionalities in small diameter SWNTs, and their impact on the electronic and mechanical properties of the SWNTs, is incomplete. We report a detailed study on nitrogen doping in SWNTs with diameters in the range of 0.8-1.0 nm. We show that the introduction of nitrogen in the carbon framework significantly alters the stability of certain tubes, opening for the possibility to selectively grow nitrogen doped SWNTs with certain chirality and diameter. At low nitrogen concentration, pyridinic functionalities are readily incorporated and the tubular structure is well pertained. At higher concentrations, pyrrolic functionalities are formed, which leads to significant structural deformation of the nanotubes, and hence a stop in growth of crystalline SWNTs. By correlating the influence of defined nitrogen functionalities on the electronic properties of SWNTs with different chirality we make precise interpretation of experimental Raman data. We show the double resonance G'-peak can be well-correlated to the type of nitrogen doping of SWNTs originating from the p or n-doping nature of the nitrogen incorporation. Our results are supported by experimental and theoretical data.

Poster Sessions 5+6 and Summary (Christophe Bichara)

Poster Session 5 and Exhibition

Structure and Transport at Metal-Nanotube Contacts

Jerry Tersoff

*Thomas J. Watson Research Center, IBM, Yorktown Heights, New York, United
Statestersoff@us.ibm.com*

The performance of nanoscale low-dimensional devices is typically limited by the contacts. With advances in scaling, the contact is becoming even more critical. To explore the fundamental limits for carbon nanotube transistor performance, we have calculated the device characteristics as a function of nanotube diameter and metal work function. Although the on-state current varies continuously, the transfer characteristics reveal a relatively abrupt crossover from Schottky to ohmic contacts. We find that typical high-performance devices fall surprisingly close to this Schottky-ohmic crossover. As a result, tunneling plays an unexpectedly important role even for the best devices with ohmic contacts. We also examine structural aspects of the metal-CNT contact. The metal causes unexpectedly large mechanical deformations of the CNT, and for nanotube arrays there is a critical pitch where the metal contact dewets from the substrate.

Detection and Spectroscopy of Individual Carbon Nanotubes dedicated to bio-imaging

Laurent Cagnet^{1,2}

1LP2N, Univ. Bordeaux, 33405 Talence Cedex France

2LP2N, Institut d'Optique - CNRS, 33405 Talence Cedex France

* Laurent.cagnet@u-bordeaux.fr

The optical microscopy of single molecules has recently been beneficial for many applications, in particular in biology. It allows a sub-wavelength localization of an isolated nano-object and a subtle probing of its spatio temporal nano-environment on cells as we demonstrated on live neurons^[1].

For many bio-applications, near infrared nanoprobe and/or more photostable nanoprobe than conventional fluorescent molecules or quantum dots are desirable. In this context, single walled carbon nanotube tubes are promising. A prerequisite is however to understand their optical properties in different environments including water/saline suspensions, to study their rheological/interaction behavior in crowded bio/cellular environments and further optimize their optical detection therein. Our current efforts toward these goals will be presented as well as comparisons with other near infrared probes^[2].

References

[1] Groc, J. Neuroscience, (2007); Heine, Science, (2008).

[2] Cagnet, et al, Science, (2007); Fakhri, et al, Science, (2010); Oudjedi et al, J. Phys. Chem. Lett. (2013); Duque, JACS (2013); Genin, Adv. Mat (2014)

Single-walled carbon nanotube growth from Pt catalysts by cold-wall ACCVD

Takahiro Maruyama, Hiroki Kondo, Yuya Sawaki, Ranajit Ghosh, Shigeya Naritsuka, Toshiya Okazaki, Sumio Iijima

Department of Applied Chemistry, Meijo University, Nagoya, Aichi, Japan
Department of Materials Science and Engineering, Meijo University, Nagoya, Aichi, Japan
Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
Faculty of Science and Technology, Meijo University, Nagoya, Aichi, Japan
takamaru@meijo-u.ac.jp

So far, we have reported single-walled carbon nanotube (SWNT) growth from Pt catalysts in the alcohol gas source method ^[1]. In this study, we demonstrated that SWNTs grew from Pt under very low ethanol pressure using a conventional cold-wall type chemical vapor deposition (CVD) system and the diameters and chirality of grown SWNTs were investigated using SEM, TEM, Raman and PL.

SWNT growth was carried out on SiO₂/Si substrates at 400-900°C in a cold-wall type CVD system using Pt as catalysts. When the growth temperature and ethanol gas pressure were 700-900°C and 1-3 Pa, RBM peaks were observed in the Raman spectra, accompanied with the splitting of G band. From SEM images, high-density web-like structures were observed on the substrates. These results indicate that SWNTs grew under low ethanol pressure even in the conventional CVD system, confirming that the high activity of Pt catalysts. We also estimated the chirality of SWNTs from PL and Raman spectra. Our results showed that diameters of most of SWNTs were below 1.3 nm and that the distribution of chirality was fairly narrow, compared to SWNTs grown from transition metal catalysts.

[1] T. Maruyama et al. Mater. Express 1 (2011)267.

Poster section 6 and Exhibition

Chirality dependence of the absorption cross-section of carbon nanotubes

Fabien Vialla, Cyrielle Roquelet, Géraud Delport, Silvia Morim Santos, Benjamin Langlois, Christophe Voisin, Jean-Sébastien Lauret

LPA, ENS, Paris, France

Aimé Cotton Laboratory, ENS Cachan, CNRS, Paris Sud University, Orsay, France

jean-sebastien.lauret@lac.u-psud.fr

On one hand, the synthesis methods of carbon nanotubes produce heterogeneous samples with broad distribution of (n, m) species. On the other hand, absorption spectroscopy is a common and easy tool used to determine concentrations thanks to the molar extinction coefficient. This method is however very difficult to implement for the nanotubes case. In fact it relies on the knowledge of the variation of the nanotube absorption cross-section as a function of the chiral indices. Some theoretical studies pointed a possibly strong variation of this absorption cross-section with diameter, the chiral angle and the family type $(n-m \bmod 3)$ ^[1]. On the experimental point of view, some measurements of the absolute absorption cross-section through single nanotube spectroscopy was reported for the $(6, 5)$ and $(18, 5)$ species ^[2, 3], and very recently on few chiral species through short-wave IR fluorescence microscopy ^[4].

Here, we report on a new experimental method to scale the (n, m) -dependence of the absorption cross section of single wall carbon nanotubes ^[5]. Porphyrin molecules stacked on the wall of the nanotubes provide an original way to achieve efficient and uniform photo-excitation of the whole set of chiral species present in the sample ^[6], which allows to reveal intrinsic properties of the nanotubes. We show that the absorption varies by up to a factor of 3 for zigzag nanotubes of opposite family type. Finally, we propose a phenomenological formula to evaluate quantitatively the absorption cross section of small diameter carbon nanotubes as a function of their chiral indices ^[5].

References

- [1] Y. Oyama et al., Carbon 44, 873 (2006) ; E. Malic et al., Phys. Rev. B 74, 195431 (2006)
- [2] S. Berciaud et al., Phys. Rev. Lett. 101, 077402 (2008)
- [3] D. Christofilos et al., Chem. Phys. Lett. 3, 1176 (2012)
- [4] J.K. Streit et al, Nano Letters 14, 1530 (2014)
- [5] F. Vialla et al, Phys. Rev. Lett. 111, 137402 (2013)
- [6] C. Roquelet et al., Appl. Phys. Lett. 97, 141918 (2010)

Single Carbon Nanotube Devices for Integrated Photonics

Yuichiro K. Kato

Institute of Engineering Innovation, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
ykato@sogo.t.u-tokyo.ac.jp

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 integrated photonics.

Here we discuss the use of individual single-walled carbon nanotubes for optical devices that could be integrated in silicon photonics. Their light emission properties can be controlled by coupling to silicon photonic structures such as photonic crystal microcavities [1,2] and microdisk resonators [3]. With the strong absorption polarization at the nanoscale, they allow for unconventional polarization conversion that results in giant circular dichroism [4]. More recently, we have found that excitons can dissociate spontaneously [5], enabling photodetection at low bias voltages. Ultimately, it should be possible to combine these results to achieve generation, manipulation, and detection of photons on a chip.

Work supported by SCOPE, KAKENHI, The Canon Foundation, The Asahi Glass Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The devices were fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

- [1] R. Watahiki, T. Shimada, P. Zhao, S. Chiashi, S. Iwamoto, Y. Arakawa, S. Maruyama, Y. K. Kato, *Appl. Phys. Lett.* **101**, 141124 (2012).
- [2] R. Miura, S. Imamura, R. Ohta, A. Ishii, X. Liu, T. Shimada, S. Iwamoto, Y. Arakawa, Y. K. Kato, submitted.
- [3] S. Imamura, R. Watahiki, R. Miura, T. Shimada, Y. K. Kato, *Appl. Phys. Lett.* **102**, 161102 (2013).
- [4] A. Yokoyama, M. Yoshida, A. Ishii, Y. K. Kato, *Phys. Rev. X* **4**, 011005 (2014).
- [5] Y. Kumamoto, M. Yoshida, A. Yokoyama, T. Shimada, Y. K. Kato, *Phys. Rev. Lett.*, **112**, 117401 (2014).

Poster Session 5

D1

Tuning the Threshold Voltage of Carbon Nanotube Transistors by n-Type Molecular Doping for Robust and Flexible Complementary Circuits

Huilang Wang, Peng Wei, Zhenan Bao

Department of Materials Science and Engineering, Stanford, Palo Alto, California, United States

Department of Chemical Engineering, Stanford, Palo Alto, California, United States

whl0903@stanford.edu

Tuning threshold voltage of a transistor is crucial for realizing robust digital circuits. For Silicon transistors, the threshold voltage can be accurately controlled by doping, mainly through ion implantation. However, it remains challenging to tune the threshold voltage of single-wall nanotube (SWNT) thin-film transistors (TFTs). In this work, we report a method to controllably n-dope SWNTs using 1H-benzoimidazole derivatives processed via either vacuum evaporation or solution coating.^[1] The threshold voltages of our polythiophene-sorted SWNTs TFTs can be continuously tuned over a wide range. Photoelectron spectroscopy (PES) measurements confirmed that the SWNT Fermi energy decreased with increased doping concentration. Utilizing this approach, we proceeded to fabricate SWNT complementary inverters by inkjet printing of the dopants. We observed an unprecedented high noise margin of 28V at VDD = 80V (70% of 1/2VDD) and a gain of 85. Additionally, equally robust SWNT CMOS inverters (noise margin 72% of 1/2VDD), NAND and NOR logic gates with rail-to-rail output voltage swing and sub-nanowatts power consumption were fabricated onto a highly flexible substrate for the first time.

[1] H. Wang, et al., PNAS, 2014, Accepted

D2

Novel hierarchical nanostructure based on nitrogen doped carbon nanotubes and maghemite for electrochemical water oxidation

Tiva Sharifi, Hans-Martin Berends, Johannes Messinger, Thomas Wagberg

Physics, Umea University, Umea, vasterbotten, Sweden
Chemistry, Umea University, Umea, Vasterbotten, Sweden
Physics, Umea University, Umea, vasterbotten, Sweden
tiva.sharifi@physics.umu.se

We have developed a new type of nanostructured anode material and studied its performance for catalyzing the oxygen evolving half reaction (OER) associated with electrolysis of water. The hybrid material, comprising a hierarchical iron oxide/nitrogen doped carbon nanotube structure, was used as a direct electrode for electrochemical water splitting without any further modification. The electrode is prepared in a bottom up process by CVD growth of NCNTs on the fibers of a conductive carbon paper, followed by a hydrothermal growth of iron hydroxide nanorods on the surface of the nitrogen doped carbon nanotubes (NCNTs). The iron hydroxide nanorods are then transformed to maghemite. The resulting hierarchical nanostructure exhibit large surface area, and ideal attachment of maghemite nanorods to NCNTs which are further well attached to the carbon paper. The hybrid electrode demonstrates very good electrochemical water oxidation activities in 0.1 M KOH. For a current density of 1 mA cm⁻² (geometric surface) an overpotential of only 392 mV is needed. By combining electrochemical water oxidation with isotope ratio mass spectrometry we show that only water is oxidized.

High Bias Characteristics of Individual, Suspended Carbon Nanotube p-n Junction Photodiodes

Shun-Wen Chang, Kevin Bergemann, Rohan Dhall, Jeramy Zimmerman, Stephen Forrest, Stephen Cronin

Physics, University of Southern California, Los Angeles, CA, United States

Physics, University of Michigan, Ann Arbor, MI, United States

Electrical Engineering, University of Southern California, Los Angeles, CA, United States

Physics, Colorado School of Mines, Golden, CO, United States

Electrical Engineering, Physics, Materials Science & Engineering, University of Michigan, Ann Arbor, MI, United States

Electrical Engineering, Chemistry, University of Southern California, Los Angeles, CA, United States

shunwenc@usc.edu

We have recently investigated p-n junction diodes formed by electrostatic doping of individual, suspended, single-walled carbon nanotubes (CNTs) using two gate electrodes positioned beneath a free standing nanotube that bridges source and drain electrodes. The electrostatic field imposed by the two gates polarizes the nanotube along its length, thereby allowing independent control of the "doping" in the nanotube without introducing impurities or defect states. These pn-devices exhibit rectifying diode behavior and finite photoresponse under illumination. Several interesting phenomena are observed at high bias that arise from Schottky contacts formed between the nanotube and its metal contact electrodes and electron tunneling between the n- and p-doped regions. A model is developed explaining this behavior showing evidence for plasmon-induced band gap shrinkage with electrostatic doping.

Giant Circular Dichroism in Individual Carbon Nanotubes Induced by Extrinsic Chirality

A. Yokoyama, M. Yoshida, A. Ishii, and Y. K. Kato

Institute of Engineering Innovation, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
ykato@sogo.t.u-tokyo.ac.jp

We report on the observation of giant circular dichroism in individual single-walled carbon nanotubes induced by extrinsic chirality [1]. The nanotubes are suspended over trenches on Si substrates, and helicity dependent absorption is detected through photoluminescence collected using a home-built microspectroscopy system [2]. The degree of polarization reaches a value as high as 65%, an unforeseen level of circular dichroism for single nanomaterials in the absence of magnetic fields. We find that the signal has a large dependence on the incidence angle, consistent with extrinsic chirality induced effects in which symmetry is broken by the optical wave vector. We propose that field-induced charge distribution on the substrate results in an efficient polarization conversion, giving rise to the giant dichroism. Our results highlight the possibility of polarization manipulation at the nanoscale for applications in integrated photonics and novel metamaterial designs. For example, by integrating individual nanotubes into silicon photonics [3], it should be possible to use the dichroism for polarization conversion on a chip.

Work supported by SCOPE, KAKENHI, The Canon Foundation, The Asahi Glass Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The devices were fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

[1] A. Yokoyama, M. Yoshida, A. Ishii, Y. K. Kato, *Phys. Rev. X* 4, 011005 (2014).

[2] R. Watahiki, T. Shimada, P. Zhao, S. Chiashi, S. Iwamoto, Y. Arakawa, S. Maruyama, Y. K. Kato, *Appl. Phys. Lett.* 101, 141124 (2012).

[3] S. Imamura, R. Watahiki, R. Miura, T. Shimada, Y. K. Kato, *Appl. Phys. Lett.* 102, 161102 (2013).

Large thermoelectric power of highly concentrated semiconducting single-wall carbon nanotube film

Yusuke Nakai, Kazuya Honda, Kazuhiro Yanagi, Hiromichi Kataura, Teppei Kato, Takahiro Yamamoto, Yutaka Maniwa

Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, Japan
Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
Department of Electrical Engineering, Tokyo University of Science, Katsushika, Tokyo, Japan
Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, Japan
nakai@tmu.ac.jp

High-performance flexible thermoelectric devices are highly needed. From a thermoelectric engineering standpoint, single-wall carbon nanotubes (SWCNTs) possess many desirable properties. In this work, we report our study on the thermoelectric properties of SWCNT films with different semiconducting/metallic ratios, combined with first-principles transport simulations.

We found a giant Seebeck effect in highly concentrated semiconducting SWCNT films, which shows a comparable to that of commercial Bi₂Te₃ alloys. Carrier doping on semiconducting SWCNT films leads to further improvement of the thermoelectric performance. These results are well reproduced by first-principles transport simulations based on a simple SWCNT junction model. The present study clarified that thermally resistive junctions play an important role in the giant Seebeck effect of semiconducting SWCNT films. Because major advantages of SWCNTs as a thermoelectric material is their printability and flexibility, these findings represent a major advance in the realization of emerging printed flexible thermoelectric devices. [1]

[1] Y. Nakai, K. Honda, K. Yanagi, H. Kataura, T. Kato, T. Yamamoto, and Y. Maniwa, Appl. Phys. Express 7, 025103 (2014).

Macroscale Superlubricity in Centimeters Long Perfect Double-walled Carbon Nanotubes under Ambient Conditions

Rufan Zhang, Zhiyuan Ning, Yingying Ning, Quanshui Zheng, Qing Chen, Huanhuan Xie, Qiang Zhang, Weizhong Qian, Fei Wei

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, Beijing, China
Key Laboratory for the Physics & Chemistry of Nanodevices, Peking, Beijing, Beijing, China
Center for Nano and Micro Mechanics, Tsinghua University, Beijing, Beijing, China
Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, Beijing, China
zhangrufan4201@163.com

Friction and wear are two main causes for mechanical energy dissipation and component failure, especially in micro/nano-mechanical systems with large surface-to-volume ratio. The past decade has witnessed increasing research interest in superlubricity, a phenomenon where the friction almost vanishes between two incommensurate solid surfaces, which is also called structural superlubricity. However, all experimental structural superlubricity was obtained on micro/nano-scale and mostly under high vacuum. Multi-walled carbon nanotubes (MWCNTs), composed of coaxial cylindrical graphene layers with a high aspect-ratio, are ideal candidates to study superlubricity. The MWCNT shells can slide or rotate with respect to each other. Due to the difficulty in nano-manipulation, there are only a few experimental reports on the sliding or rotational behavior of MWCNT shells in the past two decades. The measured intershell friction was much higher than the theoretical values due to the presence of defects or deformations in MWCNTs. Besides, the manipulation of individual CNTs is also a challenge because of their nanosized diameters.

Here we show that macroscale superlubricity can be realized in centimeters long double-walled carbon nanotubes (DWCNTs) under ambient conditions. Centimeters long inner shells could be continuously pulled out from DWCNTs. The intershell friction was lower than 1 nN and independent of the DWCNT length. The shear strength of the DWCNTs is only several Pascals, four orders of magnitude lower than the lowest reported value. The perfect structure of the ultralong DWCNTs used in our experiments is essential to the macroscale superlubricity. The macroscale superlubricity in DWCNTs can be understood in view of the absence of either defects or large axial curvatures in the as-employed DWCNTs and the length-independent variation of the vdW interaction between CNT shells during the pull-out process. The observation of superlubricity in ultralong DWCNTs is a promising result for many practical applications, such as ultrasensitive sensors, fine positioning devices, gyroscopes, fast switches and more.

Hierarchical Nanostructured Carbon/Sulfur Hybrid Cathode for High-Performance Lithium-Sulfur Battery

Hong-Jie Peng, Jia-Qi Huang, Meng-Qiang Zhao, Qiang Zhang, Xin-Bing Cheng, Xin-Yan Liu, Fei Wei

Department of Chemical Engineering, Tsinghua University, Beijing, Beijing, China
phj13@mails.tsinghua.edu.cn

Among various energy storage/conversion systems, lithium-sulfur batteries are considered as one of the most promising candidate due to not only very high theoretical energy density of 2600 Wh kg⁻¹ (based on lithium-sulfur redox couple) and wide operating temperature range benefiting from its unique multiple-electron-transfer chemistry, but also abundant reserves and environmental friendliness of sulfur. However, several intrinsic obstacles should be overcome for its applicably extension, including the ultra-low electrical conductivity of sulfur and its lithiated products, huge volumetric changes during charge and discharge, and the shuttling mechanism of soluble intermediate polysulfides.

Here, a hierarchical nanostructured carbon/sulfur hybrid in which the porous carbon was in situ integrated into graphene/single-walled carbon nanotube (SWCNT) hybrid matrix with small cyclo-S₈ molecule clusters was fabricated as advanced cathode material for lithium-sulfur battery application. The sp² graphene/SWCNT hybrid interlinked framework was served as robust conductive scaffold with good electrical conductivity and structure stability, while the micro-/mesoporous carbon accommodated sulfur and lithium polysulfides, provided accessibility for liquid electrolyte to active material, and suppress the shuttle behavior due to the spacial confinement. Therefore, such hierarchical all-carbon nanostructure hybridized with small cyclo-S₈ molecule clusters obtained an excellent electrochemical performance including an ultrahigh specific capacity of 1121 mAh g⁻¹ at 0.5 C, a favorable high-rate capability of 809 mAh g⁻¹ at 10 C, a very low capacity decay of 0.12 % per cycle, and an impressive cycling stability of 877 mAh g⁻¹ after 150 cycles at 1 C. As sulfur loading increasing from 50 wt % to 77 wt %, high capacities of 970, 914, and 613 mAh g⁻¹ were still available at current densities of 0.5, 1, and 5 C respectively. Even after 300 cycles at 1 C, reversible capacity of over 600 mAh g⁻¹ was achieved. Based on the total mass of packaged devices, gravimetric energy density of GSH@APC-S//Li cell was expected to be 400 Wh kg⁻¹ at a power density of 10000 W kg⁻¹, matching the level of engine driven systems. Such novel hierarchical nanostructured carbon will shed a light on advanced energy storage systems such as supercapacitors, lithium-air battery, and sodium-ion battery.

Single-Walled Carbon Nanotube Networks for Ethanol Vapor Sensing Application

Albert Nasibulin, Ilya Anoshkin, Prasantha Mudimela, Maoshuai He, Vladimir Ermolov, Oleg Tolochko, Esko Kauppinen

Dept. Applied Physics, Aalto University, Espoo, Uusimaa, Finland

Nokia Research Center,, Nokia, Espoo, Uusimaa, Finland

Institute of Materials and Technologies, Saint-Petersburg Polytechnic State University, Saint-Petersburg, Russia, Russian Federation

Dept. Applied Physics, Aalto University, Espoo, Uusimaa, Finland

albert.nasibulin@aalto.fi

Networks of pristine high quality single walled carbon nanotubes (SWNTs), the SWNTs after Ar-plasma treatment (from 2 to 12 min) and carbon nanobuds (CNBs) have been tested for ethanol vapor sensing. It was found that the pristine high quality SWNTs do not exhibit any ethanol sensitivity, while the defect introduction in the tubes results in the appearance of the ethanol sensitivity. The CNB network showed the ethanol sensitivity without plasma treatment. Both CNB and low defective (after 3 min treatment) SWNT networks exhibit significant drift in the resistance baseline, while heavily plasma-treated (9 min) SWNTs exhibited high ethanol vapor sensitivity without the baseline change. The mechanisms of the ethanol sensitivity and stability after the plasma irradiation are attributed to the formation of sensitive dangling bonds in the SWNTs and formation of defect channels facilitating an access of the ethanol vapor to all parts of the bundled nanotubes.

Carbon nanotube graphene hybrid film and its thermionic emission

Xiaoyang Lin, Feng Zhu, Peng Liu, Yang Wei, Qunqing Li, Jiaping Wang, Yang Wu, Chen Feng, Lina Zhang, Shoushan Fan

Department of Physics and Tsinghua–Foxconn Nanotechnology Research Center, Tsinghua University, Beijing, Beijing, China

pengliu@mail.tsinghua.edu.cn

We have fabricated an ultra-thin freestanding carbon nanotube/graphene hybrid film^[1]. Such a square-centimetre-sized hybrid film can realize the overlaying of large-area single-layer chemical vapour deposition graphene on to a porous vein-like carbon nanotube network. The vein–membrane-like hybrid film, with graphene suspended on the carbon nanotube meshes, possesses excellent mechanical performance, optical transparency and good electrical conductivity. The ultra-thin hybrid film features an electron transparency close to 90%, which makes it an ideal gate electrode in vacuum electronics and a highperformance sample support in transmission electron microscopy.

The pore size of the CNT film can be decreased by increasing the number of the layers^[2]. With smaller pore size, the graphene on CNT film can be Joule heated to a temperature as high as 1,800 K in vacuum without any change in the graphene structure. We have studied the thermionic emission of the graphene and derived the work function of graphene, ranging from 4.7 to 4.8 eV with the average value being 4.74 eV. Because the substrate influence can be minimized by virtue of the porous nature of the CNT film and the influence of adsorbents can be excluded due to the high temperature during the thermionic emission, the measured work function of graphene can be regarded as intrinsic.

[1]. Lin, X.Y.; Liu, P.; Wei, Y.; Li, Q.Q.; Wang, J.P.; Wu, Y.; Feng, C.; Zhang, L.N.; Fan, S.S.; Jiang, K.L., Development of an ultra-thin film comprised of a graphene membrane and carbon nanotube vein support. *Nature Communications*, 2013, 4, 3920.

[2]. Zhu, F.; Lin, X.Y.; Liu, P.; Jiang, K.L.; Wei, Y.; Wu, Y.; Wang, J.P.; Fan, S.S., Heating graphene to incandescence and the measurement of its work function by thermionic emission method. *Nano Research*, 2014, DOI. 10.1007/s12274-014-0423-1.

Robust Transistor of Single Wall Carbon Nanotube in a Network Structure, Rubber Materials and Gel

Atsuko Sekiguchi, Fumiaki Tanaka, Takeo Yamada, Kenji Hata

Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
atsuko-sekiguchi@aist.go.jp

Ambient and wearable electronics have received increasing attention for realizing a safe, secure and comfortable smart community, requiring the devices that possess a similar feelings and comparable robustness to clothes. We developed the transistor from all soft organic materials, such as single wall carbon nanotube (SWNT) in a network structure, rubber materials and gel so that all components integrally stretch and absorb applied loadings and impact. The transistor is the side-gated transistor of SWNT channel, ion-gel gate dielectric, and the conductive SWNT rubber electrodes. The transfer characteristic of the side-gated transistor shows that the transistor operates at low voltage and shows high ON/OFF current ratio of 10^4 . We evaluated robustness and stretchability of the transistor systematically by measuring the transistor performance before and after various loadings such as press, bending, stretching and twisting. Our results indicate that the transistor really combines stretchability and robustness comparable to clothes.

Waveguide-integrated light-emitting carbon nanotubes

Ralph Krupke

*Karlsruhe Institute of Technology, Institute of Nanotechnology, Karlsruhe, Baden-Württemberg,
Germany*

krupke@kit.edu

Carbon nanotubes can be envisioned as wave-guide 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 nanotubes across CMOS compatible waveguide structures and to enforce efficient coupling of light from the nanotube into the waveguide. We will show how light from an electrically-driven carbon nanotube 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 show that the spectral properties of the emitter can be controlled directly on chip with passive devices using Mach-Zehnder interferometers and grating structures. 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.

[1] S. Khasminskaya, F. Pyatkov, B. S. Flavel, W. H. P. Pernice, R. Krupke, *Advanced Materials* (2014) in press

High uniformity networks of individual SWCNTs for thin film transistors from a novel floating catalyst reactor

Antti Kaskela, Kimmo Mustonen, Patrik Laiho, Albert G. Nasibulin, Yutaka Ohno, Esko I. Kauppinen

Department of Applied Physics, Aalto University School of Science, Espoo, Southern Finland, Finland

Department of Quantum Engineering, Nagoya University, Nagoya, Aichi, Japan
Department of Applied Physics, Aalto University School of Science, Espoo, Southern Finland, Finland

antti.kaskela@aalto.fi

Single-walled carbon nanotube (SWCNT) networks have a significant potential for the future electronics, both as transparent and flexible conductive electrodes ^[1] and as thin film transistors (TFT) ^[2,3]. Controlled fabrication of reproducible and uniform SWCNT networks, with appropriate density, high individual tube fraction and controlled tube diameter and length is especially important for realisation of SWCNT-TFT based integrated circuits.

Here, we report our recent progress in developing controlled synthesis of SWCNTs by a novel type of floating catalyst reactor. Iron catalyst particles are created by physical evaporation of iron targets by an electric spark discharge. Concentration of catalyst particles can be controlled by adjusting the discharge energy and thus the concentration of SWCNTs grown in the gas phase can be controlled precisely. This allows us to reduce bundling of the SWCNTs in the gas phase, leading to SWCNT networks consisting mainly of individual tubes after membrane filtration at the reactor outlet.

In addition to high individual fraction, these SWCNT networks exhibit small mean tube diameter of 1.1 nm and mean length of 3-4 μm . To estimate the uniformity of the networks, we fabricated SWCNT-TFT arrays on Si-substrates, based on filter dissolution transfer technique ^[2]. With optimal network density, the SWCNT TFTs exhibit excellent characteristics with high charge carrier mobility of $\sim 100 \text{ cm}^2/\text{Vs}$ and high ON/OFF-ratio 1E^5 - 1E^7 . The SWCNT networks were found to be uniform over the 1cm^2 area of the test arrays, consisting of several hundred individual devices. All the tested devices with $100\mu\text{m} \times 100\mu\text{m}$ channel dimensions exhibited similar TFT-characteristics. We have also fabricated network devices with very small mean SWCNT diameter of 0.86 nm. These devices fabricated at lower reactor temperature have smaller mean SWCNT length and charge carrier mobility, but exhibit excellent uniformity and small ON-current spread.

[1] A. Kaskela, A. G. Nasibulin, M. Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov, and E. I. Kauppinen, "Aerosol-Synthesized SWCNT Networks with Tunable Conductivity and Transparency by a Dry Transfer Technique," *Nano Lett.*, vol. 10, no. 11, pp. 4349–4355, Nov. 2010.

- [2] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, "Flexible high-performance carbon nanotube integrated circuits," pp. 1–6, Feb. 2011.
- [3] D.-M. Sun, M. Y. Timmermans, A. Kaskela, A. G. Nasibulin, S. Kishimoto, T. Mizutani, E. I. Kauppinen, and Y. Ohno, "Mouldable all-carbon integrated circuits," *Nature Communications*, vol. 4, Aug. 2013.

Thin film electronics based on direct deposition of aerosol-synthesized SWCNTs

Patrik Laiho, Antti Kaskela, Kimmo Mustonen, Albert G. Nasibulin, Esko I. Kauppinen

Department of Applied Physics, Aalto University School of Science, Espoo, Southern Finland, Finland

patrik.laiho@aalto.fi

High purity single-walled carbon nanotubes (SWCNTs) can be synthesized using a floating-catalyst method^[1]. SWCNTs synthesized in this manner can be further fabricated into thin films using a variety of methods, such as membrane filtration and subsequent transfer of the film from the filter onto a substrate by pressing or dissolving the filter, and by aerosol sampling techniques such as electrostatic and thermal precipitation^[2].

Here, we report our recent progress in developing improved dry, single-step and direct deposition methods for aerosol-synthesized SWCNTs. We have designed and built new plate-to-plate thermal and electrostatic precipitators that can be used to efficiently deposit thin films of SWCNTs on a variety of substrates. These methods preserve the high quality of aerosol-synthesized SWCNTs, which give them excellent performance as transparent conducting electrodes^[3] and thin film transistors^[4,5]. Additionally, direct deposition is compatible with a wide range of substrates, doesn't require the use of special filters and eliminates substrate and SWCNT exposure to potentially harmful chemicals. The deposition method and parameters are shown to have a significant effect on the resulting SWCNT network morphology and resulting electrical properties.

[1] A. Moisala, A.G. Nasibulin, D.P. Brown, H. Jiang, L. Khriachtchev, and E.I. Kauppinen, "Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor," *Chemical Engineering Science* vol. 61, pp. 4393-4402, July 2006

[2] M.Y. Timmermans, D. Estrada, A.G. Nasibulin, J.D. Wood, A. Behnam, D-M. Sun, Y. Ohno, J.W. Lyding, A. Hassanien, E. Pop, and E.I. Kauppinen, "Effect of carbon nanotube network morphology on thin film transistor performance," *Nano Research* vol. 5, pp. 307-319, May 2012

[3] A. Kaskela, A. G. Nasibulin, M. Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov, and E. I. Kauppinen, "Aerosol-Synthesized SWCNT Networks with Tunable Conductivity and Transparency by a Dry Transfer Technique," *Nano Lett.*, vol. 10, no. 11, pp. 4349–4355, Nov. 2010.

[4] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, "Flexible high-performance carbon nanotube integrated circuits," pp. 1–6, Feb. 2011.

[5] D.-M. Sun, M. Y. Timmermans, A. Kaskela, A. G. Nasibulin, S. Kishimoto, T. Mizutani, E. I. Kauppinen, and Y. Ohno, "Mouldable all-carbon integrated circuits," *Nature Communications*, vol. 4, Aug. 2013.

Carbon nanotubes network for 10^8 on/off ratio field effect transistors

Vladimir Derenskyi, Widianta Gomulya, Jorge Mario Salazar Rios, Sybille Allard, Satria Zulkarnaen Bisri, Ullrich Scherf, Maria Antonietta Loi

Physics Department, Zernike Institute for Advanced Materials, University of Groningen, Groningen, Groningen, Netherlands

Chemistry Department and Institute for Polymer Technology, Wuppertal University, Wuppertal, Wuppertal, Germany

Physics Department, Zernike Institute for Advanced Materials, University of Groningen, Groningen, Groningen, Netherlands

Chemistry Department and Institute for Polymer Technology, Wuppertal University, Wuppertal, Wuppertal, Germany

Physics Department, Zernike Institute for Advanced Materials, University of Groningen, Groningen, Groningen, Netherlands

v.derenskyi@rug.nl

Carbon nanotubes networks in field-effect transistors (FETs) generally show limited performances with on/off ratio much inferior (10^5) respect to the one of single strand nanotube transistors (10^8). Here we report the fabrication of FETs utilizing semi-aligned networks of polymer wrapped semiconducting carbon nanotube as active layer. Semiconducting SWNTs were selected by polymer wrapping using poly-9,9-di-n-dodecyl-fluorenyl-2,7-diyl (PF12) and poly(3-dodecylthiophene-2,5-diyl) (P3DDT), and are aligned on a SiO₂ surface by Blade coating. Field effect transistors fabricated in this way show carrier mobility ranging from 0.42 cm²/Vs to 3.71 cm²/Vs and record high on/off ratio of 10^8 . FETs based on PF12-wrapped SWNT shows almost symmetric ambipolar characteristic, while devices fabricated with P3DDT-wrapped SWNTs display significantly lower electron current. This results evidence that the wrapping polymer has influence not only on the quality of SWNTs dispersion, but also on the device performance. Finally, we demonstrate the importance of controlling the wrapping polymer concentration as it has significant influence on the transport characteristics.

Characterization of Dye-Sensitized Solar Cells with Counter Electrode made of Single-Walled Carbon Nanotubes

Takaaki Chiba, Shintaro Asai, Kehang Cui, Shohei Chiashi, Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

chiba@photon.t.u-tokyo.ac.jp

Dye-sensitized solar cells (DSSCs) have attracted much attention as alternatives to conventional Si-based solar cells because of the potential low cost bulk production. Platinum, however, which is used as counter electrodes of DSSCs, is known to be the highly demanded rare metal. It is also corrosive to iodine electrolyte and hence limits the kind of electrolyte. Hence, nano carbon materials such as carbon nanotubes or graphene can be good candidates for counter electrodes ^[1]. Here, we used the vertically aligned single-walled carbon nanotube (VA-SWNT) ^[2] and metal/semiconductor separated buckypapers as counter electrodes. In addition to the J-V characteristics, impedance technique and electrochemical measurement are employed. The result shows that the charge transfer resistance between VA-SWNT and iodine electrolyte is higher than that between Pt and electrolyte and therefore VA-SWNT has lower catalytic activity to iodine electrolyte. And it is also shown that there is a possibility to improve the catalytic activity by separating semi conducting and metal SWNTs.

[1] L. Kavan, J. Yum, M. Grätzel, *Nano Lett.*, 11, (2011), 5501.

[2] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, *Chem. Phys. Lett.*, 385, (2004), 298.

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MICROFLUIDIC DEVICE WITH CARBON NANOTUBE CHANNEL WALLS FOR BLOOD PLASMA EXTRACTION

Yin-Ting Yeh, Nestor Perea-Lopez, Archi Dasgupta, Ramdane Harouaka, Mauricio Terrones, Siyang Zheng

Biomedical Engineering, The Pennsylvania State University, University Park, PA, United States

Physics, The Pennsylvania State University, University Park, PA, United States

Chemistry, The Pennsylvania State University, University Park, PA, United States

yxy155@psu.edu

The human plasma biomarker analysis is promised to be a revolution for disease diagnosis and therapeutic monitoring. However, blood plasma is a complicated body fluid. For targeted plasma biomarker detection or untargeted plasma biomarker discovery, the challenges can be as difficult as identifying a needle in a haystack. Plasma extract from whole blood is the first step for plasma biomarker analysis. We report a new microfluidic device with channel walls made of nitrogen-doped carbon nanotubes (CNxCNT) as a point-of-care device to continuously extract plasma from human whole blood. The cross flow microfiltration principle is applied in this plasma extraction device. The blood sample is transported within the double spiral channels. The plasma diffuses through the porous CNxCNT wall into the spiral plasma channel while blood cells continue to flow inside the spiral blood sample channel.

Highly Conductive CNT Thin Films for Organic Solar Cells

Amélie CATHELIN, Aminy Ostfeld, Kathleen Ligsay, Kee-Chan Kim, Siân Fogden, Graham McFarlane, Ana Arias

Linde Nanomaterials, Linde, San Marcos, CA, United States
EECS, University of California, Berkeley, Berkeley, CA, United States
amelie.catheline@linde.com

Current transparent electrodes in electronic devices are made of indium tin oxide (ITO). Although it has the best electrical properties required for electronic applications, several drawbacks, such as its cost, its brittleness, have to be overcome to comply with the next generation of organic electronic devices. In this context, carbon nanotubes (CNTs) have been under investigation for several years, due to their excellent electrical and mechanical properties, to replace the ITO electrodes.

Using high quality CNT inks, transparent and highly conductive films have been made to prepare solar cells. CNT inks have been prepared by liquid ammonia reduction in order to fully individualize the CNTs without damaging them^[1], as it is commonly done by usual dispersion techniques, such as functionalization, ultrasonication and/or ultracentrifugation. This method allows to keep long CNTs in solution with excellent electrical properties.

This work is focused on organic solar cells on glass and on flexible substrates to study the CNT properties and to compare their efficiency to ITO. Spray-coated transparent and conductive films of SWNT ink prepared by reductive dissolution show higher conductive performances than films made of SWNT aqueous dispersion and a better uniformity than spin-coated TCFs. Integration of those TCFs into solar cells show comparable power efficiency than ITO solar cells. Moreover, CNT networks can be used to prepare flexible electrodes, thus new solar cell designs can be envisioned. We show that the performance of a SWNT-based solar cell, in absolute terms and in comparison to an ITO-based control device, depends not only on the quality of the SWNT transparent electrode itself but also on the active layer material and processing.

[1] S. Fogden, C. Howard, R. Heenan, N. Skipper, M. Shaffer, ACS Nano, 2012, 6(1), pp54-62, Scalable method for the reductive dissolution, purification, and separation of single-walled carbon nanotube.

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SWNT Transparent Conductive Thin Films from SEERe-Nanotubide Inks

Siân Fogden, Amélie Catheline, Ce Ma, Kee-Chan Kim, Kathleen Ligsay, Graham McFarlane

Linde Nanomaterials, Linde, San Marcos, California, United States

sian.fogden@linde.com

Linde Nanomaterials has developed a revolutionary new single walled carbon nanotube ink. Known as SEERe- Ink, it can be used to make ‘best in class’ transparent conductive thin films suited to a wide application spectrum including solar cells, touch screens, displays, electrochromic windows and thin-film transistors. The possible applications for SEERe- Ink also extends beyond the TCF market - the potential for further SWNT functionalisation open the way possible applications to include sensors, composites and within the healthcare sector.

Using reduction dissolution technology to produce nanotubide inks, Linde Nanomaterials has been able to produce TCFs which exceed the resistivity and transparency requirements commonly quoted in the literature as 100 ohms/sq at 90% transparency without affecting the other critical properties such as haze, environment stability, flexibility, hardness, adhesion and of course, cost.

This reductive dissolution technology begins by reducing SWNTs in liquid ammonia followed by dissolution in a polar aprotic organic solvent without the need for additional sonication. This mild dissolution technique results in solutions of long, undamaged, individualized SWNTs which can be deposited using spin or spray coating to make TCFs. This technique directly addresses the critical SWNT conductivity scaling factors of purity, length and bundle size to produce commercially viable TCFs.

Carbon nanotube sponge as electrochemical capacitor electrodes capturing any capacitive particles

Kei Hasegawa, Richardo Quintero, Misato Narubayashi, Suguru Noda

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo, Japan
Department of Chemical System Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
k_hasegawa@aoni.waseda.jp

Carbon nanotubes (CNTs) have been extensively studied as a promising material for next-generation electric storage devices such as electrochemical capacitors, lithium ion batteries, and metal-air batteries. We have systematically studied the millimeter-scale growth of single-wall CNTs (SWCNTs) by chemical vapor deposition (CVD) on substrates ^[1] and realized the semi-continuous scalable synthesis of few-wall CNTs (FWCNTs) by fluidized bed CVD (FB-CVD) ^[2]. Sponge-like matrices of long SW/FWCNTs, which can be easily made by their dispersion and filtration, are attractive because of their high conductivity, specific surface area, and their small pores (several tens nm) capturing active particles with good electrical contacts. In this work, we target at electrochemical capacitors, which have the highest power density among the electric storage devices and thus need high electric conductivity for electrodes. We demonstrate the simple fabrication of hybrid electrodes with activated carbon (AC) and manganese dioxide (MnO₂) captured in CNT sponges for electrochemical capacitors with enhanced energy and power densities.

First we investigated the effect of individual and matrix structures of CNTs on the electrochemical property. 50- μm -tall vertically aligned SWCNTs (VA-SWCNTs) were grown by CVD using C₂H₂ ^[1] for 1 min and transferred to porous polymer membrane. Self-supporting 40- μm -thick random network films of SWCNTs and FWCNTs were prepared by filtrating the dispersions of SWCNTs by on-substrate growth ^[1] and FWCNTs by FB-CVD ^[2]. Electrochemical performance was measured by cyclic voltammetry with a 3-electrode cell in 1 M Na₂SO₄ aq. All CNT electrodes showed a constant specific capacitances from 5 to 1000 mV/s scan rates (equal to 0.8 s charge-discharge), showing that these three electrodes have sufficiently high electric conductivities.

Next we fabricated and evaluated the hybrid electrodes. Self-supporting AC-FWCNT hybrid films were fabricated by mixing AC and FWCNTs at a 9:1 weight ratio, dispersing them in ethanol, and filtrating the dispersion. Even with a contact only at one edge of the film, it kept a specific capacitance of 132 F/g at a high scan rate of 100 mV/s in a 1 M H₂SO₄ aq. 10 wt% FWCNTs hold and make 90 wt% AC conductive, making it possible to eliminate the capacity-less metal current correctors and insulating polymer binders ^[3]. Self-supporting MnO₂-FWCNT hybrid films were fabricated by electrodepositing MnO₂ in FWCNT matrices. By carefully adjusting the over-potential, sub- μm -sized MnO₂ particles were uniformly formed whole over the FWCNT sponge, yielding a high specific capacitance \sim 200 F/g at 2 mV/s and in a 0.5-1.0 M Na₂SO₄ aq. Any capacitive particles will be captured within CNT matrices.

Acknowledgements: We thank Profs. A. Yamada and Y. Yamada for their support on AC-CNT hybrids and Profs. T. Osaka and T. Momma for their support on MnO₂-CNT hybrids. This work is partially supported by Kakenhi #25249111 from JSPS and ALCA from JST, Japan.

[1] K. Hasegawa and S. Noda, ACS Nano 5, 975 (2011).

[2] D. Y. Kim et al., Carbon 49, 1972 (2011).

[3] R. Quintero et al., RSC Adv. 4, 8230 (2014).

Thermoacoustic Chips with Carbon Nanotube Thin Yarn Arrays

Yang Wei, Xiaoyang Lin, Kaili Jiang, Peng Liu, Qunqing Li, Shoushan Fan

Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing, Beijing, China

WeiYang@tsinghua.edu.cn

Aligned carbon nanotube (CNT) films drawn from CNT arrays have shown the potential as thermoacoustic loudspeakers. CNT thermoacoustic chips with robust structures are proposed to promote the applications. The silicon-based chips can play sound and fascinating rhythms by feeding alternating currents and audio signal to the suspending CNT thin yarn arrays across grooves in them. In addition to the thin yarns, experiments further revealed more essential elements of the chips, the groove depth and the interdigital electrodes. The sound pressure depends on the depth of the grooves, and the thermal wavelength can be introduced to define the influence-free depth. The interdigital fingers can effectively reduce the driving voltage, making the chips safe and easy to use. The chips were successfully assembled into earphones and have been working stably for about one year. The thermoacoustic chips can find many applications in consumer electronics and possibly improve the audiovisual experience.

[1] Y. Wei, X.Y. Lin, K.L. Jiang, P. Liu, Q.Q. Li, and S.S. Fan, *Nano Lett.* 13 (2013) 4795-4801.

Sub-10 μm top-gate carbon nanotube thin-film transistors based on high-speed flexographic printing process

Michihiko Maeda, Kentaro Higuchi, Shigeru Kishimoto, Takuya Tomura, Masafumi Takesue, Katsuhiko Hata, Yutaka Ohno

Quantum Engineering, Nagoya University, Nagoya, Aichi, Japan
Research and Development Center, Bando Chemical Industries, LTD., Kobe, Hyogo, Japan
maeda.michihiko@b.mbox.nagoya-u.ac.jp

Among various thin film transistors (TFTs), carbon nanotube (CNT) TFTs have advantages such as high mobility, flexibility, transparency, printability, and so on. In the previous work, we developed a fully-lithography free and non-vacuum process to fabricate CNT TFTs based on flexographic printing technique, one of high speed printing methods, and achieved a high mobility of $157 \text{ cm}^2/\text{Vs}$.^[1]

In this work, we have improved the resolution of the printing technique for miniaturizing printed CNT TFTs. Flexographic plates were fabricated by using micro-fabrication process. High-purity semiconductor CNTs were used for the channel. Top-gate CNT TFTs with a channel length of $\sim 7 \mu\text{m}$ was fabricated. The devices showed an on/off ratio of 103 and a mobility of $3.7 \text{ cm}^2/\text{Vs}$. This work was partially supported by ALCA-JST, SICORP-JST, and Grant-in-Aid of MEXT.

[1] K. Higuchi et al., Appl. Phys. Express 6, 085101 (2013).

Light emission and detection with carbon nanotubes

Lian-Mao Peng

Department of Electronics, Peking University, Beijing, Beijing, China

lm peng@pku.edu.cn

Carbon nanotubes (CNTs) are direct band gap materials that are not only useful for nanoelectronic applications, but also have the potential to make significant impact on the developments of nanoscale optoelectronic devices. In particular CNTs have been investigated for various electronic and optoelectronic device applications, such as light-emitting diodes ^[1,2], photodetectors and photovoltaic (PV) cells ^[3,4]. Semiconducting single-wall CNTs (SWCNTs) are direct-gap materials that can efficiently absorb and emit light. The unique band structure of SWCNT suggests that multiple subbands absorptions can contribute to optoelectric properties. By combining sufficient nanotubes with different diameters, it was also demonstrated that it is possible to gain a nearly continuous absorption response within a broad spectral range (from UV to infrared) to match the solar spectrum ^[5]. In addition, extremely efficient carrier multiplication (CM) effect has been observed ^[6], which may potentially lead to a higher energy conversion efficiency than that defined by the Shockley-Queisser limit. More recently, efficient photovoltage multiplication was also realized via introducing virtual contacts in CNTs, making the output photovoltage of CNT based solar cells a tunable quantity via choosing the diameter of the tube and the number of virtual contacts introduced in the device ^[7], making it possible for developing optoelectronic communications between nanoelectronic circuits and high performance infrared photodetectors ^[8-10].

References

- [1] Mueller T, M. Kinoshita M, M. Steiner M, V. Perebeinos V, Bol AA, Farmer DB and Avouris P (2010), *Nature Nanotech*, 5:27-31.
- [2] Wang S, Zheng QS, Yang LJ, Zhang ZY, Wang ZX, Pei T, Ding L, Liang XL, Gao M, Li Y and Peng LM (2011), *Nano Lett.*, 11: 23.
- [3] Lee JU, Gipp PP and Heller CM (2004), *Appl. Phys. Lett.*, 85:145.
- [4] Wang S, Zhang LH, Zhang ZY, Ding L, Zeng QS, Wang ZX, Liang XL, Gao M, Shen J, Xu HL, Chen Q, Cui RL, Li Y and Peng LM (2009), *J. Phys. Chem. C*, 113(17): 6892.
- [5] Lehman J, Sanders A, Hanssen L, Wilthan B, Zeng J and Jensen C (2010), *Nano Lett.*, 10, 3261.
- [6] Gabor, N.M., Zhong, Z.H., Bosnick, K., Park, J. & McEuen, P.L. (2010), *Science* 325, 1367.
- [7] Yang LJ, Wang S, Zeng QS, Zhang ZY, Pei T, Li Y and Peng LM (2011), *Nature Photonics*, 5:672.
- [8] Zeng Q.S., Wang S., Yang L.J., Wang Z.X., Pei T., Zhang, Z.Y., Peng L.-M., Zhou W.W., Liu J., Zhou W.Y. and Xie S.S. (2012), *Optical Materials Express* 2(6): 839
- [9] Yang L.J., Wang, S., Zeng, Q.S., Zhang, Z.Y. and Peng, L.-M. (2013) 8:1225.
- [10] Yu, D.M., Wang, S., Ye, L.H., Zhang, Z.Y., Chen, Y.B., Zhang J. and Peng L.-M. (2014) *Small* 10:1050.

Carbon Nanotube Thin Film Transistors for Printed Electronics

Kimmo Ojanperä, Antti Kaskela, Ari Alastalo, Yutaka Ohno, Esko Kauppinen

*Printed and hybrid functionalities, VTT TECHNICAL RESEARCH CENTRE OF FINLAND ,
Helsinki, Helsinki, Finland*

Department of Applied Physics, Aalto University, School of Science, Helsinki, Helsinki, Finland

*Printed and hybrid functionalities, VTT TECHNICAL RESEARCH CENTRE OF FINLAND ,
Helsinki, Helsinki, Finland*

Department of Quantum Engineering, Nagoya University, Nagoya, Nagoya, Japan

Department of Applied Physics, Aalto University, School of Science, Helsinki, Helsinki, Finland

kimmo.ojanpera@gmail.com

We present single-walled carbon-nanotube (SWCNT) thin-film transistors (TFT) fabricated on a plastic substrate using a hybrid manufacturing method. The device structure is a bottom-gate top-contact (BGTC) configuration. The SWCNT networks for the TFT channels were collected onto nitrocellulose membrane filters directly from a floating catalyst-CVD reactor ^[1]. SWCNT networks were transferred onto plastic PEN substrates, by dissolving the membrane filter by acetone ^[2]. Before the transfer process, the gate electrodes were shadow-evaporated and polyimide dielectric layer was ink-jet printed on the substrate. The source and drain electrodes were shadow-evaporated on top of the percolating SWCNT network. Finally, another layer of polyimide was ink-jet printed on top of the channel to function as a mask for O₂ plasma etching that removed the SWCNTs outside the channel area.

The TFTs were characterized by transfer and output curve measurements using a Keithley 4200 semiconductor characterization system in ambient conditions. The TFTs had parallel plate mobilities on the order of 8 cm²/Vs and on/off-ratios over 10⁵, with the measurement voltage ranging from -20 V to +20 V. The demonstrated process can be used to fabricate, for example, backplane circuits of flexible displays.

[1] Sun, D.-m., M.Y. Timmermans, Y. Tian, A.G. Nasibulin, E.I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, *Nature Nanotech.*, 2011. 6(3): p. 156-161.

[2] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, "Flexible high-performance carbon nanotube integrated circuits," pp. 1–6, Feb. 2011.

Using Nanotube Transistors for Single-Molecule Studies of DNA Polymerase I

O. Tolga Gul, Yongki Choi, Kaitlin Pugliese, Brad L. Corso, Gregory A. Weiss, Philip G. Collins

Physics and Astronomy, University of California, Irvine, Irvine, CA, United States

Chemistry, University of California, Irvine, Irvine, CA, United States

ostogu@gmail.com

DNA polymerases are critical enzymes for DNA replication, and because of their complex catalytic cycle they are excellent targets for investigation by single-molecule experimental techniques. Recently, we studied the Klenow fragment (KF) of DNA polymerase I using a label-free, electronic technique involving single KF molecules attached to carbon nanotube transistors^[1]. The nanotube sensitivity allowed a single KF molecule to be monitored over long durations as it processed thousands of template strands. Processivity of up to 42 nucleotide bases was directly observed, and statistical analysis of the recordings determined key kinetic parameters for the enzyme's open and closed conformations. Subsequently, we have used the same technique to compare the incorporation of canonical nucleotides to analogs like α -thio-dNTPs, 2-thio-dTTP or dCTP, and 6-chloro-dGTP. The analogs had almost no effect on the closed conformation, during which the nucleotide is incorporated. Instead the entire effect of the analogs was during the open conformation. The thiolated and chlorinated analogs appear to interfere with KF's recognition and binding, two key steps that determine its ensemble turnover rate.

[1] T. J. Olsen, et. al., JACS 135, 7855 (2013).

LCNDs : Photonic Functionalization of MWCNT Towards Light Conversion Nanostructured Devices

Elaine Cavalcanti Rodrigues Vaz, Audrey Nunes de Andrade, Janaína Versiani dos Anjos, Yadira I. Vega-Cantú, Ferrnando J. Rodríguez-Macías, Oscar Manoel Loureiro Malta, Petrus Santa Cruz

Department of Fundamental Chemistry, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil
elaine@inct-inami.com.br

As described by Lehn ^[1], light conversion molecular devices (LCMD) are based on the property named “antenna effect”, that summarizes the sequence of events involving selective absorption (by a ligand as antenna), energy transfer and emission (by a central lanthanide ion). Highly sensitive photonic nanodevices based on this process have been developed in our group ^[2]. In this work, carbon nanotubes were covalently functionalized by a reaction with 4-azidobenzoic acid and then complexed with Eu³⁺ salts under microwave irradiation. FT-IR and UV-vis confirmed the formation of the complexes and SEM showed that this procedure can decorate the CNT with a layer of crystalline fluorescent complexes, resulting in a highly efficient photonic CNT-Eu hybrid system we named light conversion nanostructured device (LCND). This device presents a better quantum efficiency than the non-hybrid ones.

[1] Lehn, J. M.; *Angew. Chem., Int. Ed.* 1990, 29, 1304;

[2] de Sá, G.F. et al.; *Coord.Chem. Rev.* 2000, 196, 165;

Thermoelectric devices based on sandwiched carbon nanotube forests and the effect of contact electrodes

Harrison D. E. Fan, Amir H. Khoshaman, Andrew T. Koch, Alireza Nojeh

Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada

harrison@ece.ubc.ca

Multi-walled carbon nanotube forests were grown by atmospheric-pressure chemical vapor deposition onto silicon substrates and incorporated as one of the materials in thermoelectric energy generators. In order to more carefully study the thermoelectric behavior of carbon nanotubes, the forests were transferred onto copper substrates. The first method to transfer the millimeter-long forests onto copper involved depositing the thin film catalyst directly onto copper and subsequently growing the forest directly over the top surface. The second method involved physically detaching the forest from its silicon substrate with the tip of sharp tweezers. In a symmetric copper-nanotube-copper configuration measured at temperatures between 300-380 K, this device exhibited a Seebeck coefficient of 16-20 $\mu\text{V}/\text{K}$. In comparison, our previous measurements on a symmetric silicon-nanotube-silicon device produced a coefficient as high as 132 $\mu\text{V}/\text{K}$ in a similar temperature range. The order of magnitude decrease was attributed to the absolute Seebeck coefficient of copper being much smaller than that of silicon.

Application of Nanoparticle Antioxidants to Enable Hyperstable Chloroplasts for Solar Energy Harvesting

Ardemis Anoush Boghossian, Fatih Sen, Brenna Marie Gibbons, Selda Sen, Sean Mitchell Faltermeier, Juan Pablo Giraldo, Cathy Zhang, Jingqing Zhang, Daniel Heller, Michael Strano

Chemical Engineering, California Institute of Technology, Pasadena, CA, United States

Biochemistry, Dumlupınar University, Kütahya, Kütahya, Turkey

Materials Science and Engineering, Stanford University, Stanford, CA, United States

Chemistry, Middle East Technical University, Ankara, Ankara, Turkey

Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Physics, Harvard University, Cambridge, MA, United States

Molecular Pharmacology & Chemistry Program, Memorial Sloan-Kettering Cancer Center, New York, New York, United States

arde@caltech.edu

The chloroplast contains densely stacked arrays of light-harvesting proteins that harness solar energy with theoretical maximum glucose conversion efficiencies approaching 12%. Few studies have explored isolated chloroplasts as a renewable, abundant, and low cost source for solar energy harvesting. One impediment is that photoactive proteins within the chloroplast become photodamaged due to reactive oxygen species (ROS) generation. In vivo, chloroplasts reduce photodegradation by applying a self-repair cycle that dynamically replaces photodamaged components; outside the cell, ROS-induced photodegradation contributes to limited chloroplast stability. The incorporation of chloroplasts into synthetic, light-harvesting devices will require regenerative ROS scavenging mechanisms to prolong photoactivity. Herein, we study ROS generation within isolated chloroplasts extracted from *Spinacia oleracea* directly interfaced with nanoparticle antioxidants, including dextran-wrapped nanoceria (dNC) previously demonstrated as a potent ROS scavenger. We quantitatively examine the effect of dNC, along with cerium ions, fullereneol, and DNA-wrapped single-walled carbon nanotubes (SWCNTs), on the ROS generation of isolated chloroplasts using the oxidative dyes, 2',7'-dichlorodihydrofluorescein diacetate (H2DCF-DA) and 2,3-bis(2-methoxy-4-nitro-5-sulphophenyl)-2H-tetrazolium-5-carboxanilide sodium salt (XTT). Electrochemical measurements confirm that chloroplasts processed from free solution can generate power under illumination. We find dNC to be the most effective of these agents for decreasing oxidizing species and superoxide concentrations whilst preserving chloroplast photoactivity at concentrations below 5 μ M, offering a promising mechanism for maintaining regenerative chloroplast photoactivity for light-harvesting applications.

Boghossian*, A.A.; Sen*, F.; Gibbons, B.M.; Sen, S.; Faltermeier, S.M.; Giraldo, J.P.; Zhang, C.T.; Zhang, J.; Heller, D.A.; Strano, M.S. Application of Nanoparticle Antioxidants to Enable Hyperstable Chloroplasts for Solar Energy Harvesting. *Advanced Energy Materials* 3, 881-893 (2013).

Poster Session 6

G1

Growth of Half-Meter Long Carbon Nanotubes Based on Schulz-Flory Distribution

Rufan Zhang, Yingying Zhang, Huanhuan Xie, Qiang Zhang, Weizhong Qian, Fei Wei

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing, Beijing, China
Center for Nano and Micro Mechanics, Tsinghua University, Beijing, Beijing, China
wf-dce@mail.tsinghua.edu.cn

The Schulz-Flory distribution is a mathematical function that describes the relative ratios of polymers of different length after a polymerization process, based on their relative probabilities of occurrence. Carbon nanotubes (CNTs) are big carbon molecules which have very high length-to-diameter ratio, somewhat similar to polymer molecules. CNTs are one of the strongest materials ever known. The extraordinary mechanical properties of CNTs renders them promising candidates for superstrong fibers, ballistic armors, and even space elevators. Mass production of CNTs with macroscopical length is the first step to realize their application. Gas-flow-directed chemical vapor deposition on silicon substrates is the most effective method to prepare ultralong CNTs, and significant progress has been made in the synthesis of ultralong CNTs. However, the reported longest CNTs was only 20 cm and the number density of ultralong CNTs is usually lower than several CNTs per 100 μm . Besides, it remains a question why their number density decreases so rapidly and how to synthesize meter-long CNTs. Here, we report that the Schulz-Flory distribution can be applied to describe the relative ratios of CNTs of different length produced with a floating chemical vapor deposition process, based on catalyst activity/deactivation probability. With the optimized processing parameters, we successfully synthesized 550-mm-long CNTs, for which the catalyst deactivation probability of single growth step was ultralow. The as-grown CNTs have perfect structures and extraordinary mechanical properties. They even exhibit superlubricity between their intershells. Our finding bridges the Schulz-Flory distribution and the synthesis of one-dimensional nanomaterials for the first time, and sheds new light on the rational design of process toward controlled production of nanotubes/nanowires.

References:

- [1]. R. F. Zhang, Q. Wen, W. Z. Qian, D. S. Su, Q. Zhang and F. Wei, *Adv. Mater.*, 2011, 23, 3387-3391.
- [2]. R. Zhang, Y. Zhang, Q. Zhang, H. Xie, W. Qian and F. Wei, *ACS Nano*, 2013, 7, 6156-6161.
- [3]. R. Zhang, Z. Ning, Y. Zhang, Q. Zheng, Q. Chen, H. Xie, Q. Zhang, W. Qian and F. Wei, *Nature Nanotechnology*, 2013.

- [4]. Q. Wen, R. F. Zhang, W. Z. Qian, Y. R. Wang, P. H. Tan, J. Q. Nie and F. Wei, *Chem. Mater.*, 2010, 22, 1294-1296.
- [5]. Q. Wen, W. Qian, J. Nie, A. Cao, G. Ning, Y. Wang, L. Hu, Q. Zhang, J. Huang and F. Wei, *Adv Mater*, 2010, 22, 1867-1871.
- [6]. R. Zhang, H. Xie, Y. Zhang, Q. Zhang, Y. Jin, P. Li, W. Qian and F. Wei, *Carbon*, 2012, 52, 232-238

On the Nitrogen Doping Mechanism in Small Diameter Single Walled Carbon Nanotubes; Impact on Electronic Properties and Growth Selectivity

HamidReza BarzegarGoltapehei, Eduardo Gracia-Espino, Tiva Sharifi, Florian Nitze, Thomas Wagberg

Physics, Umea University, Umea, Vasterbotten, Sweden
Department of Chemical and Biological Engineering, Chalmers University of Technology,
Gothenburg, Gothenburg, Sweden
hamid.barzgear@physics.umu.se

Despite numerous studies on nitrogen doped single walled carbon nanotubes (SWCNTs), the structural conformation and stability of nitrogen functionalities in small diameter SWNTs, and their impact on the electronic and mechanical properties of the SWNTs, is incomplete. We report a detailed study on nitrogen doping in SWNTs with diameters in the range of 0.8-1.0 nm. We show that the introduction of nitrogen in the carbon framework significantly alters the stability of certain tubes, opening for the possibility to selectively grow nitrogen doped SWNTs with certain chirality and diameter. At low nitrogen concentration, pyridinic functionalities are readily incorporated and the tubular structure is well pertained. At higher concentrations, pyrrolic functionalities are formed, which leads to significant structural deformation of the nanotubes, and hence a stop in growth of crystalline SWNTs. By correlating the influence of defined nitrogen functionalities on the electronic properties of SWNTs with different chirality we make precise interpretation of experimental Raman data. We show the double resonance G'-peak can be well-correlated to the type of nitrogen doping of SWNTs originating from the p or n-doping nature of the nitrogen incorporation. Our results are supported by experimental and theoretical data.

Loading of Metal Nanoparticle on Oxidation-free Carbon Nanotubes for Fuel Cell Application and their Durability

Tsuyohiko Fujigaya, Berber Reda Mohamed, Akiyo Nagashima, Naotoshi Nakashima

Dept. of Applied Chemistry, Kyushu University, Fukuoka, Fukuoka, Japan
fujigaya-tcm@mail.cstm.kyushu-u.ac.jp

CNT have received a great deal of attention as a supporting material for the electrocatalyst in fuel cell due to their highly graphitized surface. However, in returning to the graphitic structure, CNTs lose the metal loading efficiency compared to carbon black. Generally, CNTs are treated by a harsh oxidative treatment with strong acids, but treatment might weaken their inherent durability. We developed the oxidation-free approach, in which CNT surface was wrapped by polybenzimidazoles (PBI). The wrapped PBI on CNT surface functioned as a binding sites for metal loading and, as the results, uniform platinum nanoparticles were loaded homogeneously on CNT.

Fluidized Bed CVD of Submillimeter-Long Carbon Nanotubes Using an Internal Heat-Exchange Reactor

Zhongming Chen, Kei Hasegawa, Dong Young Kim, Toshio Osawa, Suguru Noda

Department of Chemical System Engineering, School of Engineering, the University of Tokyo, Bunkyo-ku, Tokyo, Japan

Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, Shinjuku-ku, Tokyo, Japan
zhongmingchen86@gmail.com

Low cost production of carbon nanotubes (CNTs) will open many opportunities for the practical applications such as batteries/capacitors. Fluidized bed chemical vapor deposition (FBCVD) has realized mass production of multi-wall CNTs (MWCNTs) at several hundred tons annually per plant, but such CNTs are short, thick, entangled, and thus less conductive. Large-scale, low-cost production of long and thin CNTs are of highly demanded. We previously developed an original FBCVD and realized semi-continuous production of submillimeter-long few-wall CNTs from C_2H_2 at a high yield 70% and short gas residence time ~ 0.3 s^[1]. But the high gas feed causes insufficient heating of the bead bed when scaled up. This time, we designed and developed a new FBCVD reactor having an internal heat-exchange and preheating zone and examined its performance in producing submillimeter - long CNTs using a reactor with three-times enlarged cross sectional area.

All processes for catalyst (re-)deposition, catalyst reduction, CNT growth, CNT separation, and removal of residual carbons were performed in a single fluidized bed reactor. All the gases except for the catalyst vapor were fed to the outer tube, flown down and preheated by the furnace and the hot effluent gas in the inner tube, and then flown into the inner tube through the distributor at the bottom. Catalyst vapors (aluminum-isopropoxide and ferrocene, carried by 4 vol% O_2/Ar at 20 slm) were fed directly to the bed through the catalyst line penetrating the distributor from the bottom. After catalyst deposition for 4 min, the catalyst was reduced by flowing 26 vol% $H_2/0.06$ vol% H_2O/Ar at 9.48 slm for 10 min. CVD was performed by flowing 1.1 vol% $C_2H_2/26$ vol% $H_2/600$ ppmv H_2O/Ar at 9.48 slm for 20 min. CNTs were separated from the beads by vigorously fluidizing the bed by Ar for 10 min. The residual carbon on the beads was removed by flowing 20 vol% O_2/Ar for 5 min. These processes were repeated at 745 C by changing the gas flow.

The bead bed expanded from 3 cm to 12 cm (Fig. 1d) after CVD for 20 min. The CNT yield was increased from 0.25 to 0.82 g/cycle while CNTs retained the submillimeter- long array structure. From the transmission electron microscopy (TEM) analysis, we found that the average diameter of the CNTs is 11 nm. We reduced the total supply of Ar carrier for ferrocene to one fifth and the concentration of C_2H_2 to 0.73 vol%, and realized the diameter reduction to 6.5 nm in average. The FBCVD reactor with the internal heat exchanger will realize further scale-up for practical mass production.

Acknowledgement: Partial support by JST-ALCA & Kakenhi.
[1] D Y Kim, et al., Carbon 49, 1972 (2011).

Corresponding Author: S. Noda
Tel: +81-3-5286-2769, Fax: +81-3-5286-2769, E-mail: noda@waseda.jp

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Quality Control of Electric Arc Single-Walled Carbon Nanotubes

Elena Bekyarova

Carbon Solutions Inc., www.carbonsolution.com, Riverside, CA, United States
bekyarova@carbonsolution.com

Reliable and rapid measurement of the material purity is central to the progress in the bulk production and purification of single-walled carbon nanotube (SWNT) materials. This talk will focus on the application of solution phase near-IR (NIR) spectroscopy for evaluation of carbon nanotube purity, sample preparation and homogenation. Other popular analytical techniques for characterization of SWNT materials, including thermogravimetric analysis (TGA), Raman spectroscopy, SEM and TEM will be discussed. In addition to recent advances in the purification of carbon nanotubes, I will talk about the SWNT thin film technology and its prospects for energy applications and optoelectronic devices.

Fabrication of carbon nanotube nanogap electrodes by helium-ion sputtering for molecular contacts

Cornelius Thiele, Henning Vieker, André Beyer, Benjamin S. Flavel, Frank Hennrich, David Munoz Torres, Thomas R. Eaton, Marcel Mayor, Armin Gölzhäuser, Hilbert v. Löhneysen, Ralph Krupke

Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, BW, Germany

Faculty of Physics, Bielefeld University, Bielefeld, NRW, Germany

Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, BW, Germany

Department of Chemistry, University of Basel, Basel, Basel, Switzerland

Faculty of Physics, Bielefeld University, Bielefeld, NRW, Germany

Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, BW, Germany

Cornelius.Thiele@kit.edu

Carbon nanotube nanogap electrodes have been used as electrodes to contact individual large organic molecules. However, the reliable fabrication of a truly nanometer-sized gap remains a challenge with established techniques^[1,2]. Recently, successful patterning of graphene with a helium ion beam was demonstrated^[3,4]. We now report on using helium ion beam lithography to sputter a nanogap of only (2.8 ± 0.6) nm into single metallic carbon nanotubes embedded in a device geometry. The high reproducibility of the gap size provides us with a reliable nanogap electrode testbed for contacting small organic molecules. To demonstrate its functionality, we present electrical measurements on an oligo(phenylene ethynylene) molecule, a common type of molecular wire.

[1] Guo et al., Science 311 (2006) 356

[2] Marquardt et al., Nat. Nano. 5 (2010) 863

[3] Bell et al., Nanotechnology 20 (2009) 455301

[4] Lemme et al., ACS Nano 3 (2009) 2674

Advances in bottom-up assembly of carbon nanotubes and graphene devices

Antonios Oikonomou, Maria Iliut, Aravind Vijayaraghavan

School of Materials, The University of Manchester, Manchester, Greater Manchester, United Kingdom

maria.iliut@manchester.ac.uk

Over the past few years, we have demonstrated that bottom-up device assembly of nano-carbons using dielectrophoresis (DEP) can achieve ultra-high integration densities, excellent FET device performance and can be combined with sorting to even produce single-chirality SWCNT device arrays. Recently, we have extended the DEP assembly in two main routes.

Firstly, we will present the large-scale assembly of suspended carbon nanotube and graphene devices by bottom-up DEP assembly. Suspended device fabrication is associated with a range of new technological challenges which we have overcome. These devices are ideally suited for sensors and resonator applications.

Secondly, we have succeeded in integrating carbon nanotubes into plasmonic antennae^[1], using DEP to place CNTs into a optical cavity formed by a gold nano-disc dimer. In this cavity, we observe plasmonic enhancement of Raman scattering up to 10^4 times.

Finally, I will also discuss how nitrogen-doped SWCNTs can also be assembled individually into devices using DEP. These results further demonstrates the great versatility of the DEP assembly technique for nano-carbon device fabrication^[3].

References

- [1] Heeg, S.; Oikonomou, A.; Fernandez-Garcia, R.; Lehmann, C.; Maier, S.A.; Vijayaraghavan, A.; Reich, S.; Plasmon-enhanced Raman scattering by carbon nanotubes optically coupled with near-field cavities. *Nano Letters*, 2014, Just accepted manuscript.
- [2] Oikonomou, A.; Susi, T.; Kauppinen, E.; Vijayaraghavan, A.; Growth, dispersion, and electronic devices of nitrogen-doped single-wall carbon nanotubes, *Physica Status Solidi B*, 2012, 249, 2416-2419
- [3] Vijayaraghavan, A.; Bottom-up assembly of nano-carbon devices by dielectrophoresis. *Physica Status Solidi B*, 2013, 250, 2505-2517.

Controlled Growth of Single-Walled Carbon Nanotubes and Application to CNT-Si Solar Cells

Shigeo Maruyama, Kehang Cui, Shohei Chiashi, Albert G. Nasibulin, Esko I. Kauppinen

Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
Department of Applied Physics, Aalto University School of Science, Puumiehenkuja 2, Espoo,

Finland

maruyama@photon.t.u-tokyo.ac.jp

Chemical reaction process in CVD growth of single-walled carbon nanotubes (SWNTs) will be discussed with diameter controlled CVD growth incorporating nitrogen and molecular dynamics simulations. Then, the structure controlled assembly of SWNTs for SWNT-Si heterojunction solar cells will be discussed.

We found the reversible and repeatable modification of diameter of vertical array of SWNTs by adding acetonitrile (AcN) in ethanol (EtOH) as feedstock of CVD ^[1-3]. When the nitrogen (N) is involved, the SWNT mean diameter was dramatically reduced from approximately 2.1 nm to less than 1 nm. Surprisingly, the main nitrogen configuration was found to be encapsulated diatomic N₂ molecules interior of SWNTs with the content of 1 at %. We address that the nitrogen atoms on the surface of the catalyst particle result in a change from the ‘Octopus’ to the ‘VLS’ growth mode predicted by molecular dynamics simulations.

We proposed a water vapor treatment to build up SWNTs to a self-assembled micro-honeycomb network for the application of solar cells ^[4]. The micro-honeycomb network consists of vertical aggregated SWNT walls and a buckypaper bottom. This hierarchical structure is very efficient to collect holes from the interface of Si. The heterojunction solar cell was fabricated by dry depositing the SWNT film to the 3 mm by 3 mm n-type silicon substrate. The pristine SWNT-Si heterojunction solar cell shows a record-high fill factor of 72 % as well as a power conversion efficiency (PCE) of 6 % without tuning the diameter or height of original vertically aligned SWNTs. The PCE remains stable for months in ambient condition. A PCE exceeding 10 % is achieved in the dry state after dilute nitric acid treatment.

On the other hand, heterojunction solar cells using highly transparent-conductive SWNT films from controlled bundle-diameter and long bundle length ^[5] are also promising. Here, SWNTs were synthesized by the thermal decomposition of ferrocene vapor in a carbon monoxide atmosphere, with the average diameter of approx. 2 nm. Our preliminary test result shows the highest PCE of 11 % among such CNT-Si design without chemical doping. These solar cells are stable after 6 months.

References:

[1] T. Thurakitserree, C. Kramberger, P. Zhao, S. Aikawa, S. Harish, S. Chiashi, E. Einarsson, S. Maruyama, Carbon 50 (2012) 2635.

- [2] C. Kramberger, T. Thurakitseree, H. Koh, Y. Izumi, T. Kinoshita, T. Muro, E. Einarsson, S. Maruyama, *Carbon*, 55 (2013) 196.
- [3] T. Thurakitseree, C. Kramberger, A. Kumamoto, S. Chiashi, E. Einarsson, S. Maruyama, *ACS Nano* 7 (2013) 2205.
- [4] K. Cui, T. Chiba, S. Omiya, T. Thurakitseree, P. Zhao, S. Fujii, H. Kataura, E. Einarsson, S. Chiashi, S. Maruyama, *J. Phys. Chem. Lett.*, (2013), 4, 2571.
- [5] A. G. Nasibulin, A. Kaskela, K. Mustonen, A. S. Anisimov, V. Ruiz, S. Kivistö, S. Rackauskas, M. Y. Timmermans, M. Pudas, B. Aitchison, M. Kauppinen, D. P. Brown, O. G. Okhotnikov, E. I. Kauppinen, *ACS Nano*, (2011), 5, 3214.

Automated carbon nanotube synthesis by water-assisted CVD

Pavel Nikolaev, Daylond Hooper, Benji Maruyama

, UES Inc., Dayton, OH, United States

Materials and Manufacturing Directorate, RXAS,, Air Force Research Laboratory, WPAFB, OH,
United States

pavel.nikolaev.ctr@us.af.mil

Among many techniques of carbon nanotube (CNT) synthesis available today, chemical vapor deposition (CVD) is the most popular by far due to low cost, ease of set-up, and wide range of nanotube morphologies that can be produced. The throughput of a typical research CVD system, however, is limited to a few runs per day due to time necessary for heating, conditioning, growing, and cooling steps. This makes it difficult and time-consuming to explore the multi-dimensional experimental parameter space that includes temperature, pressure, feedstock composition; catalyst and catalyst support composition. The Adaptive Rapid Experimentation and in-situ Spectroscopy (ARES) CVD system described in this contribution makes over 100 CVD experiments possible in a single day in fully automatic mode, with pre-programmed growth recipes and without user intervention. CNTs are grown in a miniature cold wall CVD reactor, with the same laser used for both thermal activation of the growth process and Raman excitation. Raman spectra are acquired in real time, enabling in-situ analysis of growth kinetics and nanotube characteristics. Further linear regression modeling allowed mapping regions of selectivity towards SWNT and MWNT growth in the complex parameter space of the water-assisted CVD synthesis. This is the first demonstration of automated experimentation combined with regression analysis applied to the CNT synthesis by CVD. This development of the automated rapid serial experimentation is a significant progress towards an autonomous closed-loop learning system: a Robot Scientist.

Simple and scalable aligned nanotube films

Daniel Tune, Joe Shapter

*Centre for Nanoscale Science & Technology, The Flinders University of South Australia,
Adelaide, SA, Australia*

daniel.tune@flinders.edu.au

The production of conductive and semitransparent thin films is one of the dominant methods of incorporating carbon nanotubes into useful devices and systems. Over the years this has been done primarily by vacuum filtration or spray deposition from very low concentration surfactant-stabilised suspensions. A recent development is the fabrication of thin films in which the nanotubes are highly aligned in one direction parallel with the surface and such films have been shown to exhibit superior properties, resulting in substantially improved devices and systems. Based on earlier work we have developed a simple and scalable process for the deposition of highly aligned nanotube films. These thin films have excellent properties compared to randomly aligned counterparts produced by other methods, with the addition of several potentially useful characteristics not found in non-aligned films.

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Hybrid Carbon Source for Single-Walled Carbon Nanotube Synthesis by Aerosol CVD Method

Ilya V. Anoshkin, Albert G. Nasibulin, Ying Tian, Bilu Liu, Hua Jiang, Esko I. Kauppinen

Department of Applied Physics, Aalto University School of Science, Espoo, Espoo, Finland
ilya.anoshkin@aalto.fi

Fabrication and Characterization of Nitrogen-Induced Single-Walled Carbon Nanotubes Field-Effect Transistors

Sungjin Kim, Theerapol Thurakitserree, Shinya Aikawa, Taiki Inoue, Shohei Chiash, Shigeo Maruyama

Mechanical Engineering, The University of Tokyo, Tokyo, Tokyo, Japan
International Center for Materials Nanoarchitectonics, National Institute for Materials Science ,
Tsukuba, Ibaraki, Japan
Mechanical Engineering, The University of Tokyo, Tokyo, Tokyo, Japan
kimsung69@gmail.com

Carbon nanotube field-effect transistors (CNTFETs) using horizontally aligned single-walled carbon nanotubes is relatively easy with high performance to fabricate devices on desired location and substrate compared with other method.^[1] CNTFETs are also expected to enable fabrication complementary circuits with high performance by control of density or carrier type using several techniques. However, there is a major impediment to the introduction of single-walled carbon nanotubes (SWNTs) to these technologies is the lack of reproducibility in SWNT synthesis and CNT-based device.

In this work, we report the synthesis and fabrication of nitrogen-induced horizontally aligned single-walled carbon nanotubes (N-HASWNTs) FETs. The growth of N-HASWNTs using chemical vapor deposition on an r-cut crystal quartz substrate using ethanol and/or acetonitrile,^[2] followed by peel off and transfer to a target substrate. Although our N-HASWNT FETs show p-type behaviors, the resulting N-HASWNTs have well-controlled density and a unique morphology, consisting of small diameter nanotubes with narrow diameter distribution (for bandgap control). N-HASWNTs can be This FET simultaneously demonstrates a mobility of $1,284 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an $I_{\text{on}}/I_{\text{off}}$ ratio ~ 106 . We also demonstrate flexible FETs using N-HASWNT with high performance.

[1] C. Kocabas, S.-H.Hur, A. Gaur, M. A. Meitl, M. Shim, J. A. Rogers, *Small*, 1, (2005), 1110.

[2] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, *Chem. Phys. Lett.* 360, (2002), 229.

Synthesis of semiconducting single-wall carbon nanotubes by hydrogen etching

Wen-Shan Li, Peng-Xiang Hou, Hong-Tao Cong, Chang Liu, Hui-Ming Cheng

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, Liaoning, China

htcong@imr.ac.cn

The most attractive and important application of single-wall carbon nanotubes (SWCNTs) is to fabricate new generation high-performance electronic devices, such as field effect transistors (FETs), integrated circuit, sensors, etc. However, each of these applications requires a pure and high quality sample that contains only or mostly semiconducting SWCNTs (s-SWCNTs). Although post-synthesis separation and in situ selective oxidation techniques have been developed for the selective preparation, the yield (surface growth), quality (more defects, decreased length), and uniformity of the s-SWCNTs obtained are still very poor.

In this presentation, we report high quality, high concentration s-SWCNTs obtained by in situ selective removal of metallic SWCNTs (m-SWCNTs) via hydrogen etching during a floating catalyst chemical vapor deposition process. We found that hydrogen preferentially reacts with m-SWCNTs in the presence of a highly active floating iron catalyst at a synthesis temperature of 1100 °C, while s-SWCNTs are mostly retained. Compared with previously reported oxidative etchants, hydrogen is much milder and does not cause structural defects in the remaining s-SWCNTs. Under an optimum condition, samples containing ~93% s-SWCNTs were obtained in bulk reproducibly. These s-SWCNTs with good structural integrity showed an oxidation resistance temperature of ~800 °C, the highest value ever reported for SWCNTs. Thin-film transistors using the s-SWCNTs as a channel material showed a high on/off ratio up to 4.0×10^5 and a high carrier mobility of $21.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Biosensors fabricated using these s-SWCNTs demonstrated an ultra-low detection limit of 10-18 mol/L for dopamine detection, which is several orders of magnitude lower than values previously reported. The above results indicate that our high quality s-SWCNTs may find application in high-performance FETs, sensors, and other electronic devices.

Growth of Single-walled Carbon Nanotubes from Opened Edges of Carbon Nanotubes

Shohei Chiashi, Takanori Umino, Taiki Inoue, Shigeo Maruyama

Mechanical Engineering, The University of Tokyo, Bunkyo, Tokyo, Japan
chiashi@photon.t.u-tokyo.ac.jp

Chirality control is one of the important topics in the single-walled carbon nanotube (SWNT) growth research field. Although some studies showed chirality selective growth for specific chirality such as (6, 5), it is still difficult to perform chirality control in growth process. It was reported that the epitaxial growth of SWNTs was one of the possible techniques for chirality controlled synthesis ^[1]. Here, we performed the SWNT growth using the opened edges of SWNTs as the growth template. In advance, horizontally aligned SWNTs (the length was 50 μm) were synthesized on crystal quartz substrates from iron catalyst nano-particles ^[2]. And then horizontally-aligned SWNTs were cut into several shorted SWNTs in length by oxygen plasma etching and SWNTs with opened edges were obtained.

The opened SWNTs were heated in air ambient (at 200 degree C, in 30 min) and water vapor atmosphere (at 400 - 900 degree C). The heating treatments were for the activation of the opened edges ^[1]. And then, CVD was performed by introduction of ethanol vapor at 800 - 900 degree C. In scanning electron microscopy, the epitaxial growth of SWNTs was observed at approximately 2 % SWNT edges. By repeating epitaxial growth CVD, 10% edges showed the epitaxial growth of SWNTs, totally. We will discuss the mechanism and yield of the repetitive epitaxial growth.

[1] J. Liu, et al., Nature Comm., 3 (2012) 1199.

[2] T. Inoue, et al., J. Phys. Chem. C, 117 (2013) 11804.

Synthesis and application of carbon nanocones as CNT substitutes for electron emission and AFM probes

Mathieu Delmas, Thierry Ondarcuhu, Florent Houdellier, Martin Hytch, Aurelien Masseboeuf, Marc Monthieux

Nanomateriaux, Cemes-CNRS, Toulouse, Midi-Pyrenee, France
Nanoscience, Cemes-CNRS, Toulouse, Midi-Pyrenee, France
Nanocaracterisation, Cemes-CNRS, Toulouse, Midi-Pyrenee, France
Nanomateriaux, Cemes-CNRS, Toulouse, Midi-Pyrenee, France
mathieu.delmas@cemes.fr

Carbon nanotubes (CNT) are thought to be an ultimate solution for a variety of applications, including AFM probes and electron emission. But due to various issues related to CNT specificities (e.g. mechanical flexibility, for both the AFM probe and electron emission applications), results are not as good as expected. In this work, we developed a type of objects based on MWCNTs individually coated with pyrolytic carbon, exhibiting unique morphological and textural features.

These morphologically complex carbon objects are produced in a two-step process. The first step requires a catalyst, to grow MWCNTs. During the second step, a multi-texture pyrolytic carbon coating is deposited onto each individual previously-grown MWCNTs. The overall object morphology can be described as a rough-surface microfibre segment ended by a smooth-surface cone at both extremities, with the original CNT protruding at both cone apexes. Hence, the cone apex dimension is equal to that of the supporting MWCNT diameter (few nanometers) whereas the microfibre to which the nanocones are attached allows easy grabbing and handling by micromanipulator tools. The inner structure, texture and nanotexture of the graphenes building the cones were fully described in earlier works ^[1] and make a quite favorable combination for anticipating optimized performances for applications such as AFM probes and electron emitting tips for TEM high performance electron source (cold-FEG).

Using Focused Ion Beam (FIB), one of these carbon-nanocone-bearing objects was mounted onto a regular but trimmed tungsten FEG emission tip used as support, and then was placed into the electron source (cold FEG type) of a TEM (Hitachi F2000). The resulting performances were outstanding ^[2], showing improved – or equivalent, for the least – parameters with respect to the best FEG source currently on the market: the beam brightness was up to five times higher, the beam coherence was significantly improved, the energy dispersion of the electron beam was better than 0.3 eV, and the unprecedented current stability make that daily tip flashing is no longer required. This superiority is explained by the mechanical stability brought by the conical shape which makes that the tip exhibits all the benefits of a regular CNT tip as predicted by de Jonge et al ^[3] without the drawbacks (typically, the tip vibration upon electron emission).

On the other hand, in order to test the performances of the carbon nanocones as AFM probes, several types of substrates were tested, and the results were compared to both the results obtained from usual silicon AFM probes on the one hand, and a variety of commercially available, so-called high resolution (HR) AFM probes (including nanotube-based) on the other hand. The carbon nanocone-based tips prepared at CEMES show good high resolution imaging capabilities, with very few artefacts. They are similar to other HR CNT-based probes regarding the lack of lateral convolution, and compare favorably when imaging close objects, with less sensitivity to water menisci.

For both applications, relatively easy and fast and therefore cost-effective mounting procedures are expected thanks to the unique overall micro/nano morphology, as well superior durability due to the perfection of the graphenes constituting the cones.

[1] Jacobsen R., Monthieux M., Carbon beads with protruding cones, *Nature* 1998 ; 385(6613) p. 211-212; Allouche H., Monthieux M., *Carbon* 2003 41(15) p. 2897-2912; Allouche H., Monthieux M., *Carbon* 2005; 43(6) p. 1265-1278; Monthieux M., Allouche H., Jacobsen R., *Carbon* 2006; 44(15) p. 3183-3194.

[2] Houdellier F., Masseboeuf A., Monthieux M., New carbon cone nanotip for use in a highly coherent cold field emission electron microscope, *Carbon* 2012; 50(5) p.2037-2044.

[3] de Jonge N. Carbon nanotube electron sources for electron microscopes. In "Advances in imaging and electron physics", Elsevier, 2009, vol. 156, p.203–233.

Catalyst control for the selective growth of Semiconductor Single-Walled Carbon Nanotubes

Shunsuke Sakurai, Maho Yamada, Hiroko Nakamura, Don N Futaba, Kenji Hata

*Nanotube Research Center, National Institute of Advanced Industrial Science and Technology,
Tsukuba, Ibaraki, Japan*

shunsuke-sakurai@aist.go.jp

Novel method to synthesize the single-walled carbon nanotube (SWNT) of semiconductor-type is reported. Selective synthesis of semiconductor-SWNT was realized by exposing the iron catalyst into the gas ambient containing small amount of H₂O just before SWNT growth.

Raman spectra (laser wavelength: 532, 633, 780 nm) from the as-grown SWNT films has suggested the preferential growth of semiconducting SWNTs with small diameter of 0.8-1.1 nm range. Importantly, high selectivity was only achieved when the yield of CNT was low, suggesting the selective growth can be achieved by adjusting the catalyst activity. High performance of field-effect transistor (FET) device was performed by using as-grown CNT film as channel of FET, where high on/off ratio (> 10,000) and mobility (c.a. 10 cm²/Vs) at a relatively short channel length (5 μm). These characteristics shows that the approach of selective growth can greatly contribute to the widespread electronics application, such as flexible electronics device. To achieve high growth selectivity, and high performance of FET, fine control on catalyst size distribution, furnace ambient, and gas flow in the heating zone is required. Details are presented in this paper.

In situ observation of carbon nanotube re-growth by scanning electron microscopy

Huafeng Wang, Chisato Yamada, Jia Liu, Bilu Liu, Xiaomin Tu, Ming Zheng, Chongwu Zhou, Yoshikazu Homma

Department of Physics, Tokyo University of Science, Tokyo, Tokyo, Japan

Department of Electrical Engineering and Department of Chemistry, University of Southern California, Los Angeles, California, United States

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Department of Electrical Engineering and Department of Chemistry, University of Southern California, Los Angeles, California, United States

Department of Physics, Tokyo University of Science, Tokyo, Tokyo, Japan

wanghf@rs.tus.ac.jp

Recently, carbon seeds like nano-diamond, fullerene fragments and nanotube segments have been used to synthesize carbon nanotube (CNT) ^[1-5]. This new route may produce high purity nanotube free from metal impurities, which will promote the application of nanotubes. In addition, researches on catalysts free nanotube seeds will contribute to understanding on the growth mechanisms of CNT. It has been demonstrated that cloning growth of CNT from seeds with certain chirality was realized ^[5]. Pretreatment including air oxidation followed by water vapor annealing is proved to be essential. To investigate the process of CNT re-growth so as to better understand it, we conducted re-growth of CNT in the chamber of scanning electron microscope (SEM). Compared with conventional chemical vapor deposition (CVD), the nanotube formation process can be in situ monitored by SEM, which might help to comprehensively evaluate the influence of experimental parameters on its growth.

Since our in situ system is a cold wall CVD, all reaction processes are conducted on the surface of substrate, which is different from conventional hot wall CVD. Therefore, the same condition for conventional CVD cannot be directly used. By varying experimental parameters, the new pretreatment as well as the growth condition suitable for this cold wall system was established, and the re-growth of nanotube from seeds with different chirality in the chamber of SEM was realized. Furthermore, multi-times re-growth of nanotube was also achieved. In situ observation on CNT formation provided a direct evidence for its cloning growth. According to our experimental results, the efficiency of re-growth was closely related with pretreatment conditions and growth parameters, especially the carbon source. We carefully studied the influences of these parameters on the re-growth of CNT. On the basis of these analyses, the growth mechanisms of nanotube synthesized from seed will be discussed.

References

- [1] Takagi, D. et al. J. Am. Chem. Soc. 131, 6922(2009).
- [2] Yu, X. et al. Nano Lett. 10, 3343(2010).

- [3] Ibrahim, I. et al. ACS Nano 6, 10825(2012).
- [4] Yao, Y. et al. Nano Lett. 9, 1673(2009).
- [5] Liu, J. et al. Nat. Commun. 3, 1199(2012).

Corresponding Author: Yoshikazu Homma
Tel: +81-3-5228-8244, Fax: +81-3-5261-1023
E-mail:homma@rs.kagu.tus.ac.jp

Direct Growth of High-Density Carbon Nanotube Arrays on Copper foils toward Thermal Interface Materials

Nuri Na, Kei Hasegawa, Suguru Noda

*Department of Chemical System Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo, Japan*

nanuri@chemsys.t.u-tokyo.ac.jp

CNTs are a candidate for future thermal interface materials (TIMs) owing to their high theoretical thermal conductivity (3000 W/m K) and mechanical flexibility. Among introduced approaches for CNT array TIMs, mounting CNT/metal foil/CNT TIMs on devices has advantages not only in avoiding any damage of electrical devices by high CNT growth temperature but also in applying to many devices conveniently. However, typical CNT arrays grown by conventional chemical vapor deposition (CVD) method have thermal conductivity far below the expected values because of their porous structure (mass density $< 0.1 \text{ g cm}^{-3}$ and porosity $> 90\%$). Previously, targeting at via-interconnects in large-scale integrated circuits (LSIs), we reported sub- μm -tall CNT arrays with a density as high as $\sim 1 \text{ g/cm}^3$, grown by CVD at $400 \text{ }^\circ\text{C}$ with careful control over the nucleation and growth of catalyst particles during sputter deposition ^[2]. In this work, we target at direct growth of such dense CNT arrays with much larger height of several tens μm on both side of copper foils.

To grow CNTs much taller, we elevated CVD temperature from 400 to $700 \text{ }^\circ\text{C}$. At such high temperature, catalyst particles got easily deactivated in the reaction with Cu. Thus we examined diffusion barrier materials used in LSIs. On diffusion barrier preformed on Cu foils, we deposited Ni, Co, and Fe catalysts by sputtering. And then we carried out CVD by feeding $\text{C}_2\text{H}_2/\text{H}_2$ at a rather low C_2H_2 partial pressure of 0.2 Torr , in order to avoid the catalyst deactivation by carbonization ^[3]. We evaluated the height and density of CNTs by scanning electron microscopy (SEM) and weight gain method. We found that Ni and Co catalyst worked well at low temperatures $\sim 400 \text{ }^\circ\text{C}$ whereas Fe worked better in growing CNTs tall at a high temperature of $\sim 700 \text{ }^\circ\text{C}$. Although the mass density of CNT arrays decreased with CVD time and thus their height, a fairly high mass density of 0.22 g cm^{-3} was achieved for a $35\text{-}\mu\text{m}$ -tall CNT array. The $90\text{-}\mu\text{m}$ -thick CNT/Cu/CNT film ($35\text{-}\mu\text{m}$ -tall CNT arrays on both sides of a $20\text{-}\mu\text{m}$ -thick Cu foil) would be attractive for TIM applications. We are now evaluating the thermal conductivity of such films.

Acknowledgement: We thank Huawei Technologies for fruitful discussion.

[1] B.A. Cola, et al., Appl. Phys. Lett. 90, 093513 (2007).

[2] N. Na, et al., NT13, P42 (2013).

[3] K. Hasegawa, et al., Carbon 49 (13), 4497-4504 (2011).

Single-walled carbon nanotube growth from Pt catalysts by cold-wall ACCVD

Takahiro Maruyama, Hiroki Kondo, Yuya Sawaki, Ranajit Ghosh, Shigeya Naritsuka, Toshiya Okazaki, Sumio Iijima

Department of Applied Chemistry, Meijo University, Nagoya, Aichi, Japan
Department of Materials Science and Engineering, Meijo University, Nagoya, Aichi, Japan
Department of Applied Chemistry, Meijo University, Nagoya, Aichi, Japan
Department of Materials Science and Engineering, Meijo University, Nagoya, Aichi, Japan
Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
Faculty of Science and Technology, Meijo University, Nagoya, Aichi, Japan
takamaru@meijo-u.ac.jp

So far, we have reported single-walled carbon nanotube (SWNT) growth from Pt catalysts in the alcohol gas source method ^[1]. In this study, we demonstrated that SWNTs grew from Pt under very low ethanol pressure using a conventional cold-wall type chemical vapor deposition (CVD) system and the diameters and chirality of grown SWNTs were investigated using SEM, TEM, Raman and PL.

SWNT growth was carried out on SiO₂/Si substrates at 400-900°C in a cold-wall type CVD system using Pt as catalysts. When the growth temperature and ethanol gas pressure were 700-900°C and 1-3 Pa, RBM peaks were observed in the Raman spectra, accompanied with the splitting of G band. From SEM images, high-density web-like structures were observed on the substrates. These results indicate that SWNTs grew under low ethanol pressure even in the conventional CVD system, confirming that the high activity of Pt catalysts. We also estimated the chirality of SWNTs from PL and Raman spectra. Our results showed that diameters of most of SWNTs were below 1.3 nm and that the distribution of chirality was fairly narrow, compared to SWNTs grown from transition metal catalysts.

[1] T. Maruyama et al. Mater. Express 1 (2011)267.

Preparation and Properties of PVDF membrane filled with carbon nanotubes

Wenyi Wang, Ningning Gao, Yanling Li, Zhengxin Liu

State Key Laboratory of Hollow Fiber Membrane Materials and Membrane Processing, Tianjin Polytechnic University, Tianjin, Tianjin, China

wenyiw@gmail.com

To investigate the polymer composites with high dielectric constant and excellent electrical conductivity at low filler concentration, we had prepared conductive hybrid ultrafiltration membranes via phase inversion by dispersing carboxyl multi-wall carbon nanotubes (MWCNTs-COOH), ranging from 0 to 10 wt.% in Polyvinylidene Fluoride(PVDF) casting solutions. The membranes had good hydrophilic, high electric conductivity and excellent mechanical properties compared to the pure PVDF film. The electric conductivity and permittivity of pure PVDF film were 10-13 S/cm and 2.8 at 100 HZ respectively, while the values were both increased with the addition of the MWCNTs content, the statistical percolation threshold for PVDF-MWCNTs membranes was found to be 5 wt.%. When at 5 wt.% MWCNTs, the values of electric conductivity and permittivity were 10-4 S/cm and 36.5 at 100 HZ respectively, moreover, the contact angle was reduced to 72.3°(the pure PVDF was 80.3°). The morphology of the film was characterized as individual and dispersed uniformly at low MWCNTs contents, whereas it was networked but also aggregated at high filler contents (≥ 5 wt.%). The mechanical strength of MWCNTs-filled binary films also increased with the increase of MWCNTs content. Our work demonstrated that the MWCNTs played a critical role in determining the structures, morphologies, conductivity and properties of ultrafiltration membranes.

Laser annealing of single-wall carbon nanotubes

Nicolas Souza Carmona, Frank Mücklich, Volker Presser

Materials Science and Engineering, Functional Materials, Saarbruecken, Saarland, Germany
Energy Materials, Leibniz Institute for New Materials, Saarbruecken, Saarland, Germany
n.souza@mx.uni-saarland.de

Most carbon nanotube (CNT) synthesis routes carry defects and impurities which are generally addressed by thermal and/or chemical post treatments. However, chemical purification often incurs in further defects, as do mechanical dispersion methods such as ultrasound. Thermal defect elimination requires atmosphere control and time-consuming temperature ramping.

Contrary to previous studies, laser radiation was found to effectively treat both problems, resulting in high-purity and -crystallinity and low-defect CNTs, with a reduced mean interdefect distance. Even mechanically induced defects could be corrected. Super-fast laser radiation times have a leg up on common oven and chemical treatments. Additionally, selective shape and site-specific parameters come into play such as interference patterns. Such arrangements of alternating tube quality, e.g. in a CNT matt, could be interesting for preferred electronic conduction paths and find applications in, e.g., interdigitated electrodes.

As is paramount to the correct evaluation of any CNT study, the starting material and its production method are presented. Then, a study of the laser power and exposure time is discussed, as characterized by Raman spectroscopy, scanning and transmission electron microscopy and thermo-gravimetric analysis. Results are contrasted with previous studies on the effect of laser radiation on CNTs.

Fabrication of infrared solar cell with controllably carrier doped stable semiconducting single-walled carbon nanotube films

Toshiki Akama, Toshiaki Kato, Yoshihiro Abiko, Rikizo Hatakeyama, Toshiro Kaneko

Department of Electronic Engineering, Tohoku University, Sendai, Miyagi, Japan

akama13@ecei.tohoku.ac.jp

Single-walled carbon nanotubes (SWNTs) are one of the most attractive materials for future high performance solar cells due to their flexible filament-like structures, high carrier mobilities, and tunable bandgap energies by controlling their diameters^[1,2]. Multiple exciton generation (MEG) in SWNTs can also be expected. For the fabrication of solar cell with SWNTs, it is necessary to establish a method for carrier type-, density-, and position-controllable doping into SWNTs. Stability of the doping is also another important issue for the practical use of SWNTs in solar cells. Recently, we have demonstrated the controllable and stable n-type carrier doping into semiconducting SWNTs thin films by position selective Cs encapsulation into SWNTs with a plasma ion irradiation method^[3]. In this study, the optoelectrical transport properties are investigated for the controllably carrier doped stable semiconducting SWNTs films. It is 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. Since pn junctions are formed along the tube axis, carrier loss caused by tube to tube junction can be minimized and high rate power generation can be expected with this pn junction embedded SWNTs solar cells.

[1] R. Hatakeyama, Y. F. Li, T. Y. Kato, and T. Kaneko, *Appl. Phys. Lett.*, 97 (2010) 013104.

[2] Y. F. Li, S. Kodama, T. Kaneko, and R. Hatakeyama, *Appl. Phys. Lett.*, 101 (2012) 083901.

[3] Y. Abiko, T. Kato, R. Hatakeyama, and T. Kaneko, *J. Phys.: Conf. Ser.*, in press.

Transfer of chemical vapour deposition grown carbon nanotubes for interconnect applications

Vimal Chandra Gopee, Owen Thomas, Ravi Silva, Jeremy Allam, Vlad Stolojan, Chris Hunt

*Materials, National Physical Laboratory, Teddington, Middlesex, United Kingdom
Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey, United Kingdom*

*Materials, National Physical Laboratory, Teddington, Middlesex, United Kingdom
v.gopee@surrey.ac.uk*

With the increase in current densities through electronic circuitry brought about by miniaturisation, replacements for traditional materials have to be found due to problems arising with electromigration and thermal coefficient of expansion mismatch. Carbon nanotubes (CNT) show promise as a replacement for traditional interconnect materials, such as copper, because they do not suffer from electromigration below a certain size and due to their superior thermal conductivity properties. A method of transposing arrays of multiwall carbon nanotubes (MWCNTs) from their growth substrates to a target metal substrate is demonstrated. MWCNT arrays, typically 300 μm in length, were produced by a chemical vapour deposition process and were shown by Raman spectroscopy to have relatively few defects. MWCNT arrays treated by oxygen plasma followed by a metallisation step were shown to have good adhesion to Sn33Pb67 solder. This paper discusses the solder-MWCNT-solder interconnects manufacturing process and their subsequent electrical characterisation. Using lithography arrays of 100x100 μm were produced and interconnects with average resistance of 5 Ω were achieved.

Relationship between Fe-Catalyzed Single-Walled Carbon Nanotubes and Fe Catalyst Nanoparticles

Hua Jiang, Antti Kaskela, Kimmo Mustonen, Albert G. Nasibulin, Esko I. Kauppinen

Department of Applied Physics, Aalto University School of Science, Aalto, Espoo, Finland
hua.jiang@aalto.fi

It has been well known that single-walled carbon nanotubes (SWCNTs) nucleate and grow on catalytic nanoparticles and the size and crystal structure of the nanoparticles play a key role in determining the chirality of the produced SWCNTs. However, it is often observed that not all nanoparticles actively catalyze growth of SWCNTs in a chemical vapor deposition (CVD) process though they appear to have similar size and structure as active nanoparticles. In addition, the correlation between the nanotube properties and that of active nanoparticles remain under discussion.

In this contribution, we have performed a comprehensive statistical analysis of morphology, size and chemical compositions of a large number of nanoparticles, including both catalytically active and inactive ones, by means of aberration-corrected high-resolution transmission electron microscopy. SWCNTs were produced by a novel floating-catalyst CVD process with Fe nanoparticles serving as catalysts for CO-disproportionation reaction. It is disclosed that active and inactive nanoparticles show no essential difference in morphology and size distribution. Though the average diameter of active nanoparticles (~3.3 nm) is over three times larger than that of SWCNTs (~1.1 nm), our results have shown that the ratio of a certain SWCNT diameter to that of an active catalyst nanoparticle varies dramatically, ranging from 1:2.2 to 1:4.3. Importantly, we discriminate at least two species of Fe nanoparticles, i.e. oxidized Fe nanoparticles and metallic BCC Fe nanoparticles. It is found that no oxidized Fe nanoparticles, but only BCC Fe nanoparticles are catalytically active for SWCNT growth. Electron diffraction analysis indicates a biased chiral distribution of SWCNTs towards high chiral angles, but no significant preference to a specific chirality is observed.

Synthesis of (6,5) and (6,4) enriched SWNTs by pulse plasma CVD

Bin Xu, Toshiaki Kato, Toshiro Kaneko

Department of Electronic Engineering, Tohoku University, Sendai, Miyagi, Japan
xu12@ecei.tohoku.ac.jp

Single-walled carbon nanotubes (SWNTs) are promising materials in various fields as they have many novel characteristics. Since SWNTs properties strongly depend on the chirality, it is inevitable to realize the chirality-controlled SWNTs synthesis for the fabrication of next-generation high performance electrical devices. In our study, we use parameter-controlled plasma CVD ^[1-3] to synthesize SWNTs and narrow down the chirality-distribution by the introduction of pulse plasma CVD.

In order to realize narrow chirality distribution of SWNTs, we optimize the parameters in two steps. Firstly, we adjust parameters of growth temperature and gas pressure to suppress the growth of large diameter SWNTs. Secondly, we optimize the time sequence of pulse plasma such as “on” and “off” time to increase the selectivity of (6,5) and (6,4) SWNTs. Through the careful optimizations, we have realized highly enriched growth of (6,5) and (6,4) SWNTs. The detailed effects of plasmas on the selective growth of (6,5) and (6,4) SWNTs are also investigated.

[1] Z. Ghorannevis, T. Kato, T. Kaneko, and R. Hatakeyama, *J. Am. Chem. Soc.*, 132 (2010) 9570.

[2] T. Kato and R. Hatakeyama, *ACS Nano*, 4 (2010) 7395.

[3] B. Xu, T. Kato, K. Murakoshi, and T. Kaneko, *Plasma and Fusion Research*, in press.

CaH₂-assisted low temperature synthesis of metallic magnetic nanoparticle-loaded multiwalled carbon nanotubes

Liis Seinberg, Shinpei Yamamoto, Yoji Kobayashi, Mikio Takano, Hiroshi Kageyama
National Institute of Chemical Physics and Biophysics, National Institute of Chemical Physics and Biophysics, Tallinn, Harju maakond, Estonia

Institute for Integrated Cell-Material Sciences, Kyoto University, Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Kansai, Japan

Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto, Kansai, Japan
Institute for Integrated Cell-Material Sciences, Kyoto University, Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Kansai, Japan

Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto, Kansai, Japan
liis.seinberg@kbfi.ee

MWCNTs loaded with metallic Ni and Fe NP can be prepared by pyrolyzing nickel stearate or ferrocene, respectively, under a flow of acetylene at 800 - 1100 °C^[1]. In pyrolysis, metallic nanoparticles (NPs) which act as catalysts are formed in-situ via reduction of metal ions by the decomposed organic ligands upon heating. Thus, the addition of strong reducing agent which enables the formation of metallic NP catalysts at lower temperatures is expected to accomplish CNT formation at lower temperatures. Several reports in solid state chemistry have shown that CaH₂ is a fairly strong reductant for metal oxides at low temperatures (< 300 °C)^[2,3]. Our recent work demonstrated this method can also be applied to reduction of metal organic salts^[8]. Metallic Fe and Ni NPs, which are known to be efficient catalysts for MWCNT formation, can be prepared at temperatures as low as 140 °C simply by reducing the corresponding metal organic salts with CaH₂^[4].

In the current study we have successfully synthesized MWCNTs loaded with Ni or Fe NP by pyrolyzing metal organic salt with CaH₂. The use of CaH₂ enables formation of MWCNTs at 400 °C without using toxic halogen-containing precursors and assistance of plasma. This is about half of the lowest reported temperature in the pyrolysis method and among the lowest formation temperature by the typical CVD methods. The dual roles of CaH₂ are considered to be responsible for such extraordinary low formation temperature; formation of metal NPs which act as catalyst at lower temperatures and enhancement of decomposition of the carbon feedstocks. This work clearly demonstrates that CaH₂ opens a way to low temperature synthesis of MWCNTs loaded with a variety of metal NP able to catalyze CNT growth.

[1] F. Geng, et al, J. Mater. Chem 2005, 15, 844

[2] M. A. Hayward, et al, Science, 2002, 295, 1882; Y. Tsujimoto et al, Nature, 2007, 450, 1062

[3] S. Yamamoto, et al, Chem. Mater., 2011, 23, 1564

[4] L. Seinberg, et al, Chem. Commun., 2012, 48, 8237

Novel 3-dimensional nanocomposite of covalently interconnected multiwalled carbon nanotubes using Silicon as an atomic welder

Lakshmy Pulickal Rajukumar, Manuel Belmonte, Benito Roman, John Edward Slimak, Ana Laura Elías Arriaga, Eduardo Cruz-Silva, Nestor Perea-López, Aaron Morelos-Gómez, Humberto Terrones, Pilar Miranzo, Mauricio Terrones

*Department of Materials Science and Engineering, The Pennsylvania State University,
University Park, PA, United States*

INSTITUTO DE CERAMICA Y VIDRIO, CSIC, Madrid, Madrid, Spain

*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA,
United States*

*Department of Physics and Center for Two Dimensional and Layered Materials, The
Pennsylvania State University, University Park, PA, United States*

Research Center for Exotic Nanocarbons, Shinshu University, Nagano, Nagano, Japan

*Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy,
New York, United States*

INSTITUTO DE CERAMICA Y VIDRIO, CSIC, Madrid, Madrid, Spain

*Department of Physics and Center for Two Dimensional and Layered Materials, The
Pennsylvania State University, University Park, PA, United States*

lzp130@psu.edu

There is a growing interest in synthesizing three-dimensional (3-D) carbon nanotube structures with multi-functional characteristics. Here, we report the fabrication of a novel composite material consisting of 3-D interconnected multi-walled carbon nanotubes (MWNTs) with Silicon Carbide (SiC) nano- and micro-particles. The materials were synthesized by a two-step process involving the chemical coating of MWNTs with Silicon oxide, followed by Spark Plasma Sintering (SPS). SPS enables the use of high temperatures and pressures that are required for the carbothermal reduction of silica and for the densification of the material into a 3-D composite block. Covalent interconnections of MWNTs are facilitated by a carbon diffusion process resulting in silicon carbide formation as silica coated MWNTs are subjected to high temperatures. The presence of SiC in the sintered composite has been confirmed through Raman spectroscopy, which shows the characteristic peak close to 800 cm^{-1} and also Energy Filtered Transmission Electron Microscopy maps. X-ray Diffraction, Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy and High Resolution Transmission Electron Microscopy have also been used to characterize the produced material. Interestingly, the thermal property measurements of the sintered composite reveal a high thermal conductivity value (16.72 W/mK) for the material. From the electrical point of view, a 3-D variable range hopping (VRH) electron hopping was observed in the composite.

From 2D to 1D: Localized Laser-Induced Heating In Carbon Nanomaterials

Mike Chang, Gethin Owen, Alireza Nojeh

Department of Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada

Centre for High-Throughput Phenogenomics, Faculty of Dentistry, University of British Columbia, Vancouver, British Columbia, Canada

Department of Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada

mi.chang@alumni.ubc.ca

Highly localized light-induced heating of carbon nanotube forests (“Heat Trap”) ^[1] is an unusual physical property where the generated heat remains locked in place in this otherwise conducting material. This has many potential applications, such as in solar thermionics and light-activated cathodes for multi-electron beam direct-write lithography ^[2]. Through this effect, temperatures as high as $\sim 2,000\text{K}$ have been observed with a laser intensity of less than 10 W/mm^2 from a visible beam ^[3]. In this work, we study the effect of dimensionality in this phenomenon by using nano carbon of different dimensionalities. Patterned highly ordered pyrolytic graphite was used for comparison with vertically aligned carbon nanotube (VA-CNT) forests. Pseudo-one-dimensional graphene nano-ribbons with widths varying from $\sim 3\text{ }\mu\text{m}$ to $\sim 300\text{ nm}$ were created through focused ion beam patterning on highly ordered pyrolytic graphite (HOPG). VA-CNT forests were synthesized by thermal chemical vapor deposition on Fe/Al₂O₃ thin films on silicon substrates. A focused laser beam was used as the source of irradiation on the specimen at a vacuum level of 10^{-6} Torr. The increase in temperature was observed by monitoring the resulting incandescence and measuring its spectrum using an optical spectrum analyzer. Experiments were also performed on non-patterned HOPG in order to investigate the effect of going from a 2-dimensional to a quasi-1-dimensional system and compare with the behavior in nanotubes.

[1] P. Yaghoobi, M. V. Moghaddam, and A. Nojeh, *Solid State Commun.* 151, 1105 (2011).

[2] M. V. Moghaddam, and A. Nojeh, “Shaped and multiple electron beams from a single thermionic cathode,” 57th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, Nashville TN, USA, 2013.

[3] M. Chang, M. V. Moghaddam, A. Khoshaman, M. S. Ali, M. Dahmardem, K. Takahata, and A. Nojeh, “High Temperature Gradient in a Conductor: Carbon Nanotube Forest Above “Heat-trap” Threshold,” 57th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, Nashville TN, USA, 2013.

Thursday

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Towards large-area monocrystalline graphene: Growth and observations

Young Hee Lee

Department of Physics, SungKyunKwan University, Seoul, Suwon, Korea, Republic Of
leeyoung@skku.edu

Grain boundaries in graphene are formed via the stitching of islands during the initial growth stage, and these boundaries govern transport properties and related device performance. Graphene can be ideally grown from a single nucleation seed, but its growth to large-area graphene can be terminated by several unknown self-limiting growth factors. Another approach is to start with numerous nucleation seeds and allow them to grow and coalesce together to produce large-area graphene. However, graphene grain boundaries (GGBs) are inevitably formed via stitching of graphene flakes, consequently limiting the graphene quality. We will describe several growth factors to achieve monocrystalline graphene growth during CVD. Another issue is how to confirm grain boundary-free large-area graphene in centimetre scales. We will present several methods of identifying monocrystallinity of graphene in large area together with local transport phenomena at the grain boundaries.

Chirality sorting of SWCNTs using gradient elution in gel column chromatography

Hiromichi Kataura, Mayumi Tsuzuki, Takeshi Tanaka

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

h-kataura@aist.go.jp

Because single-wall carbon nanotube (SWCNT) has three different C-C bonds due to its tiny cylindrical structure, to know the precise structure of SWCNT is very important for understanding its physical properties. For this purpose, large scale separation of single-chirality SWCNT is one of the most important research targets, which enables growing a single crystal for X-ray diffraction measurement. Previously, we reported that diameter selective desorption of SWCNTs was possible using different concentration of sodium deoxycholate (DOC) in the gel column chromatography ^[1]. In this work, we have extended this method into mixed surfactant system and tried a gradient elution for DOC concentration using a high performance liquid chromatography (HPLC). In this system, we can get UV-VIS-NIR absorption spectra in situ, which showed clear chirality sorting for HiPco SWCNTs. Because "overloading effect" is not necessary in this method, this is more effective for large scale separation of single-chirality SWCNTs than the multicolumn method that we reported previously ^[2].

This work was partly supported by JSPS KAKENHI No. 25220602.

[1] Huaping Liu et al. J. Phys. Chem. C 114 (2010) 9270.

[2] Huaping Liu et al., Nat. Commun. 2 (2011) 309.

Large thermoelectric power of highly concentrated semiconducting single-wall carbon nanotube film

Yusuke Nakai, Kazuya Honda, Kazuhiro Yanagi, Hiromichi Kataura, Teppei Kato, Takahiro Yamamoto, Yutaka Maniwa

Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, Japan
Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan
Department of Electrical Engineering, Tokyo University of Science, Katsushika, Tokyo, Japan
Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, Japan
nakai@tmu.ac.jp

High-performance flexible thermoelectric devices are highly needed. From a thermoelectric engineering standpoint, single-wall carbon nanotubes (SWCNTs) possess many desirable properties. In this work, we report our study on the thermoelectric properties of SWCNT films with different semiconducting/metallic ratios, combined with first-principles transport simulations.

We found a giant Seebeck effect in highly concentrated semiconducting SWCNT films, which shows a comparable to that of commercial Bi_2Te_3 alloys. Carrier doping on semiconducting SWCNT films leads to further improvement of the thermoelectric performance. These results are well reproduced by first-principles transport simulations based on a simple SWCNT junction model. The present study clarified that thermally resistive junctions play an important role in the giant Seebeck effect of semiconducting SWCNT films. Because major advantages of SWCNTs as a thermoelectric material is their printability and flexibility, these findings represent a major advance in the realization of emerging printed flexible thermoelectric devices. ^[1]

[1] Y. Nakai, K. Honda, K. Yanagi, H. Kataura, T. Kato, T. Yamamoto, and Y. Maniwa, Appl. Phys. Express 7, 025103 (2014).

Controlled Growth of Single-Walled Carbon Nanotubes and Application to CNT-Si Solar Cells

Shigeo Maruyama, Kehang Cui, Shohei Chiashi, Albert G. Nasibulin, Esko I. Kauppinen

*Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, Japan
Department of Applied Physics, Aalto University School of Science, Puumiehenkuja 2, Espoo,
Finland*

maruyama@photon.t.u-tokyo.ac.jp

Chemical reaction process in CVD growth of single-walled carbon nanotubes (SWNTs) will be discussed with diameter controlled CVD growth incorporating nitrogen and molecular dynamics simulations. Then, the structure controlled assembly of SWNTs for SWNT-Si heterojunction solar cells will be discussed.

We found the reversible and repeatable modification of diameter of vertical array of SWNTs by adding acetonitrile (AcN) in ethanol (EtOH) as feedstock of CVD ^[1-3]. When the nitrogen (N) is involved, the SWNT mean diameter was dramatically reduced from approximately 2.1 nm to less than 1 nm. Surprisingly, the main nitrogen configuration was found to be encapsulated diatomic N₂ molecules interior of SWNTs with the content of 1 at %. We address that the nitrogen atoms on the surface of the catalyst particle result in a change from the ‘Octopus’ to the ‘VLS’ growth mode predicted by molecular dynamics simulations.

We proposed a water vapor treatment to build up SWNTs to a self-assembled micro-honeycomb network for the application of solar cells ^[4]. The micro-honeycomb network consists of vertical aggregated SWNT walls and a buckypaper bottom. This hierarchical structure is very efficient to collect holes from the interface of Si. The heterojunction solar cell was fabricated by dry depositing the SWNT film to the 3 mm by 3 mm n-type silicon substrate. The pristine SWNT-Si heterojunction solar cell shows a record-high fill factor of 72 % as well as a power conversion efficiency (PCE) of 6 % without tuning the diameter or height of original vertically aligned SWNTs. The PCE remains stable for months in ambient condition. A PCE exceeding 10 % is achieved in the dry state after dilute nitric acid treatment.

On the other hand, heterojunction solar cells using highly transparent-conductive SWNT films from controlled bundle-diameter and long bundle length ^[5] are also promising. Here, SWNTs were synthesized by the thermal decomposition of ferrocene vapor in a carbon monoxide atmosphere, with the average diameter of approx. 2 nm. Our preliminary test result shows the highest PCE of 11 % among such CNT-Si design without chemical doping. These solar cells are stable after 6 months.

References:

[1] T. Thurakitseree, C. Kramberger, P. Zhao, S. Aikawa, S. Harish, S. Chiashi, E. Einarsson, S. Maruyama, Carbon 50 (2012) 2635.

- [2] C. Kramberger, T. Thurakitseree, H. Koh, Y. Izumi, T. Kinoshita, T. Muro, E. Einarsson, S. Maruyama, *Carbon*, 55 (2013) 196.
- [3] T. Thurakitseree, C. Kramberger, A. Kumamoto, S. Chiashi, E. Einarsson, S. Maruyama, *ACS Nano* 7 (2013) 2205.
- [4] K. Cui, T. Chiba, S. Omiya, T. Thurakitseree, P. Zhao, S. Fujii, H. Kataura, E. Einarsson, S. Chiashi, S. Maruyama, *J. Phys. Chem. Lett.*, (2013), 4, 2571.
- [5] A. G. Nasibulin, A. Kaskela, K. Mustonen, A. S. Anisimov, V. Ruiz, S. Kivistö, S. Rackauskas, M. Y. Timmermans, M. Pudas, B. Aitchison, M. Kauppinen, D. P. Brown, O. G. Okhotnikov, E. I. Kauppinen, *ACS Nano*, (2011), 5, 3214.

Waveguide-integrated light-emitting carbon nanotubes

Ralph Krupke

*Karlsruhe Institute of Technology, Institute of Nanotechnology, Karlsruhe, Baden-Württemberg,
Germany*

krupke@kit.edu

Carbon nanotubes can be envisioned as wave-guide 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 nanotubes across CMOS compatible waveguide structures and to enforce efficient coupling of light from the nanotube into the waveguide. We will show how light from an electrically-driven carbon nanotube 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 show that the spectral properties of the emitter can be controlled directly on chip with passive devices using Mach-Zehnder interferometers and grating structures. 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.

[1] S. Khasminkaya, F. Pyatkov, B. S. Flavel, W. H. P. Pernice, R. Krupke, *Advanced Materials* (2014) in press

Aligning organic dipolar molecules in carbon nanotubes for nonlinear optics

Sofie Cambré, Jochen Campo, Charlie Beirnaert, Christof Verlackt, Wim Wenseleers

Experimental Condensed Matter Physics Laboratory, University of Antwerp, Antwerp, Antwerp, Belgium

sofie.cambre@uantwerp.be

The 1D character of single-walled carbon nanotubes (SWCNT) combined with their mechanical robustness, chemical inertness and wide range of diameters makes them ideal nanocontainers for various molecules. Previously, we have found that the regular, unperturbing coating of bile salt surfactants^[1], used to solubilise the SWCNTs in water, yields extremely narrow spectral linewidths, allowing to resolve the spectroscopic features of empty (pristine) and water-filled (opened) SWCNTs^[2-5], even for the thinnest tubes, where only a single file of water molecules fits inside the nanotube channel. Here, we demonstrate that this enhanced resolution even allows resolving the encapsulation of different organic molecules, through the combined effect on the vibrational and electronic properties of the SWCNTs and the encapsulated molecules, using extensive wavelength-dependent Raman and fluorescence-excitation spectroscopy. In particular I present the encapsulation of elongated dipolar molecules inside the 1D SWCNT channel. While in 3D, Coulomb interactions between such dipolar molecules result in a pairwise anti-parallel alignment, the 1D encapsulation naturally favors a polar head-to-tail alignment of the molecular dipoles, resulting in a cooperative enhancement of directional properties, such as the second-order nonlinear optical (NLO) response. The polar alignment is demonstrated by wavelength-dependent hyper Rayleigh scattering experiments (HRS)^[6-8] (i.e. second harmonic light scattering). The newly synthesized organic nanohybrids possess a giant total dipole moment and NLO response, corresponding to ~70 identically aligned molecules (HRS intensity scaling quadratically with this number). These nanohybrids form solution processible building blocks highly interesting for the development of electro-optic modulators and switches.

References

- [1] W. Wenseleers et al. *Adv. Funct. Mater.* 14, 1105 (2004)
- [2] W. Wenseleers et al. *Adv. Mater.* 19, 2274 (2007)
- [3] S. Cambré et al. *Phys. Rev. Lett.* 104, 207401 (2010)
- [4] S. Cambré et al, *ACS nano* 6, 2649 (2012)
- [5] S. Cambré et al. *Angew. Chem. Int. Ed.* 50, 2764 (2011)
- [6] E. Goovaerts et al. In *Handbook of advanced electronic and photonic Materials and Devices*, Vol.
- [9]: *Nonlinear optical materials*, Academic Press, San Diego, 127-191 (2001)
- [7] J. Campo et al. *Optics Express* 17, 4587 (2009)
- [8] J. Campo et al. *J. Phys. Chem. Lett.* .3, 2248 (2012)

Full-length selective removal of metallic single-walled carbon nanotubes by organic film-assisted electrical breakdown

Keigo Otsuka, Taiki Inoue, Shohei Chiashi, Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, Japan

otsuka@photon.t.u-tokyo.ac.jp

Horizontal arrays of semiconducting (s-) single walled carbon nanotubes (SWNTs) grown on crystal quartz substrates have potential for the use in field effect transistor channels, especially for the SWNT-based large-scale integrated circuits. However metallic (m-) SWNTs simultaneously grown in the SWNT arrays are one of the major obstacles to the realization of high-performance devices. Although many researchers have been tackling on this problem, satisfying the required purity of s-SWNTs and purification scalability is still of great difficulty.

Here we present an organic film-assisted electrical breakdown method, which creates the horizontal arrays of pure s-SWNTs by removing full length of metallic SWNTs. SWNT arrays grown on quartz substrates were transferred onto Si/SiO₂ substrates for control of the electrical conductivity of s-SWNTs. Ti/Pd electrodes were patterned for voltage application on the SWNT arrays in their axial direction, followed by organic film deposition on the SWNT arrays. Performing electrical breakdown on the SWNT arrays embedded in the films resulted in over 100 times as long removal of m-SWNTs as conventional electrical breakdown technique. Remaining s-SWNT arrays after the breakdown can be used for the fabrication of the SWNT-based integrated circuits.

Tuning the Threshold Voltage of Carbon Nanotube Transistors by n-Type Molecular Doping for Robust and Flexible Complementary Circuits

Huiliang Wang, Peng Wei, Zhenan Bao

Department of Materials Science and Engineering, Stanford, Palo Alto, California, United States

Department of Chemical Engineering, Stanford, Palo Alto, California, United States

whl0903@stanford.edu

Tuning threshold voltage of a transistor is crucial for realizing robust digital circuits. For Silicon transistors, the threshold voltage can be accurately controlled by doping, mainly through ion implantation. However, it remains challenging to tune the threshold voltage of single-wall nanotube (SWNT) thin-film transistors (TFTs). In this work, we report a method to controllably n-dope SWNTs using 1H-benzoimidazole derivatives processed via either vacuum evaporation or solution coating.^[1] The threshold voltages of our polythiophene-sorted SWNTs TFTs can be continuously tuned over a wide range. Photoelectron spectroscopy (PES) measurements confirmed that the SWNT Fermi energy decreased with increased doping concentration. Utilizing this approach, we proceeded to fabricate SWNT complementary inverters by inkjet printing of the dopants. We observed an unprecedented high noise margin of 28V at VDD = 80V (70% of 1/2VDD) and a gain of 85. Additionally, equally robust SWNT CMOS inverters (noise margin 72% of 1/2VDD), NAND and NOR logic gates with rail-to-rail output voltage swing and sub-nanowatts power consumption were fabricated onto a highly flexible substrate for the first time.

[1] H. Wang, et al., PNAS, 2014, Accepted

Relationship between Fe-Catalyzed Single-Walled Carbon Nanotubes and Fe Catalyst Nanoparticles

Hua Jiang, Antti Kaskela, Kimmo Mustonen, Albert G. Nasibulin, Esko I. Kauppinen

Department of Applied Physics, Aalto University School of Science, Aalto, Espoo, Finland
hua.jiang@aalto.fi

It has been well known that single-walled carbon nanotubes (SWCNTs) nucleate and grow on catalytic nanoparticles and the size and crystal structure of the nanoparticles play a key role in determining the chirality of the produced SWCNTs. However, it is often observed that not all nanoparticles actively catalyze growth of SWCNTs in a chemical vapor deposition (CVD) process though they appear to have similar size and structure as active nanoparticles. In addition, the correlation between the nanotube properties and that of active nanoparticles remain under discussion.

In this contribution, we have performed a comprehensive statistical analysis of morphology, size and chemical compositions of a large number of nanoparticles, including both catalytically active and inactive ones, by means of aberration-corrected high-resolution transmission electron microscopy. SWCNTs were produced by a novel floating-catalyst CVD process with Fe nanoparticles serving as catalysts for CO-disproportionation reaction. It is disclosed that active and inactive nanoparticles show no essential difference in morphology and size distribution. Though the average diameter of active nanoparticles (~3.3 nm) is over three times larger than that of SWCNTs (~1.1 nm), our results have shown that the ratio of a certain SWCNT diameter to that of an active catalyst nanoparticle varies dramatically, ranging from 1:2.2 to 1:4.3. Importantly, we discriminate at least two species of Fe nanoparticles, i.e. oxidized Fe nanoparticles and metallic BCC Fe nanoparticles. It is found that no oxidized Fe nanoparticles, but only BCC Fe nanoparticles are catalytically active for SWCNT growth. Electron diffraction analysis indicates a biased chiral distribution of SWCNTs towards high chiral angles, but no significant preference to a specific chirality is observed.

Near-band edge optical properties of h-BN: from bulk to nanolayers and nanotubes

Aurélie Pierret, Léonard Schué, Frédéric Fossard, Simona Moldovan, Ovidiu Ersen, François Ducastelle, Julien Barjon, Annick Loiseau

LEM, ONERA-CNRS, Chatillon, France, France
IPCMS, CNRS - Université de Strasbourg, Strasbourg, France, France
LEM, ONERA-CNRS, Chatillon, France, France
GEMAC, Université Versailles St Quentin - CNRS, Versailles, France, France
LEM, ONERA-CNRS, Chatillon, France, France
loiseau@onera.fr

h-BN is a wide band gap semiconductor (6.4 eV), which can be synthesized, as graphite, its carbon analog, as bulk crystallites, nanotubes and layers. These structures meet a growing interest for deep UV LED and graphene engineering. In this talk, we will review the interplay between the structure, defects and luminescence properties of different BN structures and how these properties can be further exploited for their characterization. To this aim, we carry out optical and structural characterizations by combining Photoluminescence (PL), cathodoluminescence (CL) measurements at 4K in the UV range (up to 7eV) using dedicated experimental sets-up^[1, 2] and TEM analyses using HRTEM, diffraction contrast imaging, electron tomography and Energy Loss spectroscopy (EELS).

We first examined properties of high quality single crystals^[3], and have shown that their optical properties are governed, in the energy range 5.5 – 6 eV, by strong excitonic effects^[1, 4], which have been confirmed by reliable theoretical calculations^[5, 6]. Near band edge luminescence consists of two series of lines called S and D^[2, 4]. PLE experiments indicate that binding energy of S excitons is equal to 370 meV, whereas the gap is measured to be equal to 6.4 eV^[7]. Furthermore S excitons are found to be self-trapped, due to a Jahn-Teller effect^[3, 7]. Thanks to the imaging capability of the CL, emission related to D lines, is found to be localized on defects, such as grain boundaries or stacking faults. In defect free areas, D lines completely vanish and S lines only are observed. D/S ratio can therefore be used as a qualification parameter of the defect densities present in the material [1]. This procedure has been applied to understand the first luminescence studies of few layers individual BN flakes obtained by mechanical exfoliation^[1] and has revealed that the luminescence is significantly perturbed by the exfoliation process.

Second, we have studied multi wall nanotubes made of typically 10 to 20 layers^[8]. CL images reveal that the luminescence in the 5.5 – 6eV energy range is strongly inhomogenous and oscillating. Thanks to a deep investigation combining different TEM techniques, we have shown that the tubes display a complex twisted faceted structure and that the twist period is correlated with the luminescence oscillations. Furthermore, we could show that excitons, responsible for the spectacular localization of the luminescence, are trapped to specific defects, twisted along with the faceting structure.

Finally, low-loss EELS providing an alternative approach to the nature of electronic excitations [9], we will show how it is an efficient tool to investigate the local structure and optical properties with an energy resolution below 100meV of different BN layers and nanotubes.

Acknowledgements: The research leading to these results has received funding from the European Union Seventh Framework Programme under grant agreement n°604391 Graphene Flagship. D. Golberg, T. Taniguchi and K. Watanabe from NIMS, Japan, are warmly acknowledged for providing samples (Nanotubes and HPHT single crystals).

- [1] P. Jaffrennou et al., Phys. Rev. B 77 (2008) 235422
- [2] A. Pierret et al., Phys. Rev. B 89 (2014) 035414
- [3] Y. Kubota et al., Science 317, (2007) 932
- [4] K. Watanabe et al., Phys. Rev. B 79 (2009) 193104
- [5] B. Arnaud, et al. Phys. Rev. Lett. 96 (2006) 026402
- [6] C.-H. Park et al., Phys. Rev Lett. 96 126105 (2006).
- [7] L. Museur et al., Phys. Stat. Sol. rrl, 5 (2011) 414
- [8] C. Tang et al., Chem. Commun. 12 (2002) 1290
- [9] R. Arenal et al., Phys. Rev. Lett. 95 (2005) 127601
- [4] M. Kociak, K. Hirahara, K. Suenaga, and S. Iijima, Eur. Phys. J. B 32, 457–469 (2003)

Carbon Nanotube Computer: Transforming Scientific Discoveries into Working Systems

Max Shulaker, Gage Hills, Nishant Patil, Hai Wei, Hong-Yu Chen, H.-S Philip Wong, Subhasish Mitra

Departments of Electrical Engineering and Computer Science, Stanford University, Stanford, CA, United States
maxms@stanford.edu

The miniaturization of electronic devices has been the principal driving force behind the semiconductor industry, and has brought about major improvements in computational power and energy efficiency. Although advances with silicon-based electronics continue to be made, alternative technologies are being explored. Digital circuits based on transistors fabricated from carbon nanotubes (CNTs) have the potential to outperform silicon by improving the energy–delay product, a metric of energy efficiency, by more than an order of magnitude. Hence, CNTs are an exciting complement to existing semiconductor technologies. However, carbon nanotubes (CNTs) are subject to substantial inherent imperfections that pose major obstacles to the design of robust and very large-scale CNFET digital systems:

- It is nearly impossible to guarantee perfect alignment and positioning of all CNTs. This limitation introduces stray conducting paths, resulting in incorrect circuit functionality.
- CNTs can be metallic or semiconducting depending on chirality. Metallic CNTs cause shorts resulting in excessive leakage and incorrect circuit functionality.

A combination of design and processing technique overcomes these challenges by creating robust CNFET digital circuits that are immune to these inherent imperfections. This imperfection-immune design paradigm enables the first experimental demonstration of the carbon nanotube computer, and, more generally, arbitrary digital systems that can be built using CNFETs. The CNT computer is capable of performing multitasking: as a demonstration, we perform counting and integer-sorting simultaneously. In addition, we emulate 20 different instructions from the commercial MIPS instruction set to demonstrate the generality of our CNT computer. This is the most complex carbon-based electronic system yet demonstrated. It is a considerable advance because CNTs are prominent among a variety of emerging technologies that are being considered for the next generation of highly energy-efficient electronic systems.

Excursion and Banquet

Friday

K5

Optical Spectroscopy of Individual Carbon Nanotubes

Feng Wang

*Physics Department, UC Berkeley, Kavli Energy NanoScience Institute at Berkeley Nanoenergy,
Berkeley, CA, United States
fengwang76@berkeley.edu*

Electronic and optical properties of single-walled carbon nanotubes depend sensitively on the nanotube chirality. Single tube spectroscopy provides a powerful tool to probe the chirality-dependent physics in nanotubes. In the talk, I will discuss our recent progress on optical spectroscopy of individual carbon nanotubes. I will describe a high-throughput optical imaging and spectroscopy technique that enables in-situ characterization of single tubes on substrate and in functional devices. I will also show that systematic spectroscopy of individual double-wall nanotubes indicate strong electronic coupling between the inner- and outer-wall tubes that vary strongly with the nanotube chirality.

Flexible Electronics Applications of Carbon Nanotube Thin films

Yutaka Ohno

Department of Quantum Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan
yohno@nuee.nagoya-u.ac.jp

Flexible and stretchable electronics are attracting much attention because of the variety of potential applications from flexible e-papers though wearable healthcare devices. Among various kinds of electronic materials, carbon nanotube thin films have advantages in flexibility, stretchability, and performance because of the excellent electronic and mechanical properties. Low cost manufacturing of flexible devices is also possible with good processability of carbon nanotube films. Their optical transparency is also attractive for transparent electronics applications.

In the presentation, I will talk about recent topics and progresses on flexible electronics based on carbon nanotube thin films, including capacitive touch sensors ^[1], high-mobility carbon nanotube thin-film transistors (TFTs) and integrated circuits (ICs) on a transparent plastic film ^[2], all-carbon ICs demonstrating excellent stretchability and mouldability ^[3], and high-mobility TFTs fabricated with high-speed flexographic printing technique ^[4]. The operation speed of the ICs and doping techniques ^[5,6] will also be discussed.

[1] N. Fukaya et al. (submitted)

[2] D.-M. Sun et al., Nature Nanotech.6, 156 (2011).

[3] D.-M. Sun et al., Nature Commun.4, 2302 (2013).

[4] K. Higuchi et al., Appl. Phys. Express 6, 085101 (2013).

[5] T. Yasunishi et al., phys. stat. sol. (c) 10, 1612 (2013)

[6] T. Yasunishi et al., Jpn. J. Appl. Phys. (2013)

Nucleation of Graphene and its Conversion to Single Walled Carbon Nanotube revealed

Matthieu C Picher, Pin Ann Lin, Jose Sahrma, Perla B Balbuena, Renu Sharma

*Center for Nanoscale Science and Technology, National Institute of Standards and Technology,
Gaithersburg, MD, United States*

*Department of Chemical Engineering, Texas A&M University, College Station, TX, United
States*

*Center for Nanoscale Science and Technology, National Institute of Standards and Technology,
Gaithersburg, MD, United States*

matthieu.picher@nist.gov

During catalytic chemical vapor deposition, the chirality of single wall carbon nanotubes is determined when the growing graphene nucleus wraps around the catalyst and converts into a tubular structure. Elucidating this critical process is required to develop deterministic bottom-up strategies aiming at better chiral distribution control. Direct observations of carbon nanotube growth, and theoretical modeling and simulations of the nucleation have been published but experimental atomic-resolution evidence of single-walled carbon nanotube nucleation has, until now, eluded us.

The main challenge is that nucleation involves a few atoms only and a short time scale, thus requiring a combination of high spatial and temporal resolution for direct observation. Here, we overcome the temporal resolution constraint by reducing the growth rate in order to match the temporal resolution of our recording medium. We employ an environmental scanning transmission electron (E-STEM), equipped with an image corrector and a digital video recording system, to follow SWCNT growth using Co-Mo/MgO catalyst and acetylene (C₂H₂) as a carbon source (see Methods). We present atomic-resolution movies that reveal the nucleation of graphene on cobalt carbide nanoparticles followed by its transformation to a single-walled carbon nanotube. We find that the surface termination of the faceted catalyst nanoparticles regulates the nucleation of the graphene sheet and its conversion into a nanotube. Additional density functional theory calculations show that the disparity in adhesion energies for graphene to different catalyst surfaces is critical for nanotube formation: strong work of adhesion provides anchoring planes for the tube rim to attach, while weak work of adhesion promotes the lift-off of the nanotube cap.

Raman Enhancement Effect on Two-dimensional Layered Materials: graphene, h-BN and MoS₂

Xi Ling, Wenjing Fang, YI-Hsien Lee, Paulo Araujo, Xu Zhang, Joaquin Rodriguez-Nieva, Yuxuan Lin, Jin Zhang, Jing Kong, Mildred Dresselhaus

Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, United States

Material Sciences and Engineering, National Tsing-Hua University, Hsinchu, Taiwan, Taiwan, Province Of China

Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL, United States

Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, United States

Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, United States

Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, United States

College of Chemistry and Molecular Engineering, Peking University, Beijing, Beijing, United States

Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, United States

xiling@mit.edu

Realizing Raman enhancement on a flat surface has become increasingly attractive after the discovery of graphene enhanced Raman scattering (GERS). Two-dimensional (2D) layered materials, exhibiting a flat surface without dangling bonds, were thought to be strong candidates for both fundamental studies of this Raman enhancement effect and its extension to meet practical applications requirements. Here, we study the Raman enhancement effect on graphene, hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS₂), by using the copper phthalocyanine (CuPc) molecule as a probe. This molecule can sit on these layered materials in a face-on configuration. However, it is found that the Raman enhancement effect, which is observable on graphene, hBN and MoS₂, has different enhancement factors for the different vibrational modes of CuPc, depending strongly on the surfaces. Higher frequency phonon modes of CuPc (such as those at 1342, 1452, 1531 cm⁻¹) are enhanced more strongly on graphene than that on h-BN, while the lower frequency phonon modes of CuPc (such as those at 682, 749, 1142, 1185 cm⁻¹) are enhanced more strongly on h-BN than that on graphene. MoS₂ demonstrated the weakest Raman enhancement effect as a substrate among these three 2D materials. These differences are attributed to the different enhancement mechanisms related to the different electronic properties and chemical bonds exhibited by the three substrates: (1) graphene is zero-gap semiconductor and has a non-polar C-C bond, which induces charge transfer (2) h-BN is insulating and has a strong B-N bond, while (3) MoS₂ is semiconducting with the sulfur atoms on the surface and has a polar covalent bond (Mo-S) with the polarity in the vertical direction to the surface. Therefore, the different Raman enhancement mechanisms

differ for each material: (1) charge transfer may occur for graphene ; (2) strong dipole-dipole coupling may occur for h-BN and (3) both charge transfer and dipole-dipole coupling may occur, although weaker in magnitude, for MoS₂. Consequently, this work studied the origin of the Raman enhancement (specifically, chemical enhancement), and identifies h-BN and MoS₂ as two different types of 2D materials with potential for use as Raman enhancement substrates.

Thermodynamics of Quasi-Epitaxial Assembly of FMN around various (n, m)-SWNTs

Fotios Papadimitrakopoulos, Roholah Sharifi, Milinda Samaraweera, José A. Gascón

Chemistry, Institute of Materials Science, Storrs, CT, United States

papadim@ims.uconn.edu

The helical assembly of self-organized flavin mononucleotide (FMN) around single-walled carbon nanotubes (SWNTs) presents among the highest organization order in nanotube surfactants. In this contribution, we quantitatively analyze and model for the first time the cooperative hydrogen bonding of adjacent flavin moieties as well as the concentric π - π interactions between the isoalloxazine moieties and the underlying graphene lattice as a function of (n,m)-SWNT chirality. For this we use dissociation thermodynamics of FMN-wrapped (n,m)-SWNTs dispersed in both H₂O and D₂O as a function of FMN concentration. The binding strength of these FMN assemblies has been assessed in terms of ΔH , ΔS and ΔG . Atomistic molecular simulations were used to modeled these data and link their dependence in terms of nanotube diameter (d_t) the chiral angle (ϕ). The findings of this study provide the first quantitative proof of the quasi-epitaxial assembly of FMN around various (n,m)-SWNTs. This study demonstrates the architectural fidelity of FMN-wrapped SWNTs that closely emulates the dissociation mechanics of double-stranded DNA in its aqueous solutions.

Distinguishing individual and ensemble carbon nanotubes by Raman spectroscopy

Asmus Vierck, Emanuele Poliani, Florentina Gannott, Manuel Schweiger, Jana Zaumseil, Janina Maultzsch

Institute for solid state physics, TU Berlin, Berlin, Berlin, Germany
Nanomaterials for Optoelectronics Group, Institute of Polymer Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Bavaria, Germany
Institute for solid state physics, TU Berlin, Berlin, Berlin, Germany
avierck@physik.tu-berlin.de

Raman spectroscopy on single-walled carbon nanotubes (SWCNTs) is one of the most powerful methods to analyse their structural, optical, and electronic properties. While Raman studies are usually performed on mixed SWCNT ensembles, it is essential to investigate the inherently distinct Raman signal of the underlying individual tubes.

Using isopropanol as a precursor, our samples were grown from patterned iron catalyst particles by CVD in a tube furnace system. Using ST-cut quartz as a substrate, we obtain perfectly aligned, mostly individual tubes, as confirmed by Raman spectroscopy, AFM and SEM imaging.

We present Raman spectra acquired under different excitation wavelengths from many individual SWCNTs and compare them to those of SWCNTs in areas with higher density that interact with each other. We assess the inherent variation of the acquired Raman signal along individual tubes statistically and discuss whether the Raman spectra from nanotube ensembles can be modelled by a superposition of individual SWCNT spectra. We show the importance of our findings when e.g. using the Raman intensities of D and G modes for the determination of defect concentration or their position and lineshape for deducing the metallic / semiconducting content of the sample.

