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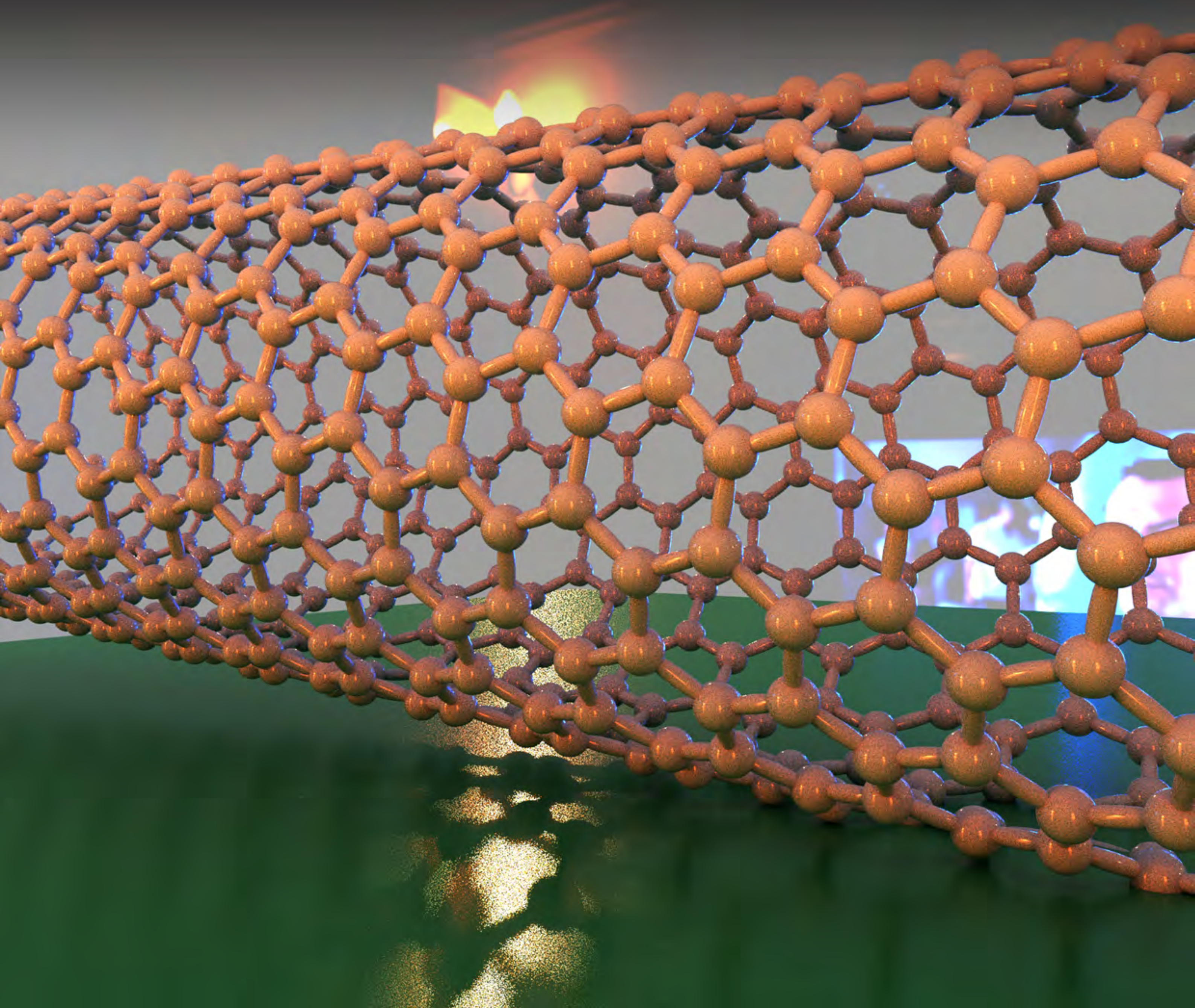

Making the Structures of Aligned and Identical Carbon Nanotubes

- A road towards the applications of carbon nanotubes

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Since Iijima's finding in 1991, the carbon nanotube has become one of the most popular and exciting research fields. A variety of applications of carbon nanotubes have been expected and demonstrated based on their unique properties. Many growth methods for carbon nanotubes have been developed, among which catalytic chemical vapor deposition has become a dominating production technique. However, the as-grown pristine product is usually a mixture of tangled carbon nanotubes with diverse microstructures, which become a big hurdle for their applications. In spite of many post-growth purification, cutting, sorting, and assembling technologies being developed, in-situ direct growth of desired carbon nanotube structures is always highly preferred from the beginning. This presentation reviews the longtime efforts and advances in controlled growth of carbon nanotubes with specific chirality and aligned structures, such as vertically aligned carbon nanotube arrays on substrates, free-standing horizontally aligned carbon nanotube films, horizontally aligned semiconducting carbon nanotubes on substrates, etc. Some interesting applications based on such carbon nanotube structures are also presented.

Graphene Materials: Properties, Fabrication and Applications

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Graphene is a single-atom-thick sheet of hexagonally arranged, sp2-bonded carbon atoms that is not an integral part of a carbon material but is freely suspended or adhered on a foreign substrate, and has excellent properties, such as high mechanical strength and modulus, high thermal and electrical conductivities, very stable thermal and chemical stabilities, and unique electronic properties. Graphene materials, overarching terms for the collection of two-dimensional materials that contain the word “graphene”, including multilayered materials (N less than about 10), chemically modified forms (graphene oxide, reduced graphene oxide), and materials made from graphene precursors, are expected for various applications.

Synthesis of graphene materials in a large quantity at reasonable cost is very important. Basically, graphene can be synthesized by mechanical exfoliation, epitaxial growth, chemical exfoliation, CVD and chemical synthesis from small molecules. Among them, chemical exfoliation of graphite and CVD on different substrates are the most-widely-used two methods.

Due to their unique and outstanding properties, graphene materials may have wide applications in many fields, from electronics to new energy field, and from transportation to space as low-weight structural materials, including composites, anti-corrosion coatings, conductive inks, energy storage devices, electronics, optoelectronics, photonics, sensors and bio-sensors, bio-medical materials and devices, thermal management materials, etc. However, great efforts are highly needed for the research and development, and commercialization and market explorations of graphene materials.

Origin and Control of Spectral Diversity from sp^3 Defect States of Single Wall Carbon Nanotubes

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Low-level covalent functionalization of single wall carbon nanotubes (SWCNTs) introduces new photoluminescent defect states appearing 100-300 meV to lower energy than the normal band-edge E_{11} exciton emission.[1,2] Exciton localization at the defect sites gives rise to new functionality, including single photon emission at room-temperature and at telecom wavelengths.[3,4] One challenge in harnessing the defect-state emission is that, even for single chirality samples, emission over a broad spectral window (~100-200 nm range) is observed. A better understanding of the origins of this spectral diversity is required to arrive at strategies for narrowing the emission window. We present a single-tube low-temperature spectroscopic study paired with TD-DFT modeling of defect-state behavior for aryl diazonium sp^3 functionalized SWCNTs. We show that the spectral diversity arises from the potential for 6 different aryl binding configurations to occur on the nanotube structure. Each configuration is a chemically distinct species, with its own defined electronic structure and emitting behavior.[5,6] We further explore the structural dependence of this behavior and show that chirality may be used as a parameter for limiting emission wavelengths. Furthermore, TD-DFT modeling paired with kinetic studies shows that aryl diazonium binding is limited to ortho-only configurations.[7]

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Graphene Nanoribbons as a New Semiconductor Family

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Graphenes and graphene nanoribbons (GNRs), their geometrical cutouts, are new additions to the carbon family. Indeed, graphenes hold enormous promise as materials for energy technologies. GNRs are regarded as a new generation of semiconductors superior to i) silicon in view of the required miniaturization of printed circuits and superior to ii) classical conjugated polymers due to better band structure control. Above all, graphene as a two-dimensional polymer and GNRs are true challenges for materials synthesis.

In our “bottom-up” synthesis of GNRs, repetitive cycloaddition in solution is shown to afford branched polyphenylene polymers which serve as precursors for perfectly “graphitized”, solution-processable GNRs as long as 600 nm. An alternative on-surface synthesis utilizes immobilization of suitable monomers and in-situ STM-control of the polymerization to secure structural perfection. A further option is to employ chemical vapor deposition by introducing oligophenylene monomers as initial building blocks. Only these three methods of controlled synthesis ensure sufficient structural precision over, for example, the nature of the edges. Our approach is thus superior to methods of lithiography or unzipping carbon nanotubes.

It is a synthetic breakthrough which leads to new materials science and physics. We fabricate field effect transistors from, both, single GNRs and GNR networks and compare the performance with that of conjugated polymers. Of particular importance is the synthesis of GNRs with zig-zag edges because they provide edge localized states. The associated spins reveal long correlation times. These characteristics provide entries to spintronics and even quantum computing.

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High-Resolution Microscopy and Spectroscopy of Individual Carbon Nanotubes Enable Brain Imaging at the Nanoscale

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Over the last two decades the optical microscopy of single molecules has been crucial 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 such as in cells and in biological tissue [1]. However, for many bio-applications, near infrared nanoprobes and/or more photostable nanoprobes than conventional fluorescent molecules or quantum dots would be desirable [2]. In this context, luminescent single walled carbon nanotube tubes are unique due to their unusual dimension, optical properties and rigidity. A prerequisite to the application of carbon nanotubes in high-resolution bio-imaging is however to understand their fundamental optical properties which are based on subtle and sensitive excitonic processes [3] but also to study their rheological/interaction behavior in crowded bio/cellular environments [4] and finally to optimize their optical detection in specific biological environments [5]. Our continuous efforts toward achieving these different goals will be presented as well as recent applications for imaging the brain at the nanoscale [6].

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Carbon Nanotube based High Performance CMOS Devices and Integrated Systems

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Carbon nanotube (CNT)-based electronics has been considered one of the most promising candidates to replace Si complementary metal-oxide-semiconductor (CMOS) technology, which will soon meet its performance limit. In particular CNTs have been investigated for various electronic and optoelectronic device applications, such as sub-10nm CMOS devices which outperform that of state-of-the-art Si based CMOS devices in both speed and power consumption [1-5], as well as idea material for monolithic optoelectronic integration with complementary MOS-compatible signal processing circuit [6-8].

Prototype device studies on individual CNTs revealed that CNT based devices have the potential to outperform Si CMOS technology in both performance and power consumption. With a well-designed device structure and in combination with graphene, it is showed that high-performance top-gated CNT FETs with a gate length of 5 nm can be fabricated. A scaling trend study revealed that sub-10 nm CNT CMOS FETs significantly outperform Si CMOS FETs. In particular, the 5 nm CNT FETs approach the quantum limit of FETs and involve only approximately one electron per switch. The contact length of the CNT CMOS devices has been scaled down to sub-10 nm, and the smallest CMOS inverter yet reported with a total pitch size of 240 nm is demonstrated. These results show that CNT CMOS technology has the potential to substantially outperform that of Si when approaching the quantum limits of a binary logic switch and to extend mainstream CMOS technology in the post-Moore era [1].

Significant progress has been made in fabricating carbon nanotube low-power devices. An efficient way to reduce the power is to lower the supply voltage V_{DD}, but this voltage is restricted by the 60 millivolts per decade thermionic limit of subthreshold swing (SS) in FETs. A Dirac source (DS) with a much narrower electron density distribution around the Fermi level than that of conventional FETs was recently proposed and demonstrated using CNT to reduce SS [2]. In particular, a DS-FET with a carbon nanotube channel provided an average SS of 40 millivolt per decade over four decades of current at room temperature and high device current. When compared with state-of-the-art Si 14-nanometer node FETs, a similar I_{on} is realized but at much lower supply voltage of 0.5 versus 0.7 volts for Si, and a much steeper SS below 35 millivolts per decade in the off-state.

High purity semiconducting CNTs have also been used as active channel materials for various optoelectronic de-vices, including light emit-ting diodes and photodiodes [6], and as a general platform for building three-dimensional optoelectronic integrated system [7-8].

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Interfaces between Small Molecules and Semiconducting Single-Walled Carbon Nanotubes for Precise Control Over Energy and Charge Transport

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Semiconducting single-walled carbon nanotubes (s-SWCNTs) are attractive as components in energy harvesting applications because of their strong and energetically tunable optical absorption, and high charge carrier mobilities due to the delocalized nature of the π-electron system. Inherent in energy harvesting systems are the needs to balance multiple competing processes: (1) absorb energy over appropriate regions of the electromagnetic spectrum (visible, infrared, UV) to generate energetic species (excitons, charges, phonons) within the active layer; (2) transport, transfer, or interconvert the excitations in a controlled manner using interfaces; and (3) collect the appropriate energetic species efficiently to produce useful work. SWCNTs are unique nanomaterials within energy harvesting schemes, in that they naturally provide a high degree of interfacial surface area (both external and endohedral) for creating energetically tuned interfaces that can direct energy and charge carriers in specific ways.

This presentation will highlight the critical roles played by interfaces between small molecules and s-SWCNTs in a variety of model energy harvesting systems. Small molecule dyes encapsulated within s-SWCNTs can be used to sensitize the surrounding SWCNTs to visible light *via* ultrafast excitation energy transfer.[1] Interfaces between s-SWCNTs and small molecule electron acceptors can be used to efficiently dissociate photo-generated excitons *via* photo-induced charge transfer, producing the long-lived separated charges needed for efficient solar energy harvesting.[2] Ground-state charge transfer between s-SWCNT and small molecules with appropriate energetics can be used to sensitively tune the majority carrier density (both for holes and electrons) within s-SWCNTs, facilitating efficient thermal energy harvesting.[3] Within each of these systems, I will highlight our efforts aimed at understanding the detailed connection between the thermodynamics, kinetics, and molecular structure at play at the molecule/s-SWCNT interface. Such fundamental understanding of these model interfaces can inform the design of more efficient energy harvesting systems other opto-electronic devices.

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2. Long-lived Charge Separation at Heterojunctions Between Semiconducting Single-walled Carbon Nanotubes and Perylene Diimide Electron Acceptors. *J. Phys. Chem. C* **2018**, *Article ASAP.*
3. Large *n*- and *p*-type thermoelectric power factors from doped semiconducting single-walled carbon nanotube thin films. *Energy & Environmental Science* **2017** *10*, 2168.

2D Material Inks for Electronics, Optoelectronics and Photonics

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The two-dimensional (2D) material family covers diverse and distinct but complementary optoelectronic properties. When considering large-scale manufacturability of electronic, optoelectronic and photonic devices of these 2D materials, their solution processability offers a cost effective and realistic option. Functional ink formulation and well-controlled printing of these materials to ensure high device-to-device repeatability is central to this argument.

For ink formulation of these 2D materials, which can be best described as "powders", solvents and ink rheological properties play a critical role in printing and device fabrication as well as the ultimate device performance [1,2]. Starting with inkjet printing, I will discuss key ink formulation strategies of these novel 2D materials and printed devices. I will show that the choice of unique solvent blends allows us to engineer counteracting Marangoni flows in drying droplets. This enables uniform, reliable inkjet printing towards scalable development of printed electronic, photonic and optoelectronic devices of a range of 2D materials [2,3]. In the latter half of my talk, I will move into printing on conformable substrates as well large format print technologies and show that a combination of advanced materials printed by traditional graphics printing and contemporary electronics could promote simple, yet powerful and inexpensive technologies.

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Fused Organic Networks for Energy Conversion and Storage

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Together with graphene,[1] conjugated two-dimensional (2D) organic networks have attracted immense interest due to their unusual electronic, optoelectronic, magnetic and electrocatalytic properties. In addition, their tunable structures and properties promise to offer various opportunities in various applications. However, even after years of intensive exploration of 2D materials in science and technology, facile and scalable methods capable of producing stable 2D networks with uniformly decorated heteroatoms with/without holes remain limited. To overcome these issues, new layered 2D fused organic networks have been designed and synthesized (Fig. 1a and 1b). They have uniformly distributed heteroatoms,[2] holes with heteroatoms[3] and transition metal nanoparticles on the holes.[4] The structures were confirmed by scanning tunneling microscopy (STM). Based on the stoichiometry of the basal plane, they were, respectively, designated C_3N, C_2N and M@C_2N (M = Co, Ni, Pd, Pt, Ru) (Fig. 1c). Their electronic and electrocatalytic properties were evaluated by electrooptical and electrochemical measurements along with density-functional theory (DFT) calculations. The results suggest that these newly-developed 2D organic networks offer promising opportunities, ranging from wet-chemistry to device applications.

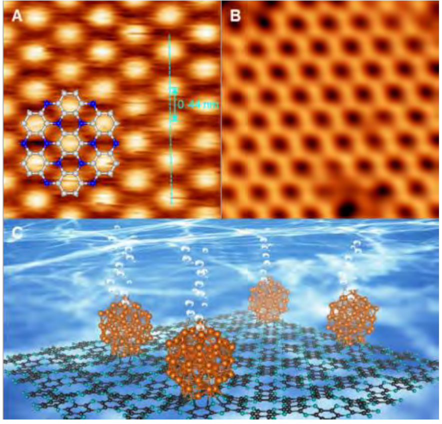

Fig. 1. Scanning tunneling microscopy (STM) images of 2D organic networks: **A,** C_3N; **B,** C_2N. **C,** Schematic representation of metal (M) nanoparticles on C_2N (M@C_2N).

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Wafer-Scale Crystalline Carbon Nanotubes: Physics and Applications

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We have recently developed a controlled vacuum filtration technique to fabricate wafer-scale "crystalline" films (1 inch [1] or 2 inches [2] in diameter) of highly aligned and densely packed single-wall carbon nanotubes (SWCNTs). We have further built unique SWCNTs architectures and devices by stacking and doping these aligned films. In this talk, we summarize our recent accomplishments using these unique samples. We have observed intersubband plasmons (ISBPs) in gated and aligned SWCNT films [3]. For parallel polarization, interband exciton absorption peaks disappeared as carriers were injected, whereas, for perpendicular polarization, a new peak due to an ISBP appeared and grew as the carrier density increased. We have also made the first direct observation of a cross-polarized exciton peak in optical absorption spectra for an aligned undoped (6,5) film [4], which allowed us to quantitatively estimate the oscillator strength of this transition and the effective dielectric constant of this film. We further built an exciton-polariton architecture by incorporating an aligned (6,5) film inside a Fabry-Pérot microcavity. This system displayed a continuous transition from the ultrastrong-coupling regime to the weak-coupling regime through facile polarization control [5]. The obtained dispersion surfaces revealed the existence of two equienergy arcs in momentum space that are bounded by exceptional points. Furthermore, the vacuum Rabi splitting exhibited cooperative enhancement when the number of excitons was increased by increasing the SWCNT film thickness. Finally, we have recently demonstrated that aligned SWCNTs work as hyperbolic thermal emitters that are stable at temperatures greater than 100 K [6]. Aligned SWCNT films exhibited polarized thermal emission with a spectral peak near the epsilon-near-zero frequency, while deeply sub-wavelength-sized cavities showed resonantly enhanced midinfrared radiation.

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Optical and Thermoelectric Properties of Fermi Level Tuned and Aligned Single Wall Carbon Nanotube Thin Films

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Single wall carbon nanotubes (SWCNTs) are one-dimensional materials with sharp van Hove singularities. Preparation of SWCNTs with a selected electronic structure, fabrication of their aligned thin films[1] and tuning their Fermi level allow us to reveal unique phenomena, which cannot be observed or correctly understood in conventional SWCNT random networks. For example, we observed anomalously large optical absorption for perpendicular polarization to the tube axis in highly doped aligned SWCNTs, which is related to intersubband transition plasmon phenomena in SWCNTs.[2] In this talk, first I discuss the background of this unique properties.

Next, I discuss interesting thermoelectric phenomena in fermi level tuned and aligned SWCNTs. In our society, a large amount of heat at relatively low temperature, which is emitted from factories, houses, human bodies, and so on, is left unused. Development of high-performance flexible thermoelectric devices is crucial to efficiently convert such unused waste heat into electric power. Understanding of relationships between electrical conductivity σ, Seebeck coefficient S, and thermal conductivity κ in thin films of flexible materials and tuning of these parameters is of great importance to improve the performance. SWCNTs are a model of one-dimensional flexible materials, and will play important roles for realization of high-performance flexible thermoelectric devices. Since the seminal study by Hicks and Dresselhaus,[3] the thermoelectric properties of low dimensional materials have been intensively studied, but it still has been of great importance to experimentally clarify how the one dimensional electronic structures can influence and enhance its thermoelectric properties. For flexible thermoelectric applications, we must evaluate the thermoelectric properties in a thin film situation of the materials. Although the thermoelectric properties in a single rope situation of the materials are well understood, thermoelectric properties in the form of thin films are still under discussion. For example, in conventional solid metallic materials, there is a trade off between S and σ, such as increase of S leads to decrease of σ, however, in the case of SWCNTs sometimes we can observe the breaking of the trade-off.[4] Moreover, it is not clear whether the Wiedemann-Franz law is applicable in thin films. Femi level tuned and aligned SWCNTs allow us to investigate the details of the background because we can systematically change the electronic structure, location of Fermi level, and conditions of contacts between the tubes. In this talk, I will present recent our results about thermoelectric properties of Fermi-level tuned and aligned SWCNTs and discuss how electronic structure, location of Fermi level, current with respect to the tube axis influence on the S, σ of SWCNT thin films.

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Cardiovascular disease as a (nano)particle-induced occupational disease

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Epidemiological studies link inhalation of particles to increased risk of cardiovascular disease. Inhaled particles may induce cardiovascular disease by several different mechanisms including translocation of particles to systemic circulation, activation of airway sensory nerves resulting in autonomic imbalance and particle-induced pulmonary inflammation and acute phase response.

The acute phase response is the systemic response to acute and chronic inflammatory states caused by for example bacterial infection, virus infection, trauma and infarction. It is characterized by differential expression of ca. 50 different acute phase proteins including C-reactive protein (CRP) and Serum amyloid A (SAA). Blood levels of CRP and SAA are closely associated with risk of cardiovascular disease in epidemiological studies. The acute phase protein SAA is causally related to atherosclerosis and cardiovascular disease. Overexpression of SAA leads to increased plaque progression and inhibition of SAA synthesis leads to lowered plaque progression in APOE -/-mouse models [1].

We have shown that inhalation and airway exposure to different particles induces pulmonary acute phase response in mice [2]. The pulmonary acute phase response correlates with the total surface area of the deposited particles, neutrophil influx into the lung and with blood concentrations of acute phase proteins.

In a recent controlled human exposure study, inhalation of ZnO particles induced systemic acute phase response in a dose-dependent manner at doses well below the current occupational exposure limit in many countries [3]. This calls for re-evaluation of the current occupational exposure limits taking risk of cardiovascular disease into account and underscores cardiovascular disease as an occupational disease [4].

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Effective theory for the twisted bilayer graphene

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The recent discovery of the superconductivity and strongly correlated insulating state in the twisted bilayer graphene (TBG) attracts enormous attention [1,2]. TBG is a sandwitch of two graphene layers stacked with a rotational orientation [Fig.1(a)]. There a slight rotation gives rise to a long-period moiré pattern, substantially modifying the electronic property. Due to the huge moire pattern, the unit cell of TBG includes more than 10,000 carbon atoms. It is a challenging problem to theoretically describe the many-body physics in such a complex system.

Here we develop an effective theory to describe the many-body physics in TBG [3]. By using the realistic band model and with the aid of the maximally localized algorithm, we construct the Wannier orbital, which works as the effective composite “atom” on the moiré pattern. The effective atomic orbital has a characteristic three-peak structure [Fig.1(b)], and it leads to unexpected properties of many body states. For example, we find that an electronic excitation can be viewed as a pair creation of the fractional charges in units of e/3, which would possibly give rise to exotic physics. Our effective model dramatically reduces the fundamental complexity of the electronic system in TBG, and it would be greatly beneficial to future theoretical studies. It opens the way to explore the many-body physics in TBG.

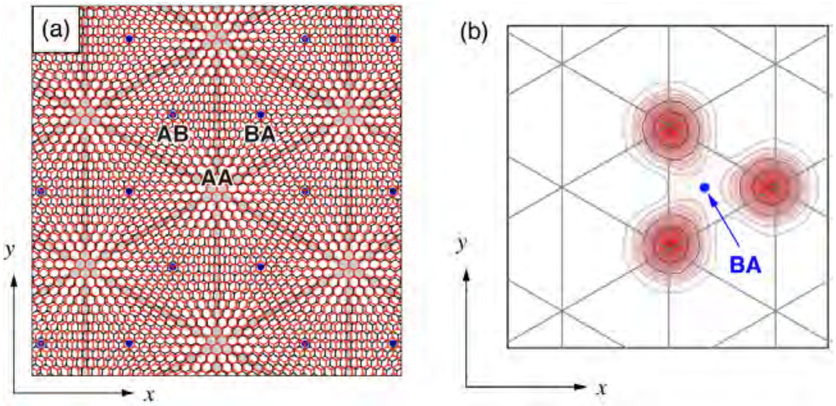

Fig. 1 (a) Atomic structure of TBG with $\theta = 3.89^{\circ}$
(b) A maximally localized Wannier orbital in the low-energy flat band of TBG with $\theta = 1.05^{\circ}$.

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Dark exciton dynamics in atomically thin 2D materials

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Monolayers of semiconducting transition metal dichalcogenides (TMDs) build a new class of atomically thin two-dimensional materials. They exhibit a remarkably strong Coulomb interaction giving rise to the formation of tightly bound excitons. In addition to regular bright excitonic states, there is also a variety of dark states that cannot be accessed by light due to the required momentum-transfer or spin-flip.

To model the exciton physics in TMD monolayers, we apply a microscopic approach combining semiconductor Bloch equations with the Wannier equation providing access to time- and momentum-resolved optical response and the non-equilibrium dynamics in TMDs. In this talk, we review our recent work focusing on:

(i) Uncovering the full exciton landscape including bright as well as momentum- and/or spin-forbidden dark excitonic states (Fig. 1a) [1].

(ii) Demonstrating signatures of dark excitonic states by probing the intra-excitonic 1s-2p transition directly after optical excitation and after exciton thermalization [2].

(iii) Activating momentum-forbidden dark excitonic states via efficient coupling with molecules suggesting a dark-exciton-based sensing mechanism for molecules (Fig. 1b,c) [3].

(iv) Providing a fully quantum mechanical description of formation, thermalization, and photoemission of interlayer excitons in TMD-based heterostructures [4,5].

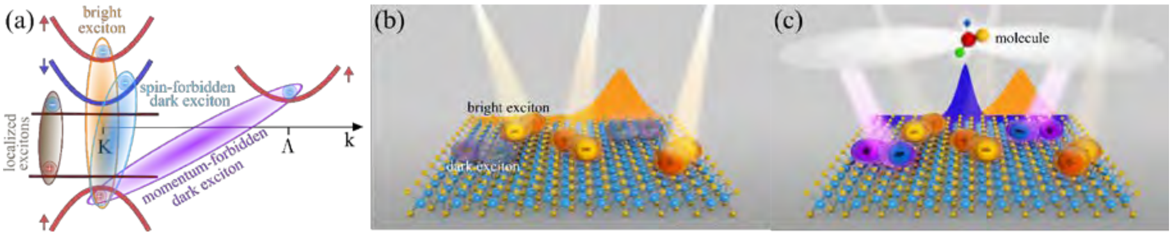

Fig.1 (a) Exciton landscape including bright and dark states. (b) An optical pulse can only excite bright excitons resulting in a pronounced peak in optical spectra (orange). (b) In presence of molecules, dark excitons can be also excited via an efficient exciton-molecule coupling. The resulting additional peak (blue) can be exploited for sensing of molecules.

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In-Situ TEM Studies on Phase Transition Mechanism of TMDs by Alkali Metal Intercalation

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In-situ transmission electron microscopy (TEM) method is powerful in a way that it can directly correlate the atomic structure with physical and chemical properties. By using the homemade in-situ TEM holders, the properties at nanoscale under various physical stimuli have been studied, including mechanical, electrical, and optical properties. For example, the physical properties of individual carbon nanotubes with known chirality have been reported previously. For this work, the real-time imaging of solid state electrochemical processes at atomic scale has been carried out by in-situ TEM. In this presentation, we will review our progress on the studies of phase transition mechanism of the two-dimensional layered transition metal dichalcogenides (TMDs) by alkali metal intercalation.

Probing Luttinger Liquid in Single Walled Carbon Nanotubes

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UC Berkeley

Interacting electrons in three-dimensional metals are described remarkably well by quasi-particles in the Fermi liquid theory. At one dimension (1D), however, Coulomb interactions can modify the electron behavior qualitatively and lead to a new type of electron system—the Luttinger liquid. A Luttinger liquid can exhibit fascinating quantum phenomena distinctly different from conventional metals, such as anomalous correlation function and density of states with power-law scaling and spatially separated collective charge and spin excitations. Single Walled carbon nanotubes provide the ideal platform to explore Luttinger liquid physics due to the strong one-dimensional quantum confinement. I will discuss our combined electrical and optical studies to correlate the unusual electron tunneling and plasmon excitations of a Luttinger liquid. I will also show that distinctly different plasmon behavior emerge in electrically gated metallic and semiconducting carbon nanotubes, which are described by the linear Luttinger liquid and nonlinear Luttinger liquid, respectively.

Controlling the inner dielectric environment of carbon nanotubes to tune their optical properties

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The optical properties of single-wall carbon nanotubes (SWCNTs) are extremely sensitive to their external and internal environment. For example, filling the endohedral cavity with water molecules results in characteristic shifts and broadening of both the SWCNTs' radial breathing mode vibrational frequency and their optical (electronic) transitions, as well as a quenching of their emission.[1] Although mostly ignored in literature, solvent ingestion effects are substantial, and can also be used to passivate the nanotube interior, by controlled manipulation of the endohedral environment prior to dispersion.[2]

In this work, specific and tunable modification of the optical properties of SWCNTs is demonstrated through the direct encapsulation of guest molecules with widely varying dielectric constants. Over 30 different compounds with static dielectric constant varying from 1.8 to 109 have been encapsulated inside the SWCNTs and their spectroscopic analysis, in comparison to unfilled (empty) SWCNTs, demonstrates for the first time experimentally that the general effect of filler static dielectric on the nanotube optical properties corresponds to a monotonic energy reduction (red-shifting) of the optical transitions with increased magnitude for higher dielectric constants.

Systematic two-dimensional fitting of the fluorescence-excitation spectra enables the direct comparison of this red shifting as a function of nanotube diameter, modulus and chirality. In addition to these spectral shifts, the filling with dielectric molecules also reveals a general increase of fluorescence intensity with lower dielectric constants, with some fillers approaching the emission efficiencies of empty SWCNTs.

Our investigation hence demonstrates a new degree of modulation of the SWCNTs' optical properties by simple endohedral ingestion of various guest molecules.

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Aligned Carbon Nanotube Transistors and Neuromorphic Computing

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Carbon nanotubes hold great potential but also face significant challenges for various electronic application. Regarding nano- and RF electronics, obtaining high-density horizontally aligned carbon nanotubes with high semiconducting purity (>99.99%) has been an important but challenging goal. Here we report record radio frequency (RF) performance of carbon nanotube transistors based on combined use of a self-aligned T-shape gate structure, and well-aligned, high semiconducting purity, high-density polyfluorene-sorted semiconducting carbon nanotubes, which were deposited using dose-controlled, floating evaporative self-assembly method. These transistors show outstanding direct current (DC) performance with on-current density of 350 μA/μm, transconductance as high as 310 μS/μm, and superior current saturation with normalized output resistance greater than 100 kΩ·μm. These transistors create a record as carbon nanotube RF transistors that demonstrate both the current-gain cutoff frequency (ft) and the maximum oscillation frequency (fmax) greater than 70 GHz. Furthermore, these transistors exhibit good linearity performance with 1 dB gain compression point (P1dB) of 14 dBm and input third-order intercept point (IIP3) of 22 dBm.

In addition, I will present aligned carbon nanotube (CNT) synaptic transistors for large-scale neuromorphic computing systems. The synaptic behavior of these devices is achieved via charge-trapping effects, commonly observed in carbon-based nanoelectronics. In this work, charge trapping in the high-k dielectric layer of top-gated CNT field-effect transistors (FETs) enables the gradual analog programmability of the CNT channel conductance with a large dynamic range (i.e., large on/off ratio). Here, we demonstrate exceptional uniformity of aligned CNT FET synaptic behavior, as well as significant robustness and nonvolatility via pulsed experiments, establishing their suitability for neural network implementations. Additionally, this technology is based on a wafer-level technique for constructing highly aligned arrays of CNTs with high semiconducting purity and is fully CMOS compatible, ensuring the practicality of large-scale CNT+CMOS neuromorphic systems. We also demonstrate fine-tunability of the aligned CNT synaptic behavior and discuss its application to adaptive online learning schemes and to homeostatic regulation of artificial neuron firing rates. We simulate the implementation of unsupervised learning for pattern recognition using a spike-timing-dependent-plasticity scheme, indicate system-level performance (as indicated by the recognition accuracy), and demonstrate improvements in the learning rate resulting from tuning the synaptic characteristics of aligned CNT devices.

Nanomechanical characterization of the Kondo charge dynamics in a carbon nanotube

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Suspended single wall carbon nanotubes are at cryogenic temperatures both extraordinary nano-electromechanical systems and prototypical clean and defect-free single electron devices. The interaction of the corresponding two fields of physics allows for many interesting studies. In particular, by measuring the gate voltage dependence of the transversal vibration frequency, the evolution of the charge on a quantum dot embedded in the nanotube can be evaluated at high precision.

We apply this technique to the limit of strong Kondo correlations between a nanotube quantum dot and its contacts [1]. The current through the nanotube displays a clear odd-even pattern (i.e., a “Kondo ridge” at odd electron number) as a function of gate voltage. The time-averaged charge on the quantum dot, however, shows no such odd-even pattern, and can be well modeled via sequential tunneling only. We conclude that the Kondo current is carried via virtual occupation of the quantum dot alone. This is in excellent agreement with recently published results coupling a nanotube to a coplanar waveguide resonator [2], where the transmitted radio-frequency phase depends on the compressibility of the electronic system.

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A General Gelation Strategy for Nanowires: Functional Gels for Wearable 3D Printing Electronics

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Abstract

Additive manufacturing, in which three-dimensional (3D) functional architectures are rapidly prototyped via printing, has in recently years emerged as the promising approach to increase product sophistication while reduce material waste and energy consumption. The development for additive manufacturing of future electronic devices hinges on the availability of 3D printable functional materials. We report a versatile strategy to obtain stable gel with nanowires for 3D printing of electronic devices. Inorganic metallic and non-metallic nanowires, widely studied one-dimensional (1D) functional nanomaterials that are generally difficult to disperse in solvents for printing, can be effectively cross-linked, or hinged, by a small amount of graphene oxide nanosheets. The resulting 3D network forms a dynamically stable suspension in water, in a similar fashion as hydrogels in which 1D polymer chains are cross-linked via hydrogen bonding. Functional gels of silver nanowires, zinc oxide nanowires, and manganese oxide nanowires have all been prepared and printed into various 3D and self-supported architectures via extrusion-based 3D-printing. The electrical conductivity of the 3D-printed silver nanowire conductor can reach over 40,000 S/cm right after solidifying at ambient condition. The feasibility of these nanowire gels is demonstrated by fabricating wearable electronics of thin-film field transistor, UV-detector and micro-supercapacitor with promising performance via extrusion-based 3D-printing.

Keywords: Extrusion-based 3D printing, functional nanowire gel, gelation, wearable printed electronics, graphene oxide

Temperature depenence on the double-resonance Raman process for two dimensional Transition Metal Dichalcogenides

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Two-dimensional transition metal dichalcogenides (TMDs) are composed of stacks of atomically thin layers, that can be exfoliated until a single layer. This lead to the discovery of interesting properties related to their electronic and phonons structure. Resonant Raman scattering is a very strong technique to investigate their excitons, phonons and exciton-phonon coupling. Recently, Carvalho et al [1] reported a double resonance Raman study for monolayer and bulk MoS_2, in which the assignment of second-order peaks was proposed considering combinations of Transversal acoustic and Longitudinal acoustic phonons (TA and LA respectively) at M and K points participate of the process. That experiment was done by varying the incident photon energy, almost continuously, across the excitonic levels. However, photoluminescence measurements reveal a dependence of the excitonic levels energy with the sample temperature. In this work, we study the dependency of monolayer MoS_2 Raman spectra with temperature and excitation energy. In special, we are interested in the physics of the double resonance peaks and the way it changes with the in-situ variation of the sample temperature. The dependence of the excitonic levels with the temperature is responsible for a selection of phonon wavevectors during the double-resonance process. The experiments were performed on bulk and monolayered samples with in-situ temperature variation from 80 to 700K for different laser excitation energies. A temperature resonance behaviour for the double-resonant Raman peaks was observed and explained considering both temperature dependence of the phonon wavenumber and the exciton energy.

Acknowledgements

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Electron hydrodynamics in graphene: introduction and status

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Transport in systems with many particles experiencing frequent mutual collisions (such as gases or liquids) has been studied for more than two centuries and is accurately described by the theory of hydrodynamics. It has been argued theoretically for a long time that the collective behavior of charge carriers in solids can also be treated by the hydrodynamic approach. However, despite many attempts, very little evidence of hydrodynamic electron transport has been found so far.

Graphene encapsulated between hexagonal boron nitride (hBN) offers an ideal platform to study electron hydrodynamics as it hosts an ultra-clean electronic system with the electron-electron mean free path being the shortest lengths scale in the problem. In this presentation we will discuss why electron hydrodynamics has not been observed before and how it manifests itself in electron transport. In particular, it will be shown that electrons in graphene can behave as a very viscous fluid (more viscous than honey) forming vortices of applied electron current [1], as it is shown in the figure. We will discuss the approaches which can be used to measure the viscosity of electron liquid [2] and its behavior in presence of magnetic field. Last but not least, we will discuss how electron hydrodynamics can be used for the development of resonant terahertz photodetectors.

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Graphene Materials in Antimicrobial Nanomedicine

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Graphene materials (GMs), such as graphene, graphene oxide (GO), reduced GO (rGO), and graphene quantum dots (GQDs), are rapidly emerging as a new class of broad-spectrum antimicrobial agents. Here we describe their state-of-the-art and potential future covering both fundamental aspects and biomedical applications. First, the current understanding of the antimicrobial mechanisms of GMs is illustrated, and the complex picture of underlying structure–property–activity relationships is sketched. Next, the different modes of utilization of antimicrobial GMs are explained, which include their use as colloidal dispersions, surface coatings, and photothermal/photodynamic therapy agents. Due to their practical relevance, the examples where GMs function as synergistic agents or release platforms for metal ions and/or antibiotic drugs are also discussed. Later, the applicability of GMs in the design of wound dressings, infection-protective coatings, and antibioticlike formulations ("nanoantibiotics") is assessed. Notably, to support our assessments, the existing clinical applications of conventional carbon materials are also evaluated. Finally, the key hurdles of the field are highlighted, and several possible directions for future investigations are proposed. We hope that the roadmap provided here will encourage researchers to tackle remaining challenges toward clinical translation of promising research findings and help realize the potential of GMs in antimicrobial nanomedicine.

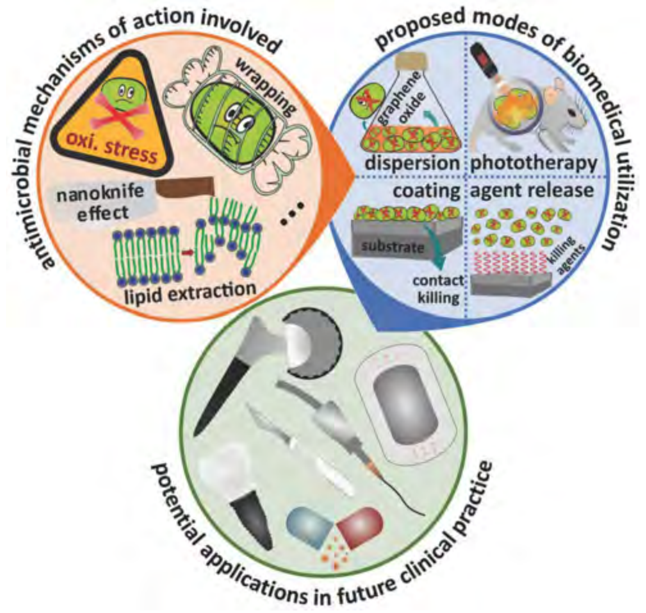

Fig. 1 Illustrative overview of the three major aspects of graphene-based antimicrobial outlined in this work: (i) "antimicrobial mechanisms of action involved" in pathogen control; (ii) "proposed modes of biomedical utilization" in proof-of-principle studies; (iii) "potential applications in future clinical practice."

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Few-layer graphene based nanocomposites for potential use in dental/biomedical applications

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Statistically, we chew around 800 times in an average meal; that's almost a million times a year. We put our teeth under huge mechanical strain, and often require fillings to repair them. Fillings are typically made of a mixture of metals, such as copper, mercury, silver and tin, or composites of powdered glass and ceramic. Typical metal fillings can corrode and composite fillings (thus far) are not very strong; Graphene on the other hand is 200 times stronger than steel and doesn't corrode, making it a prime new candidate for dental fillings. Graphene can, therefore, be used to make mechanically stronger composite-dental fillings which also do not corrode. Despite some challenges and the fact that carbon nanotubes-polymer composites are sometimes better in some particular performance, graphene-polymer composites may have wide applications in dentistry due to their outstanding properties and the availability of graphene in a large quantity and at low cost. One of the main problems, for patients, associated with dental-polymers is that of location. This stems from the fact they must be situated within the mouth and this proves to be an extremely demanding setting, where exposure to moisture, high temperatures, and abrasion from tooth brushes plus intake of food all have to be dealt with. These conditions can lead to complications such as mechanical failures which negate clinical success and over time mandates remedial work for restoration with associated cost and inconvenience. Graphene has potential applications in dental-polymer materials as it has the required mechanical properties as well as being biocompatible. Here we present new work into the application of graphene for the fabrication of potential dental-polymer materials (Fig. 1).

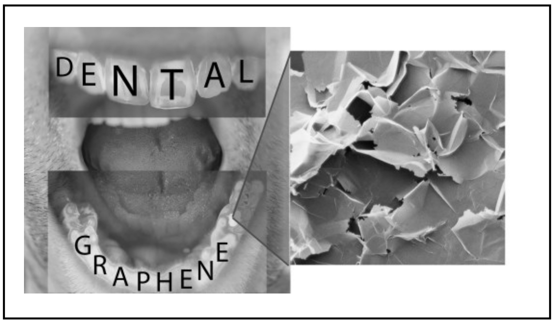

Fig.1 Helium Ion Micrograph of Few-Layer Graphene.

From Carbon-Based Nanotubes to Nanocages for Advanced Energy Conversion and Storage

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Fuel cells, supercapacitors and lithium-sulphur batteries are the typical energy conversion and storage devices of great significance in which carbon-based nanomaterials play irreplaceable role. The functionalized carbon-based nanomaterials could be applied to fuel cells to lower Pt loading by highly dispersing and immobilizing Pt-based nanoparticles, or to totally get rid of Pt with the metal-free electrocatalytic ability themselves. The abundant nanostructures and morphologies, tunable compositions, high surface area, good conductivity, small volume expansion, as well as the low cost and environmental benignity make the carbon-based nanomaterials have great potential as electrode materials of supercapacitors and lithium-sulphur batteries. In this talk I will give a brief introduction about our study on the synthesis, performance and mechanism of carbon-based nanostructures, especially the nanocages, for this kind of energy conversion and storage. Special attention will be paid to the carbon-based nanomaterials doped with electron-rich N, electron-deficient B, and the both, as well as to the dopant-free carbon nanomaterials, to elucidate the correlation of performance with electronic configuration, which is a general interesting issue in developing the advanced carbon-based energy materials [1].

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Carbon Nanotube Dry Adhesives with Performances Superior to Nature-originated Adhesions

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While chemical bonding are widely utilized in synthetic adhesives, nature-originated adhesions as exemplified by gecko and insects are mediated by van der Waals (vdW) forces, which arise from the attraction between molecules or atomic groups. As seen in geckos' feet, countless micrometre-sized setae with high aspect ratio are densely assembled onto macroscopic pads for intimate contacts with target surfaces, excelling in terms of adhesion strength among natural adhesion systems and allowing their locomotion on almost any vertical surface.

Here, we fabricated a series of CNT dry adhesives applied on rough surfaces for instance, polymer, paper, wood and even sand paper and painting wall with the roughness ranged from nanometer to millimeter scale. Roughness has been turned from "enemy" to adhesion "enhancer" that the record-high adhesion strength (135 ± 10.3 N/cm^2) was reported on the printing wall [1]. From our extensive investigation, we have elucidated the general rules governing the adhesion promotion of CNTs against roughness by increasing the effective contact area provided by CNT sidewalls. It was achieved by specific design of adhering top based on the rough surface information combined with the advanced tube structure tuning (e.g. CNT length). Furthermore, the design principles was extended to facilitate the double-sided CNT adhesives to hold substrate with distinguishably different roughness (e.g. glass and printing wall), and even three-dimensionally rough stuff (e.g. nickel foam) which is difficult to be accomplished by other adhesives.

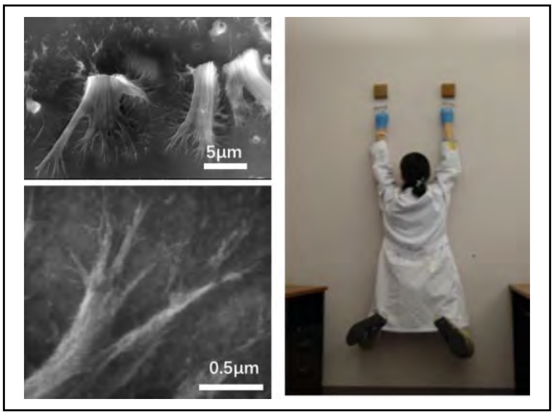

Fig.1 Demonstration of dry adhesion on painted wall. A human being of 54 kg by weight was held on the painted wall by using 6 pieces of the 2 cm × 2 cm CNT adhesives supported by two wood handles. The paint wall was partially peeled off by the three pieces of the CNT dry adhesives after deliberately taking each of the two wood handles away from the wall, indicating a very strong adhesion of the 2 cm × 2 cm CNT adhesives to the wall (scale bar: 2cm).

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Digital-Coded Isotope Labeling on Individual Single-Walled Carbon Nanotubes Grown on Crystal Quartz

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Single-walled carbon nanotubes (SWCNTs) are attracting increasing attention as an ideal material for high-performance electronics through the preparation of arrays of purely semiconducting SWCNTs. Despite significant progress in the controlled synthesis of SWCNTs, their growth mechanism remains unclear due to difficulties in analyzing the time-resolved growth of individual SWCNTs under practical growth conditions. Here we present a method for tracing the diverse growth profiles of individual SWCNTs by embedding digitally coded isotope labels [1]. Raman mapping showed that, after various incubation times, SWCNTs elongated monotonically until their abrupt termination. *Ex situ* analysis offered an opportunity to capture rare chirality changes along the SWCNTs, which resulted in sudden acceleration/deceleration of the growth rate. Dependence on growth parameters, such as temperature and carbon concentration, was also traced along individual SWCNTs, which could provide clues to chirality control. Systematic growth studies of with a variety of catalysts and conditions, which combine the presented method with other characterization techniques, will lead to further understanding and control of chirality, length and density of SWCNTs.

Part of this work was supported by JSPS KAKENHI Grant Numbers JP25107002, JP15H05760, JP17K06187 and JP17K14601. K.O. was financially supported by a JSPS Fellowship (JP15J07857).

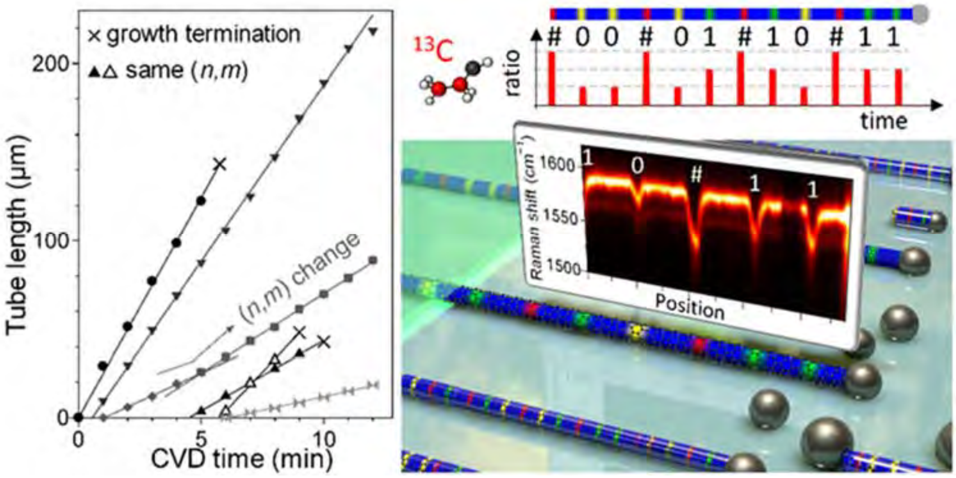

Fig.1 Growth of individual SWCNTs and schematics of digital isotope coding

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Strategies for the Chirality Control during Carbon Nanotubes' Growth

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The formation of the cap structure determines the chirality of the consequent SWCNT and the addition of the last pentagon can turn the SWCNT into one with any possible chiral angle. Therefore, the random formation of the last pentagon during SWCNT nucleation explains the even distribution of chiral angles in most SWNT samples.

During the cap formation, an external bias that affects the addition of the last pentagon may lead to the chirality-selected SWCNT growth. Detailed theoretical and experimental study suggests that the growth of (2n,n)-rich SWNT samples can be achieved by catalyst surface symmetry control.

Besides the nucleation stage, varying the chirality during SWNT growth is predicted to be another route towards the chirality-specific SWNTs synthesis. Such a predication has been successfully realized by experimental studies and the synthesized SWNTs show exact chirality distribution as predicated theoretically.

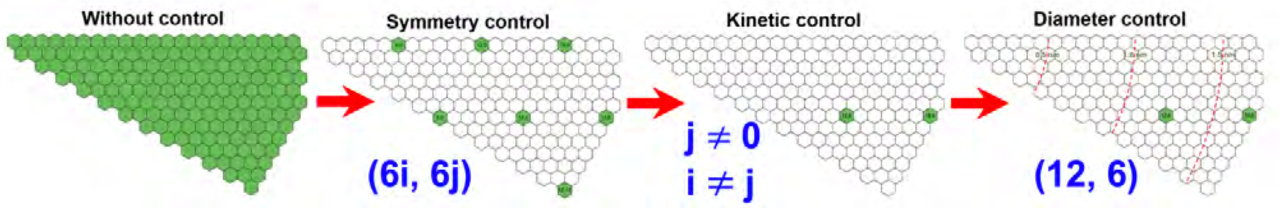

Fig. 1 The selective growth of (12,6) SWCNT by controlling the symmetry of the catalyst surface.

Growth and Characterization of Semiconducting Carbon Nanotubes for Nanoelectronics

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Carbon nanotubes (CNTs) are anticipated to be the successor to silicon in next generation integrated circuits. However, great challenges to the practical application of this concept include the need to grow horizontal semiconducting CNT (s-CNT) arrays with very high purity, and an efficient method to evaluate the purity. Here we show high throughput methods for evaluating the purity of large area carbon nanotube arrays by using SEM, with the imaging contrast coming from conductivity and bandgap[1-4]. Recently, we found that charge is generated during the CVD growth of CNTs[5-6], which inspired us to use electric field to twists the chirality of the CNTs during synthesis. As a result, nearly-defect-free s-CNTs horizontally-aligned on the substrate have been synthesized with less than 0.1% residual metallic CNT (m-CNT), thus offers a potential pathway to practical applications of CNT nanoelectronics[7].

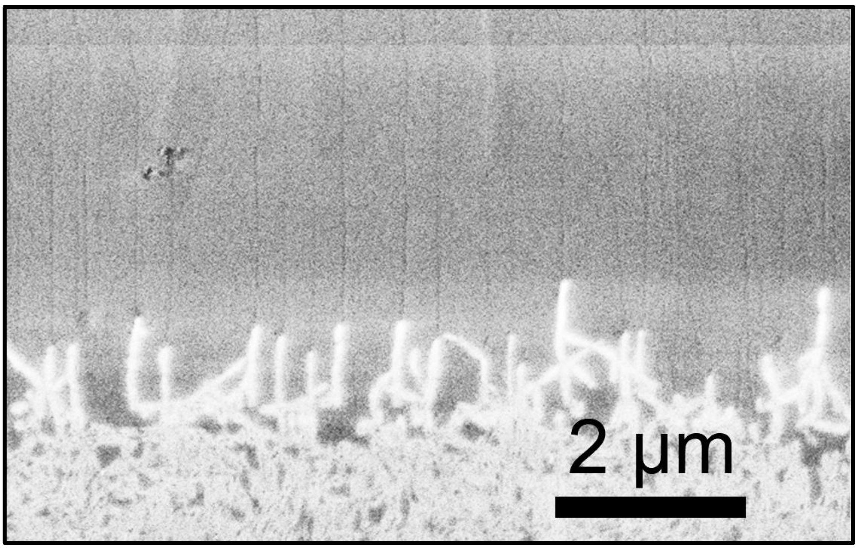

Fig.1 SEM image of the CNTs on quartz changing from bright to dark when the direction of the electric field reversed. This observation corresponds to the chirality change from metallic to semiconducting CNTs.

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Carbon Nanotube Forest Growth at 375 °C: Process Decoupling and Temperature Effect on Chiral Distribution

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We systematically study the synthesis of carbon nanotube forests by chemical vapour deposition aiming at fully controlling nanotube growth at temperatures below 450 °C. This is the allowed thermal budget for microelectronic and device manufacturing technologies. Using ultra-thin films of purely metallic Fe or Co along with process decoupling (catalyst formation/activation from nanotube nucleation/growth), we demonstrate it is possible to grow forests at temperatures as low as 375 °C. Of equal importance, the tubes appear to grow with very good alignment and well-graphitized walls. To accomplish this, it is essential to fully reduce the catalyst in ammonia (for proper activation) and finely control the amount of carbon source supplied, as low temperatures tend to easily lead to catalyst deactivation. On this basis, we propose a manufacturing process technology capable of producing nanotube forests employing microelectronic-compatible conditions, so it would allow direct nanotube integration into devices. The key requirement is to deposit the metal catalyst and proceed to restructuring into nanoparticles (and further nanotube growth) without exposition to air, hence avoiding metal oxidization. The typically high temperatures reported in the literature (600-800 °C) are largely related to the need of reducing the catalyst to purely metallic state. On the other hand, at temperatures as low as 375 °C, catalyst surface diffusion is, too, virtually negligible, and, as a result, the tubes grow with much more homogenous diameters and a narrow distribution of chiral angles, averaging seven to nine different chiralities per sample. Although the number of chiral angles is steadily observed to be below ten, further improvement appears to be extremely challenging to achieve. The essential level of narrowness in catalyst size and size-distribution requires nanoparticle control are at the very atomic level. However, that in itself exceeds the limits offered by the physical deposition methods usually employed to deposit the catalyst.

Kinetics Evolution Growth of (n, n-1) Tubes

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Semiconducting single-walled carbon nanotubes (SWNTs) with tunable bandgap are regarded as an ideal candidate for nanoelectronics applications. However, the semiconducting SWNTs obtained from traditional chemical vapor deposition (CVD) method usually have diverse structures. We herein reported a kinetic evolution growth method to enrich (n, n-1) semiconducting carbon nanotubes with tunable band gap by modulating the size of the ferromagnetic metal solid catalysts. At the low concentration of carbon source, the six-fold (1 1 1) face of ferromagnetic metal solid catalysts with certain size was served as the template for the nucleation of (n, n) tubes with three or six-fold. Due to the growth kinetics, (n, n) cap was forbidden to continue cyclic growth for the large barrier to create a new kink and has to change to (n, n-1) tube through the formation of 5|7 or 7|5 defects. Finally, (n, n-1) carbon tubes with small bandgaps, such as (13, 12), (15, 14), (16, 15) and (18, 17), could be enriched with abundance of 88.2% on quartz substrate using large size Co solid catalysts (2.4~3.6 nm) at 850ºC, and (10, 9) tubes with large bandgap were enriched about 83% at 650ºC. This design offers a new strategy for selective growth of fully semiconducting SWNTs with tunable band gap.

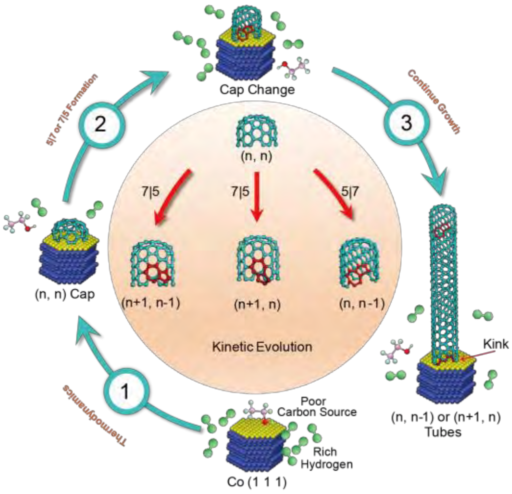

Fig.1 Schematic showing the kinetics evolution growth of (n, n-1) tubes

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High-performance single-wall carbon nanotube transparent conductive films prepared by floating catalyst CVD

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Single-wall carbon nanotubes (SWCNTs) have small diameter, good electrical conductivity, desirable light transmittance, high stability, and excellent flexibility. Therefore, they are an ideal candidate for making flexible transparent conductive films, which are an essential component of emerging flexible electronic devices. Here we prepare high-performance, large-area SWCNT transparent conductive films by a floating catalyst CVD method. As-grown floating SWCNTs were directly deposited onto a porous substrate equipped at the downstream of a CVD reactor without involving any liquid phase process. Therefore, the quality of the SWCNTs obtained is high, evidence by a high G/D ratio of Raman spectra. In addition, we selectively grew metallic SWCNT-enriched samples by tuning growth parameters and subsequent selective etching [1], and a high-performance transparent conductive film was obtained. By controlling the size of SWCNT bundles and their inter-tube resistance, the performance of SWCNT transparent conductive films were further improved, approaching that of ITO film on flexible substrates [2]. In addition to their simple and scalable film production process, good chemical stability and desirable mechanical flexibility and durability, these SWCNT films demonstrate great potential for use as transparent electrodes in various flexible electronics.

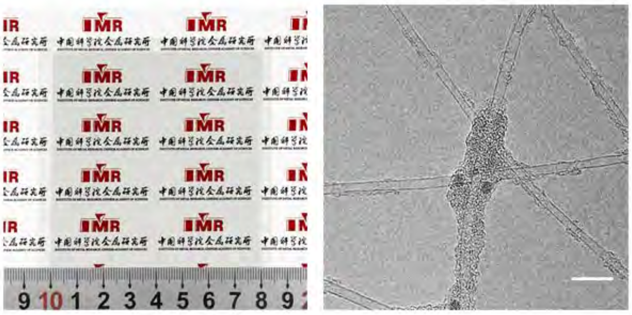

Fig.1 Transparent conductive film composed of carbon-welded isolated single-wall carbon nanotubes.

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Confined Catalysis in Carbon Nanotubes

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Carbon nanotubes (CNTs) attract wide attention for their unique physical and chemical properties due to their peculiar tubular morphology formed by the curved graphene layers. The one-dimensional nanochannels can be utilized as nanoscale containers for a series of materials and as nanoscale reactors for chemical reactions. Frequently, the nanotubes and the confined substances exhibit different properties from their respective mother parts due to the host-guest interaction, and hence resulting in nanocomposites with new properties which are not accessible by other means. For example, encapsulated metal-based (metal, metal oxide or metal carbide) nanocomposites in the form of discrete NPs or nanowires were demonstrated with potentials for applications in catalysis [1, 2], electrochemical energy storage, nanoelectronics, nanomedicine, and etc. Likewise, the chemical reactions confined within the nanotube channels also differ from those in the bulk. It was theoretically predicted that the confinement effects on metal nanoparticles become stronger with the decreasing diameter of CNTs and reach a maximum with a nanotube inner diameter of ~ 1 nm [3] However, introduction of metal nanoparticles particularly non-precious metals, within nanotubes with inner diameter smaller than 2 nm remains a challenge.

In this study, we report a versatile method which is applicable for encapsulating various non-precious metal NPs including Mo, W, V, Mn, Fe, Co inside SWNTs with a diameter of 1-2 nm in the form of oxide, metallic and carbide states [4]. The key lies in a small trick, i.e. oxidation treatment following evaporation of volatile cycloalkene metal carbonyl complexes precursors, at a temperature below their sublimation points. Studies reveal that over 95% nanotubes have been occupied by metal NPs within the channels following this method. This allows studies on their properties and the unique behavior of the catalysts within confined nanochannels, for instance in hydrogen evolution and ammonia synthesis.

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In Situ Study on Catalysts for Controlled Growth of Carbon Nanotubes

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The structure-controlled growth of single-walled carbon nanotubes (SWNTs) is an important issue for their advanced applications. The catalysts play an essential role in controlling the structure of the SWNTs [1, 2]. Revealing the role of catalyst in the working environments is crucial for understanding the controlled growth mechanism. We developed a family of tungsten-based intermetallic compounds for chirality specific growth of SWNTs. The Co_7W_6 intermetallic have high melting points (2400 °C) and very special crystal structures, acting as the structural templates with designed structures for growing SWNTs [3, 4].

Here, we demonstrated the structural and chemical stability of Co_7W_6 intermetallic catalysts at atomic level when feeding with carbon at high temperature (700-1100 °C). This was made possible by the use of using a state-of-the-art aberration-corrected environmental transmission electron microscope (ETEM) combined with electron energy loss spectroscopy (EELS). We also established *in situ* synchrotron X-ray absorption spectroscopy (XAS) operated in the atmospheric-pressure CVD and demonstrated the stable local coordination structure of Co_7W_6. No carbide formation or carbon diffusion induced structural change was observed from these *in situ* characterization. Statistical *in/ex situ* measurements of the tube−catalyst interfaces showed that all the caps and SWNTs are perpendicular to the plane of the Co_7W_6 catalysts. These results demonstrate that Co_7W_6 catalysts act as the stable structure template for the chirality controlled growth of SWNTs.

Cobalt catalyzed the SWNT growth is generally believed to via a vapor–liquid–solid mechanism. Using Co as a model catalyst, we elucidated the synergetic role played by the cooperation of Co-Co_3C in catalyzing CVD growth of SWNTs. We recorded *in situ* and at the sub-angstrom level, the carburization of cobalt nanoparticle and formation of Co_3C play an essential role in the nucleation of carbon cap and consequent growth by ETEM. These findings are crucial for the rational design of catalysts for high efficiently catalyzing SWNTs.

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The Bonding inside and outside Fullerene Cages

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As the only soluble form of elemental carbon, fullerenes can be accurately characterized with single crystal crystallography, one of the most powerful tools for atomic-resolution structural studies. Meanwhile, the sub-nanometer cavity of fullerenes is an deal platform to host a variety of metal atoms or metallic clusters, forming endohedral metallofullerenes (EMFs).[1]

Charge transfer from metal to cage in EMFs is critical to the stability of the resultant hybrid molecules and even to the chemical reactivity of the cage carbon atoms (**Fig.1**). During the last few years, results relating to the molecular structures, chemical properties and formation mechanism of EMFs have added new insights into modern coordination chemistry. For instance, it is discovered that the coordination behaviors of the encapsulated metal ions in the comfined sub-nanometer space of the cages are usually different from the situations found in bulky complexes and accordingly some materials show interesting properties and potential applications in different fields.[2,3,4]

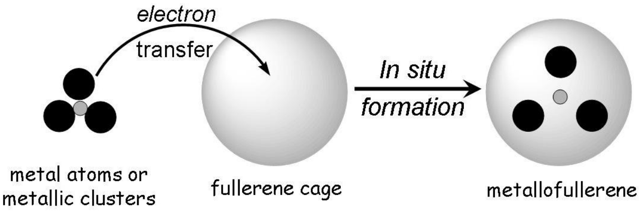

Fig.1 A Scheme showing the formation of endohedral metellofullerenes.

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Optical Spectroscopy of Individual Carbon Nanotubes with Defined Structure

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Abstract:

When the characteristic length of a material shrinks to 1 nm scale, many distinct physical phenomena, such as quantum confinement, enhanced many-body interactions and strong van der Waals inter-material couplings, will appear. To investigate the related fascinating low-dimensional physics, we need a tool to quantitatively link the atomic structures to the physical properties of these very small nano-materials. In this talk, I will introduce our recently developed in-situ TEM + high-sensitive ultrafast nano-optics technique [1], which combines capability of structural characterization in TEM and property characterization in nano-optics on the same individual nanomaterials. Several examples of using this technique to study the 1D carbon nanotube system will be demonstrated [2-3].

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Gd-metallofullerenol nanomaterial as non-toxic breast cancer stem cell-specific inhibitor

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Cancer has become the leading cause of death. The number of them who die each year from the disease could reach seventeen million. Nanomedicines hold great promise in biomedical applications especially in cancer therapeutics. The contemporary use of nanomedicines for cancer treatment has been largely limited to serving as carriers for existing therapeutic agents. Here, we provide definitive evidence that, the metallofullerenol nanomaterial $Gd@C_{82}(OH)_{22}$, while essentially not toxic to normal mammary epithelial cells, possesses intrinsic inhibitory activity against triple-negative breast cancer cells. $Gd@C_{82}(OH)_{22}$ blocks epithelial-to-mesenchymal transition with resultant efficient elimination of breast cancer stem cells (CSCs) resulting in abrogation of tumor initiation and metastasis. In normoxic conditions, $Gd@C_{82}(OH)_{22}$ mediates these effects by blocking TGF-β signalling. Moreover, under hypoxic conditions found in the tumor microenvironment, cellular uptake of $Gd@C_{82}(OH)_{22}$ is facilitated where it functions as a bi-potent inhibitor of HIF-1α and TGF-β activities, enhancing CSC elimination. These studies indicate that nanomaterials can be engineered to directly target CSCs. Thus, Gd-metallofullerenol is identified as a kind of non-toxic CSC specific inhibitors with significant therapeutic potential.

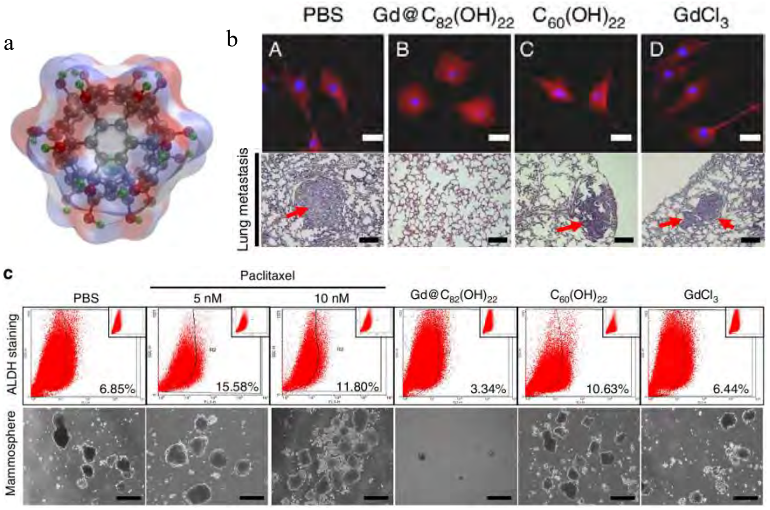

Fig.1 Gd-metallofullerenol nanomaterial as non-toxic breast cancer stem cell-specific inhibitor.

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Chirality phase diagrams for Single-Walled Carbon Nanotubes

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Since 25 years, significant progress has been achieved in the controlled synthesis of Single Walled Carbon Nanotubes (SWNTs), but we are still facing difficult issues concerning the yield and selectivity of their synthesis by Catalytic Chemical Vapor Deposition. The choice of a catalyst is critical, and hitherto made by trial and error. In fact, we don't know what are the required properties of a "good" catalyst for a selective SWNT growth.

Here, we answer this question by developing a statistical thermodynamics model, that in the case of a perpendicular growth[1,2], enables to relate the stable (n,m) tube structure, to the tube/catalyst interfacial energies for zigzag (E_{int}^{Z}) and armchair $\left(E_{int}^{A}\right)$ edges and the temperature. This model shows that, at low temperature, only zigzag or armchair tubes should be stable. Chiral tubes become stable at higher temperature because of the configurational entropy of the tube edge, that is indeed the key element of the model. This enables to produce chiral stability maps or "chirality phase diagrams" displayed in Figure 1, that makes it possible to understand under which conditions, a near armchair distribution can be obtained, and accounts for the temperature evolution of the chiral distributions reported in a number of experiments. The model[3], its relevance, usefulness, implications on our understanding of SWNT growth mechanisms, and possible improvements will be discussed.

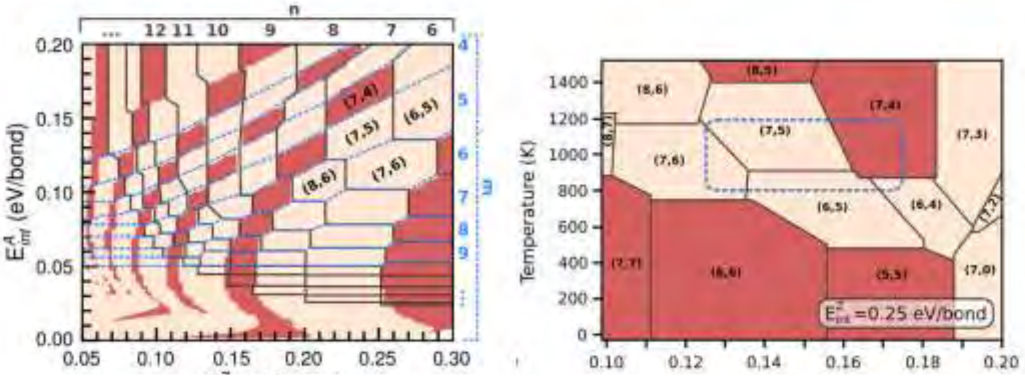

*Figure 1- **left**: Stability map at 1000 K, showing large parameter areas for armchair, and (n, n-1) (n,n-2) tubes; **right**: temperature dependent "phase diagram", calculated for* $E_{int}^{Z} = 0.25\ eV/bond$. *Red areas correspond to metallic tubes, flesh-colored ones to semiconducting tubes.*

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Raman spectra by circularly polarized light in 2D materials

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Resonant Raman spectroscopy of graphene and other two-dimensional (2D) materials have been investigated intensively for characterizing the multilayer 2D structure and their electronic structure [1]. However, it is not so well-known that circularly polarized light (CPL) change its helicity for some phonon modes in the 2D materials in which the helicity of light is defined by 1 or -1 for left or right handness (σ_+ or σ_- as shown in Fig. 1) of the CPL, respectively. For example, in the Raman spectra of G-band of graphene at 1585cm^{-1}, the CPL changes its helicity in the scattered light from the incident light as shown in Fig.1. In the transition metal dichalcogenides (TMD), on the other hand, although the in-plane Raman active mode changes the helicity, the out-of-plane Raman active mode does not change the helicity. Thus it is a natural question why the helicity changes in some Raman scattering.

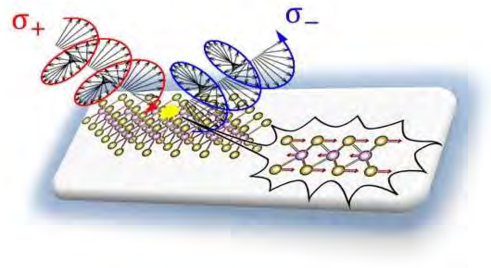

Fig.1: Circularly polarized light changes its helicity ($\sigma_+ \rightarrow \sigma_-$) in Raman scattering for in-plane phonon modes of 2D materials.

Since a photon of CPL has angular momentum of $+\hbar$ or $-\hbar$, the scattered light gets an angular-momentum quanta of $\pm 2\hbar$ from the 2D materials in the Raman scattering in the case of the helicity-changing Raman scattering. Thus we will start our discussion from the classical Raman tensor and the conservation law of angular momentum in the Raman scattering processes [2]. There are three sub-processes in the Raman scattering, (1) optical absorption, (2) emission of a phonon, (3) emission of a scattered photon [3]. In particular, in optical absorption and emission, the electron can excite by CPL only at one of the two valleys (valley is defined by energy bottom (maxima) of conduction (valence) energy band), which is known as optical valley-polarization [4]. Combining the phenomena of helicity-changing Raman spectroscopy with optical valley-polarization, we calculated resonant Raman intensity of TMDs by first principles calculation [5]. In the presentation, we will discuss origin of the helicity changing Raman spectra based on the calculated results.

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Hexagonal Boron Nitride in the Class of 2D Materials: Luminescence Properties

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Hexagonal boron nitride (hBN) is a wide band gap semiconductor (> 6 eV) of the 2D materials family, which is rapidly growing around graphene. Bulk hBN exhibits unusual optical properties. It presents a high luminescence efficiency in the deep ultra-violet range [1] despite an indirect electronic structure [2]. Recently, hBN has also become a strategic material in the fabrication of van der Waals heterostructures. Stacked with graphene and/or transition metal dichalcogenides, it can reveal the best of their physical properties [3,4]. As a key material for 2D heterostructures, it is therefore crucial to better understand hBN intrinsic properties and to capitalize them for developping relevant characterization spectroscopic techniques.

This talk will review recent advances made thanks to the development of appropriate spectroscopies to the UV range - cathodoluminescence (CL) at 4K, [5,6] angular resolved low loss EELS [7] and Raman spectroscopy [8] - combined with ab initio simulations and tight binding modeling [9,10]. We shall address in particular the long-time debate on the excitonic origin of hBN luminescence, following our previous studies on the impact of defects [6] and layer confinement on the luminescence properties [11]. The efficiency of excitonic radiative recombinations is compared for different hBN sources, ranking them in terms of crystallinity and purity [12]. Thanks to the spectral calibration of the set-up, we performed a quantitative analysis of the excitonic luminescence efficiency in a reference hBN crystal and evidenced a remarkable high value, almost two orders of magnitude higher than for diamond, although both materials present indirect bandgaps [13]. Contrary to diamond and ZnO, the hBN luminescence efficiency remains stable up to room temperature, consistently with tightly bound excitons. Ab initio calculations of the exciton dispersion in bulk hBN confirm that the luminescence is related to an indirect exciton, with a theoretical binding energy equal to 300 meV in agreement with the observed thermal stability of luminescence and standing 100 meV below the direct exciton [13].

The benefits of these findings will be shown to solve the long-standing debate on the Stoke shift in bulk hBN [13] and will be discussed for accounting low dimensionality effects observed in few atomic layers [11]. Beyond fundamental issues on the excitonic processes in lamellar crystals, these results highlight CL as a relevant characterisation [12] to accompany the integration of hBN in van der Waals heterostructures.

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Theoretical study on low-dimensional carbides for catalytic applications

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Recently, metal-free carbon-based nanomaterials attracted a lot of attention due to their potential in catalyzing several key reactions for energy conversion, especially hydrogen evolution reaction (HER). To accelerate the search for high-efficiency carbon-based catalysts, a deep understanding of physicochemical principle of the catalytic processes is required. Here, we present our recently work on underlying mechanisms governing HER processes, by investigating doping, curvature, spin, surface chemistry as well as solvation effects. For HER on MXenes, we have proposed a new descriptor with better performance compared to previous ones, which could help the fast screening of high-performance HER catalysts. [1] Further analysis based on Pourbaix diagrams shows that surface chemistry on Mo_2C during the catalytic process plays a key role in determining their performance. [2] These results offer useful theoretical insight to catalytic properties on C-based nanomaterials, which may facilitate the design of metal-free carbon-based catalysts.

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Single-walled carbon nanotubes co-axially wrapped with mono- and few-layer boron nitride nanotubes

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We propose a conceptually new structure, in which mono- or few-layer hexagonal BN seamlessly wrap around a single-walled carbon nanotube (SWCNT), and result in an atomically smooth coaxial tube consisting two different materials, as shown in Fig. 1. The structure is synthesized by chemical vapor deposition (CVD), and the length of the coaxial tubes can reach up to micrometers. As the reaction occurs on outer surface of the existing SWCNTs, we name this process conformal CVD. Various SWCNTs, e.g. vertically aligned array, horizontally aligned arrays, suspended SWCNTs, random networks and films, are employed as the starting material, and successful coating are achieved on all of them. Our characterizations confirm that the outside BN coating started locally on the wall of a SWCNT and then merged into a BN nanotube on the curved surface of the SWCNT which served as a template. The thinnest inner SWCNT that can support the BN layer growth is found to be 0.6-0.7 nm. The number of walls can be tuned from 1 to few by controlling the CVD condition. The structure of inside SWCNTs are almost not effected by the conformal CVD, as evidenced by Raman and many other characterizations. The crystallization and cleanness of the starting SWCNT template are believed to be critical for the successful fabrication of outside walls. This structure is expected to have a broad interest and impact in many fields, which include but not limited in investigating the intrinsic optical properties of environment-isolated SWCNTs, fabricating BN-protected or gated SWCNT devices, and building more sophisticated 1D material systems.

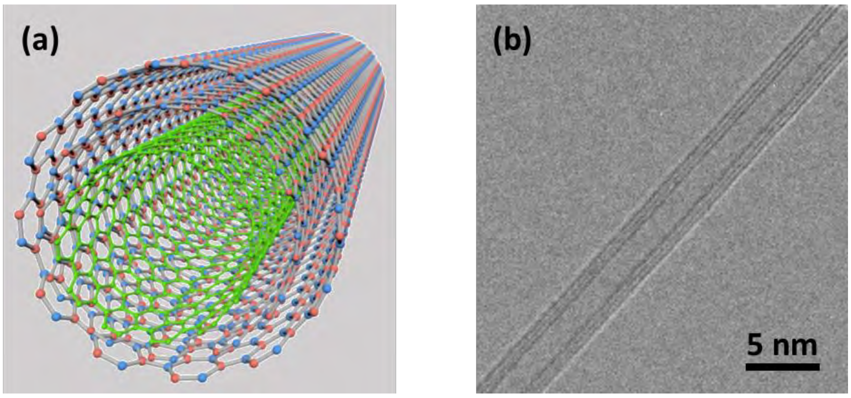

Fig. 1 (a) Schematic structure and (b) TEM image of an SWCNT wrapped with a bilayer BN nanotube.

Single-walled carbon nanotubes for flexible and stretchable electronic applications

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Unique properties of single-walled carbon nanotube (SWCNT) films, such as high porosity and specific surface area, low density, high ratio of optical transmittance to sheet resistance, high thermal conductivity and chemical sensitivity, and tunable metallic and semiconducting properties, open up avenues for a wide range of applications.

Here, we report about thin films of high quality SWCNTs produced by aerosol CVD (catalyst floating) method and use them as a key component of different flexible and stretchable electronic devices. The electrical properties of these devices can exhibit excellent characteristics compared to the traditional sensors due to a combination of high elastic moduli and outstanding electrical properties.

We report the application of the aerosol synthesized SWCNT thin films as transparent, flexible and stretchable electrodes for electrochemical double-layer capacitor (EDLC). SWCNT films exhibit extremely large specific capacitance (178 F g^{-1} or 552 μF cm^{-2}), high optical transparency and stability for 10000 charge/discharge cycles. The transparent supercapacitor can be stretched up to 120% elongation with practically no variation in the electrochemical performance during 1000 stretching cycles. For the first time, we report high-performance, stable, low equivalent series resistance (ESR) all-nanotube stretchable supercapacitor (SSC) based on single-walled carbon nanotube (SWCNT) film electrodes and boron nitride nanotube (BNNT) separator.

Also, we combined and examined a composite consisting of SWCNTs and tough hydrogels. These structures combine SWCNT film conductivity and transparency with hydrogel stretchability and biocompatibility as novel type of electrically conductive hydrogels. We further demonstrate applications of such structures as skin-like both passive electrodes and active motion sensors. A tactile sensor, a pulsometer and an electrical circuit are fabricated for the demonstration of applicability of SWCNTs in wearable electronics.

This work was supported by Skoltech NGP Program (Skoltech-MIT joint project).

Influence of Dissolved Oxygen on Defect Introduction to SWCNTs in Ultrasonic Dispersion Process

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Ultrasonic dispersion process is crucial for getting individually dispersed single-wall carbon nanotubes (SWCNTs), which is essential for the metal/semiconductor separation and following electronic device applications. A serious problem with this process is that defects are introduced in the SWCNT wall. Here, one can think that dissolved oxygen may promote the defect introduction. In this work, we tried to clarify the effect of dissolved oxygen on the defect introduction to SWCNTs.

In this work, for the assessment of defect introduction, a G/D intensity ratio of Raman spectrum was used. SWCNTs produced by electric arc discharge (AP grade, Carbon solutions INC, USA) was used as starting material. Sodium cholate 0.5 wt% aqueous solution was used as solvent, which is easily applied for following separation process. To remove the dissolved oxygen, all equipment was installed in a grove box filled with highly purified N_2 gas. We confirmed that the tip-type sonication quickly degassed dissolved oxygen and replaced to N_2. As a control, the same experiments were done in air. After the dispersion process, samples were ultracentrifuged for 30 min and upper 80% supernatant was collected. Then we measured Raman spectra of all samples using 488, 532, 633, and 785 nm lasers. Since mean diameter of AP SWCNT is around 1.4 nm, resonance of semiconducting SWCNTs were observed for 488 and 532 excitations. Interestingly, G/D ratio of SWCNTs dispersed in pure N_2 was sometimes lower than that dispersed in air. Because saturated gas concentration in water of N_2 is smaller than that of air (N_2+O_2), a "cavitation effect" was lower in pure N_2 condition. Therefore, ultrasonic power was applied to SWCNT more effectively in pure N_2 condition, which causes quicker dispersion but more defects. To see the true effect of dissolved oxygen, therefore, we had to analyze a relationship between the dispersion efficiency and the defect density. Figure 1 shows a relation between G/D ratio and the dispersion efficiency. In pure N_2 condition, G/D ratio was higher for the same dispersion efficiency. This result indicates that the ultrasonic dispersion in pure N_2 is effective to get lower defective SWCNT dispersion.

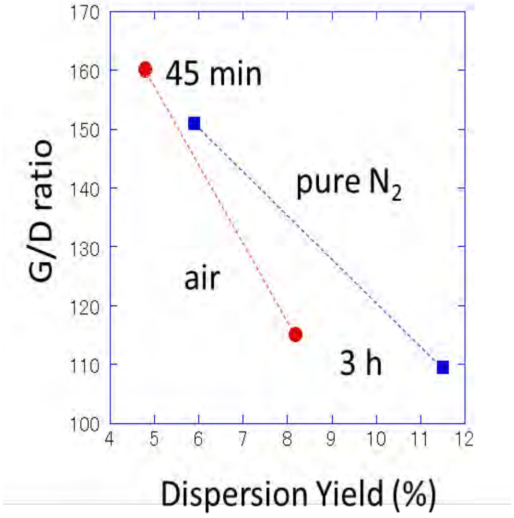

Figure 1. G/D ratio and dispersion yield

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Precise Quantification of Cut Boron Nitride Nanotubes in Liquids

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Nanotubes are potentially applicable for bio-sensing and intracellular drug delivery. Unfortunately, many related study are based on estimated small quantity of nanomaterials (µg/ml level), which has led to discrepancies in reported literature. For instance, boron nitride nanotubes (BNNTs) are chemically inert, making them a promising candidate for biomedical applications.[1] However, biomedical application of BNNTs are relatively unexplored due to the synthesis difficulty of high-quality BNNTs.[2] Reported data so far are derived from defective and low purity BNNTs and far from representable. Here we report on precise quantification of short (<500nm) and high-quality BNNTs with nanotube concentration down to ~1.3 µg/ml at an accuracy as high as 99%.

High-quality BNNTs are wide band gap materials (~6 eV with no intra-band absorption)[2-3], therefore UV-Vis absorption spectra in the visible range is not applicable for quantification. We propose a novel approach to quantify cut BNNTs by modified UV-vis spectroscopy. High-purity BNNTs (>99.9 wt%) were grown by catalytic chemical vapor deposition (CCVD).[3] The as-grown BNNTs are extracted in distilled water by sonication. The weight of the as-grown BNNTs can be precisely measured in the mg level. The extracted BNNTs was then functionalized with biocompatible PEGylated phospholipid [methoxy-poly(ethylene glycol)-1,2-distearoylsn-glycero-3-phosphoethanolamine-N conjugates (mPEG-DSPE, Mol. Wt. 5000) to make them water dispersible.[4] As functionalized BNNTs were cut by sonication to a nominal length below ~500 nm without weight lost. The as cut BNNTs were examined by field emission scanning electron microscope (FESEM) and analyze for their length distribution. These cut BNNTs are then used to generate our UV-Vis calibration curves from mg/ml to µg/ml levels. These calibration curves were further improved by a series of repeatable experiments to refine their accuracy. The accuracy of these curves is verified with another series of cut BNNT samples with a wide range of known concentrations. Our results proven that the refined calibration curves can be used to quantify concentration of cut BNNTs based on selected spectra range at an accuracy as high as 99%. The details of these quantification experiments, and the hemolysis and cell viability test results will be presented in the meeting.

Y.K.Y. acknowledges the support from the National Science Foundation, Division of Materials Research (Award No. 1261910).

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Nucleation and Growth Mechanisms of Boron Nitride Nanomaterials– Non-Equilibrium Molecular Dynamics Simulations

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Over the last few decades, catalytic chemical vapour deposition (CVD) has matured as a synthetic technique for producing many low-dimensional inorganic nanomaterials, such as carbon nanotubes, graphene and boron nitrides. However, in contrast to carbon nanomaterials, such as graphene and CNTs, little is known regarding the catalytic pathways underpinning CVD synthesis of boron nitride nanomaterials [1]. Here we present a CVD mechanism explaining the self-assembly of boron nitride nanomaterials via boron oxide CVD (BOCVD), using non-equilibrium ReaxFF molecular dynamics simulations. BOCVD involves heating solid B and a metal oxide such as MgO, FeO or Li_2O, producing B_2O_2 to react with a flow of NH_3 to form BNNTs on the walls of the reactor or on catalyst surfaces such as MgO, Fe and Ni [2]. Our simulations show that the initial steps in this reaction involve the isomerization of small $B_xN_yO_xH_z$ fragments via H transfer. Ultimately this process yields larger species that over time self-assemble into borazine rings (Figure 1(a)), the fundamental structural unit of BNNTs and hexagonal boron nitride. Our simulations also address the key roles played by H_2O and H_2 partial pressures, the presence of solid-phase catalytic nanoparticles on this mechanism (Figure 1(b)). Comparison of the BOCVD nucleation mechanism observed with that found using ammonia borane (HN_3-BH_3) also enables us to elucidate the chemical role of oxygen on the formation mechanism of BN nanomaterials.

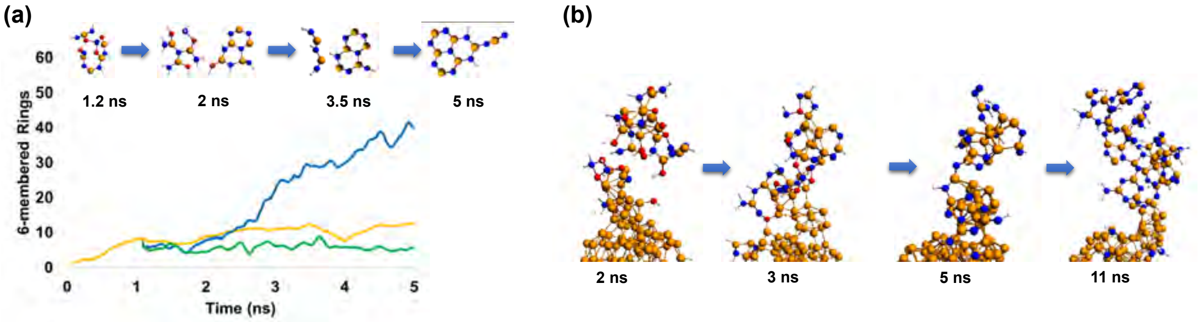

Fig. 1. (a) ReaxFF MD simulations reveal the mechanism of borazine ring nucleation during BOCVD and (b) reveal the effects of solid phase nanoparticles on BN nanomaterial nucleation.

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Improved Synthesis of Linear Carbon Chains Inside Carbon Nanotubes

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Recently we demonstrated synthesis of confined one-dimensional linear carbon chains (LCCs) inside double-walled carbon nanotubes (DWCNTs) with the shortest chains consisting of around 30 carbon atoms (polyyne) and the longest chains with a record length of more than 6000 carbon atoms (carbyne) [1]. The carbyne formation was confirmed by near-field Raman spectroscopy and its property was much tailored by its nanotube host [2]. In this presentation, I will show our recently improved methods, which allows us to control the synthesis of LCCs with different lengths and enhance the filling ratio of the chains. For example, size-controlled single-walled carbon nanotubes used as starting materials were annealed at high-temperature in high-vacuum: Thin inner tubes can be formed first [3], whereas LCCs then synthesized inside new-formed inner tubes. The length distribution of the LCCs can be then tailored by the diameter distribution of host carbon nanotubes [4]. In addition, solvents can be used as additional carbon source to increase the filling ratio of the LCCs [5]. As another example, I will show our new developed method for the LCC synthesis inside individual DWCNT [6], which helps us to easily figure out the configurations and interactions [7] between the LCCs and the host nanotubes.

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SWNT thin films for 3D electronics applications

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We introduce the industrial scale, ISO 9001:2008 certified direct dry printing (DPP) manufacturing of single walled carbon nanotube (SWNT) based transparent conducting films (TCF) for touch sensors with electrical properties on par with those of ITO-on-PET, and with optical as well as mechanical properties i.e. bendability and flexibility better than those of ITO, metal nanowire and metal mesh [1,2]. All carbon transparent, flexible and stretchable TFT-FETs have been made using percolating SWNT network as the semiconductor and SWNT TCF as the source, drain, gate and interconnect material [3,4], demonstratig capability to produce 3D devicve structures. Studies on the SWNT synthesis from CO with trace amounts of CO_2 using the ferrocene based floating catalyst chemical vapor deposition (FC-CVD) show that SWNT networks consisting of long, clean and highly individualized SWNTs exhibit substantially improved TCF performance [5]. TCFs made from individual tubes with 4 micron mean length show 63 ohms/sq sheet resistance at 90 % transparency. Patterned SWNT-based TCFs show 69 ohms/sq sheet resistance at 97 % transmittance and 29 ohms/sq at 87 % transparency [5]. We present recent results on SWNT (n,m) control in the FC-CVD synthesis processes using ethylene, ethanol and toluene as the carbon sources [6,7]. In addition, we will present current status of industrial manufacturing of SWNT based commercial touch sensor products for the emerging 3D sensor markets.

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High strength and high toughness carbon nanotube fiber and film

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The fabrication of macroscopic assemblies of carbon nanotubes (CNTs) such as fibers and films is an essential step towards real applications. All the macroscopic assemblies developed so far exhibited low tensile strengths ($\leq$ 2.5 GPa), and it appeared to be a big challenge to transfer the outstanding properties of individual CNTs to the macroscopic scale. In this presentation, we report a new method for preparing CNT fiber and film and strength improvement to 8.0 GPa with a Young's modulus of 150 GPa, and tensile elongation of 8%. The alignment and packing density of the CNTs in the fiber and film are found to be important factors affecting the mechanical properties. Our CNTs are continuously produced by a spray pyrolysis approach, self-assemble into to a hollow cylindrical assembly in a tube reactor and then condense as a fiber or film on a winding apparatus. This method offers good suitability for scaled up production.

Constructing Carbon Nanotube Networks for Electrochemical Energy Storage

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Lightweight thin-film energy storage devices with high energy density and power density are highly needed. In this talk, I will briefly introduce our recent work on the preparation and structure optimization of carbon nanotube films and their utilization for thin-film energy storage devices, which include, 1) direct growth and assembling light-weight, large-area, flexible and highly conductive CNT films used for electrodes of batteries and supercapacitors; (2) development of an electrochemical activation approach, which could active CNT film and enhance the electrochemical and loading sites; (3) activated CNT film deposited with capacitive materials performed as both the electrochemical electrode materials and current collectors for flexible supercapacitors with high capacitive activities; (4) activated CNT film loaded with oxygen catalysts constructed all-in-one air electrodes, combining the catalysts, current collectors and gas-diffusion electrodes for flexible Zn-air battery.

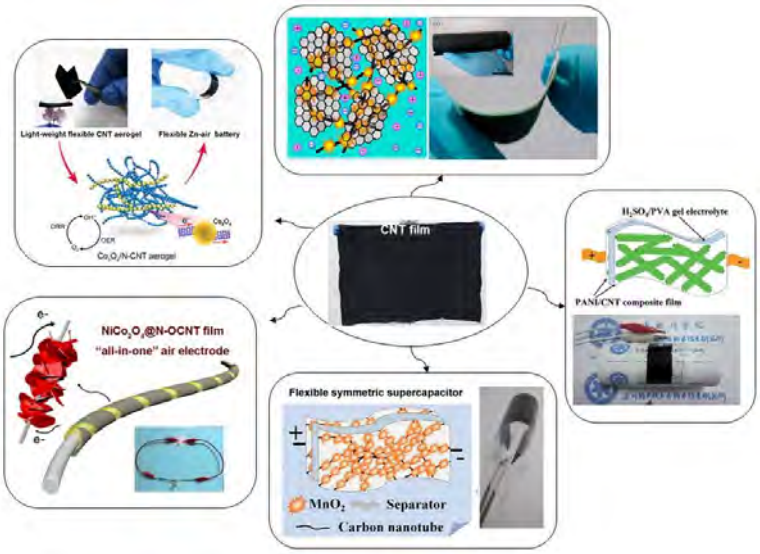

Fig.1 Carbon nanotube networks for energy-storage devices

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Carbon Nanotube Sponges and Energy Storage Applications

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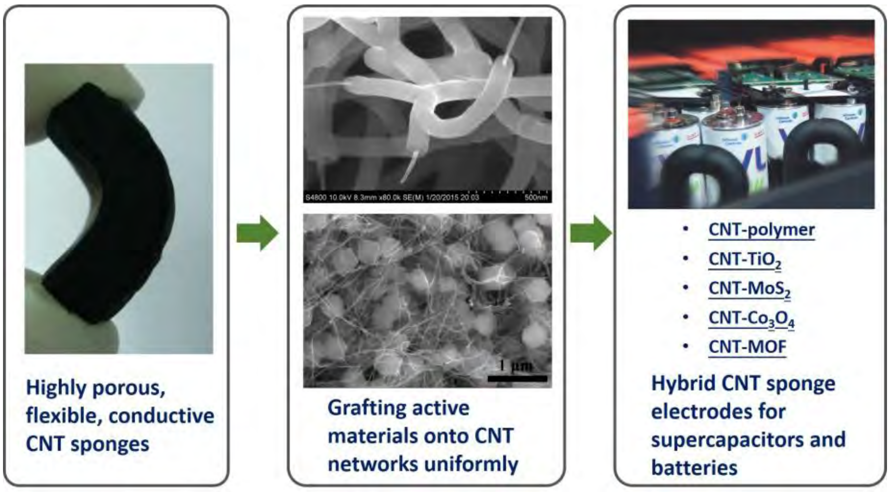
Development of advanced energy storage systems such as supercapacitors and rechargeable batteries demands high performance electrode materials. Carbon nanotube (CNT) sponges are bulk aerogel-like materials made from three-dimensionally overlapped multi-walled nanotubes. They are light-weight, highly porous and flexible, with many potential applications such as adsorption, catalysis, sensors and electrodes. In this presentation, I will describe the synthesis method, structural characteristics and unique properties of CNT sponges in the context of macroscopic CNT or graphene-based assemblies. Using the sponge as a three-dimensional isotropic porous template, we have fabricated various hierarchical composite materials with tailored microstructures and interesting properties. Examples include CNT-pseudo polymer composite sponges could serve as compressible electrodes for supercapacitors, CNT-MoS_2 and CNT-Co_3O_4 core-shell sponges act as high-capacity lithium ion battery anodes, and CNT-MOF hybrid networks for lithium-sulfur batteries.[1-6] CNT sponges thus provide a universal platform for manufacturing functional nanocomposite materials and exploring a wide range of applications particularly in energy and environmental areas.



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Hierarchical Structured Carbon Materials for Flexible and Wearable Electronics

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The development of flexible electronics and equipment attracts significant interests in recent years. Carbon materials are one kind of ideal materials for flexible electronics. It is of great importance to explore low cost and scalable preparation approaches for high performance flexible carbon materials-based wearable electronics. Herein, we use carbon materials, including carbon nanotubes, graphene, and natural mass derived carbon (such as silk, celluse) as the key materials and develop a series of flexible wearable sensors, wires and energy devices [1-5]. The hierarchical structures of the carbon materials plays important roles in achieving flexible devices with desired performance. We further demonstrated their applications and show their great potentials for applications in wearable electronics and smart textiles. Our strategy provides new approaches for the low-cost and high performance production of carbon-based flexible and wearable electronic materials, shedding light on their practical applications in next-generation electronics.

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Wearable electronics based on graphene materials

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Graphene has attracted great interests from both academia and industry partners since 2010, when Nobel Prize was awarded to Prof. Andre Geim and Prof. Konstantin Novoselov for groundbreaking experiments regarding this two-dimensional material.

In this talk, I will review some of our work on using graphene in wearable electronics such as sensors and RFID tags. Unique properties of graphene materials were explored to be applied in 5G communications and internet of things.

Encapsulation of 2D materials inside carbon nanotubes: towards an enhanced synthesis of single-layered metal halides

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The formation of low dimensional systems is a powerful tool for tuning the physical properties of materials. The unique characteristics of two-dimensional (2D) nanomaterials make them highly attractive for a wide range of applications. A variety of approaches have been explored to synthesize and control their size, morphology and crystal structure. Template-directed synthesis represents a convenient and versatile route and both organic and inorganic-based materials are usually employed for this purpose. Since carbon nanotubes (CNTs) can have a wide range of diameters and lengths, their inner hollow cavity can be filled with a large variety of compounds. Furthermore, the presence of CNTs might create synergistic effects with the filling material, resulting in unique properties and superior performance. Despite their interest, the number of reports on single-walled inorganic nanotubes is limited because the formation of their multi-walled counter parts is favored during the synthesis. Here we report on the synthesis of individual layers of several 2D van der Waals solids, namely CeI_3, $CeCl_3$, $TbCl_3$ and ZnI_2[1], and PbI_2[2] using CNTs as directing agents. Recent theoretical studies reveal that these heterostructures, consisting of single-layers and a carbon host can substantially enhance the visible light response, suggesting potential applications in novel 2D optoelectronics and photovoltaics[3]. Once confined, the metal halides can adopt different structures including single-layered metal halide nanotubes, which formation is greatly enhanced by increasing the temperature of synthesis[1]. This opens up a new strategy for the isolation of individual layers of a wide variety of metal halides, a family of 2D materials that has been barely explored.

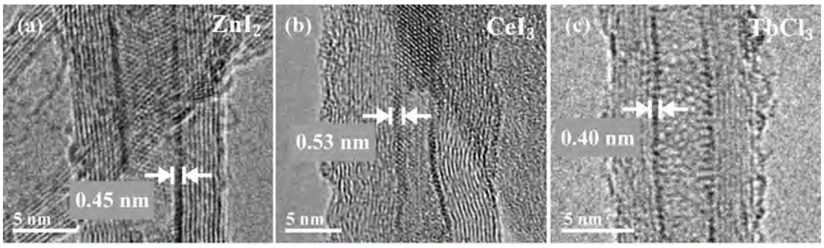

Fig.1 HRTEM images of (a) ZnI_2@MWCNTs, (b) CeI_3@MWCNT and (c) $TbCl_3$@MWCNTs.

[1] Sandoval S., Pach E., Ballesteros B., Tobias, G. Carbon **123**, 129 (2017).

[2] Cabana L., Ballesteros B., Batista E., *et al.* Adv. Mater. **26**, 2016 (2014)

[3] Zhou M., Duan W., Chen Y., Du A. Nanoscale **7**, 168 (2015).

High-Yield Production of MoS_2 and WS_2 Quantum Sheets from Their Bulk Materials

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Mass production of two-dimensional quantum sheets (2D QSs) is highly desired to fully exploit their properties. Herein, we present a general strategy for the high-yield production of molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) QSs by a sequential combination of salt-assisted ball-milling and sonication-assisted solvent exfoliation of their bulk materials. Such a strategy enables reproducible production of intrinsic and defect-free MoS_2 and WS_2 QSs with exceedingly high yields of 25.5 and 20.1 wt %, respectively. By precipitation-redispersion treatment, the QSs can be redispersed in a wide range of solvents with redispersion concentration up to 20 mg/mL or even higher. Remarkable nonlinear absorption saturation is demonstrated in the QSs-poly(methyl methacrylate) (PMMA) hybrid thin film with loading content of merely 0.1 wt %. Our method provides an avenue toward mass production and full exploration of 2D QSs.

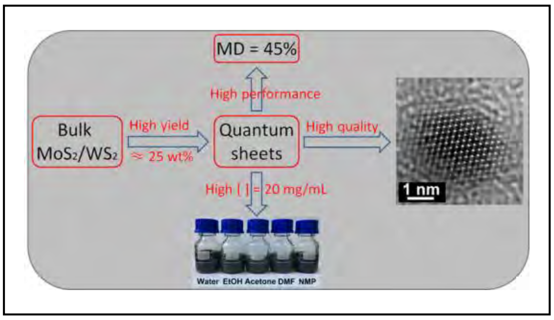

Fig.1 "4H" character of the MoS_2 and WS_2 quantum sheets.

[1] C. Han, Y. Zhang, P. Gao, S. Chen, X. Liu, Y. Mi, J. Zhang, Y. Ma, W. Jiang, J. Chang, Nano Lett. **17**, 7767 (2017).

Growing highly-pure semiconducting carbon nanotubes by electro-twisting the helicity

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Carbon nanotubes (CNTs) are anticipated to be the successor of silicon in next generation integrated circuits. However, one great challenge to the practical application of this concept is the need to grow horizontal semiconducting CNT arrays with very high purity. Here we show that this roadblock can be eliminated by switching the direction of an applied electric field during synthesis. This electro-renucleation approach twists the chirality of the CNTs to produce nearly-defect-free s-CNTs horizontally-aligned on the substrate with less than 0.1% residual metallic CNT. In principle, this residual percentage can be further reduced to less than 1 ppm simply by tuning the CNTs' diameters to around 1.3 nm. Electro-renucleation thus offers a potential pathway to practical applications of CNT electronics and opens up a new avenue for large-scale selective synthesis of semiconducting CNTs and other nanomaterials.

Direct Synthesis of Aligned Semiconducting Graphene Nanoribbon Arrays

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We have discovered how to drive graphene crystal growth with a large shape anisotropy through control of kinetics on the surface of Ge(001) single crystal wafers via CH_4 chemical vapor deposition. This discovery enables the direct synthesis of narrow, armchair, semiconducting nanoribbons. The ribbons are self-orienting, self-defining, and have smooth edges. The ribbons exhibit exceptional transport properties (e.g., high on-state conductance and on/off ratio at room temperature) and provide a promising pathway towards the direct integration of high-performance nanocarbon electronics onto conventional semiconductor wafer platforms. This presentation will detail the synthesis of these ribbons with widths as narrow as 1.7 nm, the synthesis of seeded arrays of nanoribbons, the elucidation of their structure, and the characterization of their promising charge transport properties.

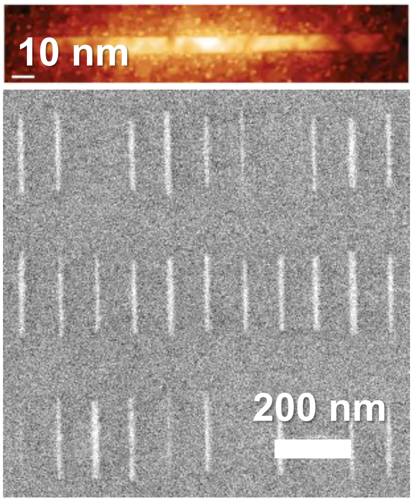

Fig. 1 (Top) STM image of single 10 nm nanoribbon on Ge. (Bottom) SEM image of nanoribbon array.

[1] R. M. Jacobberger, M. S. Arnold, et al., *Direct Oriented Growth of Armchair Graphene Nanoribbons on Germanium*, NATURE COMMUNICATIONS, 6, 8006 (2015).

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Approaching Metre-Sized Single-Crystal Graphene

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A foundation of the modern technology that uses single-crystal silicon has been the growth of high-quality single-crystal Si ingots with diameters up to 12 inches or larger. For many applications of graphene, large-area high-quality (ideally of single-crystal) material will be enabling. Since the first growth on copper foil a decade ago, inch-sized single-crystal graphene has been achieved. We present here the growth, in 20 minutes, of a graphene film of 5 × 50 cm2 dimension with > 99% ultra-highly oriented grains. This growth was achieved by: (i) synthesis of sub-metre-sized single-crystal Cu(111) foil as substrate; (ii) epitaxial growth of graphene islands on the Cu(111) surface; (iii) seamless merging of such graphene islands into a graphene film with high single crystallinity and (iv) the ultrafast growth of graphene film. These achievements were realized by a temperature-driven annealing technique to produce single-crystal Cu(111) from industrial polycrystalline Cu foil and the marvellous effects of a continuous oxygen supply from an adjacent oxide. The as-synthesized graphene film, with very few misoriented grains (if any), has a mobility up to ~ 23,000 cm^{2}V^{-1}s^{-1} at 4 K and room temperature sheet resistance of ~ 230 Ω/□. It is very likely that this approach can be scaled up to achieve exceptionally large and high-quality graphene films with single crystallinity, and thus realize various industrial-level applications at a low cost.

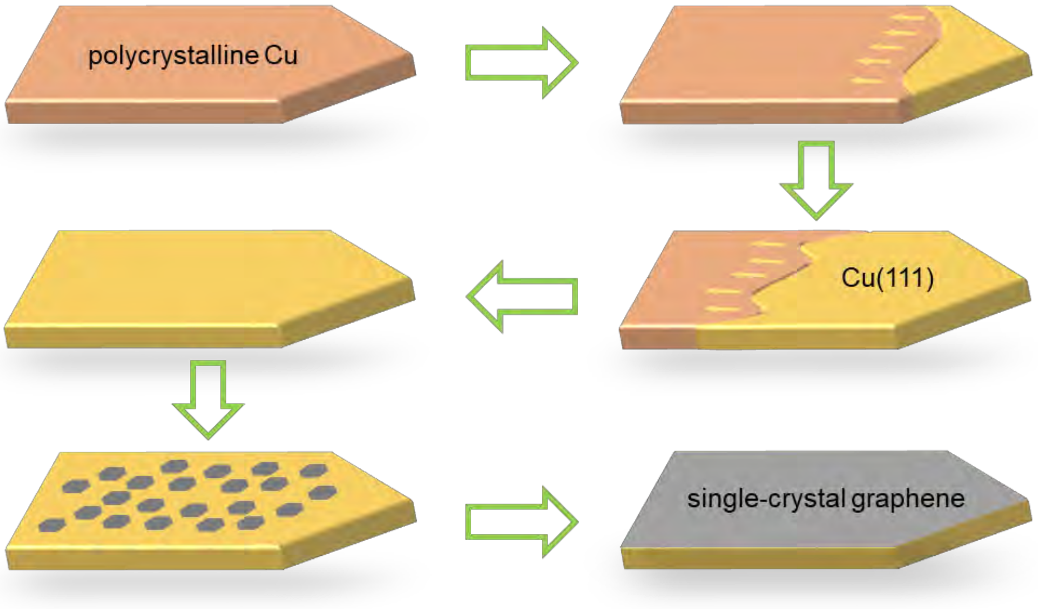

Fig.1 The schematic diagram of the epitaxial growth of single-crystal graphene.

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Highly conductive nanocomposite enabled by an accordion-like graphene network

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Abstract

Graphene reinforced polymer nanocomposites can have favorable electrical properties, making them promising in electromagnetic, electrochromic and photovoltaic devices. Using graphene to fabricate nanocomposites with specific electrical properties requires that the dispersion of graphene in polymer matrix is well controlled, which however remains a big challenge. Here, we propose two intriguing designs, i.e., slightly oxidizing graphene sheets and hot drawing nanocomposites, resulting in a uniform, dense and highly aligned graphene network. The achieved conductivity of nanocomposites is as high as 25 S m^{-1} at 6.25 wt% of graphene, which is 8 and 2 orders of magnitude higher than those of polymer matrix and nanocomposites without hot drawing, respectively. Furthermore, prototypes of heating films and flexible supercapacitors made of the highly conductive nanocomposites both exhibit high performance.

Encapsulation and Polymerisation of Arsenic and Phosphorus Inside Single-wall Carbon Nanotubes.

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Single-wall Carbon Nanotubes (SWCNTs) are one of the most exciting materials to have been discovered due to their range of useful and tuneable properties. Shortly after their discovery, they were filled with a range of materials to examine how one-dimensional confinement can affect the filling material. Arsenic and phosphorus display some of a diverse ranges of allotropes, the most famous being the tetrahedral molecular units that these elements can form. Here, we report that P_4 and As_4 can been encapsulated and stabilized within SWCNTs. Phosphorus has been shown to form tetrahedra inside the SWCNTs from both melt and vapour filling procedures from either white phosphorus or red phosphorus respectively[1]. Arsenic has also been observed to form tetrahedra within the SWCNTs when starting from grey arsenic[2]. The SWCNT can successfully stabilize the tetrahedra against the highly exothermic reaction with atmospheric oxygen and has also prevented yellow arsenic from converting back to grey arsenic. Transmission electron microscopy was used to visualise the composites and revealed that the tetrahedra can convert readily to chain structures when confined. Arsenic exhibited similar behavior to red phosphorus in this regard with more filled tubes showing the polymerized structures as opposed to tetrahedral units. When white phosphorus has been used, more tetrahedra have been visualised. The energies of the possible chain structures were determined computationally highlighting a delicate balance between the extent of polymerization and the SWCNT diameter. Experiments have also begun trying to stabilize antimony tetrahedra.

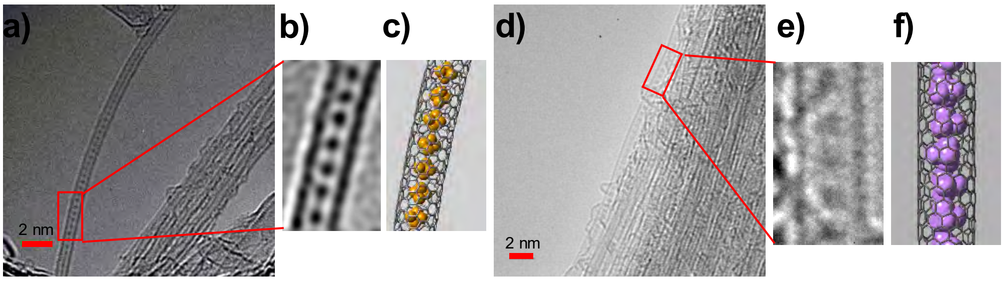

Figure 1. (a) Encapsulated white phosphorus tetrahedra. (b) Zoom of highlighted region in (a). (c) Molecular representation of encapsulated white phosphorus. (d) Encapsulated yellow arsenic tetrahedra (e) Zoom of highlighted region in (d). (f) Molecular representation of encapsulated yellow arsenic.

[1] Hart, M.; *et al.*, *Angew. Chem. Int. Ed.* **2017,** *56* (28), 8144-8148.

[2] Hart, M.; *et al.*, **2018** – submitted.

Temporal and spatial evolution of hydrocarbons and catalytic precursors in gas phase and on the substrate during CVD growth of carbon nanotubes

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Floating catalyst chemical vapor deposition (FCCVD) is commonly considered as one of the most attractive process for the production of carbon nanotubes (CNTs). Understanding the phenomena occurring during the FCCVD synthesis of CNTs is critical to improve the process selectivity and scalability, in particular, the temporal and spatial evolution of carbon and catalytic precursors as function of the synthesis conditions, as shown in Figure 1. The chemical compositions and nanoparticle activity could significantly influence the structural characteristics and the growth rates of the carbonaceous products. In this presentation, we would like to present some results obtained during past several years as well as our understanding about the CNT formation mechanism. Firstly, we made a great effort on characterization of the evolution of the nanoparticles in the gas phase during the CNT synthesis by different microscopy and spectroscopy techniques [1]. Their roles during CNTs growth were analyzed by correlating nanoparticle nature with the morphology of CNTs grown on the substrate along the reactor axis. Then, the effect of reductive gas-hydrogen on hydrocarbon decomposition and CNT growth has also been investigated under commonly used experimental conditions [2]. Hydrogen interferes with the decomposition of catalytic precursors, thus influencing the size and availability of catalyst nanoparticles. These understandings are helpful to approach application- & design- directed CNT growth and organization, and improve its production efficiency.

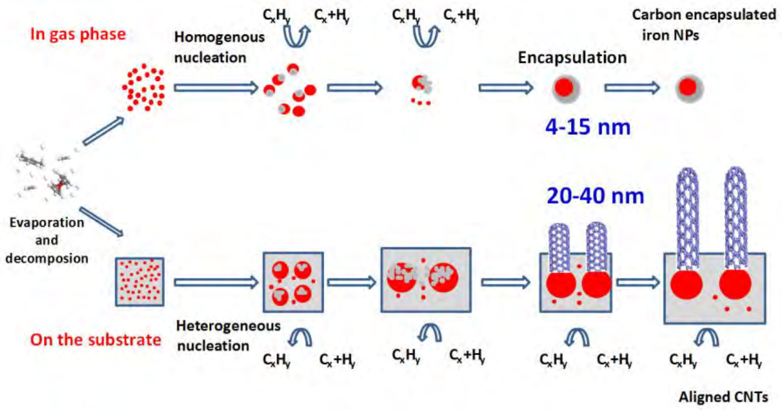

Fig.1 Schematics showing the evolution of hydrocarbons and catalytic precursors in gas phase and on the substrate [1].

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Growth of coiled amorphous carbon nanotube array forest and its electromagnetic wave absorbing properties

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CNTs have both metal and semiconductor characteristics [1]. Meanwhile, CNTs have special helical structures and chirality [2], which will produce special new electromagnetic effects. As for the performance, the unique mechanical, electrical and magnetic characteristics of CNTs indicate that it will surely have a broad application in the new stealth materials for electromagnetic wave absorption [3,4].

Coiled amorphous carbon nanotube (CACNT) array with unique three-dimensional spiral structures has drawn much attention due to their potential applications such as high-performance electromagnetic wave absorbers, micro-/nano-scale solenoids, heaters and springs. CACNT was prepared by chemical vapor deposition method. The experimental results indicated that the length of as-prepared CACNT array was about 30 mm. The electromagnetic wave absorbing properties were studied through comparison among CACNTs, CACNT-La$(NO_3)_3$, CACNT-(Fe, Co, Ni) and CACNT-reduced graphene oxide (RGO). The experimental results showed the maximum frequency bandwidth of CACNT-(Fe, Co, Ni) was 6.4 GHz below 5 dB and 2.3 GHz below 10 dB separately. Compared to the pure CACNTs, all the frequency bandwidth had been broaden after adding the modified agent. Meanwhile, the additive of rare earth ions La^{3+} could effectively increase the maximum absorption peak (17.94 dB at 8.96 GHz).

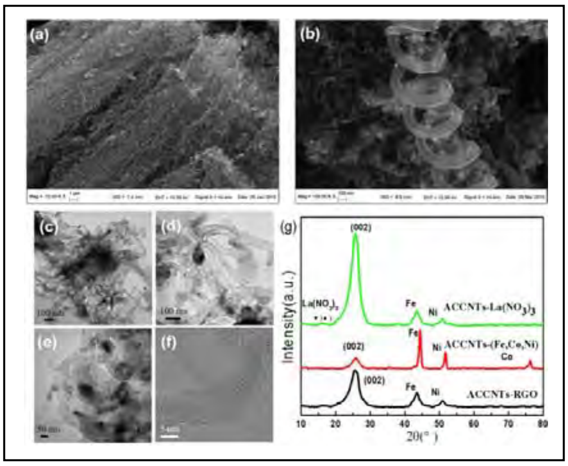

Fig.1 (a) SEM image of CACNTs; (b) Enlarged image of CACNTs; (c) TEM image of CACNT-La$(NO_3)_3$; (d) TEM image of CACNT-RGO; (e) TEM image of CACNTs; (f) TEM image of CACNT curvature; (g) XRD spectra of CNT-La$(NO_3)_3$, CNT-(Fe, Co, Ni) and CNT-RGO

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Growth of Boron Nitride Nanotubes by Chemical Vapor Deposition

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Boron nitride nanotubes (BNNTs) have some properties distinguished from their CNTs analogue, and can be used in a variety of engineering fields. However, the synthesis of them has been proved to be difficult so far, especially in the horizontal tube furnace. Recently, we demonstrated that BNNTs can be successfully fabricated in such tube furnace by low pressure chemical vapor deposition [1]. Also, Ni-Y alloy nanoparticles can effectively catalyze the growth of BNNTs with small diameter and few walls, which are resulted from their strong dissolubility for both the boron and nitrogen atoms [2]. It is so exciting that gram-scale BNNTs have been obtained by directly annealing the mixture of Li_3N and B_2O_3 in NH_3 [3]. We also found that B_2O_3 and ammonium tungstate can be served as alternatives of metal oxides in the boron oxide chemical vapor deposition method (CVD) [4, 5], which can eliminate the formation of borates, thus resulting in improved boron utilization and catalyst activity.

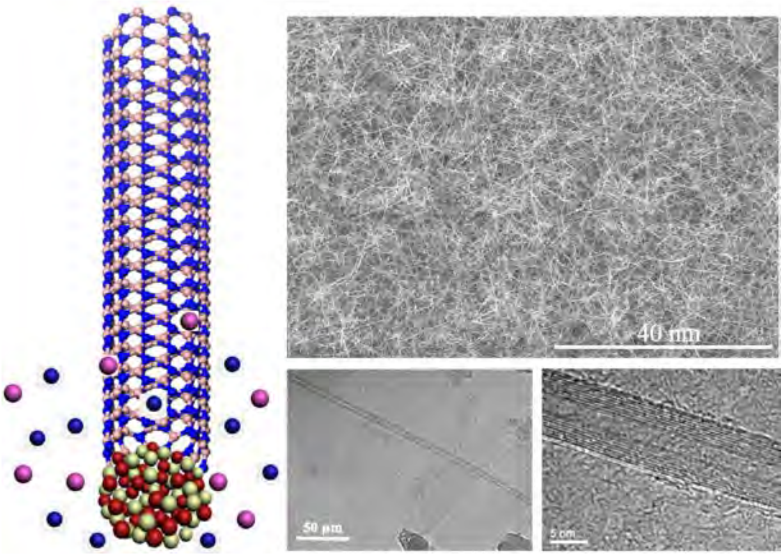

Fig.1 Typical formation schematic, SEM, and TEM images of the BNNTs.

[1] Liangjie Wang, Taotao Li, Yagang Yao, *et al*. Chem. Phys. Lett. **652**, 27 (2016).

[2] Liangjie Wang, Taotao Li, Yagang Yao, *et al*. Nanoscale, **9**, 1816 (2017).

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[5] Songfeng E, Chaowei Li, Yagang Yao, *et al*. Nanotechnology, **29**, 195604 (2018).

Graphene and Anologous 2D Materials: Large Area Growth and Transfer Methods

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Graphene and other 2D materials have been widely used in optoelectronic detectors, flexible sensors, and cell culture with the merits of extraordinary physical, chemical and mechanical properties as well as biocompatibility. For these applications, graphene need to be high quality, large scale and homogeneity. Hence, the techniques for the synthesis of large scale high quality graphene has been developed by chemists. Chemical vapor deposition (CVD) has advantages of facile setup, low cost and compatibility with conventional semiconducting process as well as potential for mass production. We employed CVD to produce strictly monolayer graphene over both Cu substrates and Si/SiO$_2$ substrates. We succeeded in transferring triangle MoS$_2$ single crystalline domain onto the Ag dimer nanoparticles to enhance the photoluminescence of MoS$_2$.

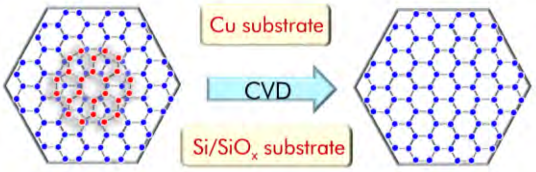

Fig.1 Strictly monolayer graphene have been synthesized over both Cu and Si/SiOx substrates with chemical vapor deposition method.

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Synthesis of large-area adlayer-free monolayer graphene films by chemical vapor deposition

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Synthesis of graphene films on Cu substrates by chemical vapor deposition (CVD) is the most popular method to produce large-area graphene films.[1,2] To date, precise control on the number of graphene layers as well as the uniformity over a large area is still very challenging. Recent studies on the magic-angle graphene superlattices shows exciting properties and potential applications.[3,4] The magic-angle graphene superlattices can be achieved by stacking two MLGs with specific rotational angles, which has to be adlayer free. Furthermore, adlayers deteriorate the quality of graphene film and affect its performance in applications, especially those requiring homogeneity.[5,6] In this work, with a further understanding of the factors affecting adlayer growth, the synthesis of large-area adlayer-free monolayer graphene (MLG) films was achieved up to tens of squared centimeters in area by just using untreated Cu foil and a normal CVD process. The criteria for the growth of adlayer-free MLG were investigated. In addition to the normal mode of MLG growth in which MLG domains grow up and then merge to form the whole continuous film, an abnormal mode was observed where the adlayers grow first but then decrease or completely disappear with the elongation of growth time after the first layer was fully merged. Mechanisms for the two growth modes are discussed. The study is not only of great significance for the industrial production of large-area adlayer-free MLG films but also instructive for the synthesis of homogeneous few-layer graphene.

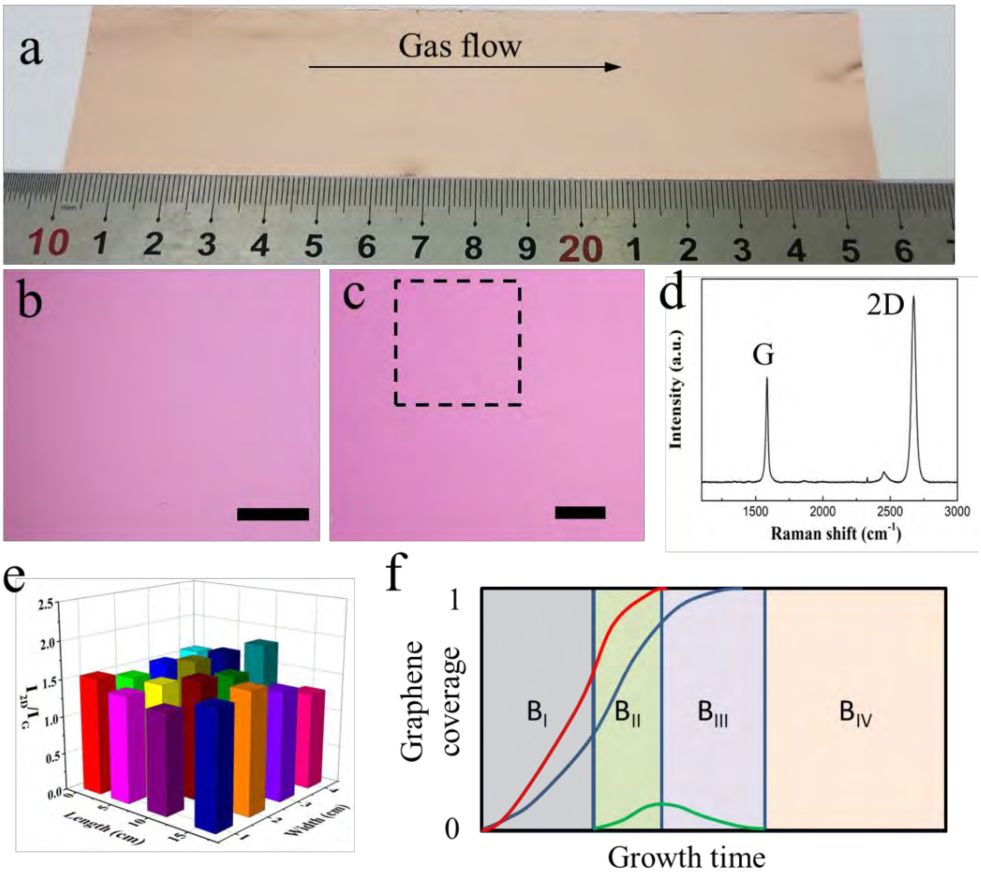

Fig.1. Characterization of large-area adlayer-free MLG. (a) The photograph of the CVD-grown graphene film on Cu substrate of 4 × 15.6 cm^2. (b) and (c) The OM images of the graphene film transferred onto the 285-nm SiO_2/Si substrate with low and high magnifications, respectively. The darker lines in (c) are graphene wrinkles, indicating the existence of graphene. Scale bars in (b) is 0.5 mm and in (c) is 10 µm. (d) Typical Raman spectrum of the transferred graphene film indicating it is MLG with the single Lorentz shape 2D peak and high quality with non-detectable D peak. (e) Distributions of I_{2D}/I_G over the whole large piece MLG. (f) Schematic plots of the two synthesis modes of adlayer-free monolayer graphene films. The blue curve corresponds to the MLG coverage v.s. growth time of the A mode, where MLG domains nucleate, grow up, and finally merge together to form a continuous adlayer-free MLG film. No adlayer appears during the whole process. The red curve corresponds to the MLG coverage v.s. growth time while the green curve corresponds to the adlayer coverage v.s. growth time of the B mode, respectively. In the B mode there are typically four stages: B_I, initially, MLG domains nucleate and grow up; B_{II}, then, adlayers nucleate and grow up; B_{III}, once the Cu surface is fully coverage with the MLG, adlayer growth terminates as well and the adlayer domains decrease; B_{IV}, finally, all adlayers dissappear.

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Synthesis of Oriented Graphene Nanoribbons Embedded in Hexagonal Boron Nitride

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Here, we report the successful growth of GNRs directly on hexagonal boron nitride (h-BN) substrates with smooth edges and controllable widths via templated growth using chemical vapour deposition (CVD). The applicability of graphene for future digital devices is often questioned due to its intrinsic gapless nature. Nanoribbons offer a potential solution, but both the width and edges must be precisely controlled. By employing the in-plane epitaxy of graphene in nano-trenches of h-BN, we have realized ZZ-oriented graphene nanoribbons with a controlled width and smooth edges. The GNRs feature a tunable band gap, enabling sub-10-nm GNR FETs with on-off ratios greater than 10^4. Our results demonstrate that it is possible to resolve the fundamental gapless limitation of graphene, paving the way for the realization of graphene-based digital electronics that can operate at room temperature.

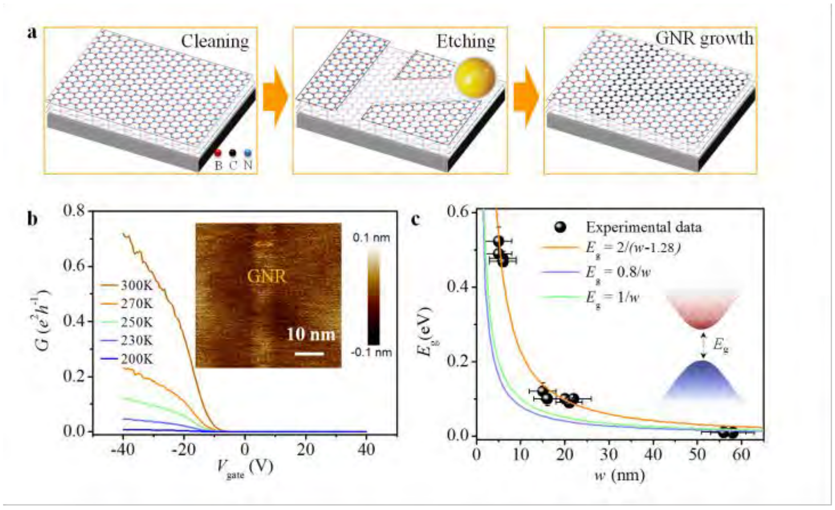

Fig.1 Formation of GNRs in h-BN trenches and electronic transport of a sub-5 nm GNR FET.

[1] S. Tang, **H. Wang**, *et al.* Scientific Reports 3, 2666 (2013).
[2] S. Tang, **H. Wang**, *et al.* Nature Communications 6, 6499 (2015).
[3] L. Chen, **H. Wang**, *et al.* Nature Communications 8, 14703 (2017).
[4] L. Chen, **H. Wang**, *et al.* Nanoscale, 9, 11475–11479 (2017).

A carbon-welded isolated single-wall carbon nanotube network with near-ohmic joint contacts

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Single-wall carbon nanotubes (SWCNTs) are ideal for fabricating transparent conductive films because of their small diameter, good optical and electrical properties and excellent flexibility. However, a high intertube Schottky junction resistance, together with the existence of aggregated bundles of SWCNTs, leads to a degraded optoelectronic performance of the films. We report a network of isolated SWCNTs prepared by an injection floating catalyst chemical vapor deposition method, in which crossed SWCNTs are welded together by graphitic carbon. Investigation of isolated SWCNT-based field-effect transistors shows that the carbon-welded joints convert the Schottky contacts between metallic and semiconducting SWCNTs into near-ohmic ones, which significantly improves the conductivity of the transparent SWCNT network. In consequence, pristine SWCNT films show a record low sheet resistance of 41 ohm $\square^{-1}$ at 90% transmittance for 550-nm light. After HNO_3 treatment, the sheet resistance further decreases to 25 ohm $\square^{-1}$. Organic light-emitting diodes using this SWCNT film as anodes demonstrate a low turn-on voltage of 2.5 V, a high current efficiency of 75 cd A^{-1} and excellent flexibility.

[1] S. Jiang, P.-X. Hou, *et al*. Ultrahigh-performance transparent conductive films of carbon-welded isolated single-wall carbon nanotubes. Sci. Adv. **4**, eaap9264 (2018).

CVD Growth of Fingerprint-like Patterned 3D Graphene Film for Ultrasensitive Pressure Sensor

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With the rapid development of wearable devices, flexible pressure sensors with high sensitivity and wide workable range are highly desired. In nature, there are many well-adapted structures developed through natural selection, which inspire us for the design of biomimetic materials or devices. Particularly, human fingertip skin, where there are many epidermal ridges serving to amplify external stimulations, might be a good example to learn from for highly sensitive sensors. In this work, based on unique CVD-grown 3D graphene films which mimic the morphology of fingertip skin, we fabricated flexible pressure sensing membranes which simultaneous showed high sensitivity of 110 kPa^{-1} for (0-0.2 kPa) and wide workable pressure range (up to 75 kPa). Hierarchical structured PDMS films molded from natural leaves were used as the supporting elastic films for the graphene films, also contributing to the superior performance of the pressure sensors. The pressure sensor showed low detection limit (0.2 Pa), fast response (<30 ms), and excellent stability for more than 10,000 loading/unloading cycles. Based on these features, we demonstrated its applications in detecting tiny objects, sound, and human physiological signals, showing its potentiality as wearable electronics for health monitoring and human/machine interface.

[1] K. Xia, C. Wang, M. Jian, *et al*. Nano Res. **11**, 1124 (2018)

[2] C. Wang, X. Li, E. Gao, *et al*. Adv. Mater. **28**, 6640 (2016).

[3] M. Zhang, C. Wang, H. Wang, *et al*. Adv. Funct. Mater. **27**, 1604795 (2016)

Alcohol Catalytic Chemical Vapor Deposition of Single-Walled Carbon Nanotubes from Platinum-group metal catalysts

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For the application of single-walled carbon nantoubes (SWCNTs) to the electronics field, SWCNTs having small-diameters and homogeneous chirality is important. At present, Fe, Co and Ni have been widely used as catalysts for SWCNT growth by chemical vapor deposition (CVD). However, due to Oswald ripening, these metals are apt to aggregate during SWCNT growth, resulting in enlargement of the SWCNT diameter and the chirality distribution. In this study, we performed SWCNT growth by alcohol catalytic CVD using platinum-group metal catalyst (Pt, Ru and Rh). These metals have high-melting points (>1700ºC) and the suppression of aggregation would be anticipated. In addition, we attempted SWCNT growth at low temperature using these metal catalysts.

SWCNT growth was performed using a gas source-type CVD system in a high vacuum using ethanol as feedstock gas. The grown SWCNTs were characterized by scanning electron microscopy (SEM), Raman spectroscopy and transmission electron microscopy (TEM).

By optimizing the ethanol gas supply, SWCNTs were grown from Pt, Ru and Rh catalysts when the growth temperature between 400 and 700ºC. Irrespective of the metals, the diameter and chirality distribution became narrower as the growth temperature decreased. Fig. 1 shows Raman spectra of SWCNTs grown from Pt, Ru and Rh when the growth temperatures were 400 - 450ºC. The distribution of Radial breathing mode (RBM) peaks shows that the diameters of most SWCNTs grown from Pt catalysts were below 1 nm, that is, small-diameter SWCNTs were grown from Pt catalysts [1]. On the other hand, the diameter of SWCNTs grown from Ru catalysts was about 1.0 nm, but had narrow chirality distribution. We also succeeded in SWCNT growth below 300ºC from Rh catalysts by optimizing the growth condition [2]. Based on the SWCNT diameter and catalyst particle size, we will discuss the difference in the growth mechanism of SWCNTs from these catalysts.

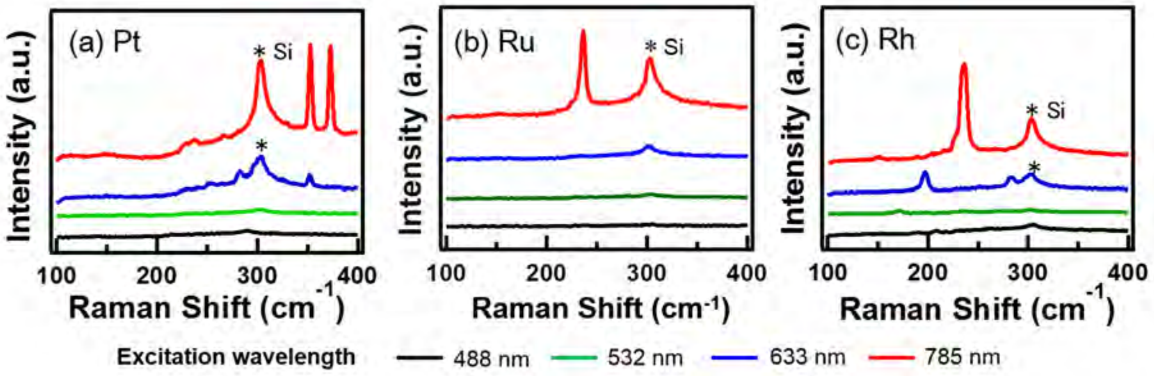

Fig.1 Raman spectra of SWCNTs grown from Pt, Ru and Rh catalysts.

[1] T. Maruyama, H. Kondo, R. Ghosh, A. Kozawa, S. Naritsuka, Y. Iijizumi and S. Iijima, Carbon **96**, 6 (2016)
[2] T. Maruyama, A. Kozawa, T. Saida, S. Naritsuka and S. Iijima, Carbon **116**, 128 (2017)

Mechanism Study of Bilayer Graphene in Chemical Vapor Deposition by Isotope Labeling

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Bilayer graphene (BLG) has attracted enormous interest due to its outstanding mechanical, chemical, electrical and thermal properties with various potential applications. By the diffusion of carbon atoms through the Cu pocket, BLG was synthesized on the outer side with methane using chemical vapor deposition (CVD). And a few bilayer regions showed distinct Raman spectra by carbon isotope labeling due to the different stacking order of two graphene layers. [1]

In this work, we studied the growth mechanism of BLG using carbon isotope labeling and Raman spectroscopy. Results show that the growth of the BLG reveals several different modes. For most of the BLG, they maintain their AB- or non-AB-stacked structures with the first layer during the growth since their nucleation, but for some of them the stacking structures can suddenly change during the growth. Moreover, we also observed that the BLG can nucleate tens of minutes later during the growth (not together with the first layer), with a AB- or non-AB-stacking with the first layer. This work enables us to have a deep understanding of graphene growth mechanism as well as the layer control for large scale BLG using CVD.

[1] Wenjing Fang, Allen L. Hsu, Roman Caudillo, *et al*. Nano Lett. **13**, 1541 (2013).

Hydrogen Function on Controlled Growth of Semiconducting Single-Wall Carbon Nanotubes with Uniform Structures

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Semiconducting single-wall carbon nanotubes (s-SWCNTs) with same chirality or similar bandgaps are highly demanded for fabricating high performance nano-electronic devices [1]. In our previous work, a strategy that combined catalyst-structure design with *in-situ* etching was proposed to obtain s-SWCNTs with a narrow band-gap distribution [2]. Partial carbon-coated Co nanoparticles with uniform size distribution were synthesized by a block copolymer self-assembling technique, and used as catalysts for guaranteeing the carbon nanotube nucleation as perpendicular mode. By using H_2 as *in-situ* etchant, high purity s-SWCNTs with a very narrow bandgap distribution were synthesized. In this work, we further investigated the function of H_2 on selective growth of s-SWCNTs by using Fe nanoparticles with uniform size as catalysts. It's found that H_2 not only served as etchant, but also modulate the carbon content decomposed from carbon source.

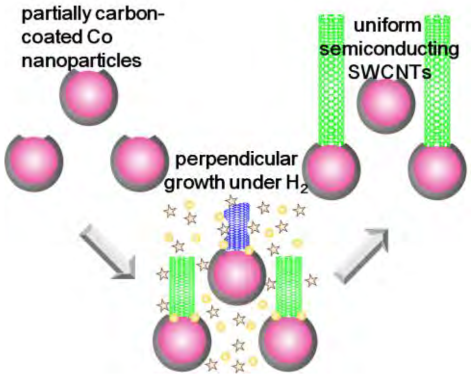

Fig.1 Schematic showing the controlled growth of s-SWCNTs with uniform structures.

[1] F. Zhang, P-X. Hou, C. Liu, *et al*. Carbon **102** (2016).

[2] F. Zhang, P-X. Hou, C. Liu, *et al*. Nat. Commun. 7:11160 (2016).

Controllable Synthesis and Device Applications of Transition Metal Dichalogenides

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Keywords: Transition metal dichalogenides (TMDs); Chemical vapor deposition (CVD); Heterostructure; Controllable synthesis; Interface engineering

Transition metal dichalogenides (TMDs) has excellent optical and electrical properties and is expected to be used in electronics, optoelectronics, catalysis and other fields. Controllable synthesis of TMDs heterostructure is still a challenge. MoS_2/WS_2 heterostructure was synthesized by a two-step chemical vapor deposition (CVD) and its growth mechanism was explored. It was found that the diffusion plays an important role in the growth of anisotropic heterostructure materials. Also the mechanism explains the fact that the final structure of the heterostructure is irrelevant to the growth order. Also, graded-alloy MoS_2/WS_2 was prepared with the same method. By means of interfacial engineering, the surface roughness of the dielectric layer is controlled and a high performance field-effect transistor device is successfully prepared. For MoS_2 transistors fabricated on crested, corrugated substrates, almost two orders of magnitude was increased in carrier mobility compared to standard devices and very high saturation currents. With comprehensive investigation of different dielectric environments and morphologies, we demonstrated that the substrate's increased corrugation is the dominating factor driving the performance enhancement. We showed that the strategy is universally valid for the other semiconducting TMD materials, either p-doped or n-doped, opening them for the applications in heterogeneous integrated electronics.

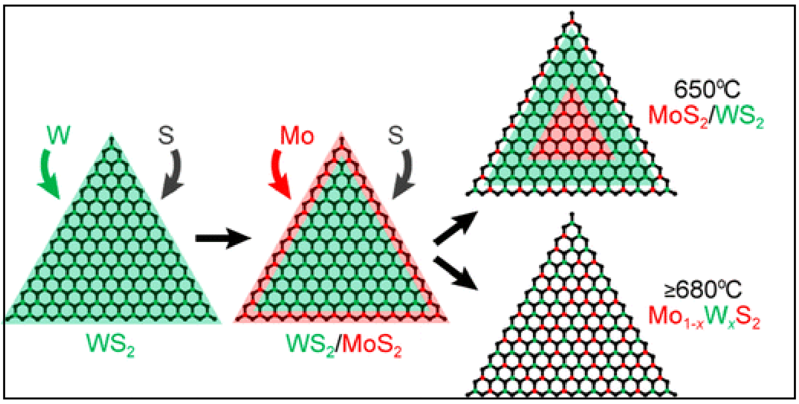

Fig.1 Proposed growth stages of $MoS_2/Mo_{1-x}WxS_2$ heterostructures.

Repeated CNT synthesis by resetting $CoAl_2O_4$ and $NiAl_2O_4$ catalysts

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We achieved repeated synthesis of carbon nanotubes (CNTs) by resetting the catalyst nanoparticles (NPs). It is well known that the catalyst NPs get coarsened through Ostwald ripening [1] during chemical vapor deposition (CVD), resulting in CNT growth termination, and no way has been known to reset the coarsened catalyst nanoparticles (NPs). We had Co and Ni NPs segregating out from their spinel films under reducing environment and dissolving in the spinel films under oxidizing environment.

$CoAl_2O_4$ and $NiAl_2O_4$ nanopowders were synthesized by liquid-feed flame spray pyrolysis [2] and sintered in air to yield flexible, dense films (30±10 μm in thickness) without any NPs on surface. The films were then reduced in H_2/Ar at 1100 ˚C, on which NPs were found. Then CNTs were grown by CVD by flowing C_2H_2/H_2/Ar at 1100 ˚C ((1) in Fig. 1 and 2). The oxidation treatment of the CNTs/spinel samples in O_2/N_2 at 1100 ˚C yielded the spinel films without CNTs nor NPs ((2) in Fig. 1 and 2). We repeated the reduction-CVD-oxidation treatment for three cycles and confirmed similar CNT growth on the spinel.

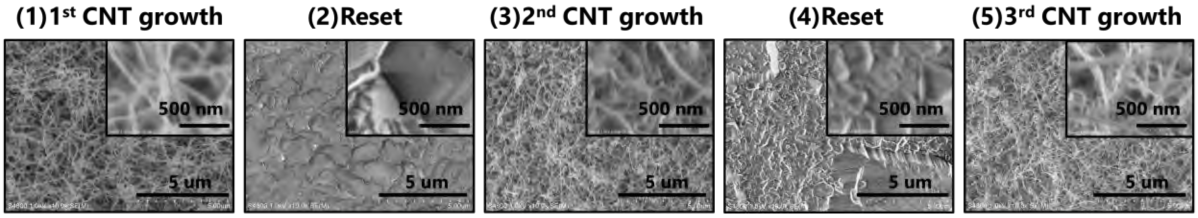

Fig. 1 Repeated CNT growth on $NiAl_2O_4$ film

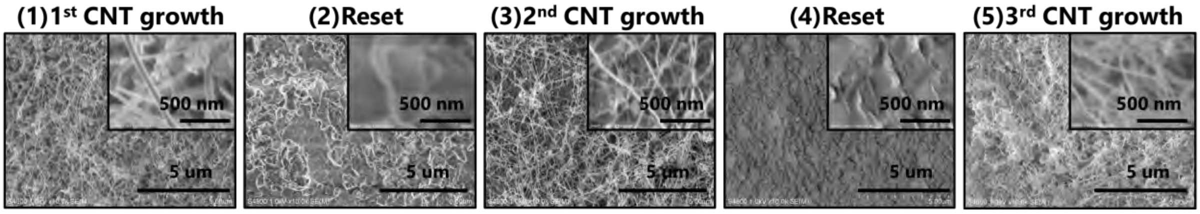

Fig. 2 Repeated CNT growth on $CoAl_2O_4$ film

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[2] J. Azurdia et al., JACS **89**, 2749 (2006).

The Controllable Growth of Fractal Dimension Atomic-layer SnS_2 Catalyzed by Potassium Atom

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Keywords: SnS_2; Potassium; Controllable growth; Fractal dimension;

Two-dimensional (2D) layered metal dichalcogenides (LMD) have become essential for their ultrathin thickness and potential applications in engineering next-generation electronics and optoelectronics. SnS_2 as one of important 2D LMD, the controllable growth of fractal dimension monolayer SnS_2 is also crucial, while it has never been reported and remains challenging. Herein, we report the direct synthesis of fractal dimension large-area uniform atomic-layer SnS_2 through a facile chemical vapor deposition process. The uniform monolayer film with the edge length of SnS_2 dendritic crystal larger than 500 μm can be achieved within a quite short time of 5 min, the morphology is controlled accurately by time, temperature and the amount of sulfur powder. This highly efficient growth is proven to be facilitated by potassium catalysts according to our experimental facts and density functional theory calculations. This work provides insights into the direct synthesis highly uniform 2D LMD with the advantages of low cost, easily transferrable, and compatible with direct applications.

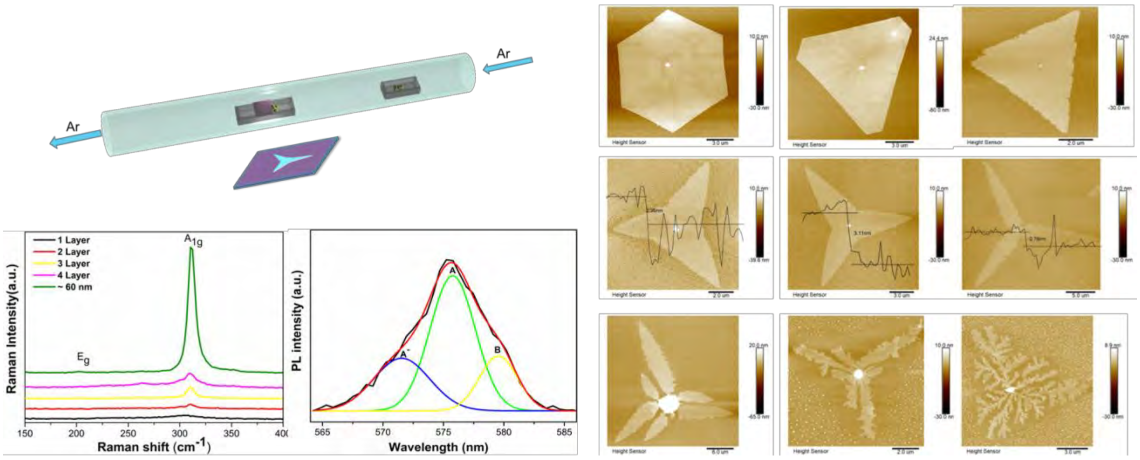

Fig.1 The controllable growth of fractal dimension atomic-layer SnS_2

Scalable synthesis of high-purity aligned semiconducting ultralong carbon nanotubes

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Immense values of semiconducting carbon nanotubes (s-CNTs) have been offered as the building elements for ultrascaled devices[1]. However, efforts through either *in-situ* synthesis or sorting strategies failed to duplicate nondestructive pure s-CNT arrays. The highest purity ever reported of the horizontally aligned s-CNTs is merely 97%, hampering the long-standing dream for outstanding optoelectronics. Here, we demonstrate an optimized chemical vapor deposition (CVD) method for selective synthesis of high-purity aligned s-CNTs. An established tip-mode molecular diffusive model reveals an exponential dependence of the catalyst activity probability on the energy barrier of carbon dissolution rate. Under such theoretical direction, a new recipe was explored to reliably obtain high-purity (>99%) s-CNTs by adjusting the growth temperature and feedstock flow rate. Careful Raman and electrical characterizations verified the high purity of s-CNTs tandem with excellent performances in transistors. We expect that this optimized CVD method will provide a novel route for scalable synthesis of aligned s-CNTs, even serving the target for 2020 electronics proposed by IBM[2].

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[2] Franklin, A. D. Nature 498, 443-444 (2013).

Preparation of long linear carbon chain inside multi-walled carbon nanotubes by hydrogen arc discharge with cooling system

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Carbyne, infinitely long carbon chain, is predicted to own a high specific stiffness, which is two times more than carbon nanotube and graphene [1]. Unfortunately, the high chemical activity even hampers the existence of free long linear carbon chain (LLCC), and the length of carbon chain is limited up to 44 atoms in solution to the date. In 2003, Zhao *et al*. found that carbon nanotube can be an excellent reactor and protector to contain high-activity LLCC inside, and named this new 1D carbon allotrope as carbon nanowire (CNW) [2]. Now, LLCC inside single, double, multi walled carbon nanotubes are expressed as LLCC@SWCNTs, LLCC@DWCNTs, LLCC@MWCNTs, respectively. Recently, Shi *et al*. successfully prepared high-yield LLCC@DWCNTs samples, including an ultra-long linear carbon chain (more than 6000 atoms) [3]. Here, a cooling enhanced hydrogen arc discharge technique was developed to improve the purity and yield of LLCC@MWCNTs samples, and the strong Raman peaks from 1780 cm^{-1} to 1880 cm^{-1} was observed as the typical sign of *sp* hybridized atomic strings. With cooling assistance, the narrow scope of suitable condition to prepare LLCC@MWCNTs by hydrogen arc discharge was largely expanded, and the high-purity LLCC@MWCNTs samples were easily mass-produced. A close relationship between the growth situation of MWCNTs and the yield of LLCC@MWCNTs was studied. This work will provide a new way to improve the growth yield of LLCC@MWCNTs and will benefit the further studies and applications of this new 1D carbon allotrope.

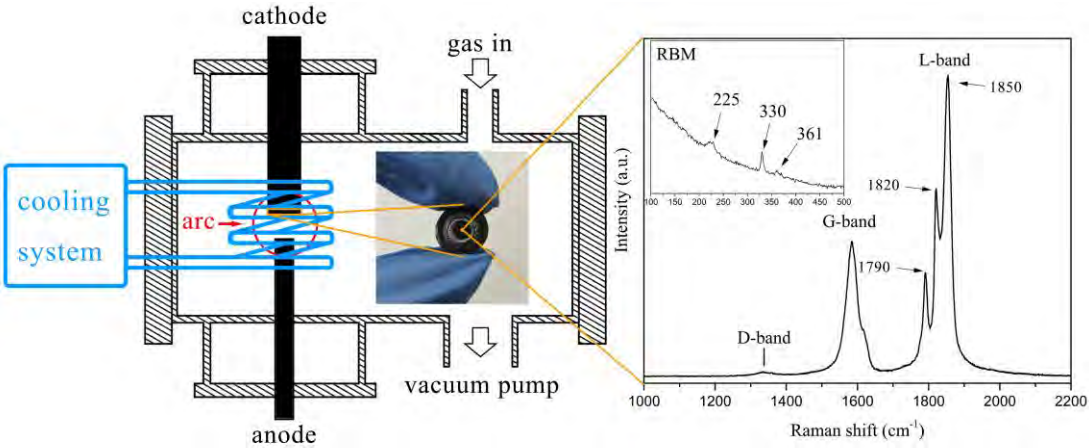

Fig.1 Illustration of the instrument and the typical Raman spectrum of LLCC@MWCNTs samples.

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[2] X. Zhao, Y. Ando, Y. Liu, *et al*. Phys. Rev. Lett. **90**, 187401 (2003).
[3] L. Shi, P. Rohringer, K. Suenaga, *et al.* Nat. Mater. **15**, 634 (2016).

Single-Walled Crystalline Molybdenum Oxide Nanotubes with Carbon Nanotube Templates

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Inorganic nanotubes[1] have drawn great research interests because of its potential applications in optoelectronic, electrochemical and biochemical devices. Tubular structures in nanoscale, especially single-crystalline nanotubes[2], are challenging to synthesize, while only few kinds of nanotubes were widely used indeed. And template-based methods[3] show high effectiveness for many inorganic materials which cannot spontaneously form tubular structures. Carbon nanotubes (CNTs) are considered as ideal templates since they were well studied both in scientific research and industrial production with outstanding electronic and mechanical properties. However, few efforts to grow inorganic nanotubes with CNT templates showed probable single-crystalline nature.

Here, we report the vapor deposition of molybdenum oxide (MoO_3) with single-crystalline tubular structure on ultralong CNTs. The chiral vectors and angles of MoO_3 nanotubes (MONTs) are defined. Diverse chiral angles of single-walled MONTs are concentrated to make the [001] direction nearly parallel to tube axis. The mechanism on the formation and epitaxial of single-crystalline nanotubes is discussed for general materials with monolayer dispersion feature. Based on the mature CNT production techniques, massive CNTs could be transformed into other tubular structures with diverse functions, greatly promoting the development of 1D multi-functional materials and composites.

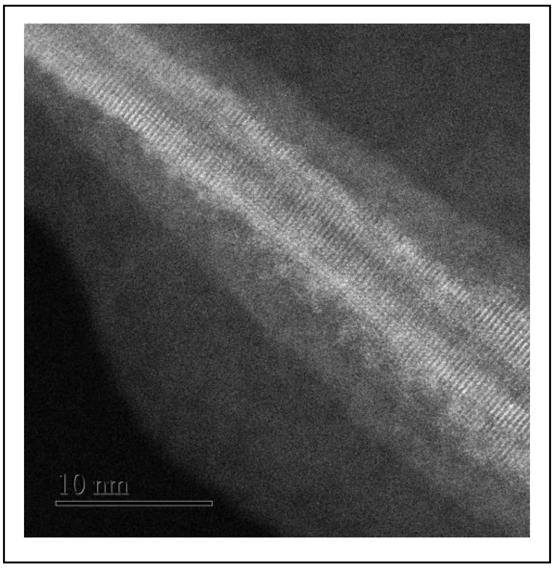

Fig.1 HAADF STEM images of MONTs.

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[2] Goldberger, J. *et al.* Nature **422**, 599-602 (2003).

[3] Ajayan, P. M., Stephan, O., Redlich, P. & Colliex, C. Nature **375**, 564-567 (1995).

On Al synthesis, Morphology Control and Heat Transfer Application of Carbon Nanotubes

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Al is widely used as a material for various heat exchangers because of its high thermal conductivity, small mass density, and high plasticity. The device performance has been improved by making the fins finer, however, it is getting more and more difficult to make finer structure (< 1 mm) at large scale. Carbon nanotubes (CNTs) also have high thermal conductivity and small mass density. In addition, simple fabrication of fine structure is possible via their self-organization process. Here we propose CNT-Al hybrid heat exchangers by growing micro-fins of CNTs directly on the conventional Al fins.

CNT arrays can be grown directly on Al sheets by chemical vapor deposition (CVD), however, their height remained 0.1 mm or less due to the low melting point of Al (660 °C). We recently realized 1.1 mm-tall CNT arrays by CVD at 600 °C (Fig. 1a) [1]. To prevent the deactivation of Fe catalyst pre-sputtered on Al, the C_2H_2 source was fed at low concentration with CO_2 additive at high concentration. This method enabled tall CNT arrays but in a long CVD time (1.1 mm in 12 h). Then we elevated the C_2H_2 concentration and fed ferrocene (Fc) simultaneously, to grow CNTs fast and deposit Fe catalyst continuously. This method enabled >0.5 mm-tall CNT array in 2 h. Al sheet was prepatterned by using an pen-ink for selective catalyst deactivation, and the resulting CNT array was shrunk by wetting with ethanol and successive drying (Fig. 1b). Finally we examined the heat dissipation performance using plate heater and N_2 gas flow. Compared with the Al sheet, no change was observed with uniform CNT arrays and with shrunk CNT fins set perpendicular to the flow. Whereas the performance improved about twice with the CNT fin arrays set parallel to the flow (Fig. 1c). It is surprising to obtain such significant improvement despite of the incomplete fin structure. CNT roughness may induce vortex and make boundary layer thinner. Detailed analysis is now underway.

Fig. 1. (a) Heights of CNT arrays grown on Al substrates [1], (b) SEM of the CNT fins formed by ferrocene-assisted CVD without sputtered Fe catalyst, and (c) heat dissipation performance of Al with various CNT fins.

[1] S. Miura, et al., *Carbon* **130**, 834-842 (2018).

Freestanding Graphene/polymer Microtube with Multiple Structure

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Graphene has been widely used for the fabrication of various materials with different structure due to its excellent mechanical, electrical and thermal properties, such as graphene fiber[1] and graphene film[2].

Here in, we develop a simple method to fabricate freestanding graphene/polymer hollow microtubes. With a template-based CVD process[3], we have obtained various structure microtube samples. With different polymer coating, different mircotubes with different performance including mechanical and optics have been proved. And with pre-modified hard templates, we also could prepared some samples with more complicated structure such like helix microtube. More importantly, with the properties such as high electrical conductivity of inside graphene layer and the viscoelasticity of the polymer outside layer, applications of the sample could be possible combined with both components. This study paves the way toward the versatile production of freestanding graphene/polymer hollow microtube with multiple morphologies, which has essential significance in many important fields such as catalysis, fluidics and sensors.

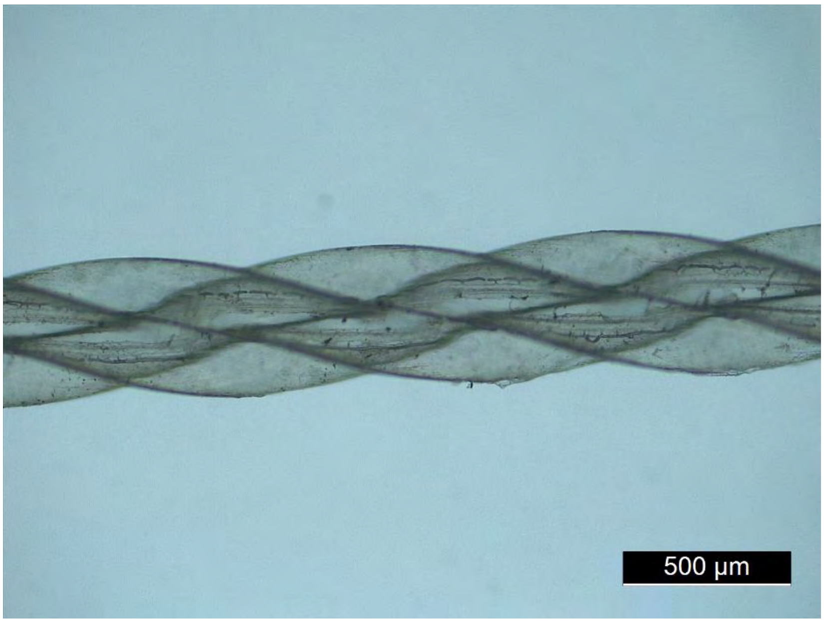

Fig.1 The optical microscope image of the helix graphene/PMMA microtube .

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[3] N. Duc Dung, S. Suzuki, S. Kato, *et al*. Acs Nano **9**, 3206 (2015).

Synthesis of Holey Graphene by Microwave Assisted Method

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Holey graphene, which contains a high specific surface area and nanopores in the two-dimensional basal plane, has aroused great interest in recent years. We developed a microwave-assisted method for preparing holey graphene. Microwave absorbing nanoparticles MxOy (M=Fe/Co/Ni) were supported on graphene oxide (GO) by a solution method. Under microwave conditions, the absorbing nanoparticles convert the microwave into heat and so etch the surrounding carbon atoms to create pores on graphene. Holey graphene with different size of pores were prepared by controlling the etching conditions. Raman and IR data showed that both the defects and the oxygen-containing groups of holey graphene decreased compared with graphene oxides. The as-prepared holey graphene can be used to enhance the electrochemical performance of supercapacitors.

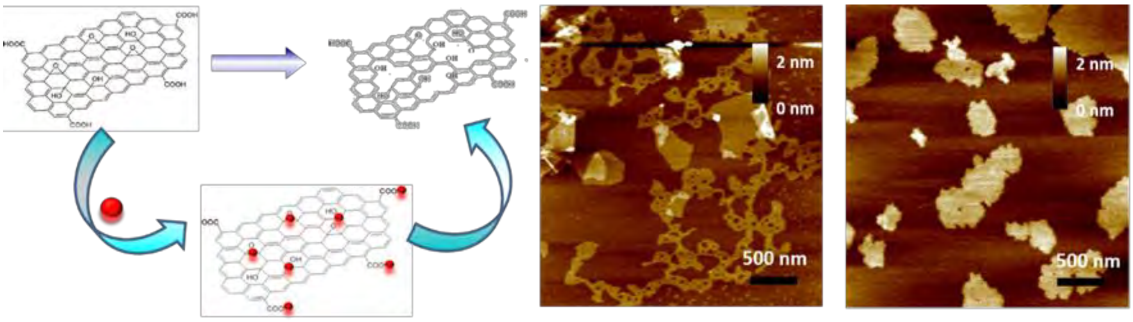

Fig.1 Schematic for the synthesis of holey grapheme and the AFM images of as-prepared holey graphene.

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Microwave-assisted Regeneration of Single-walled Carbon Nanotubes from Carbon Fragments

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Directly growth of chirality-controlled SWNTs with metal catalyst free strategy, like cloning or epitaxial growth, has suffered from the low efficiency[1,2]. The underlying problem is the activation of seed edge. Here an unexpectedly efficient microwave-assisted pathway to regenerate SWNTs from carbon fragments on Si/SiO_2 substrate is demonstrated *via* Raman spectroscopy and atomic force microscopy characterization. In this attempt, microwave irradiation provides fast heating to remove polar groups bonded to carbon nanotubes and reduce the spontaneous closure of tubes' open-ends[3]. The survived SWNT and carbon fragments connected to it after plasma treatment are simply microwaved and then served as the template for regeneration. SEM and AFM characterizations indicate the efficiency of the regeneration could reach 100%. And the chirality of regenerated SWNT has been remained compared to original SWNT. The microwave-assisted regeneration is found to be highly effective and would be applied to improve the cloning efficiency of carbon nanotubes potentially.

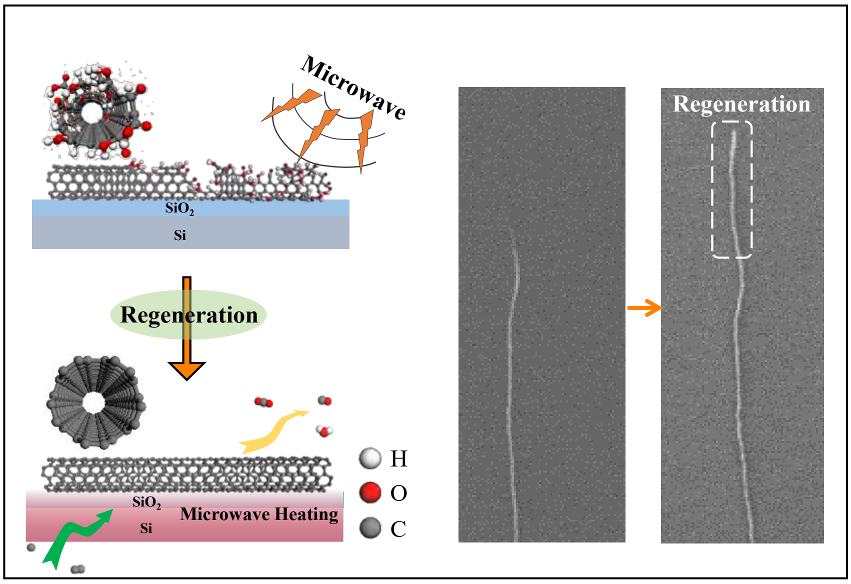

Fig.1 Title of the figure.

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[3] M. Kim, E. Haroz, Y. Wang, *et al*. Nano Lett. **7**, 15 (2007).

Synthesis of High Quality Single-Wall Carbon Nanotubes by Floating Catalyst Chemical Vapor Deposition

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High crystallinity and high purity single-wall carbon nanotubes (SWCNTs) are highly desired for practical applications including construction high performance transparent conductive films and electronic devices, as well as spinning into high strength and conductive CNT fibers[1]. In this work, high quality SWCNTs are controlled synthesized by an injection floating catalyst chemical vapor deposition method. Briefly, ferrocene and sulfur, which serve as a catalyst precursor and growth promoter, respectively, were dissolved in toluene solution, which were injected into a quartz tube reactor by a syringe pump[2]. The vaporized ferrocene and sulfur were carried into the reaction zone by mixed H_2 (carrier gas) and CH_4 (carbon source) for the growth of the SWCNTs. The growth temperature was set to be 1100 °C and the heating zone of the reactor is about 60 cm in length. By optimizing the growth parameters of SWCNTs, high purity and high crystallinity SWCNTs with uniform diameter distribution (Fig. 1) were synthesized. Raman spectra demonstrated a high G/D ratio of 146, verifying the high quality of SWCNTs. It is also found that the conductive properties and diameter distribution of SWCNTs can be effectively controlled by changing hydrogen content, which is very promising for many advanced applications of SWCNTs such as SWCNT-based electronics.

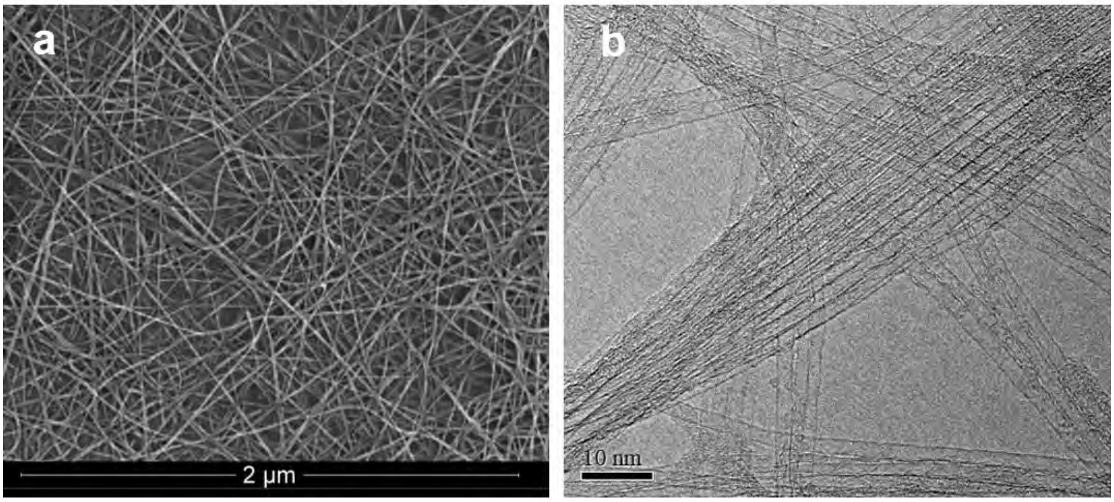

Fig.1 Typical SEM (a) and TEM (b) images of SWCNTs

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All *in-situ* process for dense CNT forest growth by mist CVD

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To realize various carbon nanotube(CNT)-based applications, it is necessary to improve the CNT production techniques to control the CNT structure and production cost. Conventional CNT growth consists of three steps including formation of a catalyst support layer, a metallic catalyst layer and a CNT growth. Therefore, the multiple steps made the CNT production process complicated, resulting in difficult structure control and higher production cost.

In this study, we developed a simple *in-situ* chemical vapor deposition (CVD) process, which conducted successively the formation of Al_2O_3 support layer, Fe catalyst nanoparticles and CNT growth. The Al_2O_3 and Fe deposition were conducted by mist CVD with precursors of Al(III) acetylacetonate and ferrocene, respectively, dissolved in ethanol. In this process, first Al_2O_3 were deposited and then Fe were deposited on a thermally oxidized Si substrate, by flowing each precursor solution mist with Ar as a carrier gas. After these depositions, CNT were grown by thermal CVD process with acetylene as a carbon source.

Figure 1 (a) and (b) show SEM images of CNT forest grown on a SiO_2 and the mist-deposited Al_2O_3, respectively. Both samples were multi-walled CNT. The CNT forest on the SiO_2 had a height of 40.6 μm. On the other hand, the height of CNT forest on the Al_2O_3 was higher than on the SiO_2, resulting in 814.0 μm. These results clearly indicate that catalytic activity of the Fe catalyst was enhanced by inserting the Al_2O_3 layer. So far, the Al_2O_3 buffer layer deposited by sputtering have been reported to have an effect of enhancement of catalytic activity on the CNT growth. In the present study, the Al_2O_3 layer deposited by mist CVD also showed the similar enhance effect.

The CNT forest with mist-deposited Al_2O_3 before self-growth termination is shown in Fig. 2. As can be seen, a CNT web was drawn out from the forest. The CNT had high alignment from top to bottom of forest without tangled structure. CNTs are bundled strongly on the entire substrate, resulting in the good spin-capable. The present process is a compatible method to large-scale CVD system for mass production of spin-capable CNT forest.

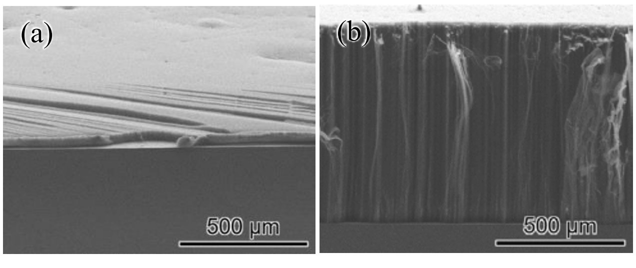

Fig. 1 SEM images of grown CNT by *in-situ* mist CVD on (a) SiO_2 and (b) mist-deposited Al_2O_3 layer.

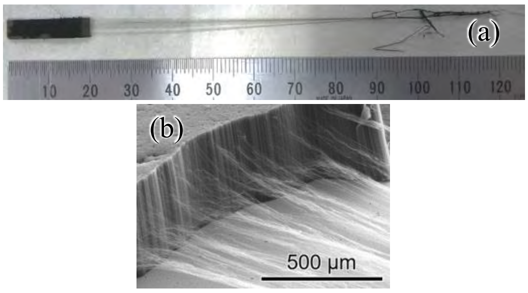

Fig. 2 (a) A CNT web drawn out from CNT forest grown on Al_2O_3. (b) SEM image of the CNT.

Effect of catalytic species on ethanol dissociation studied by *ab initio* molecular dynamics

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The quality and quantity of carbon nanotubes (CNTs) largely depend on the combination of the catalyst and the carbon source used for the synthesis. One successful method to produce CNT with high purity is to use ethanol as the carbon source and FeCo alloy as the catalyst[1]. When using ethanol as the carbon source, it is important which C–O bond or C–C bond dissociates during the process[2], which depends on catalysts used. In order to develop a better catalyst, it is required to know the mechanism of the dissociation process.

In this study, the dissociation process of ethanol (CH_3CH_2OH) and carbon mono oxide (CO), which is generated by C–C bond dissociation of ethanol, is investigated by *ab initio* molecular dynamics simulation for three different catalysts Fe, Co and FeCo. It has been observed that the C–C bond dissociates on FeCo catalyst while it does not on Fe catalyst from the same fragment, CH_3CO. The difference between two cases is found in the interaction between the oxygen atom of CH_3CO and the metal atom in the catalyst. When the C–C bond dissociates, the oxygen atom is detached from the catalyst while the oxygen atom is kept on the catalyst when C–C bond does not dissociate (Fig.1). On the other hand, C–O bond of ethanol is more often dissociated on Fe catalyst. Moreover, C–O bond of carbon monoxide is also dissociated on Fe catalyst. From the result, it can be proposed that one advantage of alloy catalyst is that it is able to firstly dissociate C–C bond in ethanol and then dissociate C–O bond of generated carbon monoxide on Fe site. In the presentation, our recent results will be introduced after the brief review of recent computational works on this topic.

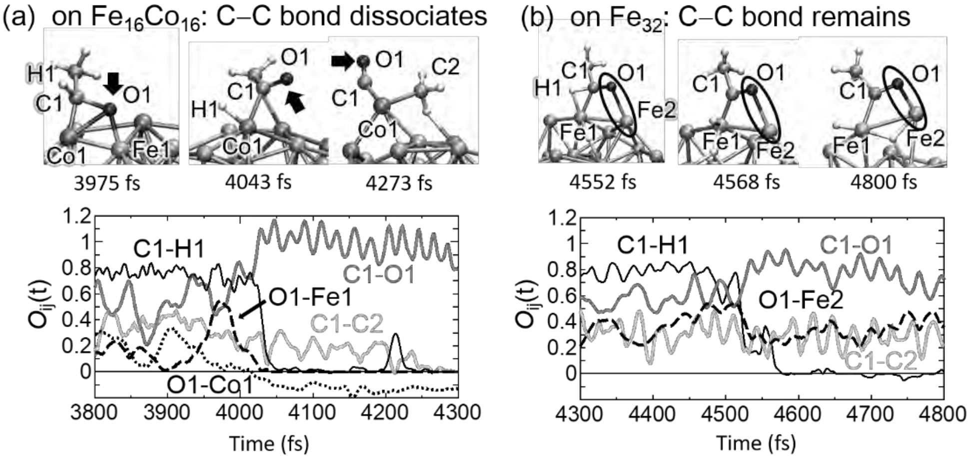

Fig.1 Snapshots of the atomic configuration and time evolution of bond-overlap populations $O_{ij}(t)$ during the reaction of (a) $CH_3CHO \rightarrow CH_3CO \rightarrow CH_3+CO$ on $Fe_{16}Co_{16}$ and (b) $CH_3CHO \rightarrow CH_3CO$ on Fe_{32}.

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Facile preparation of mesostructured porous carbons via metal-organic coordination reaction.

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Several researches have been developed to synthesize porous carbon because of its wide applicability as an energy storage material. However, it is difficult to control the microstructure of porous carbon which played an important role for accessible ion transport in electrochemical reaction. In this work, we developed a facile synthesis method for making unique mesostructured porous carbons, based on metal organic coordination. Metal salts are used as metal linker and organic materials are used as precursors, each of which cannot be carbonized by themselves. These precursors can be carbonized through metal-organic coordination and form unique flower like 3-dimensional structures without complicated processes. We confirmed that morphology and thickness of porous carbon are easily controlled according to the ratio of precursors and reaction conditions. Therefore, this study can be extended to managing macroscale-porosity of the synthesized carbon for the application in energy storage system.

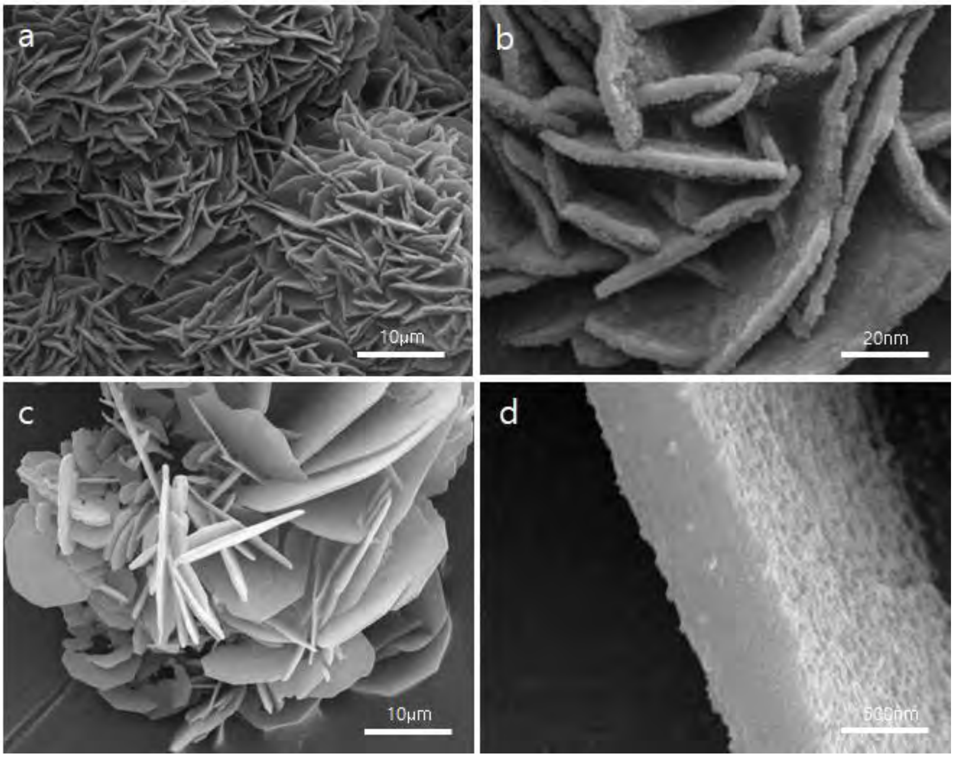

Fig.1 SEM images of metal-organic coordination based mesostructured porous carbon.

Synthesis of Metallic-Enriched Single-Wall Carbon Nanotubes by Using Bimetallic Nanoparticles as Catalysts

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Metallic single-wall carbon nanotubes (m-SWCNTs) can endure ultrahigh current densities due to ballistic electron transport, which can be used as electrodes and interconnectors in circuits and for the fabrication of transparent conductive films [1]. However, it still remains to be a big challenge to in-situ synthesize pure m-SWCNTs on a large scale. Bimetallic nanoparticles with high melting point have shown great potential in catalyzing the growth of SWCNTs with specific chirality [2-3]. Tungsten, which possesses highest melting point in known metallic elements, is used to promote the melting point of catalysts so that they can keep crystalline structure at high temperature. In this work, we focused on the exploration of iron and tungsten bimetallic catalysts for the controlled growth of m-SWCNTs in bulk by using an injection floating catalyst chemical vapor deposition methods. Toluene and C_2H_4, ferrocene and $W(CO)_6$, thiophene were used as the carbon sources, catalyst precursors, and growth promoter, respectively. We systematically investigated the effect of thermodynamical and kinetical parameters on electrical conductivity of SWCNTs. Under optimized conditions, metallic-enriched SWCNTs (~79%) were obtained.

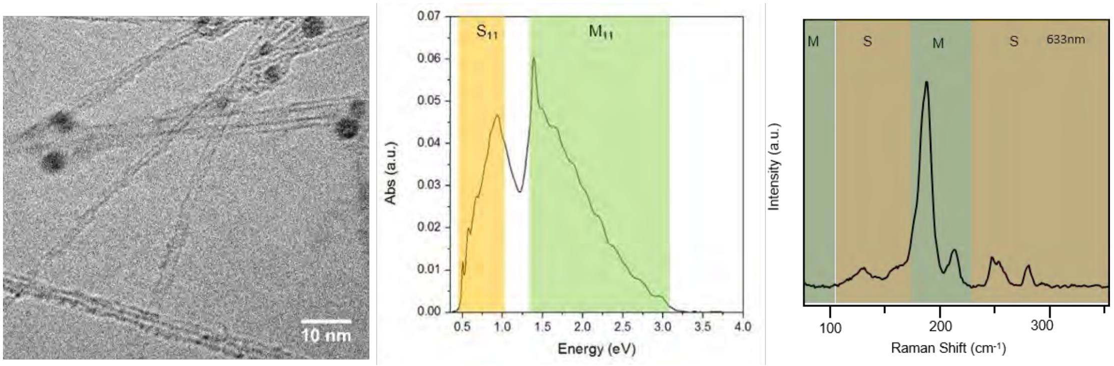

Fig. 1 TEM, absorption spectrum and Raman spectrum characterizations of SWCNTs.

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Proper Solvents Enhance the Yield of Linear Carbon Chains inside Carbon Nanotubes

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Linear carbon chains (LCCs) as a typical sp^1-hybridized 1D carbon allotrope have attracted increasing research interests and explorations because of their advantaged optical and electrical properties of true 1D structure. Previously, LCCs have been synthesized inside carbon nanotubes (CNTs) directly by arc-discharge method [1] or indirectly by post-treatment [2]. For the later, especially, long LCCs consisting of more than 6000 carbon atoms has been realized recently by high-temperature annealing of double-walled CNTs. Unlike the short chains as insulator, the LLCCs are semiconductors since their band gaps were determined between 1.8 and 2.3 eV [3], shining a light on the future research on such LLCCs. Generally, the yield of the LCCs is still low because of the limited residual carbon inside the nanotubes as the carbon source of the LCC formation. Inspired by this, here we show that extra carbon sources introduced from different solvents allows to enhance the yield of both short and long LCCs. Several types of carbon-containing solvents, have been filled inside single-walled CNTs. These solvents can be decomposed at high-temperature and transformed into small inner CNTs, and then LCCs were formed inside those inner tubes. The results show that the yields of both of the short and long LCCs increase around 2 times with the help of specific solvents at optimized temperature. This route provides larger quantity of LCCs to explore their properties and applications in the future.

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[3] Shi L, *et al.* Electronic band gaps of confined linear carbon chains ranging from polyyne to carbyne. Physical Review Materials 2017, 1 (7), 075601

CNT-based transparent conductive films and high-performance fibers from floating-catalyst CVD

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The carbon nanotube (CNT) synthesis is a key process to accelerate the fulfilment of various CNT-based applications with extraordinary properties. Because of its low set-up cost and high production yield, scalability, and degree of control, floating catalyst chemical vapor deposition (FCCVD) is now widely used among several techniques of CNT synthesis available. Specifically, macroscale CNT architectures, e.g., films and fibers, can be directly fabricated based on FCCVD. Herein, high-performance CNT films are produced in two ways based on FCCVD. One is CNT aerosol from CO-FeCp2 FCCVD directly deposited into CNT films on filters in room temperature [1]. The effect of CO2 as promoter on yield, morphology, and chirality distribution of SWCNTs is systematically studied. In addition, the high-performance transparent conductive films (TCFs) of CNTs (Fig.1a) are fabricated a simple dry transfer method. With appropriate amount of CO2, CNT TCFs exhibit improved performance up to 86.8 Ω/sq. at 90 % transmittance with AuCl3 doping. The excellent performance of CNT films is attributed to the enrichment of metallic SWCNTs and optimized geometry, e.g., long, straight and small bundles. Another is CNT aerosol transformed into CNT aerogel for tubular film fabrication in FCCVD. Based on the hydrocarbon-FeCp2 FCCVD, the tubular CNT films can be directly and continuously produced (Fig.1b). The optimized synthesis process manifests a high carbon efficiency (~ 60%), high extrusion yield (hundreds of meters per hour), and stable controllability in the fabrication of freestanding films with excellent transparent and conductive performance. Moreover, the continuous CNT fibers can be directly fabricated by shrinking tubular CNT films with liquid (Fig.1c) [2]. With acid treatment, the fibers' strength and electrical conductivity reach up to 2 GPa and 4.3 MS/m, which are promoted by 200% and almost one order of magnitude than as-synthesised fibers, respectively.

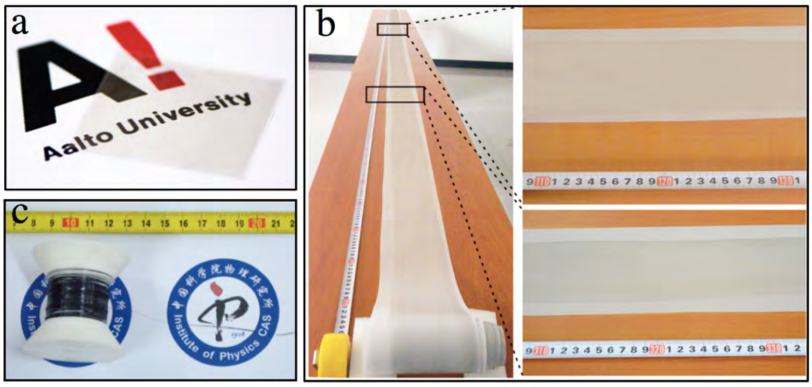

Fig.1 The CNT film and fiber from FCCVD

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Chirality-Selective Synthesis of Single-Walled Carbon Nanotubes

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Chiral-selective synthesis of single-walled carbon nanotubes (SWNTs) by chemical vapor deposition (CVD) has been challenging in carbon nanotube research field. Despite of the efforts in the past two decades, a complete understanding to catalytic synthesis of SWNTs is still lacking, precluding a ration synthesis of SWNTs with enriched species.

In this contribution, we will first address the evolution of catalysts during CVD process, where phase separation between different components are observed with the assistance of environmental transmission electron microscopy [1, 2]. Although alloy formation is lacking in both FeTi and FePt catalysts, the respective presence of Ti and Pt affects the catalytic behaviors of active Fe component, favoring the synthesis of large-chiral-angle SWNTs when applying CO as the carbon source [1, 2].

Subsequently, the roles of the carbon source in determining SWNT growth mode are clarified. Compared with CH_4, CO facilitates the nucleation of SWNTs with perpendicular mode, resulting in the synthesis of SWNTs with small diameters [3], which provides a strategy for chiral-selective of small-diameter SWNTs, like (6, 5) species. A number of catalysts, such as Fe-MgO, FeMn-MgO [4], Co-MgO [5] and Ni-MgO [6], is applied for preferentially growing (6, 5) nanotube using CO as the carbon source. During growth process, unreduced metal cations have strong binding energy with the reduced metal counterparts, constraining the aggregation of metal particles. Remarkably, the Co-MgO catalyst affords the synthesis of small diameter (6, 5) SWNT even at a temperature as high as 800 ºC, which could be correlated with the unique SWNT tip-growth mode [5]. Furthermore, by alternating carbon sources from CO to CH_4 during CVD process, SWNT intramolecular junctions are fabricated [7]. The creation of SWNT junctions is attributed to the different growth modes adopted by SWNT when using different carbon sources (**Fig .1**).

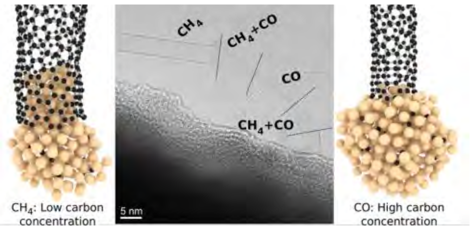

Fig.1 SWNT growth mode regulation leads to the formation of junctions.

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[4] M. He, P.V. Fedotov, A. Chernov, *et al*. Carbon **108**, 521 (2016).
[5] M. He, T. Yang, D. Shang, *et al*. Chem. Eng. J. **341**, 344 (2018).
[6] M. He, X. Wang, L. Zhang, *et al*. Carbon **128**, 249 (2018).
[7] M. He, Y. Magnin, H. Jiang, *et al*. Nanoscale **10**, 6744 (2016).

Aerosol Synthesis of Single Walled Carbon Nanotubes from Ethylene for High Performance Transparent Conducting Films

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Transparent conducting films (TCFs) are critical components of many optoelectronic devices that pervade modern technology. Due to their excellent optoelectronic properties and flexibility, single-walled carbon nanotube (SWNT) films are regarded as an important alternative to the conventional transparent conducting material, i.e the brittle indium tin oxide. Herein, we have developed aerosol synthesis of SWCNTs using C_2H_4-H_2-N_2 system for high performance thin SWNT film fabrication. For the first time, ethylene has been used as the only carbon source for high-quality SWNT synthesis in FCCVD with N_2 as the main carrier gas, which makes the growth process economical, safe and environmental friendly. The electron diffraction (ED) analysis indicates that chirality of the SWNT randomly distributes between armchair and zigzag structures and the proportion of metallic SWNTs is around 38%. High-performance TCFs of SWNTs are directly fabricated with deposition of SWCNT aerosol on the filters in room temperature. Specifically, CNT TCFs exhibit improved performance up to 51 Ω/sq. at 90 % transmittance after HNO_3 doping with the optimized synthesis process. The excellent conductivity of the SWNT TCFs is attributed to long tubes (mean length 13 um) and low bundling with 29 % of individual tubes. This high-performance SWCNT TCFs have great potential in flexible electronics, photovoltaic [1] and electrochemistry [2].

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[2] Tavakkoli, M, et al. *Angewandte Chemie* 127.15 (2015): 4618-4621

Growth of High-density Single-walled Carbon Nanotube Arrays by Multiple Catalysts Reactivation

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Single-walled carbon nanotube (SWCNT) arrays have been regarded as a leading candidate in electronic devices to replace silicon. Towards this goal, SWCNT samples should be high density, high selectivity and high orientation. Recently, many researchers focused on improving the density of SWCNTs by both direct growth and post-treatment methods. Direct growth method could obtain SWCNT samples with high quality, but the density could not face the requirement. Basically, the most critical issue to affect the density in direct growth process is the poisoning phenomenon of catalysts. Recently, researchers tried to solve this problem by catalyst designing or processing multiple-cycle growth.

In this work, we designed multiple catalysts reactivation process by introducing H_2 treatment to improve the array density of SWCNTs. During the experiment, we found that the efficiency of catalyst reactivation decreased with the increase of the cycle times. Based on this phenomenon, we proposed two possible types of catalyst poisoning: Physical Poisoning (PP) and Structural Poisoning (SP). Catalysts with PP are covered by carbon and prevented from contacting with the carbon feedback, while catalysts with SP transform to other stable structures without activation. Thus, only poisoned catalysts with PP type could be reactivated during H_2 treatment process, for H_2 could act as etchants to remove the surface carbon on catalysts. With this method, we obtained the SWCNT arrays with the density of 18 tubes/µm. Furthermore, we studied the relationship between the PP ratio and the carbon solubility in different catalyst. It was found that PP ratio increased with the decreasing carbon solubility, which showed better performance in catalyst reactivation process.

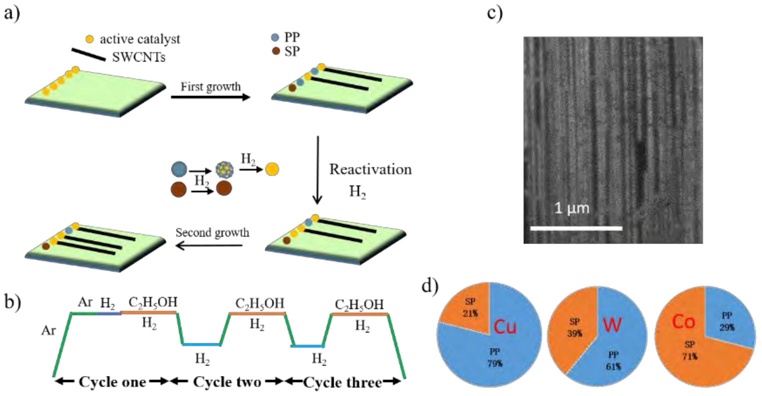

Fig.1 Schematic illustration and results of our method. (a) Schematic illustration of the reactivated process. (b) Experimental flow diagram of multiple-cycle growth method. (c) SEM of the obtained high density of SWCNTs. (d) The distribution of PP and SP ratio of different metals (Cu, W, Co).

Synthesis of highly crystalline multilayer graphene on graphene template by high growth temperature

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Multilayer graphene with a turbostratic structure different from the order stacking has a weak interlayer coupling between layers. The incommensurate stacking structures sometimes exhibit the extraordinary electrical transport properties such as high carrier mobility due to the pseudo-monolayer band structure [1,2] and superconductivity due to the superlattice formation [3]. In previous study, we reported a synthesis of graphene layers on mechanically exfoliated graphene flakes and graphene nanoribbons as a growth template using chemical vapor deposition (CVD) with ethanol [4]. The structural analysis using Raman spectroscopy indicates that the grown graphene layers has a turbostratic structure. Unfortunately, the crystallinity of grown graphene layers is not sufficient compared with the graphene template due to low growth temperature (720ºC). In this study, we investigated the growth of graphene layers on graphene template (mechanically exfoliated, CVD and SiC graphene) under high temperature condition above 1300ºC.

Figure 1 shows the Raman spectra observed from the multilayer graphene at growth temperature of (a) 1300ºC and (b) 720ºC. The peak in the D-band region shows a broad shape and strong intensity at low growth temperature, and the grown graphene layers are low crystallinity. At high growth temperature, the intensity and the full with at half maximum of the D-band peak decreases. Moreover, the peak shape in the 2D-band region reflecting the stacking structure is fitted by a single Lorentz function, suggesting the formation of turbostratic stacking. Figure 2 shows the atomic force microscope (AFM) images of graphene at (a) 1300ºC and (b) 1400ºC. Disk-shaped graphene sheets with a height of 0.34 nm corresponding to the monolayer height are formed. At higher growth temperature, graphene sheet shows a hexagonal shape. The graphene has the two kinds of edge structure (zig-zag and armchair). This means that the selective growth of edge structures becomes apparent by improving the crystallinity with higher growth temperature, and the hexagonal graphene sheet is composed of single crystal. The growth behavior strongly depends on the growth temperature rather than the graphene template type. This indicates that the synthesis approach of turbostratic multilayer graphene can be developed in the large area using CVD and SiC graphene template.

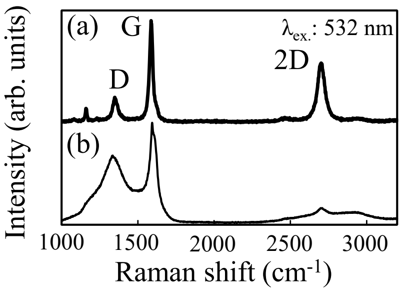

Fig. 1 Raman spectra observed from the multilayer graphene at growth temperature of 1300ºC and 720ºC.

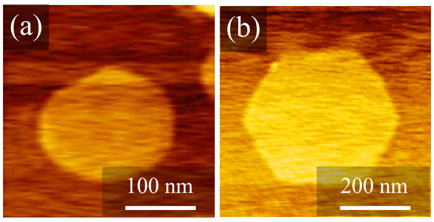

Fig. 2 AFM images of grown graphene sheet on SiC graphene template at growth temperature of 1300ºC and 1400ºC.

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Atmospheric moisture storable aerogel based on graphene oxide linked by multivalent metal chlorides

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Graphene oxide(GO) has abundant oxygen functional groups which enable it to have a good hydrophilicity. Therefore, GO is easy to interact with metal-ions through many supramolecular interactions. In this work, we present that GO aerogel attracts moisture in atmosphere and store water through 3D structure using coordination bond between GO and multivalent metal-ions. Several metal chlorides spontaneously attract moisture in air. When relative humidity was over 80%, the GO aerogel absorbed moisture is 6.6times heavier than dried GO aerogel. The ability of storing water showed a maximum of 12400%. When metal chlorides are not enough to coordinate with GO, GO aerogel can’t attract moisture in air. Additionally, through reduction of part of GO aerogel to increase mechanical property of 3D structure, we obtain stable GO aerogel in aqueous solution.

Metal-phenolic compounds derived 3D graphite nanoballs as a highly reversible anode

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In general, it is difficult to expect the characteristics of amorphous carbon in graphitic carbon. Here, we present a distinctive design based on polyphenol and transition metal on 3D structured Graphite nanoballs (GNBs). GNBs are simply derived with homogeneous carbon hollow shells composed of 20-30 layers by pyrolysis of metal-phenolic compounds. Due to their an abundance of mesopores, these hollow shells are available as a cage to contain and disperse other materials such as Sn nanoparticles. This approach has the potential to improve the properties of lithium-ion batteries as a highly reversible anode.

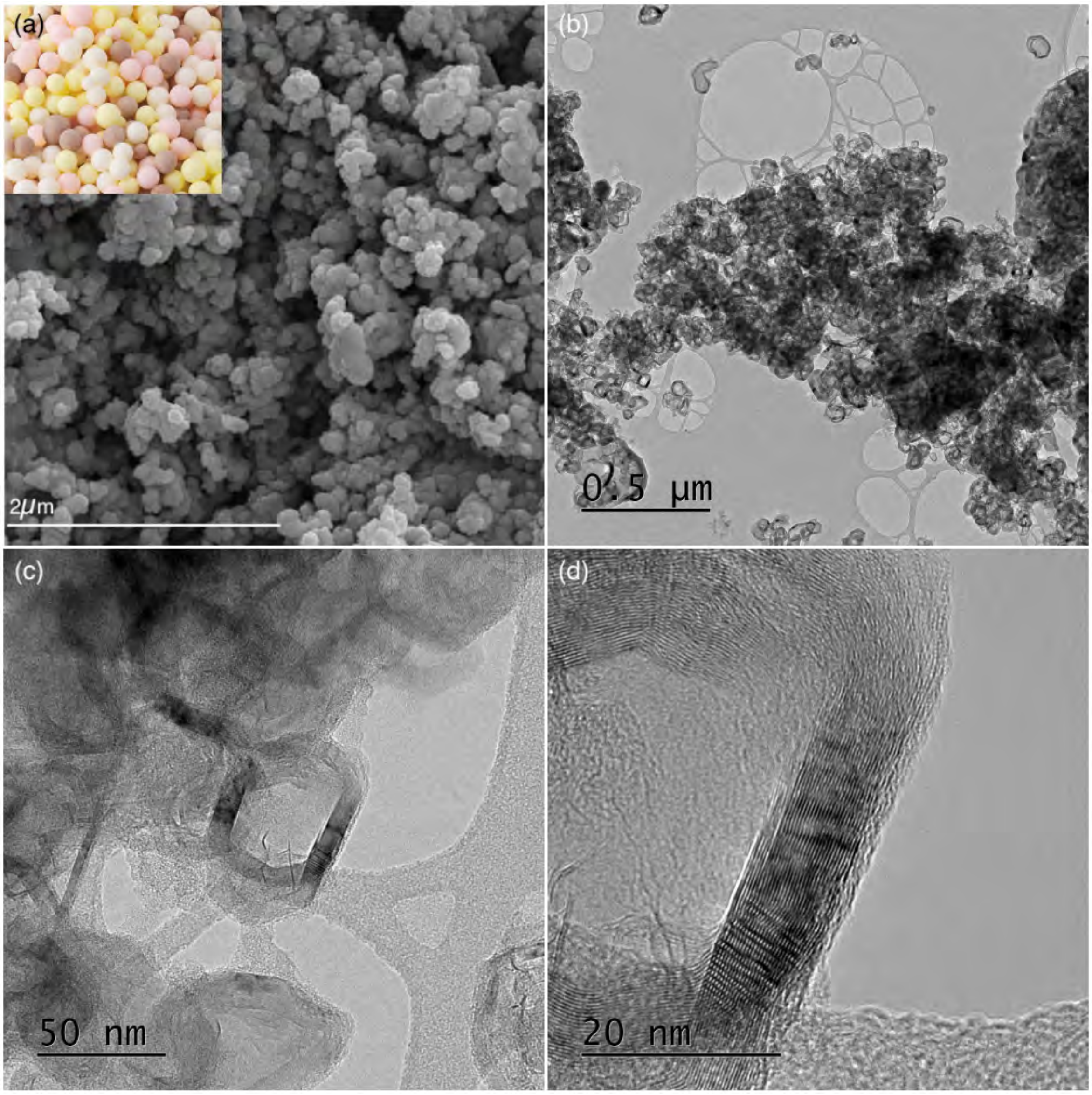

Fig. 1. SEM (with scheme) and FE-TEM micrographs of the bead-like 3D Graphite nanoballs

Two-dimensional metallic tantalum disulfide as a hydrogen evolution catalyst

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Two-dimensional metallic transition metal dichalcogenides are emerging as prototypes for uncovering fundamental physical phenomena, such as superconductivity and charge-density waves, as well as for engineering-related applications. However, the batch production of such envisioned transition metal dichalcogenides remains challenging, which has hindered the aforementioned explorations. Herein, we fabricate thickness-tunable tantalum disulfide flakes and centimetre-sized ultrathin films on an electrode material of gold foil via a facile chemical vapour deposition route. Through temperature-dependent Raman characterization, we observe the transition from nearly commensurate to commensurate charge-density wave phases with our ultrathin tantalum disulfide flakes. We have obtained high hydrogen evolution reaction efficiency with the as-grown tantalum disulfide flakes directly synthesized on gold foils comparable to traditional platinum catalysts. This work could promote further efforts for exploring new efficient catalysts in the large materials family of metallic transition metal dichalcogenides, as well as exploiting their applications towards more versatile applications.

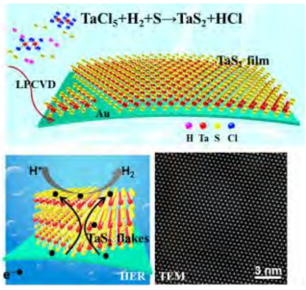

Fig.1 Two-dimensional metallic tantalum disulfide as a hydrogen evolution catalyst

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Selective growth of semiconducting single-wall carbon nanotubes using SiC as a catalyst

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Semiconducting single-wall carbon nanotubes (s-SWCNTs) without metal impurities are highly desired for use in high-performance field effect transistors as a channel material[1]. Here we use SiC nanoparticles as a catalyst to selectively grow s-SWCNTs. The Si atoms on the surface of the SiC nanoparticles are found to be depleted during thermal treatment[2-3], and carbon atoms are exposed, which leads to the formation of carbon nanocaps on the SiC nanoparticles. Under a hydrogen atmosphere, the chemically active metallic carbon caps are preferentially etched away so that high purity s-SWCNTs with a content of ~95% without any residue metal impurities are obtained by the chemical vapor deposition of ethanol and can be used to fabricate high-performance thin film transistors.

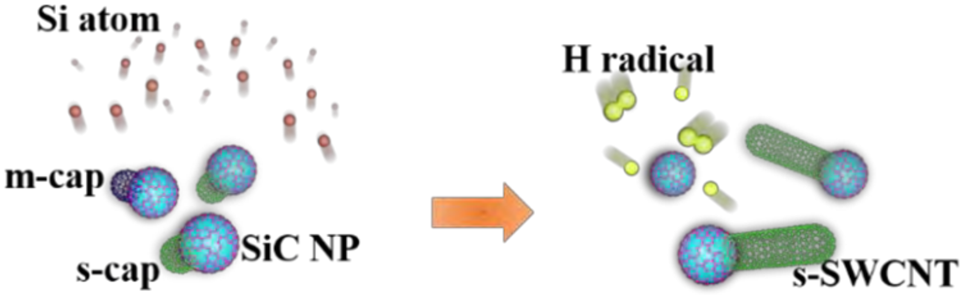

Fig.1 Semiconducting SWCNTs were selectively grown from SiC nanoparticles by the chemical vapor deposition of ethanol, where the caps of any metallic SWCNTs were preferentially etched by active H radicals.

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Title: Nitrogen-doped carbon nanotubes with encapsulated Fe nanoparticles as efficient oxygen reduction catalyst for alkaline membrane direct ethanol fuel cells

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Abstract: We designed a facile method for the synthesis of ORR catalysts with iron nanoparticles encapsulated in bamboo like structure of N-doped carbon nanotubes. It is cost effective method using rich-nitrogen molecules, pretreated KJ600 and $FeCl_3$. Finally, pyrolyzed catalyst (Bg-CA-M)-Fe-C-800°C exhibited the efficient ORR performance with the onset potential 1.10 V, half-wave potential 0.93 V and 4 electron transfer number per oxygen molecule in 0.1 M NaOH solution. (Bg-CA-M)-Fe-C catalyst has high ORR activity (0.578 mA mg^{-1} at 1 V and 2.66 mA mg^{-1} at 0.95 V) with low H_2O_2 yield less than 1%. At 1.0 V, the mass activity of (Bg-CA-M)-Fe-C@800°C can reach approximately 43% of that of Pt/C (1.35 A $gcat^{-1}$). XPS measurements revealed that ORR activities of catalysts directly correlate with pyridinic and pyrrolic nitrogen active species. The high catalyst durability and methanol-crossover tolerance can be attributed as an alternative to noble metal catalysts in the fuel cell. The direct ethanol fuel cell (DEFC) with (Bg-CA-M)-Fe-C as cathode catalyst displayed 64 mW cm^{-2} peak power density and maximum current density 350 mA cm^{-2} at 0.84 V open circuit voltage.

Key words: Carbon nanotubes (CNTs), Direct ethanol fuel cell (DEFCs), Oxygen reduction reaction, Pyrolyzed Fe/N/C, Active sites

Reference:

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Thermophoretic deposition of single-walled carbon nanotubes to form thin films with tunable characteristics

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A number of promising bright applications, thin films of single-walled carbon nanotubes are still challenge us to solve both applied and basic issues. While aerosol CVD (floating catalyst) method has proven itself to provide versatile and tailorable source for the thin films, transfer of carbon nanotubes from gas phase to a substrate offers bonus opportunities for fine tuning.

Here, we discuss thermophoretic deposition of carbon nanotube aerosol – non-invasive approach for direct tangential transfer of aerosol structures under the temperature gradient providing, for example, films of extremely low thickness (sub-percolation surface concentration) on non-porous substrates. In the present work we systematically asses the influence of intrinsic properties of carbon nanotubes (length, morphology, diameter etc.) on the thin film performance with special attention to the origins and peculiarities of carbon nanotube behavior within the field of high temperature gradient.

The data obtained show poor predictive ability of the classical models for thermophoretic deposition of aerosol to describe the deposition of carbon nanotubes. In the present work we address the reasons of this disagreement focusing on developing appropriate model as well.

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Growing 1-inch-size horizontal arrays of highly-pure semiconducting carbon nanotubes

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Carbon nanotubes (CNTs) are anticipated to be the successor of silicon in next generation integrated circuits. However, one great challenge to the practical application of this concept is the need to grow horizontal semiconducting CNT arrays with very high purity. Here we show that this roadblock can be eliminated by switching the direction of an applied electric field during synthesis. This electro-renucleation approach twists the chirality of the CNTs to produce nearly-defect-free s-CNTs horizontally-aligned on the substrate with less than 0.1% residual metallic CNT. In principle, this residual percentage can be further reduced to less than 1 ppm simply by tuning the CNTs' diameters to around 1.3 nm. Electro-renucleation thus offers a potential pathway to practical applications of CNT electronics and opens up a new avenue for large-scale selective synthesis of semiconducting CNTs and other nanomaterials.

Control of $^{12}C/^{13}C$ isotope in CNT grown from nanodiamond

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Phonon scattering in CNT significantly increases by introducing ^{13}C into the graphitic lattice of ^{12}C [1], and increases locally near the abrupt interface formed between ^{12}C- and ^{13}C-CNT regions [2]. Isotope-controlled CNT has a potential advantage for the applications such as thermoelectric materials. In this study, CNTs composed of ^{12}C and ^{13}C were grown by chemical vapor deposition (CVD) from the growth seed of nanodiamond and metal catalyst. CNT growth proceeds via Vapor-Liquid-Solid (VLS) mechanism for the metal catalyst, whereas via Vapor-Solid-Surface-Solid (VSSS) mechanism for the nanodiamond [3]. The effect of growth mechanism on isotope composition was examined by Raman spectroscopy. The G-band frequency $\omega_{13C+12C}(x)$ depends on the ^{13}C ratio $(0 \le x \le 1)$ in CNT, and $\omega_{13C+12C}(x)$ is given by [4]:

$$\omega_{13C+12C}(x) = \omega_{12C}\sqrt{12/\{12(1-x)+13x\}}$$

Fig.1 is a Raman image and Raman spectra of CNTs grown by switching carbon feedstock ^{12}C ethanol to ^{13}C ethanol. CNT grown from Co exhibits G bands at the frequency for the mixture of ^{12}C and ^{13}C near the interface, indicating the formation of $^{12}C/^{13}C$ mixed phase. As for the CNT grown from ND, very sharp transition of G bands from ^{12}C to ^{13}C demonstrates very abrupt interface formation between ^{12}C and ^{13}C regions. Fig.2 is Raman spectra of CNTs grown using the mixture of ^{12}C- and ^{13}C-ethanol as the carbon feedstock. When the ^{13}C fraction in gas phase is 1 % and 99 %, the CNT grown from ND and Co exhibits the very similar ^{13}C fraction in the Raman spectra. As for the ^{13}C fraction of 21 % and 50 % in gas phase, the ^{13}C fraction in CNT grown from ND is very close to that of the gas phase, and notably higher than that for Co catalyst. These results show that isotope composition is strongly affected by the growth mechanism for ND (VSSS) and Co (VLS), and ND is more suitable for isotopic control in CNT than Co.

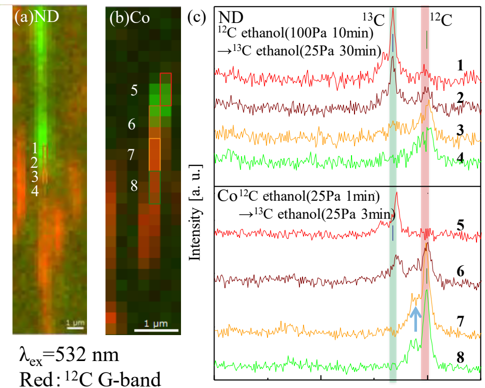

Fig.1: Raman images of G-band region observed from CNTs grown from ND (a) and Co (b).
(c) Raman spectra obtained at the points indicated in (a) and (b).

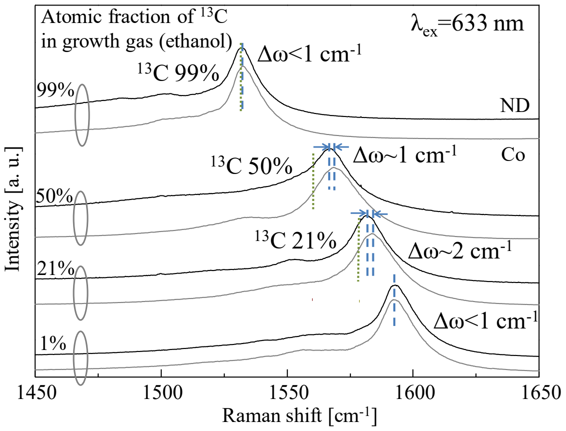

Fig.2: Raman spectra of G-band region observed from CNTs grown from ND and Co. The green dotted lines represent the positions of G-bands composed of the respective ^{13}C fraction.

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Nitrogen-doped Double-walled Carbon Nanotubes: Synthesis and Supercapacitor Performance

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Carbon nanomaterials are widely used as a material for electrochemical sources of energy storage and supercapacitors. Carbon nanotubes (CNTs) attract attention as an electrode material for supercapacitors because their outstanding optical, electronic, thermal, mechanical and chemical characteristics. As a rule, the method of catalytic chemical vapor deposition (CCVD) is used for selective large-scale synthesis of CNTs. In this case, CCVD synthesis is a multivariable process with the ability to control parameters such as catalytic metals (Fe, Co, Ni) and their combinations, carbon sources (CH_4, C_2H_2 or C_2H_4), temperature of synthesis.

The incorporation of a heteroatom in CNT structure significantly affects their electronic structure. It is well known that doping of CNTs with various elements such as nitrogen, boron or potassium allows changing both electronic and chemical properties of nanotubes. Replacing carbon with a nitrogen atom leads to an improvement in the conductivity of nanotubes. The mainly number of works is devoted to the synthesis and study of nitrogen-doped multi-walled CNTs (N-MWNTs) due to the simplicity of synthesis and scale production of MWNTs. Works devoted to the synthesis of nitrogen-doped single-walled CNTs (N-SWNTs) are significantly less. Finally, the works related to the synthesis of nitrogen-doped double-walled CNTs (N-DWNTs) are even less because of the complexity of N-DWNTs synthesis. DWNTs combine the best properties of MWNTs and SWNTs such as excellent mechanical, chemical and electrical characteristics. In this case, DWNTs are particularly interesting for modifying the outer layer with the internal state unchanged.

In the present work, CCVD synthesis of N-DWNTs was carried out in a horizontal quartz tube reactor with a length of 2 m and a diameter of 10 cm with a constant temperature zone of about 15 cm. Catalyst $MgO_{0.99}(Co_{1-x}Mo_x)_{0.01}O$ was synthesized by explosion method. The reaction mixture of gases CH_4 and H_2 was bubbling through CH_3CN and fed to CVD reactor. N-DWNTs with different nitrogen contents were obtained depending on the temperature and time of synthesis. The obtained N-DWNTs were characterized by transmission electron microscopy. The type and amount of incorporated nitrogen were determined using X-ray photoelectron spectroscopy. N-DWNTs have demonstrated promising results as an electrode material in supercapacitors.

This work was supported by the Russian Foundation of Basic Research (grant 16-53-150003) and PRC CNRS/RFBR (Grant No 1023).

Scalable synthesis of highly porous nanocarbon materials by ultrahigh temperature process for graphene oxide and cellulose nanofiber composites

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It is known that defect of graphene oxide (GO) can be repaired under inert gas by high temperature treatment. However, AB stacking formation is unavoidable during this graphitization, leading to superior properties degradation of single layer graphene. Turbostratic stacking is considered to be a promising candidate to tackle this issue and preserve monolayer graphene properties, because theoretical calculations predict the electronic structure of the turbostratic graphene is very similar to that of the single-layer graphene [1]. Our former research on GO film using ultrahigh temperature process had achieved formation of turbostratic stacking structure in restored graphene film [2], but the turbostratic structure formation is limited near the sample surface. In this study, we investigated scalable formation of turbostratic graphene with porous GO sponge, and extended the process to nanocarbon composites combined with cellulose nanofiber (CNF), in order to improve turbostratic occupation, spacing controllability and mechanical strength toward future practical applications.

Monolayer GO flakes dominated by tens μm size was synthesized by chemical exfoliation [3], and used as precursor. Initially, porous cm-scale GO sponge obtained by freeze-drying was treated at ultrahigh temperature under ethanol/Ar environment. As shown in Fig. 1(a)-(I), the Raman spectrum illustrated that R (fraction of AB stacking) was 15%, indicating that turbostratic stacking fraction was about 85%. After that, GO/CNF composite sponge prepared by freeze-drying of CNF and GO dispersion was treated thermally under the same condition. Raman spectrum, Fig. 1(a)-(II), indicated that CNF did not restrain formation of turbostratic stacking and reduce process. Occasionally, as shown in Fig. 1(a)-(III), notably intense 2D bands were observed, suggesting inhomogeneity of graphene stacking in the composite. In order to improve homogeneity, GO/CNF sponge was prepared by new process of rapid cooling and pH control (pH=8), and the graphene was synthesized by the thermal process under the same condition. I(2D)/I(G) observed for the new process samples shows narrower deviation, compared with that by the initial process (Fig. 1(b)), revealing a more homogeneous dispersion. Pore size of the porous graphene sponge was observed to be smaller (~2-8 μm) by the new process (Fig. 1(c), (d)). These results demonstrate that self-standing porous turbostratic graphene film can be produced in large scale by the thermal process at ultrahigh temperature for homogeneous dispersion of GO and GO/CNF mixture.

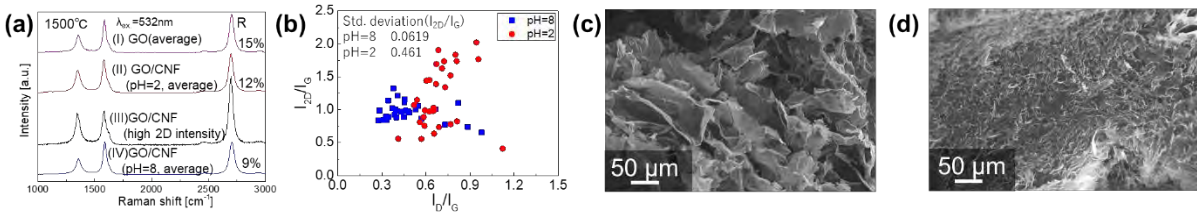

Fig.1 (a) Raman spectra of GO and GO/CNF, (b) I(2D)/I(G) deviation for initial and new processes, SEM images of the sample prepared by (c) initial and (d) new processes.

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Spacer Thickness Dependence of Enhanced fluorescence in Au Nanorod @Mesoporous Silica@Carbon-Dots nanocomposites

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Abstract： In this paper, well-defined $Au_{nanorod}$@$mSiO_2$@C-Dots nanocomposites were synthesized through layer-by-layer assembly technology with a Au nanorod core, mesoporous silica spacer and an Carbon-Dots shell. The fabricated nanocomposites were characterized by X-ray diffraction, UV-vis absorption spectroscopy and transmission electron microscopy. The spacer thickness of the mesoporous silica could be simply controlled from 15 nm to 50 nm by varying the amount of silica precursor and the reaction time. The strongest fluorescence enhancement is achieved when the optimized silica thickness is around 30 nm, resulting in about 5-fold enhancement. The emission intensity of the $Au_{nanorod}$@$mSiO_2$@C-Dots nanocomposites is highly dependent on the spacer thickness of silica.

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Nucleation and Growth Investigation of Boron Nitride Nanotube towards the Control of Morphology in Chemical Vapour Deposition

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Structurally analogous to carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) exhibit similar mechanical and thermal properties. However, BNNTs offers additional extraordinary features such as greater thermal and chemical properties, electrical resistance, and naturally absorbs radiation. These properties have attracted massive interest to researchers due to the wide range applications such as fuel efficiency particularly in space applications, thermal management for batteries and devices[1], and biomedical applications serving as scaffold to the growth of tissues. In order to use BNNTs to these applications, one must enable to acquire large scale production.

Although few teams were able to reach yields of up to ca. 20g[2], the final morphology of the up-scaled BNNT suffers entanglement. Compared to the research done in CNTs in which fundamentals of the synthesis such as the chemistry are abundantly available, fewer efforts have been done to investigate such degree of understanding BNNTs while much on up-scaling BNNTs. It must be realized that in order to produce high yields of BNNTs, the fundamental science particularly the nucleation and growth of BNNTs must be understood.

Herein, my entry will present our group's discovery concerning the nucleation and growth of BNNTs[3] through state-of-the-art equipment in University of Oxford. Short time reaction revealed significant amount of in-situ generated nanospheres having tail-like structures and these were found to be the initial growth of BNNTs. Magnesium, a component of the precursor, was found to play a vital role that served to generate the intermediate species and medium for the diffusion of BN species to the formation of BNNTs. The proposed mechanism is shown in a schematic illustration below. This finding led us to design an experimental set-up that allows the control of three important factors for the formation control; namely (a) B species, (b) N species, and (c) catalyst. Different morphologies were obtained by controlling the dimension of the catalyst particles. We believe that this is a fundamental work crucial for the up-scaling the production.

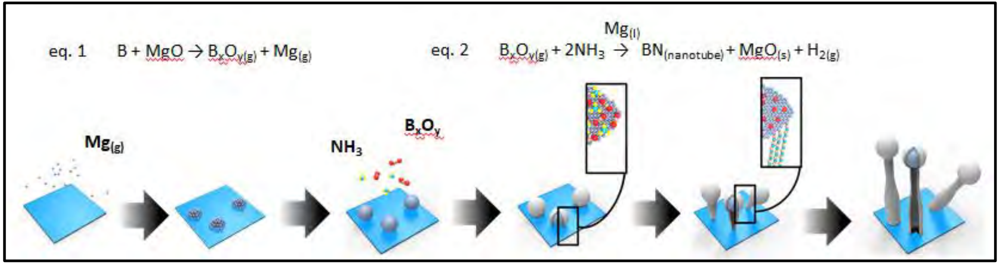

Fig.1 Proposed mechanism on the nucleation and growth of boron nitride nanotubes.

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Chemical Vapor Deposition of Two-Dimensional Metallic Vanadium Diselenide and Raman Characterization of the Phase Transition

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ABSTRACT

Two-dimensional (2D) metallic vanadium diselenide (VSe_2) have renewed interest due to the enriched physical properties and potential applications as the high-performance functional nanomaterial. Herein, we have investigated the synthesis and phase transitions of 2D metallic vanadium diselenide (VSe_2). The synthesis has been done by chemical vapor deposition (CVD) using hexagonal boron nitride (*h*-BN) and mica as substrates. High-quality VSe_2 flakes have been obtained and characterized by transmission electron microscopy (TEM). Temperature-dependent Raman characterization between 300 K and 40 K has been conducted and revealed remarkable changes of Raman modes at 110 K, indicating charge density wave (CDW) phase transitions. Temperature-dependent electrical measurements have also supported the phase transitions observed in Raman characterization.

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Direct optical polymerization and lithography of two-dimensional conjugated microporous polymers

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Two-dimensional conjugated microporous polymers (2D CMPs) have been attracting immense research interest due to their unique structure, desirable properties and wide applications[1,2]. However, the preparation of large-area patterned and multilayer 2D CMPs on arbitrary substrates, which is useful for their fundamental study and practical applications in organic electronics and large-area integrated devices, has remained not been achieved. Here we report a wafer-scale patterning method for preparation of 2D conjugated microporous polymers (CMPs) films on arbitrary substrates via photomask-assisted solid-state photopolymerization under ambient conditions. The 2D CMP patterns were controllable prepared with variable geometric photomasks, and multilayer films could be constructed by layer-by-layer stacking methods. As a proof of concept, the obtained multilayer stacked 2D CMP films onto reduced graphene oxide (rGO) substrate were used as electroactive layer to fabricate memory devices. The devices exhibited thickness dependent electrical properties, the resistive switching behavior could be investigated when two or three layer stacking of 2D CPM were used, the three layer 2D CMP based device showed higher On/Off ratio. Therefore, combining this solid-state photopolymerization with photomask technique provide an effective strategy to prepare large-area patterned conjugated polymer sheets, and this strategy could be further realized for other 2D materials and their integrated devices.

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Controlled Growth of Single-walled Carbon Nanotubes Using Graphene Oxide supported $CoWO_4$ as Catalyst Precursors

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Preparation of the uniform and well-dispersed catalysts is crucially important for the controlled growth of single-walled carbon nanotubes on substrates [1]. Tungsten-based intermetallic catalyst with high melting points can act as the structural templates for chirality specific growth of SWNTs [2-4]. Graphene oxide (GO) have been widely used as dispersants and templates to prepare well-dispersed nanoparticles on surface [5].

Here, we used GO supported cobalt tungstate as the catalyst precursors instead of the previously used molecular clusters to prepare tungsten-cobalt catalysts. The as-prepared catalyst precursors are well dispersed on the GO platforms with uniform size. The intermetallic W_6Co_7 structure of the catalysts after the annealing and reduction process was confirmed by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The SWNTs grown possess a uniform diameter. Semiconducting species of high purity were prepared at suitable conditions.

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Direct synthesis and in situ characterization of monolayer parallelogrammic rhenium diselenide on gold foil

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Rhenium diselenide ($ReSe_2$) has recently garnered great research interest due to its distorted 1T structure, anisotropic physical properties, and applications in polarization-sensitive photodetectors [1-3]. However, $ReSe_2$ synthesized by chemical vapor deposition (CVD) is usually a multilayer/polycrystalline material containing numerous grain boundaries, thereby hindering its further applications. Here we describe the direct CVD growth of high-quality monolayer $ReSe_2$ single crystals with a parallelogram shape arising from its anisotropic structure on a gold foil substrate. In particular, we use low-energy electron microscopy/diffraction combined with scanning tunneling microscopy/spectroscopy to determine the atomic-scale structure, domain orientation/boundaries, and band features of monolayer $ReSe_2$ flakes grown directly on gold foils. This work may open new opportunities for the direct synthesis and in situ characterization of CVD-grown monolayer $ReSe_2$.

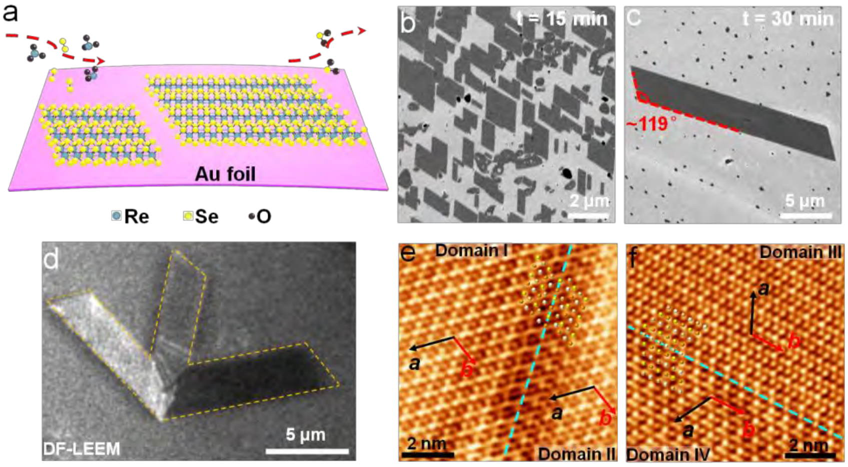

Fig.1 (a) Schematic diagram of the surface-mediated growth of $ReSe_2$ on the Au foil. (b, c) Typical SEM images of the parallelogram-shaped $ReSe_2$ achieved at different growth times: (b) 15 min and (c) 30 min. (d) DF-LEEM image showing remarkably different contrasts for the three merged parallelograms. (e) STM image (−0.003 V, 12.64 nA; 8.3 nm × 8.3 nm) with the fitted atomic models superimposed. The yellow dots with color gradients represent the upper Se atoms with different STM contrasts. The GB and the *a*-axis and *b*-axis of domains I and II are marked by a blue dashed line and black and red arrows, respectively. (f) STM image (−0.005 V, 30.77 nA; 8.30 nm × 8.30 nm) with the fitted atomic models superimposed.

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Multiple-cycle Deposition of Pure Metal Catalyst to Grow High-density SWNT Arrays

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Single-walled carbon nanotube (SWNT) has been considered as one of the most promising candidate to replace silicon in integrated circuits. The density of SWNT arrays is essential which can limit the performance of devices. Recent years, many efforts have been achieved to grow high-density SWNT arrays by controlling the morphology and dispersion of catalysts. However, it is still a challenge to obtain SWNT arrays with a density more than 80 SWNTs μm^{-1} on quartz. Herein, we develop a new method of multiple-cycle deposition of pure metal catalyst and obtain horizontally aligned SWNT arrays with density more than 80 SWNTs μm^{-1} on quartz. The catalysts obtained by vapor deposition have very high reactivity and can be removed by a short time annealing, which is essential to multiple-cycle growth. Besides, by controlling the cycle times, we can synthesis SWNT arrays with different density varying from 10-80. Using these arrays, we can get a relation between current density and density of SWNTs, which indicates the potential of SWNTs in nanoelectronics.

Formation of Precipitated Free Zone in CNT/7055Al Composite

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7055 aluminum alloy is one of the highest strength aluminum alloys and is widely used in the aerospace industry. By adding a small amount of CNTs into 7055Al alloy, it is expected that strength of 7055Al alloy can be further increased without density penalty. In this study, the bulk CNT/7055Al composites were fabricated. 1.5wt.% of CNT was firstly dispersed uniformly in 7055Al powder by high energy ball milling, and the mixed powder was condensed using vacuum hot pressing. The composite billets were hot extruded at 370°C and 420°C and followed by solution and artificial aging treatment (T6). Tensile tests were conducted, microstructures were examined by optical microscopy, scanning electron microscopy and transmission electron microscopy. The tensile strength of the composite extruded at 370 °C was 830MPa, and the elongation was 1.05%, while the tensile strength and elongation of the composite extruded at 420°C were decreased to 807MPa and 0.24%. Microstructures examination indicated that some coarse grains were formed in the ultrafine grains matrix due to liquid phase formation during sintering, and some large precipitates segregated along the boundaries between coarse and fine grains were observed in the billet. After extruded at 370 °C, there still existed many residual precipitates at the boundaries between the coarse and fine grains, while in the composite extruded at 420 °C, the segregation of precipitates almost disappeared. After T6 treatment, the large precipitates in the composites extruded at both temperatures disappeared, and precipitate free zones (PFZ) were observed at the boundaries between the coarse and fine grains in the composite extruded at 420°C, while PFZ were absent in the composite extruded at 370°C. The PFZ was main reason for the variation of mechanical properties with the extrusion temperatures. Effect of the extrusion temperature on the formation of PFZ was discussed.

Keywords: Carbon nanotube, Aluminum matrix composite, Precipitated free zone, Mechanical properties

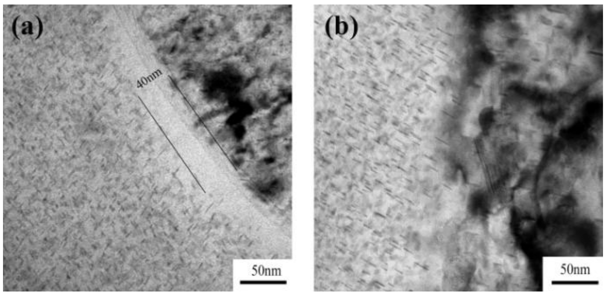

Fig.1 Precipitate phase distribution at boundaries between coarse and fine grains in CNT/7055Al composites after T6: (a) extruded at 420°C; (b) extruded at 370℃

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Design and fabrication of Nanoparticles for radiotherapy enhancement

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The concept of nanoradiosensitization warm from ten year ago, and the nanomaterial-mediated tumor radiosensitization method is mainly focused on the enhancement of intracellular radiation energy deposition by high Z nanomaterials. Recently, various new radiosensitizing approaches based on nanomaterials are successively reported, such as catalyzing ROS generation, consuming intracellular GSH, overcoming tumor hypoxia and various synergistic radiotherapy ways. These strategies may open a new avenue for enhancing radiotherapy therapeutic effects and avoiding its side effects. Hence, to improve the efficacy of RT and reduce its toxic effects, we developed several strategies to enhance the RT therapeutic effects based on nanoparticles. For example, to enhance the radiation sensitivity of hypoxic cancer cells, photothermal therapy or gene therapy based on nanomaterials are employed and combined with RT to improve the therapeutic effects. To generate more free radicals, nanocatalyst that could react with H_2O or H_2O_2 to induce abundant intracellular ROS generation are also used. These strategies may have potential for further clinic applications.

Fabrication of MoO_3/Mo_2C Layered Heterostructures by Direct Thermal Oxidation of Mo_2C

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Two-dimensional (2D) materials, including transition metal carbides (TMCs) exhibit many excellent and novel physical properties, in comparison to the corresponding bulk material. Particularly, molybdenum carbide (Mo_2C) with high hardness, melting point, stability and anti-corrosion at high temperature is greatly potential to be applied in superconductivity, chemical sensing, field-effect transistor, energy storage and so on. In this report, we will introduce the thermal stability of high-quality and ultrathin mono-crystalline Mo_2C, which were synthesized by the method of chemical vapor deposition (CVD), and propose a facile method to fabricate Mo_2C/MoO_3 heterostructures. We have investigated that the thermal properties of Mo_2C in oxygen atmosphere by analyzing its temperature-dependent Raman spectroscopy and *I-V* curve. The Raman peak of Mo_2C (~ 143 cm^{-1}) shows no changes below 300°. However, with the increasing temperature, a Raman peak at the position of 820 cm^{-1} appears at 350°, demonstrating the emergence of MoO_3. And the characteristic peak of Mo_2C cannot be observed at 450°, which indicates that the Mo_2C is completely oxidized to MoO_3. The oxidation process is from top to bottom of the few-layers Mo_2C. In addition, the Mo_2C/MoO_3 vertical heterostructure shows conducting behaviors below 400° but semiconducting properties above 400°, which is revealed by its *I-V* curve. Accordingly, it is feasible to obtain a semiconductor/metal layered heterostructure by conveniently controlling the oxidation process of Mo_2C and tune the relevant properties.

Synthesis of Narrow Diameter and BN Wrapped Vertically Aligned Single-Walled Carbon Nanotubes

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Hexagonal boron nitride (hBN) has been attracted many attentions as a new substrate or dielectric to improve the mobility of two-dimensional material for electrical and optical studies. In this work, firstly we demonstrate a new possibility for controlling the diameter of vertically aligned single-walled carbon nanotubes (VA-SWNTs) by alcohol catalytic chemical vapor deposition (CVD). [1] The synthesis of high density arrays is achieved by combining two unfavorable conditions: low temperature and mono-metallic cobalt catalyst, neither of which were previously found to be efficient for the growth of VA-SWNTs. Using this recipe, the diameter of as-synthesized VA-SWNTs is within a narrow distribution, which is with 85% of the SWNTs between 1.6 to 2.4 nm. The characterization of the cobalt catalyst is performed by in-plane transmission electron microscopy (TEM) directly on SiO_2 TEM grid and the growth mechanism is discussed based on these results in this work. Moreover, BN nanotubes are directly synthesis on VA-SWNTs to capsulate them to form a coaxial structure using ammonia borane (BH_3NH_3) as the precursor by CVD technique. This unique structure of VA-SWNTs encapsulated within BN nanotubes is well investigated by TEM, Raman spectroscopy, scanning electron microscope and time-domain thermoreflectance methods.

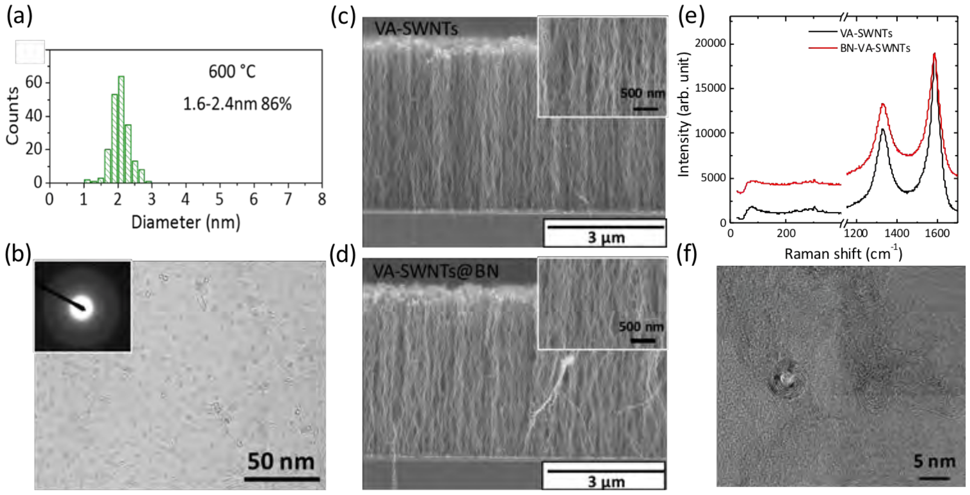

Fig. 1 (a) Histogram for the diameter of VA-SWNTs synthesized at 600°C; (b) TEM characterization of the cobalt catalyst; SEM images of (c) VA-SWNTs (d) VA-SWNTs encapsulated within BN nanotubes; (e) Raman characterization; (f) TEM image of VA-SWNTs encapsulated within BN nanotubes.

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On the Growth and Form of Graphene

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Growing large-area single-crystal monolayers is the holy grail of graphene synthesis, which holds great promises in understanding growth mechanisms and development of high-profile optoelectronic applications. Nucleation, growth and coalescence of individual graphene domains on the substrate in chemical vapor deposition are the fundamental steps that determine the perfection of a continuous film. In this work, the efficiency of growth and the quality of as-grown films are explored through time evolution of domain shapes and surface coverage of graphene on the substrate. Phase-field modeling results demonstrate the critical roles of the deposition flux, edge-attaching kinetics and surface diffusion of carbon sources in modulating the shape evolution and rate of growth. The contrast in kinetics-limited and surface-diffusion-limited regimes is remarkable, as characterized from the shape evolution, which is considered as an indicator of the growth mechanism. Synthesis strategies to improve the growth efficiency and film quality are further discussed based on these findings.

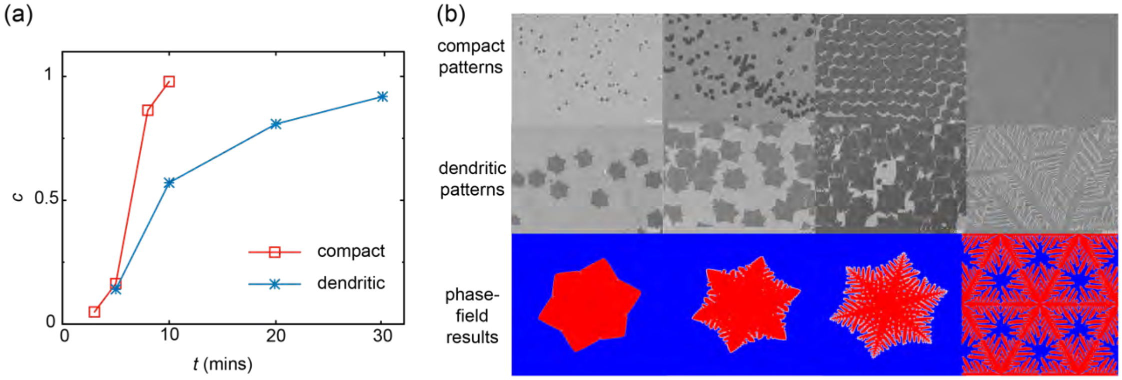

Fig.1 (a) The evolution of graphene surface coverage measured in experiments (b) The growth patterns obtained from experiments and phase-field modeling

Synchronous immobilization and conversion of polysulfides on VO_2-VN composites targeting high-rate lithium–sulfur batteries

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Lithium–sulfur (Li–S) batteries are deemed as one of the most promising next-generation energy storage systems. However, their practical application is hindered by existing drawbacks such as poor cycling life and low Coulombic efficiency due to the shuttle effect of lithium polysulfides (LiPSs). We herein present an *in-situ* constructional VO_2-VN composite which combines the merits of ultrafast anchoring (VO_2) with conducting (VN) to accomplish smooth immobilization-diffusion-conversion of LiPSs across the VO_2/VN interface. Such synchronous advantages have effectively alleviated the polysulfide shuttling, promoted the redox kinetics, and hence improved the electrochemical performances of Li–S batteries. As a result, the sulfur cathode based on VO_2-VN/graphene host exhibited an impressive rate capability with ~1105 and 935 mAh g^{-1} at 1 C and 2 C respectively, and maintained a long-term cyclability with a low capacity decay of 0.06% per cycle within 800 cycles at 2 C. More remarkably, favorable cyclic stability can be further attained with a high sulfur loading (13.2 mg cm^{-2}); Even at an elevated temperature (50 °C), the cathodes still delivered superior rate capacity. Our work emphasizes the importance of immobilization-diffusion-conversion of LiPSs with respect to the redox kinetics in Li–S batteries and is expected to shed fresh light upon the rational design of hetero-phase materials to dictate multi-reactions in other conversion type cathodes that is associated with charge and mass transport.

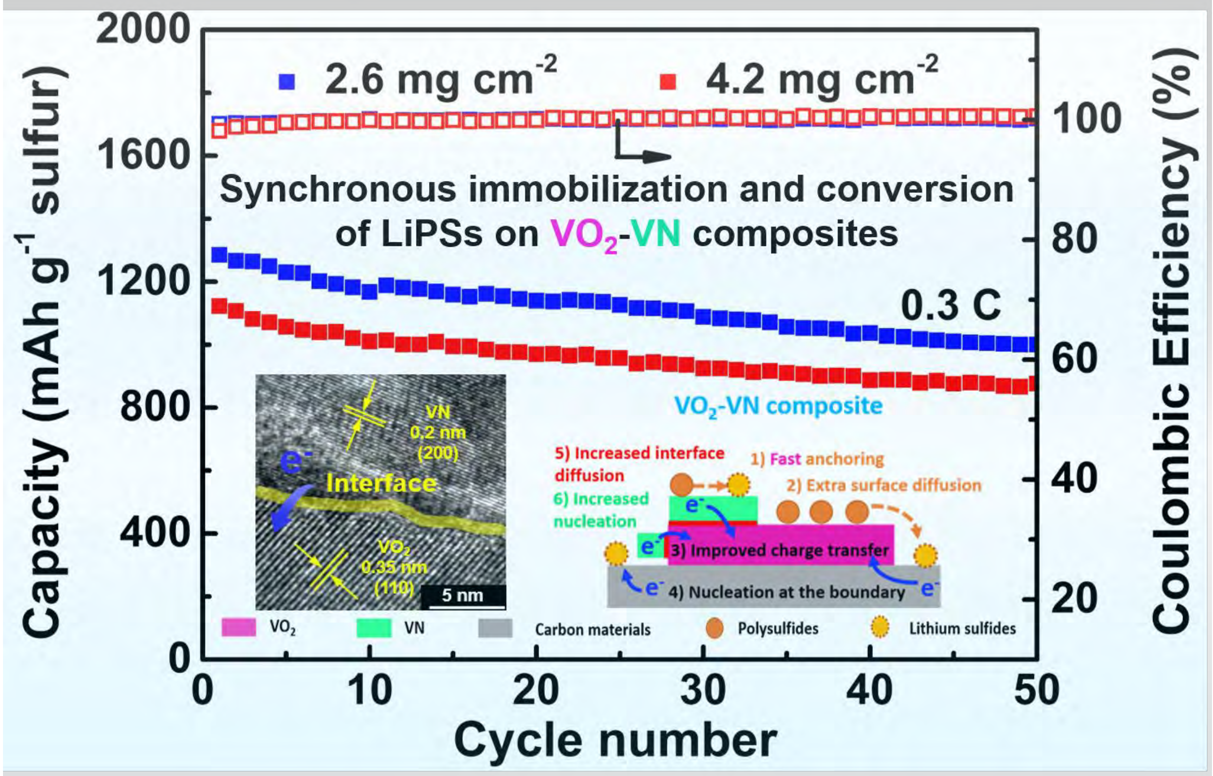

Fig.1 Synchronous immobilization and conversion of polysulfides on VO_2-VN composites targeting high-rate lithium–sulfur batteries

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Ferrofluid Filled PMMA/Graphene Microtubes and Its Application as a Magnetic Sensors

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Hollow graphene tube architectures with diameters in the range from microns to sub-millimeters have been fabricated from graphene oxide through template-assisted hydrothermal reaction[1] or coaxial two-capillary spinning strategy[2]. On the other hand, similar structures are also obtained by chemical vapor deposition (CVD) method with Cu (or Ni) wires or meshes as hard templates[3]. Notably, the latter strategy possesses merits of high quality and control of layer number of graphene "wall" of the tubes. Such CVD graphene microtubes, which could be as thin as only one atomic layer, not only could act as functional tubes/channels for microfluidic and lab-on-chip researches, like those tubes from graphene oxide, but also has the potential to be platforms for some fundamental investigations of interactions between intrinsic graphene and varies of fluidics/filling components in the tubes. However, most previous reports of CVD graphene microtube architectures finally utilized collapsed morphology of the microtubes (like graphene ribbons), which lose the specialty of such architectures.

Herein, with the modified tube furnace and optimized conditions of atmospheric pressure CVD (APCVD), we could continuous and theoretically unlimitedly synthesize high-quality graphene with 2~3 layers on commercial copper wires. After coating of PMMA and etching in $FeCl_3$ solution, the freestanding graphene microtubes with assisted outer PMMA layer (~4 μm) are obtained, which have diameters of 200 μm. Through simple but precise connections with injection units, the microtubes are filled with commercial ferrofluids or galinstan based ferrofluids. The investigations for its responsiveness of external magnetic field demonstrate potentials for it as a multifunctional sensor and as model for further research on interactions between graphene and static/dynamic ferrofluids.

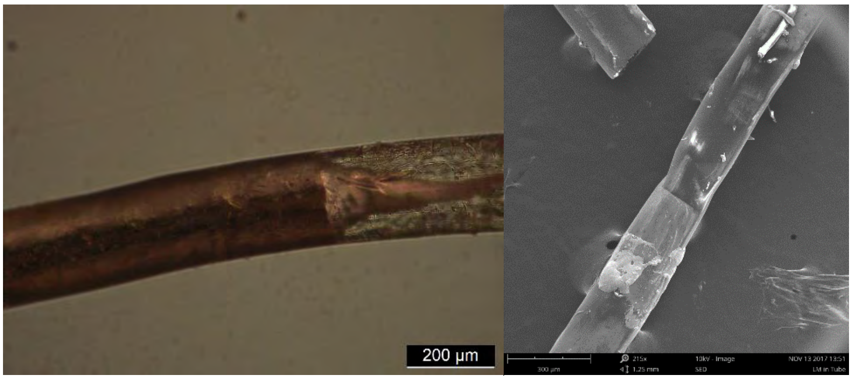

Fig.1 Photograph and SEM image of the ferrofluids filled PMMA/graphene microtubes

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From synthesis to applications of photovoltaic perovskite nanowires

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In the last few years, the organolead halide perovskite $CH_3NH_3PbI_3$ and its derivatives have been found to be very efficient light harvesters and ambipolar semiconductors revolutionizing the field of solid-state solar cells. Its low temperature fabrication process allowed designing simpler solar cell architectures (i.e. from mesoscopic to planar junctions), which yielded efficiencies exceeding 20%. The major research area in this field is photovoltaic device engineering although other applications such as solar water splitting, field-effect transistors (FETs), thermoelectric devices, light emitting diodes and lasers are also being explored.

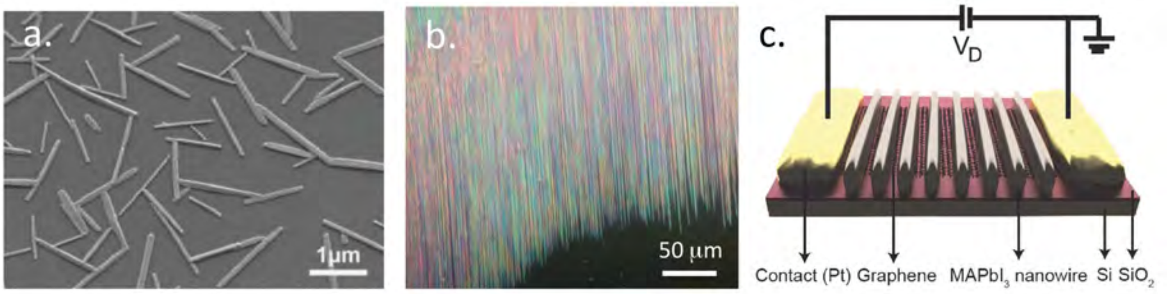

Fig1. a). SEM image of nanowires of $CH_3NH_3PbI_3$ produced by slip-casting method [1]; b) Optical microscopy image of nanowires synthesized by graphoepitaxial liquid-solid growth in open nanofluidic channels[2]; c) Sketch of a characteristic photodetector device based on $CH_3NH_3PbI_3$ nanowire/graphene structure [2].

Recently, we discovered that this photovoltaic perovskite could be synthesized in a nanowire (NW) form [1]. The NWs were produced by a relatively simple method called slip-coating[1]. In a thin layer of solution using DMF as solvent, during its evaporation, NWs of rectangular cross section were grown in the tens of microns of length (see figure 1a) and of sub-micron thickness. In the follow-up method it was shown, that with the graphoepitaxial liquid-solid growth in open nanofluidic channels, NWs of well defined sizes and densities could decorate wafer size surfaces [2].

Beyond scientific curiosity it has turned out that these crystalline structures have an excellent performence in photodetectors. Combined with graphene or carbon nanotubes, the devices [3, 4] show outstanding responsivity, as high as 10^6 A/W [2]. Moreover, at nanoscale one can achieve much better functional integration of $CH_3NH_3PbI_3$ than with granular thin films of the same material, which altogether promise a wider range of applications such as heterojunctions, tandem solar cells, LEDs and other optoelectronic devices.

In this presentation, the synthesis of NWs, their basic physical characterization and representative applications will be reported.

Acknowledgment: The work has been performed in collaboration with Endre Horváth, Márton Kollár, Alla Arakcheeva, Andrea Pisoni, Xavier Mettan, Bálint Náfrádi, Károly Holczer, László Mihály, Hugo Dil and many others. The research was partially supported by the ERC Advanced Grant (PICOPROP#670918).

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Using a Graphene Oxide Catalyst Support to Achieve High Density, Long Carbon Nanotubes Synthesized by Gas-Flow Guided Method

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Gas-flow guided growth of carbon nanotubes (CNTs) has attracted much attention due to its ability to produce extremely long (up to centimeter scale) and highly crystalline CNTs with horizontal alignment. [1,2] However, a very low density of CNTs (typically ~ 1 CNT / 100 μm) was the biggest obstacle for the above technique to realize the practical application. Researches have reported numerous approaches to overcome this problem by modifying the catalyst [3] or catalyst support. [4,5]

In this study, we achieved a high density (20 CNTs / 100 μm) of long and highly crystalline CNTs by developing a novel catalyst system using a graphene oxide support layer. Catalyst was prepared by drop-casting the mixed dispersion of iron oxide (Fe_3O_4) nanoparticles and graphene oxide flakes onto SiO_2/Si substrate. CNTs were grown by transferring the catalyst substrate directly into the pre-heated furnace at 900 °C with the reactant gases flowing (CH_4, H_2, and He). Density of the grown CNTs was found to be ~20 CNTs / 100 μm. In contrast, the density of CNTs grown from the catalyst without graphene oxide was below 2.2 CNTs / 100 μm, which highlights the significant role of the graphene oxide. Grown CNTs were measured to possess long length (5 mm) and high crystallinity (D/G ratio of Raman peaks <0.01). Typical diameter of the CNTs was 2-6 nm revealed by atomic force microscopy (AFM). Parametric study of the growth conditions further revealed that immediate feeding of the carbon feedstocks after catalyst reduction was also critical for the growth of high density CNTs.

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Directed synthesis of carbon nanotube arrays for energy storage and conversion

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Recent efforts have demonstrated that the construction of hierarchical, uniform 3D carbon nanotube (CNT)-based architecture can largely enhance the electrochemical performance of the electrodes due to their increased surface area and abundant mesopores for mass transport. However, how to achieve well-defined, highly-efficient CNTs electrodes via material design and synthesis exploration remains a big challenge. Recently, we have achieved the synthesis of a series of free-standing 3D CNT arrays via “atom economic” heating-volatilization-deposition (HVD) method by using transition metal oxides (hydroxides) nanoarray as catalysts and waste gases (*e.g.,* CO, C_2H_4, CH_4, etc) that release from solid organic precursor or liquid fuels as carbon sources. For example, we successfully fabricated free-standing 3D nitrogen-doped carbon nanotube (NCNT) arrays via HVD approach. The as-synthesized materials show a hierarchical cactus-like morphology, consisting of well-distributed NCNTs vertically grafted on both sides of LDH&Co_3O_4-derived nanoarrays. Interestingly, the 3D NCNT array electrode displays satisfactory activity and stability in both ORR and OER, even superior to the commercial Pt/C (for ORR) and IrO_2 (for OER) electrocatalysts. Besides, the as-obtained 3D NCNT arrays can also act as micro-substrate to support ultrahigh mass loading CoNi-LDH (>10 mg cm^{-2}) for high-rate supercapacitors. In addition, we also synthesized well-defined oxygen-rich CNT (O-CNT) array via a facile and scalable ultrafast “barbecue” approach. Remarkablely, the as-obtained 3D O-CNT array electrode can serves as a promising Li-metal host with a low Li deposition overpotential and a flat voltage profile at various current densities, as well as long-term durability.

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Material Patterning via manipulating the Marangoni Flow

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In the solution-based techniques, the formation of a thin liquid film is essential and substrate heating is often used to accelerate the evaporation. Therefore, Marangoni flow forms spontaneously due to the surface tension variation caused by the temperature gradient, ineluctably affecting the transfer and distribution of the materials. By using a top-heating-bottom-cooling (THBC) setup, a steady Marangoni flow with a single vortex was created in the thin liquid film which benefits the material patterning. We then succeeded in preparing ordered structures of functional materials ranging from inorganic, organic, hybrid, to biological categories under THBC conditions. Harnessing the Marangoni flow to manipulate the mass transfer by engineering the temperature gradient shows to be a general strategy with great feasibility to pattern functional materials toward practical applications.

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Self-Divided Droplets on Liquid Surface

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We studied the behavior of a free triple-phase (liquid-liquid-air) system with tunable phase contact lines. A spontaneous self-division process was observed, in which the floating volatile organic droplets automatically split and divide into small droplets with temperature-dependent tunable feature sizes which range from several microns to submicron scales. C_{60} was used as a probe material to track this process since C_{60} minimally affects the surface property of the solvent. The spherical and dumbbell-shaped aggregates were observed. This observation also indicates that the spontaneously formed droplets may be further used as micro-sized vessels to facilitate the synthesis and assembly of materials.

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Van der Waals Epitaxial Growth of 2D Metallic Vanadium Diselenide Single Crystals and their Extra-High Electrical Conductivity

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Peking University

Two-dimensional (2D) metallic transition metal dichalcogenides (MTMDs) have recently emerged as a new class of materials for the engineering of novel electronic phases, 2D superconductors, magnets, as well as novel electronic applications. Herein, we report the van der Waals epitaxial growth of monocrystalline, 1T-phase, few-layer metallic VSe_2 nanosheets on an atomically flat mica substrate *via* a "one-step" chemical vapor deposition (CVD) method. The thickness of the VSe_2 nanosheets is precisely tuned from several nanometers to several tenths nanometers. More significantly, the 2D VSe_2 single crystals are found to present excellent metallic feature, as evidenced by an extra-high electrical conductivity of up to 10^6 S m^{-1}, 1-4 orders of magnitude higher than that of various conductive 2D materials. The thickness-dependent CDW phase transitions are also examined through low-temperature transport measurements. The present results open a new path for the synthesis and property investigations of nanoscale-thickness 2D MTMDs crystals.

Growth of Carbon Nanotubes Using Cobalt Silicide as Catalyst

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Abstract: Tungsten-cobalt intermetallic catalysts have been developed to synthesize single-walled carbon nanotubes (SWNTs) with specified chiralities due to the unique structure[1-3]. Here we choose a different kind of intermetallic compounds--cobalt silicide as catalyst to grow carbon nanotubes. We found that the diameter distribution of SWNTs was narrow using ethane as carbon source. From Raman spectra, 70% of RBM peaks distributed from 140cm^{-1} to 150cm^{-1}(excited by three different lasers), and 20% of RBM peaks concentrated at ~193cm^{-1}(excited by 785nm laser). However, when we used ethanol as carbon source, the selectivity disappeared while its density highly increased. We supposed that the oxygen atom in ethanol would change the structure of catalysts during the reaction.

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Controlled Growth of SWNTs Using $CoWO_4$ Nanoparticles as Catalyst Precursor

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Single-walled carbon nanotubes (SWNTs) with special structure and excellent performance are regarded as one of the most promising candidates as building blocks in the next generation electronics. The Controlled synthesis of the structure and properties enriched SWNT samples for large-scale integrated carbon nanotube devices is a great challenge. We have developed a novel tungsten-based intermetallic compound catalyst by using heteropolyacid containing W and Co as a precursor. The catalyst has a high melting point and a lower crystal structure symmetry, acting as a structural template for the growth of carbon nanotubes with specific chirality [1-4]. However, the complex preparation process and the pH sensitivity of the specific composition of tungsten heteropolyacid is not conducive to large-scale production in the future. Therefore, it is important to find a catalyst precursor with simple preparation procedure and good stability.

Recently, we have tried to use uniform $CoWO_4$ nanoparticles, which were prepared in water-in-oil microemulsions, as catalyst precursor. By adjusting the conditions of chemical vapor deposition, we achieved the diameter, conductivity and chirality controlled growth of SWNTs on Si / SiO_2 substrates.

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Synergetic Role of Co_3C in Co-Catalyzed Growth of Carbon Nanotubes Revealed by Environmental TEM

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The metal catalysts play important roles in the growth of carbon nanotubes (CNTs) [1]. It was reported that solubility of carbon in transitional metal nanoparticles such as Fe, Co, and Ni are believed to associate with the CNT growth [2-5]. The provision of direct experimental evidence for the active catalysts with atomic resolution under high temperature environment is, however, very challenging.

Here, we elucidated the synergetic role played by Co_3C in Co-catalyzed chemical vapor deposition growth of CNTs by an aberration-corrected environmental TEM. By revealing the formation of Co_3C in Co at the atomic scale, we found that the formation of Co_3C was depended on the carbon feeding conditions and only partially carbonized Co nanoparticles are effective for the nucleation of CNTs. These findings are crucial for the rational design of catalysts for controlled growth of CNTs.

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Layer-by-Layer Assembly of Catalyst Precursor to Grow Horizontally Aligned Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) are promising materials in various applications. In many applications, e.g. electronics, well-aligned SWNTs with specified chirality are preferred [1]. We developed a new family of catalysts, i.e. tungsten-based intermetallic compounds, which have very high melting point and maintain their specific crystal structure during the chemical vapor deposition (CVD) process, to epitaxially grow chirality-specific SWNTs [2-5]. Here we report a layer-by-layer (LbL) method to prepare the tungsten-based bimetallic catalyst precursor on quartz substrates to obtain horizontally aligned SWNTs. This method allows more precise control over catalyst composition and particle size and catalyst patterning on pre-identified locations.

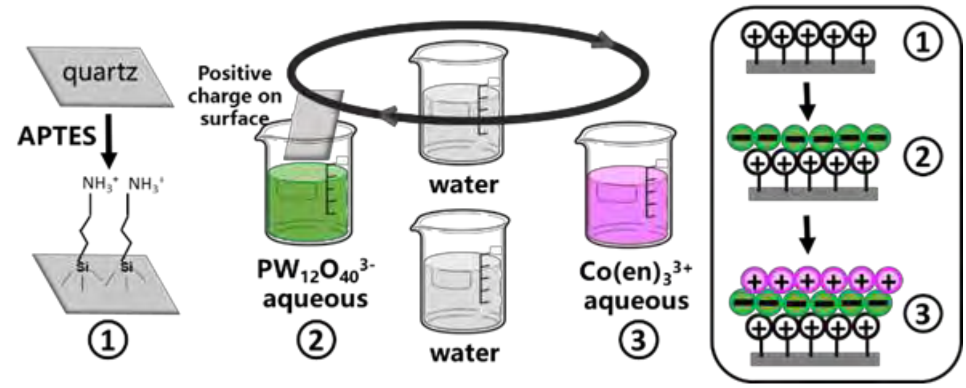

Figure. Schematic diagram of the layer-by-layer assembling of the catalyst precursor on quartz substrate obtained by repeated immersion cycles in solutions of $Na_3PW_{12}O_{40}$ and then $Co(en)_3Cl_3$.

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Methanol Enhanced Chemical Vapor Deposition of Vertically Aligned Carbon Nanotube Forests

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Vertically aligned carbon nanotube (VACNT) forests with unique structural properties (e.g. long, aligned, high specific surface area) has opened up many important applications such as touch panels, flexible charge collectors, supercapacitors, gecko-foot-mimetic dry adhesive, water purification and desalination devices and so on.

However, efficient and facile method to grow ultralong VACNT forests still needs further development. Here we add methanol to suppress the formation of amorphous carbon and maintain the activity of catalysts. With the addition of methanol, the ultrathin iron film catalyst forms large-scale, millimeter-long, high-density, uniform VACNT forests, which may have great potential in various applications.

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Rapid Response and High Temperature Carbon Nanotube Film Heaters Targeting Synthesis of Various Nanomaterials

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Heaters are widely used in materials synthesis and processing such as high-temperature chemical reactions and localized high temperature processing.[1] Conventional heating solutions are limited by factors such as low maximum heating temperatures and slow ramp rates. These limitations will hinder many processes that are desirable for materials synthesis and processing. The carbon nanotube (CNT) film with the ultrasmall heat capacity per unit area, is suitable for building special heaters.[2] Herein, we developed CNTs based heaters to function as high-performance thermal supply with high temperature (2500 k) and ultrafast heating rate (2000 K/s). The CNT film heaters can be applied to a wide range of materials synthesis, such as fast growth of graphene on insulating substrates, pulsed growth of ultra-high-density CNT arrays and a library of atomically-thin metal chalcogenides. More applications can be further developed based on the CNT film heaters.

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Ultratransparent and Stretchable Graphene Electrodes

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Graphene, together with other two-dimensional (2D) materials, are promising building blocks for both conventional semiconductor technologies and the nascent flexible nanotechnology. However, due to its intrinsic stiffness and strength, it is challenging to utilize them in stretchable electronics. For example, CVD graphene transferred onto a polydimethylsiloxane (PDMS) elastic substrate can only maintain its conductivity up to 6% strain[1] and transistor can maintain electrical functional at stretching up to 5%[2]. The above stretchability is far less than the minimum required value (~ 50%) for wearable health monitoring sensors and electronic skin. To address this challenge, graphene kirigami-approach has recently been explored[3]. However, this method requires suspended graphene and is extremely complicated in fabrication and operation.

Here, to achieve highly stretchable large-area graphene devices, we developed an all graphene nanostructure that confines graphene scrolls in between stacked graphene layers, namely multi-layer G/G scrolls (MGG). MGG consists of three-dimensional conductive paths, which bridge the fragmented domains to maintain conductivity of the resulting transparent graphene film. Bi- and tri-layer MGG supported on an elastomer exhibited significantly less reduction in conductivity even at the strain up to 100%. An all-carbon transistor fabricated using MGG as electrodes retained 60% of its original performance at 120% strain. This is the first demonstration of highly stretchable and ultra-transparent graphene-based transistors. The concept reported here should be applicable to other 2D materials and thus opens up a new route toward stretchable 2D electronics[4].

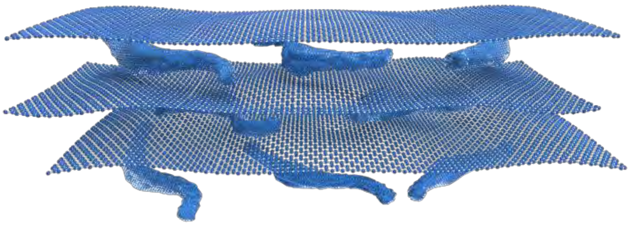

Fig. 1. Structure of multilayer graphene/graphene scrolls (MGG)

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Smart Carbon Nanotube Composite Fibers

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Wearable smart textiles that have functionalities like sensor, actuator, and electromagnetic shielding are becoming increasing interesting research field due to the proliferation of modern society's demand for wearable electronics and protection of environmental electromagnetic pollution. The development of nanotechnology makes these smart textile composites available recently. Here, we report several types of smart nano-composite fiber which can be used as textile humidity sensor, strain sensor and electromagnetic interference (EMI) shielding performance.

Textile-based humidity sensors can be an important component of smart wearable electronic-textiles and have potential applications in the management of wounds, bed-wetting, and skin pathologies or for microclimate control in clothing. Several approaches have been previously conducted to transfer conventional capacitive and resistive humidity sensors onto textiles. However, major challenges remain to be overcome. For example, the durability of electrodes prepared by printing and deposition remains an important issue to be addressed. In addition, the sensitivity of sensors made of conductive yarn electrodes depends strongly on the wettability of the textile substrate into which the electrodes are woven, which may limit these sensors' applications. To solve these challenges, we fabricate a wearable textile-based humidity sensors using high strength (~750 MPa) and ultra-tough (energy-to-break, 4300 J g-1) single-walled carbon nanotube (SWNT)/poly(vinyl alcohol) (PVA) filaments using a wet-spinning process. The conductive SWCNT networks in the filaments can be modulated by adjusting the intertube distance by swelling the PVA molecular chains via the absorption of water molecules. Textile-based humidity sensors using a 1:5 weight ratio of SWCNT/PVA filaments showed high sensitivity and excellent reversibility under different relative humidity conditions. We also demonstrated that our sensor can be used to monitor human sweating.

Magnetic nano-composite fibers are the topic of intense research due to their potential breakthrough applications such as smart magnetic field response devices and electromagnetic interference (EMI) shielding. However, clustering of nanoparticles in polymer matrix is a recognized challenge for obtaining a property-controllable nano-composite fiber. Another challenge is that the strength and ductility of the nano-composite fiber decrease significantly with the increasing weight loading of magnetic nanoparticles in the fiber. Here, we report high-strength SWNT/permalloy nano-particle (PNP)/PVA multi-functional nano-composite fibers fabricated by wet spinning. The weight loading of SWNT and PNP in the fiber were as high as 12.0% and 38.0%, respectively. The tensile strength of the fiber was up to 700 MPa. The electrical conductivity reached 96.7 S/m. The saturation magnetization (Ms) was as high as 24.8 emu/g. The EMI attenuation of a fabric woven from the prepared fiber approached to 100%, when tested by electromagnetic wave with a frequency higher than 6 GHz. Our study demonstrates that a magnetic field response device can be designed by using the fabricated multi-functional nano-composite fiber. Textile strain sensor will also be discussed in this talk. These smart textiles pave a new way for the design of novel wearable smart textiles.

Assembly of Aligned Semiconducting SWCNTs via Introducing Inter-Tube Electrostatic Repulsion

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Abstract:

Semiconducting single-walled carbon nanotubes (sc-SWCNTs) have exceptional electronic properties and have been proposed as a replacement for silicon in high-performance logic devices. [1] One key challenge of realizing these devices is to produce aligned array film of high purity sc-SWCNTs with uniform inter-tube pitch. Recent approaches in the alignment of sc-SWCNTs are mainly based on the direct growth of aligned arrays via chemical vapor deposition (CVD) and deposition from solution. [2-4] However, achieving the large-area sc-SWCNTs aligned film with uniform inter-tube pitch remains to be a challenge.

Here, we use a double-liquid-layer dip-coating method for assembling aligned sc-SWCNTs from organic solvents. By liquid sealing for organic solvent, a certain thickness of water-layer can be used to adjust the self-assembly time of sc-SWCNTs, which can be fully rearranged to achieve alignment. In general, SWCNT are easy to form bundles during assembly process due to inter-tube Van der Waals force. Via a non-covalent modification of sc-SWCNTs in organic solution, the sc-SWCNT bundles can be effectively suppressed by introducing the electrostatic repulsion between the sc-SWCNTs. Large-area aligned sc-SWCNT thin films with uniform inter-tube pitch can be prepared through this fast and scalable method.

Key words: sc-SWCNTs, aligned, self-assembly, electrostatic repulsion, dip-coating

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Bifunctional Catalytic Electrodes Derived from Zeolitic Imidazolate Framework and Carbon Nanotube for Flexible Zn-Air Batteries

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To accommodate with the growing demand of a safe and stable energy supply for flexible electronics devices, rechargeable flexible zinc-air batteries have gradually attracted many researchers attention and can be a promising new generation energy storage devices for its many excellent properties. Herein, we reported a freestanding bifunctional film air electrode via simple approaches for flexible Zn-air batteries[1]. Firstly, ZIF-67 was in-situ synthesized in the polyvinyl pyrrolidone dispersed CNTs solution, then the ZIF-67@PVP-CNT film was obtained after vacuum filtering. Finally, the network structure of N-doped carbon nanotube wrapped cobalt-N/porous carbon particles (Co-N/C@NCNT) was fabricated by the treatment of pyrolysis and acid-pickling[2].In this flexible Zn-air batteries, Carbon nanotube offered conductive and crosslinked networks for Co-N/C particles. Moreover, the existence of abundant Co-N and N-C active sites endow the free-standing flexible film with high bifunctional oxygen electrocatalytic activity for both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER). The propertity tests show that Co-N/C@NCNT film exhibits a low overpotential (270mV at 10 mA/cm^2) for OER and a positive half-wave potential(0.836V, vs. RHE) for ORR, which are comparable with commercial 20 wt% Pt/C catalyst. the flexible Zn-air batteries we prepared are hopeful to provide a flexible and safe energy supply for modern energy storage and conversion apparatus[3].

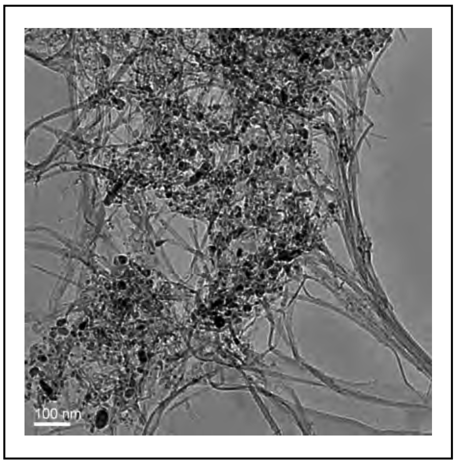

Fig.1 TEM image of Co-N/C@NCNT

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Mechanism of SiO_x particles formation during CVD graphene growth on Cu substrates

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For graphene grown on Cu substrate via chemical vapor deposition (CVD), numerous nanometer particles are distributed along the graphene grain boundaries or evenly on the circumjacent substrate surface. Despite their relatively small size, the particles form new nucleation centers of graphene or destroy the graphene membrane during growth. For clarifying the origin of particles, the formation process was studied by etching graphene at high temperature with different atmospheric pressures. Thus, we demonstrated that the formation of the particles is closely related to the competition of hydrogen and oxygen during growth; we also confirmed that SiO_x was the composition of particles through energy dispersive spectrometry (EDS) measurement in transmission electron microscopy (TEM). Finally, based on the formation mechanism, we proposed efficient approaches to reduce SiO_x particles that improve the quality of graphene during actual preparation via CVD.

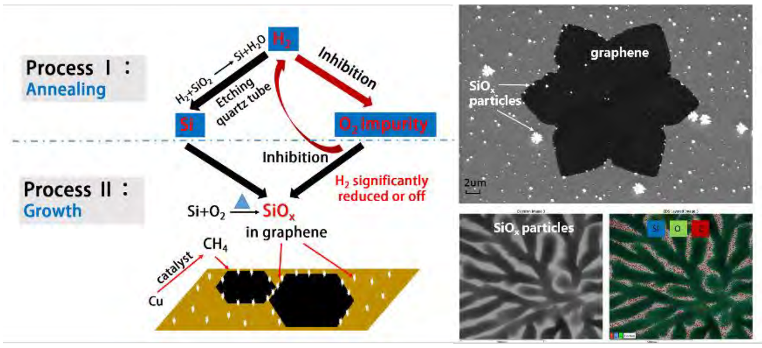

Fig.1 Mechanism of SiOx particles formation during CVD graphene growth on Cu substrates.

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Ultralight graphene-based elastomers

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Graphene possesses a combination of exceptional mechanical and electrical properties. These extraordinary properties make graphene an excellent building block for assembling macroscopic materials for widespread applications. This talk will first introduce the synthesis of extremely low density graphene-based elastomers by design and engineering of their hierarchical cellular structure. This talk will then focus on discussing their dynamic mechanical and electromechanical properties. This new class of elastomer reveals a combination of extremely low density, superelasticity and good electrical conductivity, which shows great potential for making next generation flexible electronics.

Keywords：graphene；elastomer；aerogel；flexible electronics；ultralight

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Free-standing single-walled carbon nanotube/polyaniline films for solid flexible supercapacitor

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Carbon nanotubes (CNTs) have been intensively investigated as fillers for polymeric composites thanks to one-dimensional nanostructure, narrow distribution size, excellent electronic properties, highly accessible surface area and high stability.[1, 2] Composites of conducting polymers and carbon nanotubes (CNTs) have exhibited great promise as supercapacitor electrodes by combining their individual advantages.[3, 4]

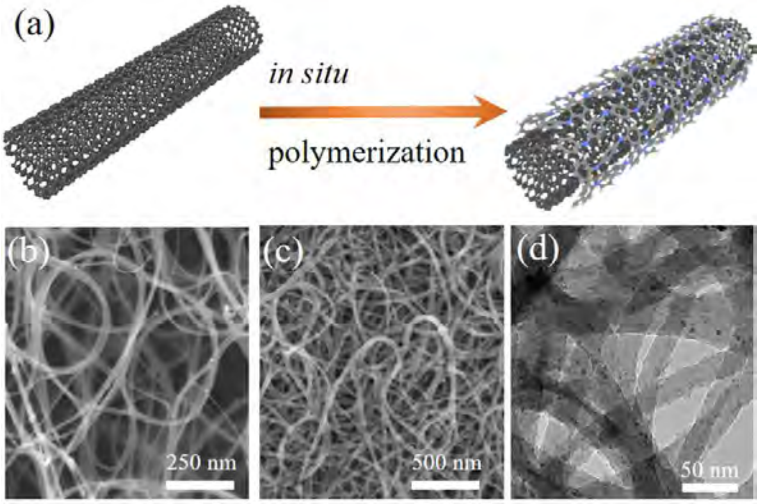

Fig 1. (a) Schematic illustration for preparation process of PANI/SWCNTs film. (b) SEM of SWCNTs film. (c) SEM and (d) TEM of ANI/SWCNTs film.

Herein, a "skeleton/skin" method was employed to prepare free-standing hybrid films via *in situ* polymerization of aniline monomer in acid media, where single-walled carbon nanotubes (SWCNTs) films with minimized defects served as templates. The strong interaction in such conjugated systems greatly improves the charge-transfer reaction between PANI and SWCNTs. The as-prepared SWCNTs/PANI hybrid films were used for fabricating solid flexible supercapacitors without metallic current collectors or any addictive, demonstrating the great potential as thin film electrode for application in flexible supercapacitors.

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Towards carbon nanotube networks of highly-defined structure and properties

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Despite being made just of carbon, carbon nanotubes (CNTs) show a great deal of structural complexity in terms of the particular arrangement of carbon atoms in a tube [1]. The order, denoted by so-called chiral index, often has got a predominant effect on the electrical, optical, thermal and other properties. Unfortunately, despite many efforts, we still have not got a universal strategy to produce CNT networks of a selected chirality at the macroscopic level.

In this contribution, I will demonstrate how we have attempted to solve the problem of sorting of the material [2,3] for the manufacture of CNT films of highly-defined structure [4,5]. Both small- and large-diameter CNTs were differentiated according to diameter, electronic character (metallic/semiconducting) and chirality. A selection of these materials was then made into macroscopic ensembles to characterize their properties. The obtained materials were found very promising for a wide range of optical and electrical applications.

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Less-Defective Dispersion of Individual SWCNTs using Repetitive Sonication–Ultracentrifugation Process

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Single-wall carbon nanotubes (SWCNTs) are promising for building block of future electronic devices due to their high carrier mobility. Well known problem of this material is that the as-synthesized SWCNT is always a mixture of metallic (M-) and semiconducting (S-) ones and post-purification is necessary. Within this decade anionic surfactant based M/S separation techniques have been highly improved and are very useful as post-purification of SWCNTs. For the M/S separation, however, bundled SWCNTs need to be dispersed into individual forms using ultrasonic dispersion. It is also well known that this process unavoidably generates structural defects on the SWCNTs that degrade device performance. To minimize the defect introduction keeping high dispersion yield, the sonication process has to be optimized. Shirae et al. [1] reported that a repetitive sonication–centrifugation process can produce less-defective and longer SWCNT dispersion suitable for conductive film. For the M/S separation, however, we need individually dispersed SWCNTs, which require stronger sonication and ultracentrifugation process. In this study, therefore, we aimed to obtain highly-dispersed and less-defective SWCNTs using repetitive sonication-ultracentrifugation process.

Pristine SWCNTs were sonicated in sodium cholate (SC) aqueous solution for relatively short time and then ultracentrifuged. Supernatant was collected as individually dispersed SWCNT solution. A sediment was dissolved in SC solution again and was used for the second cycle of the sonication and ultracentrifugation. The repetitive sonication–ultracentrifugation process was repeated until the total sonication time reaches 150 min. Fig. 1 shows G/D Raman intensity ratio of each supernatant and the sum of the collected SWCNT as supernatant for 20 and 30 min sonication case. Result for 150 min one-time sonication is also indicated. Clearly, 20 min sample shows higher G/D and higher yield than for 30 min and 150 min ones for any intermediate sonication time. This result strongly suggests that shorter sonication time is better for getting better quality SWCNTs with higher yield. Only one but serious problem is time and effort. We have to further optimize a cost-effective process towards high-performance device applications. Detailed discussion will be given in the presentation.

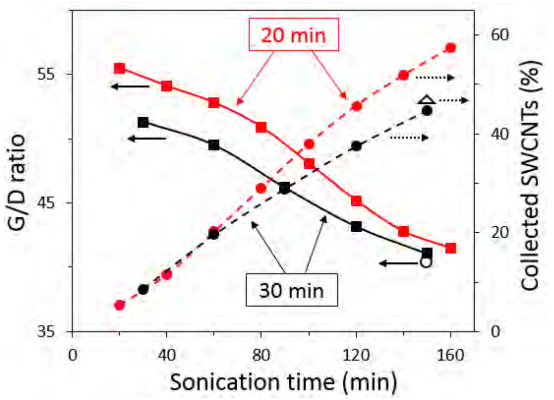

Fig. 1. The G/D ratio of dispersed SWCNTs as a function of sonication time. And, the amount of collected SWCNTs with the increasing of sonication time. The open cycle and triangle indicate the G/D ratio and the amount of SWCNTs dispersed by one cycle of sonication for 150 min, respectively.

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Development of Functional Materials and their Integration for Application of Printable Electronics

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The National Research Council (NRC) is the premier research organization of the Canadian Government. The Printable Electronics (PE) program in NRC develops key technologies for printed electronic devices including – materials, inks, printing, and additive manufacturing – in order to enable a competitive and sustainable PE sector in Canada. Progress has been made over the last 15 years, yet many challenges remain at the materials, fabrication and integration level, limiting performance and commercialization. This presentation covers our semiconducting single-walled carbon nanotube (sc-SWCNT) enrichment and conductive molecular ink development for transistor fabrication and gas sensors via solution based processes [1-9]. I will highlight our recent progress in understanding sc-SWCNT enrichment using conjugated polymers, with special consideration given to the effects of solvent parameters and doping on yield and purity of the final product [3-5]. Developments in conductive molecular inks will also be described [6,7]. Challenges and advances associated with using polymer-based dielectrics will be discussed [8]. Such transistor packages have enabled the realization of fully inkjet-printed transistors as a result of the excellent electronic and mechanical properties of sc-SWCNTs[3]. A demonstration of a fully additive printing process to make TFT backplanes via R2R printing will also be highlighted [9]. We believe that the development of such new functional materials and their successful integration in printing technology will enable additive manufacturing of electronic devices with new capabilities.

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Selective dispersion of metallic single-walled carbon nanotubes with imidazolium-based ionic liquids

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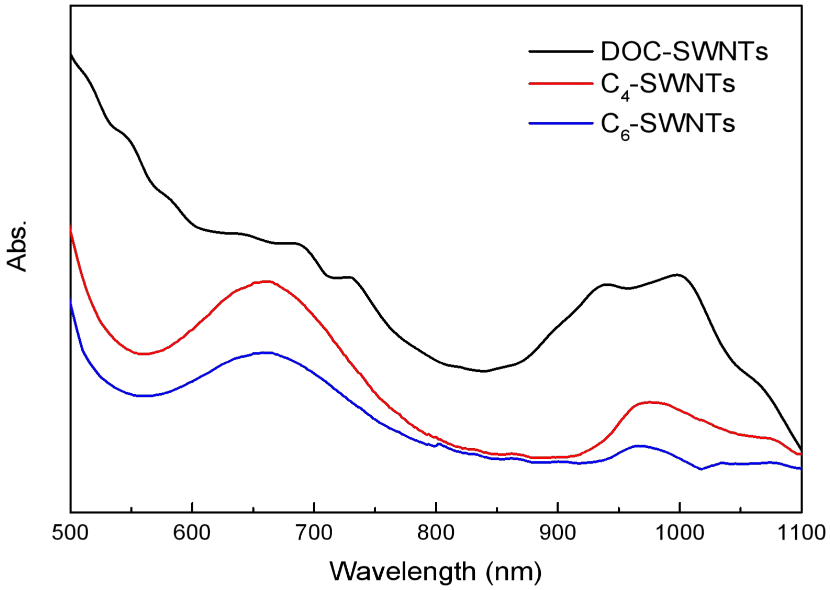
It was reported that single-walled carbon nanotubes (SWNTs) can be dispersed in the chemically modified imidazolium-based ionic liquid (IL)[1,2]. In this context, imidazolium-based ILs modified by C2, C4, C6 and C8 n-alkyl chains were synthesized and applied to the dispersion of arc-discharged SWNTs. Fourier transform infrared spectroscopy (FTIR) confirmed that the n-alkyl chains were successfully attached to the imidazole ring. According to the results of UV-vis-NIR spectroscopy, the above imidazolium-based ILs showed varying selective dispersing ability towards metallic SWNTs in aqueous solution, among which 1-butyl-3-methylimidazole fluoroborate was the most effective one for the dispersion and enrichment of metallic SWNTs. The complexes of ILs and SWNTs were treated with concentrated sodium hydroxide solution for the destruction of imidazolium-based ILs, and the SWNTs dissociated were deposited on a 0.22 μm filter membrane for Raman spectrum characterization. In line with the results of resonant Raman scattering, metallic arc-discharged SWNTs were selectively extracted by the aqueous solution of imidazolium-based ILs, especially those metallic ones with chirality index of (20,8), (12,8), (27,0) and (7,7).



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Mass Enrichment of High-purity Metallic and Semiconducting Single-walled Carbon Nanotubes

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As-grown single-walled carbon nanotubes (SWCNTs) are typically the mixtures of metallic (M-SWCNTs) and semiconducting (S-SWCNTs) components, thus hindering their widespread applications, such as nano-electronic devices. Nowadays, it still remains a challenge to produce SWCNTs with unique electrical conductivity in large quantity. In our studies, high-purity M-SWCNTs and S-SWCNTs were respectively obtained in milligram quantity by the simple and low-cost approaches, which can easily scale up. Firstly, we developed an simple method for directly enriching M-SWCNTs using NO_2 as oxidant to selectively remove the S-SWCNTs at a low temperature (220 ℃). The enriched M-SWCNTs have more than 90% purity. Secondly, we also developed an efficient approach to enrich s-SWCNTs through electrochemical etching and short-time heating in air. In a produce period of only several minutes, milligrams of S-SWCNTs with high purity of 95 wt% can be obtained. Our work paves the new way for low-cost and scalable enrichment of M-SWCNTs and S-SWCNTs, which are promising materials for nano-electronic devices.

Scalable process to reduce catalyst content below 0.01% in HiPCO Single walled carbon nanotubes

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HiPCO is a well-known process for continuous production of single walled carbon nanotubes (SWCNT). As produced material using Rice HiPCO has ~30wt% catalyst content. This has been reduced to around 10% by the NoPo HiPCO process. Applications in biology, electronics, composites etc. require at least 3 orders of magnitude lesser catalyst. A 0.2wt% iron in SWCNT is highly toxic for biological applications [1]. Mechanical strength of the nanotube composites shows degradation at catalyst junction [2]. Hence removal of catalyst to very low levels is critical to realize more practical applications. The existing techniques are either not capable of removing 99.99% catalyst or the yield is very low or high destroying rate [3].

Here we report an efficient, economic and scalable method for reducing iron catalyst content to below 0.01%. The 3-step process is carried out with acid treatment followed by low temperature oxidation and another round of acid treatment. The process exploited here is oxidation of the carbon impurities to gaseous phase as CO_2 and removal of oxidized catalyst debris using acid treatment as reported earlier. Stability of SWCNT at these temperatures does not allow any damage to the nanotubes.

The purified material was characterized using TGA (Final mass 0.01%), Raman (GD ratio 20), SEM and TEM as shown in Figure below. This process was designed to be scalable. The gas phase oxidation can be done in a belt heater followed by repeated acid wash.

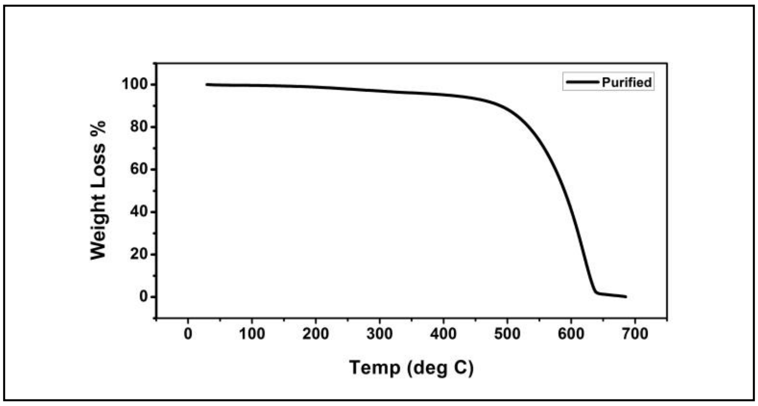

Fig.1 . TGA graph of purified SWCNT

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High quality s-SWCNT inks for highly reproducible Field Effect Transistors

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High-quality semiconducting single-walled carbon nanotube (s-SWCNT) inks in toluene obtained by conjugated polymer wrapping have been used in the last years for the fabrication of highly performing field effect transistors displaying mobility up to 50 cm^2/Vs and on/off ratio above 10^8 [1–3]. However, performances of device fabricated from inks that are only few weeks old show a marked decrease in performance, indicating the limited shelf lifetime of the toluene-based inks. In this work, we report the use of o-xylene as applicator solvent to obtain high quality and very stable s-SWCNT inks. Charge carrier mobilities of the field effect transistors obtained by the new ink at parity of concentration, show an increase up to five-fold in magnitude compared with the devices prepared from toluene solution. More importantly, the device-to-device performance showed an increase in reproducibility. Atomic force microscopy micrographs showed that this is due to the fact that the s-SWCNT network in devices fabricated using o-xylene is more homogeneous than for devices fabricated from toluene based inks. Finally, the o-xylene inks maintain their initial properties for longer than four months. This very long shelf lifetime opens possibilities for the industrial use of these inks.

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Selective etching of single-walled carbon nanotubes produced by arc discharge

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Abstract: Semiconducting single-walled carbon nanotubes(s-SWNTs) are promising materials for electronic devices. Since metallic single-walled carbon nanotubes (m-SWNTs) are more active compared to semiconducting ones, oxidative etchants such as H_2O and NO_2, have been used to inhibit the formation of m-SWNTs during the chemical vapor deposition or to remove the m-SWNTs in the preformed SWNTs. Here we choose CO_2 and H_2O as mild etchants to selectively remove m-SWNTs in the SWNTs produced by arc discharge method.

We found that when carbon nanotubes were etched by H_2O, the ratio between H_2O and H_2 is crucial to the selectivity. In addition, the existence of H_2 can ease the decrease of density after etching.

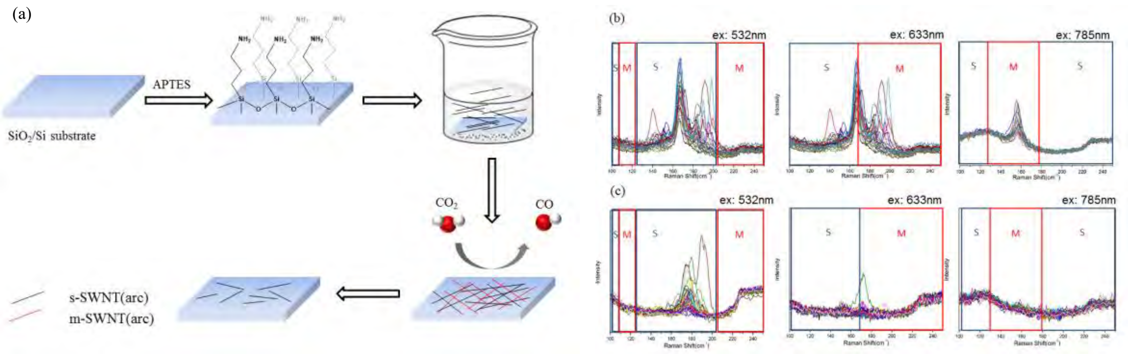

Figure 1. (a) The schematic illustration of etching process. (b,c) Raman specta of SWNTs before (b) and after (c) etching.

Polymer-Sorted Chiral Semiconducting Carbon Nanotube Networks with Improved Charge Carrier Transport

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Semiconducting single-walled carbon nanotubes (s-SWNTs) are considered to be an ideal material to replace silicon for the next generation nano-electronics. While carbon nanotubes with specific chirality are desirable for their high uniformity in construction and energy band. However, it is difficult to acquire chiral single-walled carbon nanotubes thin film with high quality until now.

Herein, we provide a reliable and simple method that sorts chiral SWNTs utilizing conformation and energy level matching between conjugated polymer and SWCNTs. The polymer with fluorene and pyridine moiety was used to extracted large-diameter single-chirality species (10,8) from raw HiPCO SWNTs, with diameter about 1.24nm and chiral angle α=26.33 degree. With precisely control the dip-coating procedure, we successfully fabricated high density chiral SWNTs thin-film. The corresponding thin-film transistor (TFT) devices show mobility as high as $57.9\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ and on-off ratio about 10^6. The performance of these chiral SWNT devices is almost five times higher than the devices using semiconducting HiPco SWNTs. And the good performance of the device should attribute to the reduced tube-tube junction barrier. Our results demonstrate that highly selected, chiral s-SWNTs lead to excellent device characteristics. In the following work, we will scaling-down the channel length further in order to reduce the number of junctions within the SWNT network.

Keywords: chiral, single-walled carbon nanotube, random network, transistor

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Separation of left- and right-handed semiconducting single-walled carbon nanotube enantiomers using achiral amino acid surfactant

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KEYWORDS: chirality and enantiomer separation, amide acid surfactant, density gradient ultrscentrifugation

ABSTRACT: Synthesized single-walled carbon nanotubes (SWNTs) are racemic mixtures of various (n, m) species with different electronic types, which greatly impeded their practical applications and fundamental research. In this paper, achiral amino acid surfactant sodium N-cocoyl sarcosinate not only displayed selectivity toward s-SWNTs, but also could further separate the sorted s-SWNTs by the chirality indices (n, m) and left- and right-handedness with the aid of density gradient ultracentrifugation (DGU). However, only different (n, m) species of SWNTs were

separated after DGC treatment when surfactant in density gradient medium changed from N-CS to SDS (sodium dodecyl sulfate), which gave us a hint that the exerted external forces on the dispersant/SWNTs complexes might affect the separation results. In addition, the pH-response of amide acid surfactant enables isolation of dispersant-free SWNTs.

Doping of holey graphene by nitrogen

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The inclusion of heteroatoms in graphene lattice leads to changes in the structure, reactivity, and electronic properties of the material. The heteroatoms can be incorporated into the lattice during synthesis or by post-treatment. The last way is more easily realized when graphene layers contain defects, which can form chemical bonds with dopants. In this work, a starting material for nitrogen doping was holey graphite with atomic vacancies "holes" in basal planes formed during a treatment of graphite oxide (GO) with concentrated hot sulfuric acid [1,2]. Atomic size of nitrogen is close to that of carbon, which allows replacing up to 20% of carbon atoms without a strong distortion of graphene planes. Nitrogen can be incorporated into graphene lattice in various forms like graphitic, pyridinic, or pyrrolic nitrogen, -NH_2 and NO_x species. N-doped graphene materials are interesting for the use as an anode material in lithium-ion batteries as well a catalyst support, wherein the nitrogen atoms will be the binding centers for catalytically active species [3]. Holey graphite (HG) was prepared by a heating of GO in H_2SO_4 at 200 and 280°C. For nitrogen doping, the obtained HG200 and HG280 samples were treated in concentrated ammonia solution at 80°C for 15 hours. To remove water and oxygen-containing groups, the products were annealed under argon at 400 °C and 800ºC for one hour. Transmission electron spectroscopy found the holes of ~2 nm in graphene layers. The measurements detected about 4–5 at% of nitrogen in the products. Analysis of the XPS N 1s lines revealed that nitrogen predominantly binds along the graphene edges by replacing the neighboring carbonyl groups. In HG200 and HG2800 samples, nitrogen occurred mainly in pyrrolic, amino groups and pyridinic form, respectively.

The work was supported by the Russian Science Foundation (Grant 16-13-00016).

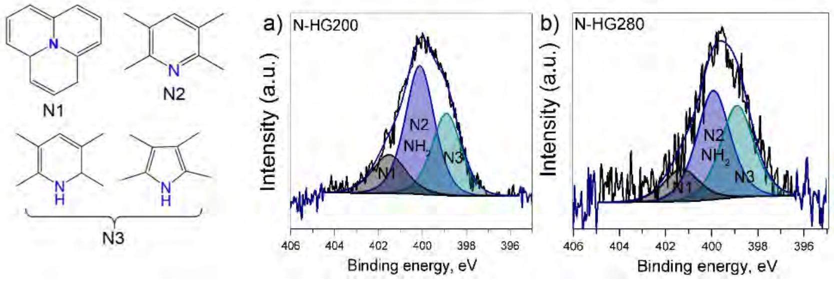

Fig.1. XPS N1s spectra of N-doped a) HG200, b) HG280 samples.

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Controlled Doping of Monolayer WS_2 with Niobium

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Keywords: Tungsten sulfide(WS_2); Niobium; Chemical vapor deposition (CVD); P-type doping; Density functional theory(DFT)

Tungsten sulfide(WS_2) has attracted a great deal of attention in photoelectric application due to its high mobility, low off-state current and high on/off ratio, which is considered as potential materials for next-generation transistor materials. Doping of the WS_2 can endow some new properties. Here, we control the doping concentration of niobium atoms in WS_2 by an one-step chemical vapor deposition (CVD), realizing p-type doping of WS_2, changing different doping concentration to control the energy band of WS_2. Density functional theory(DFT) is employed to provide the relationship between doping concentration and energy band. With increasing doping concentration, photoluminescence(PL) changes from 2.0 eV to 1.7 eV, the transfer characteristics show that WS_2 changes from n-type semiconductor to metal after Nb doping, which demonstrate that optical and electrical properties of WS_2 is changed by Nb doping. Our work provides an one-step method for p-type doping of WS_2, and reveal the effect of doping Concentration on Electrical and Optical Properties.

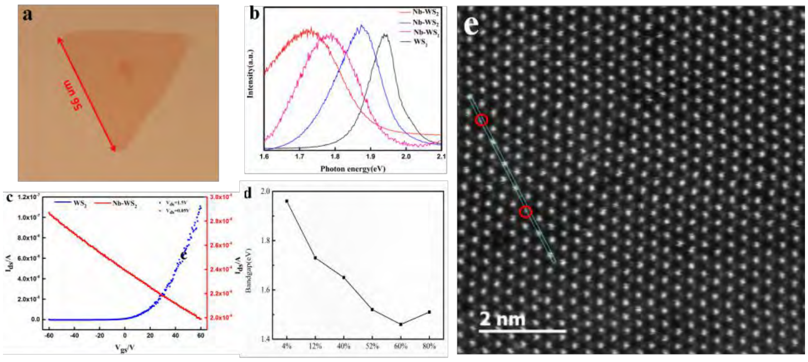

Fig.1 (a) Optical image of Nb-WS_2. (b) PL spectra of monolayer pure WS_2 and Nb-WS_2. (c) Transfer curve of pure WS_2 and Nb-WS_2. (d) Spectra of PL changes with doping concentration. (e) STEM image of Nb-WS_2.

Atomic layer deposition of iron oxide on carbon nanotubes fiber for high-power supercapacitor electrodes

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With the rapid development of wearable electronic technology, flexible energy storage device has attracted increasing attentions. Carbon nanotube (CNT) fiber assembled by individual CNTs along the macroscopic one dimensional direction have advantages to be used as flexible electrode, due to excellent electric conductivity, high strength and large specific area[1]. However, energy storage capacity relying solely on CNT fiber itself is limited. The preparation of enhanced energy storage fiber via composite or modification has been proved to be an effective strategy[2]. In this work, continuous CNT fiber has been spinning from chemical vapor reaction in a horizontal reactor[3]. Atom layer deposition process was adopted to composite iron oxide in CNT fiber for enhanced flexible super-capacitor electrode. The result of morphology characterization showed that iron oxide was well-dispersed in CNT fiber net, which resulted in obvious increase on the electrochemical properties. Electrochemical measurements revealed enhanced capacitance of up to 105 Fg^{-1} with 30 cycles iron oxide deposition, which was two times more than that of raw CNT fiber.

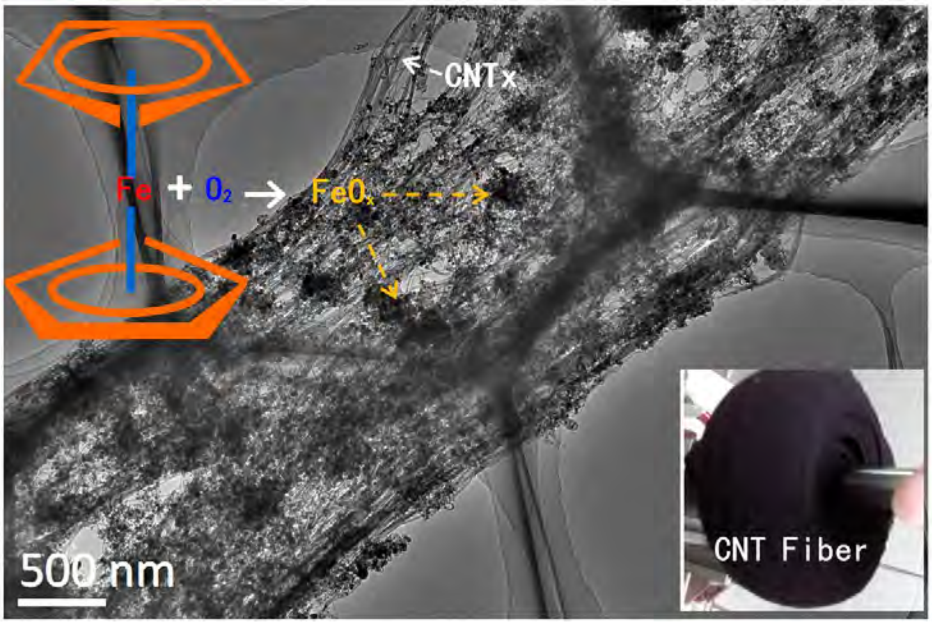

Fig.1 Atom layer deposition FeOx on CNT fiber using ferrocene and oxygen as precursors.

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Plasma functionalization of powdery nanomaterials using porous filter electrode and sample circulation

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Compared with wet processes, dry functionalization using plasma is fast, scalable, solvent-free, and thus presents a promising approach for grafting functional groups to powdery nanomaterials. Previous approaches, however, had difficulties in maintaining an intimate sample-plasma contact and achieving uniform functionalization. Here, we demonstrate a plasma reactor equipped with a porous filter electrode that increases both homogeneity and degree of functionalization by capturing and circulating powdery carbon nanotubes (CNTs) via vacuum and gas blowing. Spectroscopic measurements verify that treatment with O_2/air plasma generates oxygen-containing groups on the surface of CNTs, with the degree of functionalization readily controlled by varying the circulation number. Gas sensors fabricated using the plasma-treated CNTs confirm alteration of molecular adsorption on the surface of CNTs. A sequential treatment with NH_3 plasma following the oxidation pre-treatment results in the functionalization with nitrogen species of up to 3.2 wt.%. Our approach requiring no organic solvents not only is cost-effective and environmentally friendly, but also serves as a versatile tool that applies to other powdery micro or nanoscale materials for controlled modification of their surfaces.

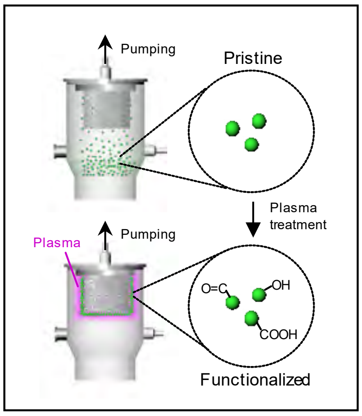

Fig.1 A schematic diagram showing plasma functionalization of powdery materials captured by a porous filter electrode.

Effect of functionalization by ultraviolet irradiation in ambient and argon atmosphere of carbon nanotubes

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The functionalization of carbon nanotubes can be used for different application, such as transistors charge carrier concentration control, gas sensors, implants in medicine etc. There are three main methods of functionalization: chemical functionalization [1], chemical sorption [2] and diffusion [3]. Chemical sorption of different functional groups on nanotube surface is a simple and effective method of functionalization, compare to the others.

For the functionalization by physical sorption, the ultraviolet treatment was used to insert the oxygen and hydroxyl groups. For the fuller picture of the process, the effect of ultraviolet treatment on carbon nanotubes was investigated in air and argon atmosphere. Structures with mesh of single-walled carbon nanotubes located on the PET substrate with gold contacts (Skoltech, Russia) on top were treated for 10-50 minutes under ultraviolet irradiation with a radiation power of 50 W at a wavelength of 254 nm (Svetolit, Russia). For studying changes in morphology, chemical composition and structure of carbon nanotubes atomic force microscopy (NT-MDT, Russia) and Raman spectroscopy (NanoScanTech, Russia) was used.

As can be seen on fig. 1 (a), the G` peak is smoothing, which can be attributed to functional groups inserting, while on fig. 1 (b) clearly shows separate G` peak. Also, the changes in ratio of intensities I_D/I_G qualitatively shows the changes in concentration of sp^3- hybridization and defect formation in different atmospheres. The ratio of I_D/I_G for nanotubes, functionalized in air changed from 0.10 to 0.23 (10 min and 50 min respectively), while for nanotubes, functionalized in argon from 0.06 to 0.10 (10 min and 50 min respectively). Such changes in spectrums of samples, treated in air atmosphere can be attributed to functional group insertion on the surface of carbon nanotubes. Also, the growth of PET peaks on fig. 1(a) shows, that air is interacting with substrate surface.

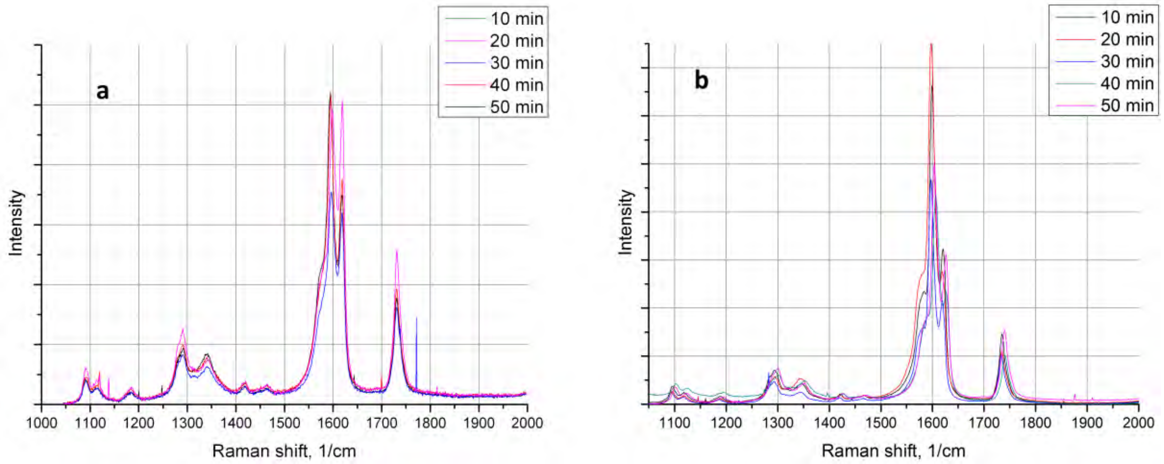

Fig.1 Raman spectra of carbon nanotubes, treated by ultraviolet irradiation in air (a) and argon (b).

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Filling of carbon nanotubes with different morphologies of a metal halide

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The filling of the internal channel of carbon nanotubes (CNT) has been widely investigated. Various methods exist to encapsulate a wide variety of substances and one of the most popular is the use of melts of inorganic compounds. This method relies on surface tension and capillary forces and can result in novel types of structures, particularly when the crystal is formed under volume constraints.

One system that has gathered attention is the inclusion of gadolinium species in CNTs. The ion Gd(III) is a known magnetic resonance imaging contrast agent because it is intrinsically paramagnetic. Recently, the halide GdI_3 was encapsulated in the form of solid rods or tubes within multiwall CNTs (MWCNT) and WS_2 nanotubes. These GdI_3@NT systems (where @ means encapsulated in) represent promising moisture-protective storage vehicles for the paramagnetic Gd(III) ion.

Our previous observations of tube-in-tube configuration in GdI_3 filled MWCNTs [1], prompted the search for this type of novel structure in smaller diameter hosts such as double- and triple-walled CNTs. We describe the structure and composition of this and a number of other configurations, all of which were obtained with the melt-phase filling method. The final samples consisted of mixed encapsulation products spanning from the mono-elemental iodine chain to the internal atomic layer deposition of the binary halide.

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Femtosecond Laser Maskless Patterning of Carbon Nanomaterials

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Carbon nanomaterials are very promising candidates for future photonic and electronic applications [1]. Ultrafast laser processing can be used to ablate and modify the properties of nanomaterials through maskless patterning with submicrometer resolution. In this report we show the results of electronic and optoelectronic device fabrication via femtosecond (fs) laser processing of carbon nanotubes (CNTs), graphene and graphene oxide (GO) structures.

Carbon nanotubes and graphene were grown by CVD technique and transferred onto Si substrates with 300 nm SiO_2 layer. Graphene oxide was produced by modified Hammers method and transferred onto polyethylene terephthalate substrates. We used 515 nm 280 fs pulsed laser to process the structures. The samples were characterized by optical, atomic force and scanning electron microscopy, Raman and X-ray photoelectron spectroscopy.

The nonlinear effects such as selective ablation, local oxidation of CNTs and graphene, and reduction of GO were studied [2-4]. We observed a significant photocurrent generation in fs laser oxidized field effect transistors based on graphene and CNTs (Fig. 1). Upon analysis of experimental data, the photo-thermoelectric effect is proposed as the main mechanism of photocurrent generation in modified transistor structures. The results show the possibility of fabrication and modification of carbon nanomaterials using maskless laser patterning technique.

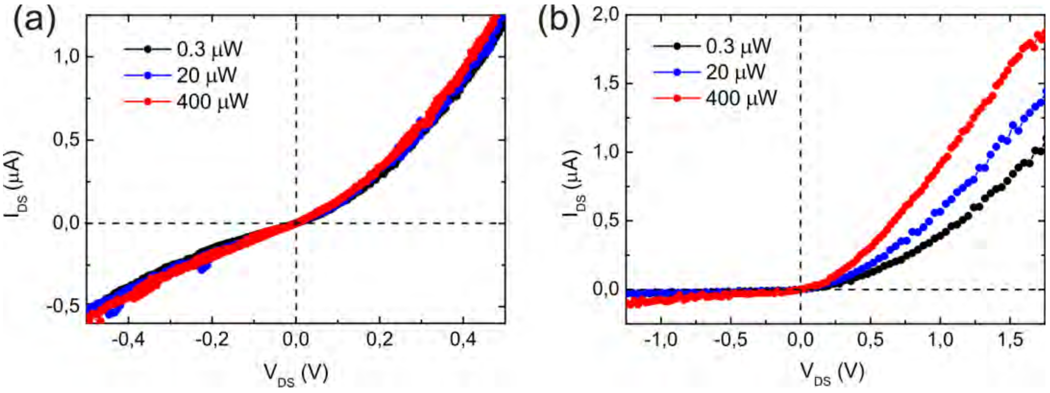

Fig.1 Output current-voltage characteristics of pristine (a) and oxidized (b) CNTs via fs laser pulses upon 470 nm diode illumination.

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Removable Carbon Nanotube Tape for wide-range-temperature application

Various adhesive is widely used in laboratories, in particular, specialized adhesive is needed in extreme conditions. However, most of conventional adhesive is made up of polymers that would be ineffective when temperature lies outside the region of -50 to 1000℃ (e.g. epoxy resin). Besides, residue of conventional adhesive is difficult to remove. Here we show a carbon nanotube (CNT) dry adhesive tape directly drawn from super-aligned carbon nanotube array (SACNT). It can provide appreciable adhesion strength up to 5N/cm2 and maintain its performance over an extremely wide temperature range from -269℃ (4K) to 1000℃). Another advantage is that the CNT tape can be easily removed without contaminating sample. Besides, compared to vertically-aligned multi-walled carbon nanotubes adhesive, the effective contact area of our CNT tape is 700 times higher, thus it consumes much fewer carbon nanotubes and is more economical. Last but not least, the anisotropic electrical and thermal conductivities of CNT tape guarantee its further application in many fields.

Photoelectrocatalytic degradation of pollutants at MnOx/g-C3N4 photoanode under visible light irradiation

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Beijing Forestry University

Graphite-like carbon nitride (g-C_3N_4) as a metal-free conjugated semiconductor photocatalytic material, has been considered to be a promising visible light activated candidate for degrading pollutants. However, the typical efficiencies of unmodified g-C_3N_4 for photoelectrochemical application were not impressive. Ultrafast recombination of photogenerated electron-hole and insufficient sunlight absorption have limited the practical application of g-C_3N_4. In this work, we demonstrate that the manganese oxide (MnO_x)/g-C_3N_4 composites synthesized by one-step thermal decomposition method exhibit enhanced photoelectrochemical efficiency. MnO_x/g-C_3N_4 photoanodes exhibit a remarkable enhancement of photoelectrocatalytic activity. The photoelectrocatalys were characterized by X-ray diffraction (XRD), The fourier transform infrared (FTIR) spectra, ultraviolet-visible (UV-vis) spectrometer, photoluminescence (PL) spectra, X-ray photoelectron spectroscopy (XPS). Its photoelectrocatalytic performance was investigated via electrochemical measurements cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) in a three-electrode system in a solution containing 0.1 M Na_2SO_4. The characterization results showed that the successful introduction of MnO_x into the bulk g-C_3N_4 can increase the visible light absorption range of semiconductors and reduce the band gap. The fitted values of Eg were 2.35eV, 2.34eV, 2.32eV, 2.30eV for pristine g-C_3N_4, 2%MnO_x/g-C_3N_4, 5%MnO_x/g-C_3N_4, 10%MnO_x/g-C_3N_4, respectively. The photocurrent densities was an elevation with the increase the contend of MnO_x. 10%MnO_x/g-C_3N_4 exhibits optimal photoelectrocatalytic performance. It can be seen that photocurrent density measured with MnO_x/g-C_3N_4 (2.5 mA cm^{-2} at 1.25 $V_{Ag/AgCl}$) electrode is higher than that of pure g-C_3N_4 (0.007 mA cm^{-2} at 1.25 $V_{Ag/AgCl}$). The EIS analyses were performed to analyze the phenomenon. The MnO_x/g-C_3N_4 electrode showed the fastest interfacial electron transfer which is in accordance with its enhanced photoelectroactivity. For this, given its high conductivity, MnO_x was introduced into g-C_3N_4 to captured photogenerated holes and reduced photogenerated electrons-hole recombination. This composite catalytic material is a potential application in photoelectrocatalytic oxidation of organic contaminants.

Photoelectrocatalytic degradation of pollutants at MnO_x/g-C_3N_4 photoanode under visible light irradiation

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Graphite-like carbon nitride (g-C_3N_4) as a metal-free conjugated semiconductor photocatalytic material, has been considered to be a promising visible light activated candidate for degrading pollutants. However, the typical efficiencies of unmodified g-C_3N_4 for photoelectrochemical application were not impressive. Ultrafast recombination of photogenerated electron-hole and insufficient sunlight absorption have limited the practical application of g-C_3N_4. In this work, we demonstrate that the manganese oxide (MnO_x)/g-C_3N_4 composites synthesized by one-step thermal decomposition method exhibit enhanced photoelectrochemical efficiency. MnO_x/g-C_3N_4 photoanodes exhibit a remarkable enhancement of photoelectrocatalytic activity. The photoelectrocatalys were characterized by X-ray diffraction (XRD), The fourier transform infrared (FTIR) spectra, ultraviolet-visible (UV-vis) spectrometer, photoluminescence (PL) spectra, X-ray photoelectron spectroscopy (XPS). Its photoelectrocatalytic performance was investigated via electrochemical measurements cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) in a three-electrode system in a solution containing 0.1 M Na_2SO_4. The characterization results showed that the successful introduction of MnO_x into the bulk g-C_3N_4 can increase the visible light absorption range of semiconductors and reduce the band gap. The fitted values of Eg were 2.35eV, 2.34eV, 2.32eV, 2.30eV for pristine g-C_3N_4, 2%MnO_x/g-C_3N_4, 5%MnO_x/g-C_3N_4, 10%MnO_x/g-C_3N_4, respectively. The photocurrent densities was an elevation with the increase the contend of MnO_x. 10%MnO_x/g-C_3N_4 exhibits optimal photoelectrocatalytic performance. It can be seen that photocurrent density measured with MnO_x/g-C_3N_4 (2.5 mA cm^{-2} at 1.25 $V_{Ag/AgCl}$) electrode is higher than that of pure g-C_3N_4 (0.007 mA cm^{-2} at 1.25 $V_{Ag/AgCl}$). The EIS analyses were performed to analyze the phenomenon. The MnO_x/g-C_3N_4 electrode showed the fastest interfacial electron transfer which is in accordance with its enhanced photoelectroactivity. For this, given its high conductivity, MnO_x was introduced into g-C_3N_4 to captured photogenerated holes and reduced photogenerated electrons-hole recombination. This composite catalytic material is a potential application in photoelectrocatalytic oxidation of organic contaminants.

Carbon nanotube supported carbon-nitrogen-iron composites as catalysts for oxygen reduction reaction

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Replacing precious and nondurable platinum-based catalysts by economical and commercially available materials in the oxygen reduction reaction (ORR) is a key issue addressed in contemporary fuel cells and metal–air batteries. Nitrogen-doped porous carbon materials, especially zeolitic imidazolate frameworks (ZIFs), have been extensively investigated as the ORR catalysts, wherein the introduced nitrogen atoms could enhance the catalytic activity by inducing active defect sites and adjusting the electronic structures. However, the direct carbonization of independent ZIF crystals cannot achieve the consecutive conductive network required for device application, which also result in insufficient performance. [1-3]

Here, we synthesized a novel ORR electrocatalyst of Fe-doped N-containing carbon anchored on carbon nanotubes (OCNT@NC-Fe). To ensure homogenous in situ growth of ZIF-8 on CNTs, the deficient functional groups on the surface of CNTs are enriched with the amide carbonyl groups of polyvinyl pyrrolidone, which would coordinate with Zn^{2+} and thus facilitate the uniform nucleation of ZIF-8 on the surface of CNTs. During the nucleation process of ZIF-8, $Fe(acac)_3$ was added and trapped in the cage of ZIF-8 simultaneously. After carbonization, the catalyst showed excellent ORR performance with a half-wave potential ($E_{1/2}$) of 0.84 V, which outperformed commercial Pt-C. It is expected that this core–shell CNT@ZIFs structures and their derivatives show better performance in fuel cells and metal–air batteries.

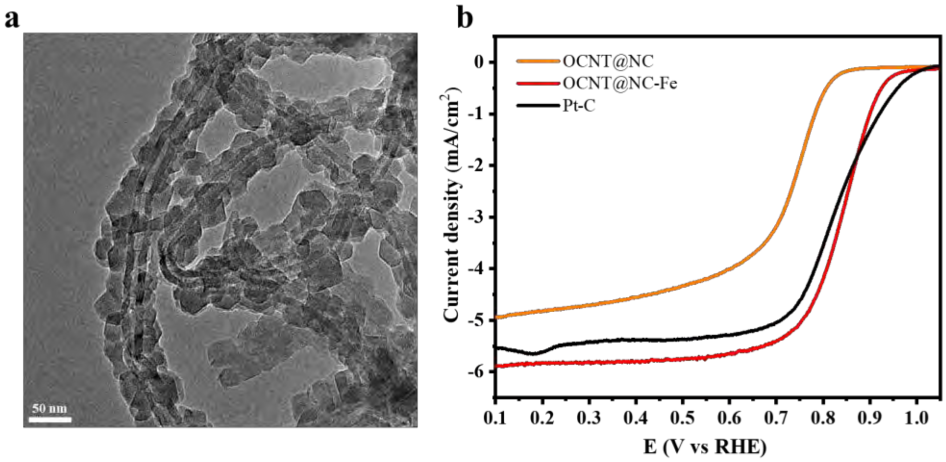

Fig.1 (a) TEM image of OCNT@ZIF-8. (b) ORR polarization curves for OCNT@NC, OCNT@NC-Fe, Pt-C at 1600 rpm in O_2-satuarated 0.1 M KOH electrolyte**.**

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Low-Dimensional Nanostructure Property Measurements in a Transmission Electron Microscope

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Modern methods of *in situ* high-resolution transmission electron microscopy (TEM) allow one to not only manipulate with a nanoscale object at the nanometer-range precision but also to get deep insights into its physical and chemical statuses [1]. Dedicated TEM holders combining the capabilities of a conventional high resolution TEM instrument and atomic force sensors, biased electrical scanning tunneling microscopy probes, optical fibers and miniaturized thermal couples became the powerful tools in low-dimensional nanomaterial properties' analysis.

This contribution reports on the most recent successes in utilizing the regarded *in situ* TEM methods by the author groups. The objects of interest are diverse. They include BN, C, ZnO CdS and MoS_2 two- one- and zero-dimensional nanoscale materials, *e.g.* nanosheets, nanotubes, nanowires, and nanoparticles. The key point of all experiments is that the nanomaterial electromechanical, optical, optoelectronic and thermal data are acquired on an individual nanostructure level under ultimately high spatial, temporal and energy resolution achievable in TEM, and thus can directly be linked to its morphological, structural and chemical peculiarities.

Applications of *in situ* TEM methods for the analysis of fading kinetics of Li- and S-ion nanobattery electrodes, mechanical properties of BN nanotube/light metal structural nanocomposites, photocurrent behavior in inorganic nanowires under their bending, spatially-resolved defect-induced cathodoluminescence signals in one-dimensional nanostructures, comparative fracture toughness of multilayered C and BN nanosheets, defect-induced softening and Joule heating-induced hardening of C nanotubes and many other striking nanoscale phenomena will be demonstrated [2-4]. The author acknowledges the key contributions from Drs. C. Zhang, D. M. Tang, M.S. Wang, W. L. Wei, O. Cretu, Z. Xu, K. Firestein, J. Fernando, and N. Kawamoto, and the Australian Research Council (ARC) for awarding a Laureate Fellowship (Project FL160100089).

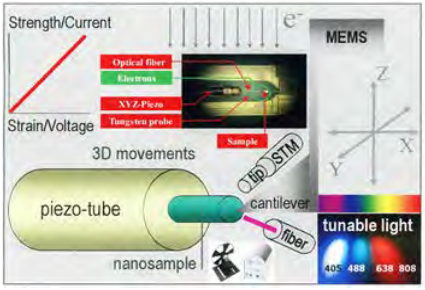

Fig. 1. A sketch showing diversity of *in situ* TEM tests performed.

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Ultrafast Carrier Thermalization and Relaxation Dynamics in Few - Layer MoS_2 Atomic Layers

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Studies of highly energetic carrier dynamics in semiconductors are essential for various problems in modern physics and technology [1–3]. In the experiments reported here, femtosecond optical pulse techniques are used to excite a non-equilibrium carrier population, which temperature cannot yet be defined, in two-dimensional (2D) MoS_2 atomic layers and to probe the initial carrier thermalization and subsequent hot carrier cooling processes. Time constants associated with the initial and the subsequent processes are determined to be around 20-fs and 600-fs in average (see Fig. 1a), respectively [4]. By monitoring the two dynamics processes as functions of excitation pulse fluence and lattice temperature, we can identify the effects of carrier-carrier and carrier-phonon interactions during these early stages of carrier relaxation dynamics. In addition, following narrowband resonant photoexcitation of the exciton A transition, the sub-picosecond to picosecond relaxation dynamics of the electron and the hole at the K valley are separately interrogated by a broadband probe pulse (see Fig. 1b). The ultrafast individual electron and hole relaxation pathways are separately discerned [5,6]. This provides the conceptual framework for understanding the electron and hole transport properties of transition-metal dichalcogenide-based electronic devices.

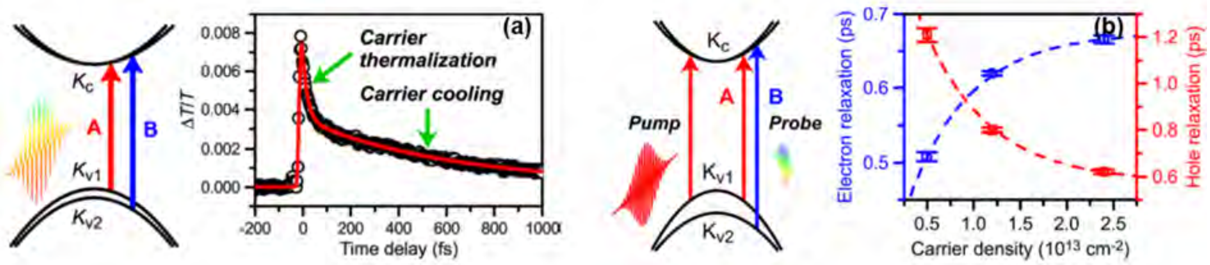

Fig. 1. (a) ΔT/T time trace probed at 655 nm with 3-fs time step to show the initial extremely fast carrier thermalization and subsequent carrier cooling processes. The red solid line is fitted to the data with an exponential function (τ_1 = 19.7±0.5 fs). The left side shows the schematic illustration for The A and B excitonic transitions in MoS_2 correspond to the transitions from the Spin-orbit-split K_{v1} and K_{v2} valence bands, respectively, to the conduction band K_c. (b) The electron and hole relaxation lifetimes are found to exhibit opposite trends in their pump fluence dependence. Also shown on the left the Schematic illustration for the band-selective probing of ultrafast electron and hole relaxation dynamics in MoS_2.

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Carbon Nanotube Bundles with Tensile Strength over 80 GPa

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Carbon nanotubes (CNTs) are regarded as one of the strongest known materials. When assembled into fibres, however, its strength becomes impaired by defects, impurities, random orientations and discontinuous lengths. Fabricating CNT fibres with strength reaching that of a single CNT has been an enduring challenge. During the past years, we successfully synthesized centimetres long CNTs with perfect structures and extraordinary mechanical properties. However, it still remains unknown that, when bundled together, whether a CN bundle can keep the tensile strength as high as that of singles ones. Here we demonstrate the fabrication of centimetre long CNT bundles (CNTBs) with tensile strength over 80 GPa using ultra-long defect-free CNTs. The tensile strength of CNTBs is controlled by the Daniels effect due to the non-uniformity of the initial strains in the components. We propose a synchronous tightening and relaxing strategy to release the non-uniform initial strains of the CNTB components. The fabricated CNTBs consisting of a large number of components with parallel alignment, defect-free structures, continuous lengths and uniform initial strains exhibit the tensile strength of 80 GPa (corresponding to an engineering tensile strength of 43 GPa), which is far higher than that of any other strong fibres.

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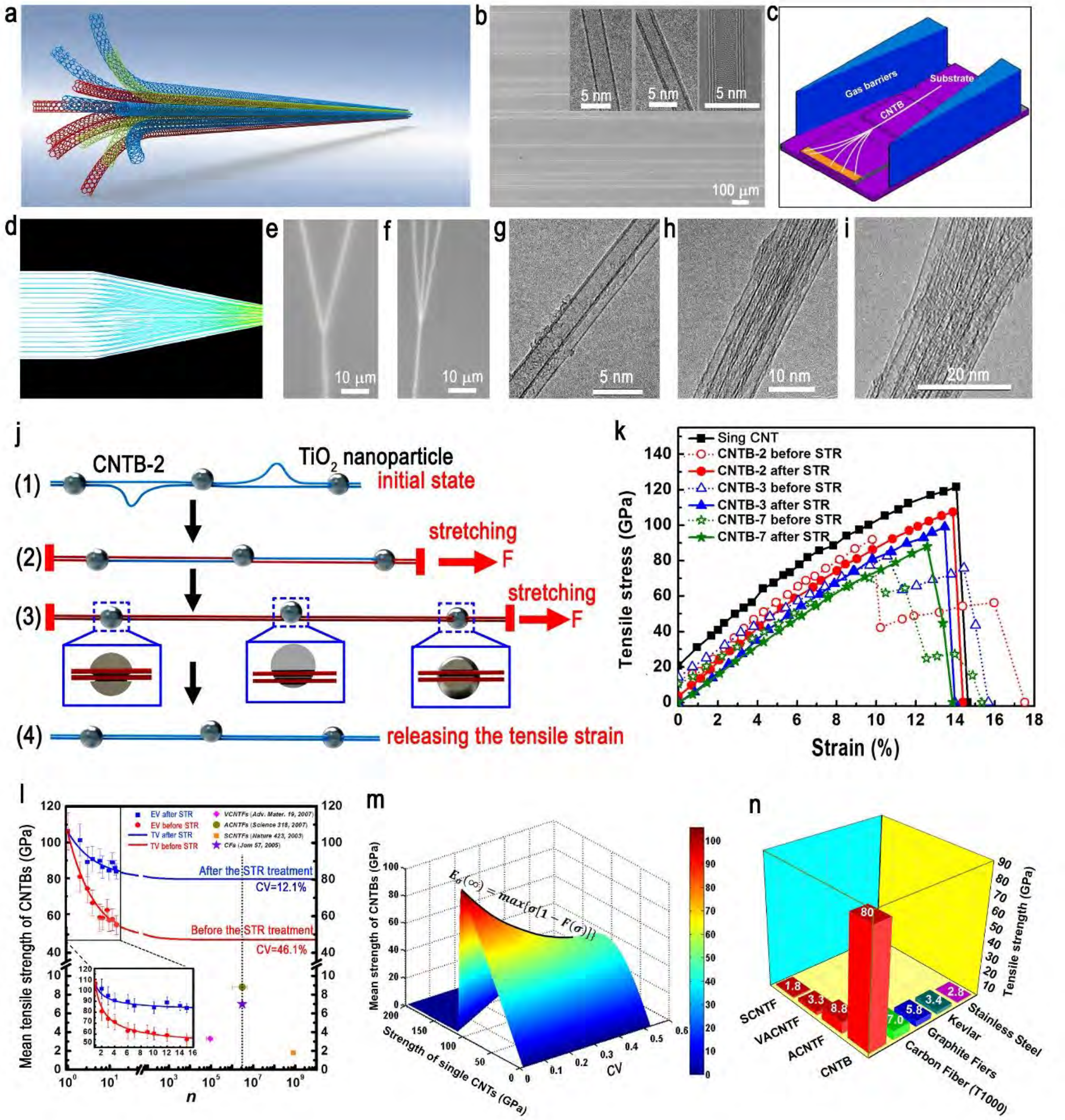

Fig.1 Fabrication of centimeters long CNT bundles and their mechanical properties. (a) Schematic illustration of ultralong CNTBs composing of ultralong CNTs. (b) SEM image of horizontally aligned ultralong CNT arrays. Inset: high-resolution TEM images of the as-grown ultralong CNTs with single, double and triple walls, respectively. (c) Schematic illustration of the in-situ fabrication of CNTBs via gas flow focusing (GFF) method. (d) Hydrodynamic simulation of streamline with the GFF. (e) and (f) SEM images of CNTBs consisting of two and three single CNTs, respectively. (g)-(i) TEM images of CNTBs with different component numbers, *i.e.*, CNTB-2 (g), CNTB-5 (h), and CNTB-10 (i). (j) Illustration of the sliding of TiO_2 nanoparticles along a CNTB-2. (k) Stress–strain curves for a single CNT, CNTB-2, CNTB-3, and CNTB-7 before and after the STR treatment. (l) The relationship between the mean tensile strength of CNTBs and their component number (n) before and after the STR treatment. (m) The relationship between the mean tensile strength of CNTBs with numerous components and the strength of single CNTs (σ) as well as the coefficient of variation (CV) (n) The strength comparison between CNTBs, high-performance commercial materials43,44, and other CNT fibers made by different methods, such as spinning from aerogels (ACNTFs)15, spinning from vertically aligned CNT arrays (VACNTFs)45, and spinning from CNT solutions (SCNTFs).

The dispersion and aggregation of graphene oxide in aqueous media

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Graphene oxide (GO), as a typical two-dimensional material, possesses a range of oxygen-containing groups and shows surfactant and/or polyelectrolyte-like characteristics. Herein, GO sheets with narrow size distribution were prepared by an ultracentrifugation-based process and the aggregation behavior of GO in pure water and an electrolyte aqueous solution were studied using laser light scattering (LLS). When adding common electrolytes, such as NaCl and $MgCl_2$, into the GO dispersions, aggregation occurs and irreversible coagulation eventually occurs too. However, the GO dispersion can still remain stable when adding excess $AlCl_3$. The zeta potential of the GO dispersion changes from negative to positive after the addition of access $AlCl_3$, indicating that electrostatic repulsion is still responsible for the dispersion of GO, which is in good agreement with the LLS results. This finding on the dispersion of GO may be applied in the solution processing of GO. It also expands the scope of the design and preparation of new GO-based hybrid materials with different functions.

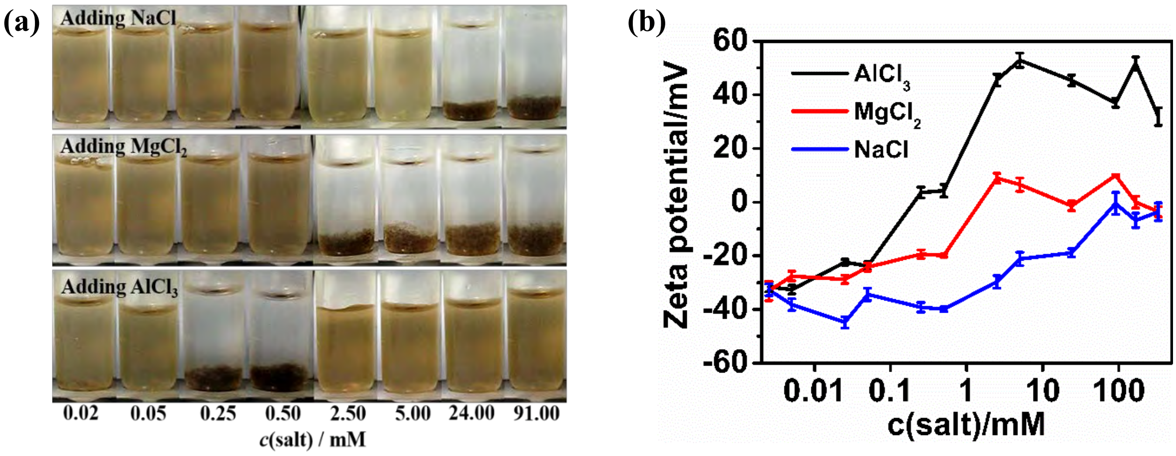

Figure: (a) Evolution of the aggregation state of GO dispersions with different concentrations of NaCl, $MgCl_2$ and $AlCl_3$ in GO dispersion solutions prepared under a centrifugal force of 150 000g; (b) The zeta potential of GO aqueous dispersions dependent on the concentration of NaCl, $MgCl_2$ and $AlCl_3$. GO sheets were prepared at 150 000g and the concentration was ~0.041 mg mL^{-1}.

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Avalanche Photoemission in Suspended Carbon Nanotubes

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We observe bright electroluminescence from suspended carbon nanotube (CNT) field effect transistors (FETs) under extremely low applied electrical powers (~nW). Here, light emission occurs under positive applied gate voltages, with the FET in its "off" state. This enables us to apply high bias voltages (4V) without heating the CNT. Under these conditions, we observe light emission at currents as small as 1nA, and corresponding electrical powers of 4nW, which is three orders of magnitude lower than previous studies. Thermal emission is ruled out by monitoring the *G* band Raman frequency, which shows no evidence of heating under these small electrical currents. The mechanism of light emission is understood on the basis of steep band bending that occurs in the conduction and valence band profiles at the contacts, which produces a peak electric field of 500kV/cm, enabling the acceleration of carriers beyond the threshold of exciton emission. The exciton-generated electrons and holes are then accelerated in this field and emit excitons in an avalanche process. This is evidenced by an extremely sharp increase in the current with bias voltage (45mV/dec). We also observe light emission at negative applied gate voltages when the FET is in its "on" state at comparable electrical powers to those reported previously (~5μW). However, substantial Joule heating (*T*>1000K) is also observed under these conditions, and it is difficult to separate the mechanisms of thermal emission from hot carrier photoemission in this regime.

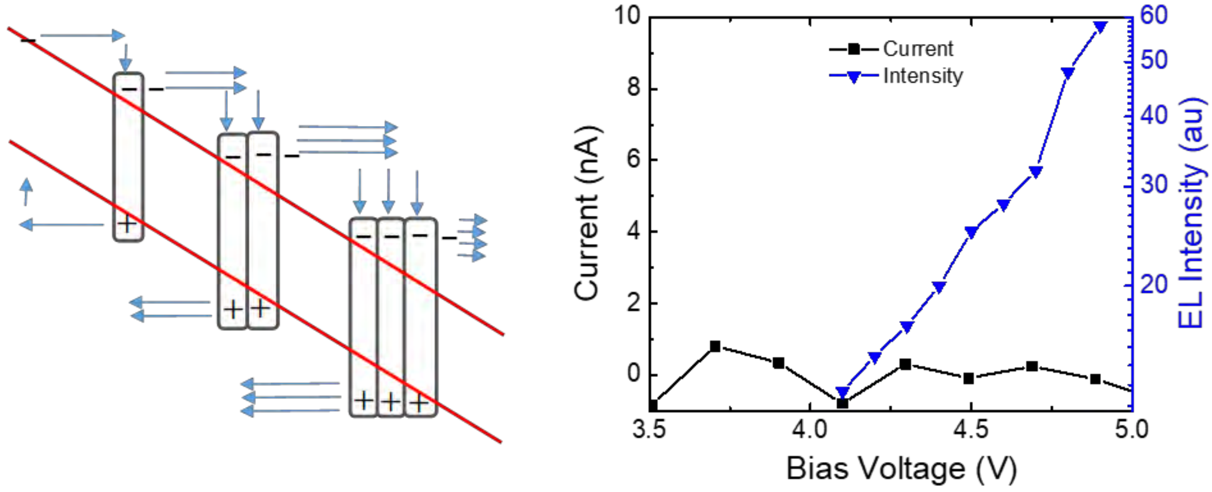

Figure1. Schematic energy band diagram illustrating the emission of photons by ballistic hot carriers in an avalanche emission processes, and log-linear plots of the electric current (left axis) and electroluminescence intensity plotted as a function of applied bias voltage.

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Nanoparticle Intercalation-Modulated Stretchable Conductive Graphene Fibers with Combined Photoelectric Properties

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Graphene fiber which shows potential superb mechanical, electrical and thermal properties poses an important role in future functional fibers and devices towards smart and wearable techniques. However, the fibers made of neat graphene sheets remain brittle and the electrical conductivity of flexible graphene/polymer composite fibers is very poor, which all together hiders the wide use of graphene fibers. Here, we demonstrate a simple wet spinning of stretchable conductive graphene fibers functionalized by TiO_2 nanoparticles with an average diameter around 100 nm through the uniform intercalation of TiO_2 nanoparticles between graphene sheets. The TiO_2 nanoparticles induce the formation of numerous winkles on the graphene sheets which all together makes the composite fibers show combined superb mechanical, electrical and photoelectric performances. With the increasing of TiO_2 from 0 to 50%, the fibers still have comparable electrical conductivities, while the breakage elongation of the graphene/TiO_2 fibers greatly increase from less than 6% to higher than 20%. With TiO_2 combined, the fibers have extra functional properties in photoelectric response, which can be further improved by oxygen plasma etching treatment. This study provides useful guidelines for the designing of functional conductive graphene fibers with highly stretchable performance towards future uses.

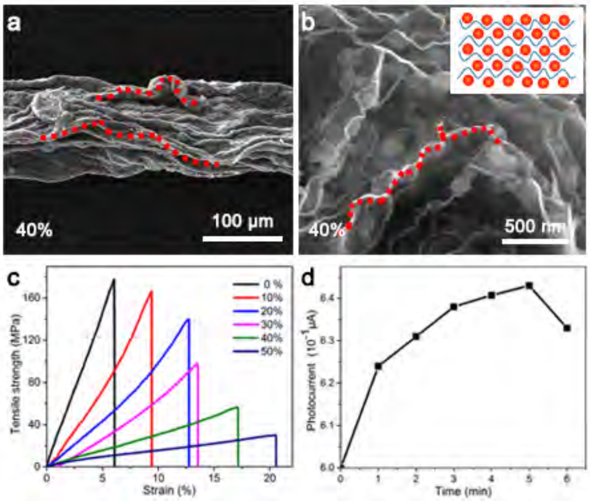

Fig. 1 SEM (a) and Cross-sectional SEM (b) images of TiO_2-graphene fiber with TiO_2 percentage of 40%. (c) Typical stress-strain curves of TiO2-graphene fiber with percentage of TiO2 from 0 to 50%. (d) photocurrent responses of TiO2-graphene fiber photoelectrodes as a function of time oxygen plasma etching.

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Grain misorientation-induced in-plane thermal conductivity variation of monolayer suspended graphene

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There has been considerable attention about the thermal transport property of large-area polycrystalline graphene because the intrinsic property of single crystalline graphene is modulated by the grain structure [1]. It is well known that grain boundaries (GBs) of graphene work as major scattering sites of charge carriers. However, the thermal transport across GBs is less understood. Here we synthesized the single and polycrystalline graphene with well-defined grain orientation by the chemical vapor deposition (CVD) method [1]. The graphene was transferred onto the holey silicon nitride membrane, and the thermal transport property of the monolayer suspended graphene was investigated by the Optothermal Raman method [1]. The grain size and grain misorientation was carefully investigated by the selected area electron diffraction analysis and dark-field transmission electron microscopy. Interestingly, the thermal conductivity dramatically decreased by the grain boundary. The grain-size dependent thermal conductivity was experimentally investigated and comparatively analyzed by the Boltzmann transport model. The relationship between the grain misorientation and thermal conductivity was then investigated. The thermal conductivity sensitively decreased as the grain misorientation slightly increased [1]. The shape of grain also affected the thermal transport. A recent progress in the lab will also be introduced.

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Optical Characterizations of Low Dimensional Metal Monohydroxides

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Metal monohydroxides represented by □-MO(OH), where M = Al, Fe, Ni, Mn, Sc, Ti, etc., have attracted considerable research interest in a wide range of fields from energy to medical science [1-4]. Crystal structures and morphologies of such of metal monohydroxides will dramatically affect their physical characteristics. Recently, we determined structures of low dimensional including 1-D crystalline structures of aluminum oxyhydroxide γ-AlOOH (pseudoboemite) at an atomic level utilizing HRTEM and ED patterns [5]. The thinnest pseudoboemite (PB) fiber found for the first time was a ribbon-like structure consists only two layers of Al-O octahedral double-sheet (with a thickness of 0.68nm that is a little bit larger than the half lattice parameter of b-axis unit cell of the boehmite crystal (b/2=0.61nm)) having a sub-micrometre length along its growing direction of c-axis. In this study, optical properties of several kinds of metal monohydroxides with different morphologies will be reported. The findings will lead to diverse interests in nucleation and growth in sol-gel processes, colloid science, polymer science, clay mineralogy, condensed matter physics, nanoscience, nanotechnology, etc.

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Fast mass transport of air through the heated aligned multi-walled carbon nanotubes

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Fast mass transport through nanopores has received considerable attention recently [1]. Here we report the effect of temperature on the mass transport of air through the vertically-aligned multi-walled carbon nanotubes (VAMWNTs) [1]. The VAMWNTs with a height of 3.4 mm were synthesized by the thermal chemical vapor deposition (CVD) method. The interstitial space among four adjacent nanotubes was defined as a unit cell control volume. The air flow through the VAMWNTs was introduced using a mass flow controller. The flow was in the transition and creeping flow regime. The non-contact heat flux was supplied to the VAMWNTs using a single-mode microwave system (2.45 GHz). The fluidic chip made of microwave-transparent materials was installed in the microwave reactor for the selective heating of the VAMWNTs. An instant volumetric heating of the VAMWNTs was achieved due to the large microwave absorption cross-section of long nanotubes (~600 cm^2 g^{-1}) [2]. The volume flow rate through the unit cell control volume was significantly higher than the Hagen-Poiseuille and Knudsen predictions [1]. A recent progress in the lab about the effect of heating on the mass transport of air through the VAMWNTs will also be presented.

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Interactions between elementary excitations, such as carriers, phonons, and plasmons, are critical for understanding the optical and electronic properties of materials. The significance of these interactions is more prominent in low-dimensional materials and can dominate their physical properties due to the enhanced interactions between these excitations. One-dimensional single-walled carbon nanotubes provide an ideal system for studying such interactions due to their perfect physical structures and rich electronic properties. Here we investigated G-mode phonon dynamics in individual suspended chirality-resolved single-walled carbon nanotubes by time-resolved anti-Stokes Raman spectroscopy. The improved technique allowed us to probe the intrinsic phonon information on a single-tube level and exclude the influences of tube–tube and tube–substrate interactions. We found that the G-mode phonon lifetime ranges from 0.75–2.25 ps and critically depends on whether the tube is metallic or semiconducting. In comparison with the phonon lifetimes in graphene and graphite, we revealed structure-dependent carrier–phonon and phonon–phonon interactions in nanotubes. Our results provide new information for optimizing the design of nanotube electronic/optoelectronic devices by better understanding and utilizing their phonon decay channels.

Properties and applications of carbon nanotube Langmuir-Schaefer thin films

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The carbon nanotubes (CNTs) are fascinating materials inspiring scientists since their discovery by Ijima in 1991 [1]. Their physical properties like electrical conductivity suggest a wide area of possible applications. A precondition for the use of CNTs in industry applications is the possibility to obtaing large scale homogeneous thin films. In recent years, there has been an intensive development of research on transparent, horizontally ordered CNT electrodes, that have the potential to replace ITO layers. Langmuir methods allow to obtain relatively large areas layers of CNTs. Despite that the individual CNTs are characterized by good electrical conductivity the resistivity of CNT thin films is too large for practical application. Main reason of the thin films high resistance is the high number of poor conductivity contacts between carbon nanotubes.

In current work we present optoelectrical properties of CNT Langmuir-Schaefer thin films and an example of their use. We have shown that the surface resistance is strictly related to the diameter of used CNT [2,3]. Moreover the results show the anisotropic feature of the nanotube layers, both optical and electrical. The differences in electrical and optical properties observed at different directions increase with the increasing surface pressure during the film transfer. The electrical properties were investigated in temperature range 300-40 K for the as deposited and annealed (373 K) CNT thin films. In those films two types of conduction mechanism can be observed: variable range hopping (VRH) and nearest neighbor hopping (NNH) [4]. Moreover, we found that the CNT Langmuir-Schaefer thin films can be used as a ultralight current collector coating in lithium-ion batteries. This modification leading to an improve electrochemical parameters such as specific capacity and charge transfer resistance [5].

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Tuning the field emission properties of ZnO nanowires in gated field emitter arrays

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Zinc oxide (ZnO) nanowires have promising applications in field emitters due to their excellent field emssion properties and simple preparation methods [1-4]. The feasibility of the applications of ZnO nanowires field emitters in field emission display and flat-panel X-ray source has been demonstrated [5-8]. Addressable field emitter arrays (FEAs) are needed for such applications and usually a micro-fabricated gated structure is adopted. For being applied in gated field emitter arrays, ZnO nanowires need to integrate with triode structures [9-10]. However, it is found that the microstructure of gated FEAs has a dramatic effect on the growth of ZnO nanowires. Therefore, how to realize uniform morphologies and good field emission properties of ZnO nanowires in gated FEAs is a crucial issue to be addressed. In this study, gated FEAs using ZnO nanowires as field emitters were fabricated by the micro-fabrication technique. In order to achieve high performance ZnO nanowires FEAs, the field emission properties of ZnO nanowires in gated FEAs were optimized, which were prepared by the thermal oxidation method. A series of experiments were designed to investigate the impacts of the doping and growth conditions on the morphology and field emission properties of ZnO nanowires. By adjusting the growth parameters, the influence of doping and oxygen vacancies on the field emission characteristics of ZnO nanowires in the device structure was studied in details, and the experimental results and analysis will be presented.

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On The Intrinsic Surface Properties of Graphitic Carbon Materials

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This talk will focus on the intrinsic surface properties of graphitic carbon materials, highlighting the effect of environmental hydrocarbon contaminants from air and water on such properties. I will show that many properties previously believed to be intrinsic to graphitic carbon are in fact due to airborne and waterborne hydrocarbon contaminations.

We previously showed that a clean Cu-supported graphene and graphite surfaces are mildly hydrophilic, with a water contact angle of *ca.* 44° and 64°, respectively [1]. These data are much lower than what have been commonly accepted for graphitic carbons (*ca.* 85°). We showed that the hydrophobicity previously associated with graphitic carbons are due to airborne hydrocarbons adsorbed on these surfaces (**Fig 1**). Our recent work showed that the same type of contamination from air and water also impacts the electrochemical activity of graphitic carbon electrodes, specifically, their heterogeneous electron transfer rate constants and double layer capacitance [2, 3]. We have developed ways to reduce such contaminations and demonstrated their effectiveness in maintaining the electrochemical performance of carbon electrodes [4].

In summary, we show that clean carbon materials behave very differently from their conventional ‘dirty’ counterparts. Precise control of environments will offer new opportunities in both fundamental research and applications of graphitic carbon materials.

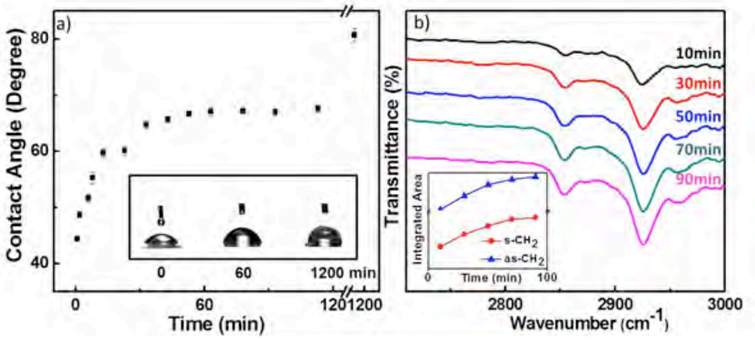

Fig.1 (a) Water contact angle measured on a graphene/copper sample as a function of air exposure time. (b) ATR-FTIR spectrum of a graphene/copper sample as a function of air exposure time. The inset shows the integrated peak area *vs* time for the peaks at 2930 cm^{-1} (asymmetric CH_2 stretching, blue) and 2850 cm^{-1} (symmetric CH_2 stretching, red). Reproduced from ref [1], copyright Macmillan Publishers Limited.

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Influence of Wrinkles on Damping Properties of Graphene Oxide Nanocomposites

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The combination of extremely large surface area, low mass density and high strength of graphene oxide (GO) made them suitable fillers of polymer for damping performance enhancement without sacrificing matrix elastic properties [1]. However, the advantages are seriously restricted due to the accumulation and self-scrolling phenomenon [2]. We propose that the GO-GO interface “stick-slip” energy dissipation [3] can be maximized if the wrinkles can be efficiently utilized. As such, sandwich structure foams with flexible polyurethane (PU) 3D cellular foams as the template and GO-ink coating as the core layer (Figure 1) were designed. As the GO content increased, the GO-GO friction appeared in high content (>0.2wt%) and the enhanced damping properties owing to the reduction of GO was observed (Figure 2). The friction force of graphene sheets observed by Atom Force Microscope (AFM) under lateral force mode reveals that the wrinkle with large coefficient of friction may play a leading role of impediment during slippage. The enhancement of damping behavior is reasoned to be attributed to the increased adhesive force and contact area between wrinkles. This work offers better understanding of how to approach the damping properties of graphene-based nanomaterials and open up a cost-effective way to develop novel nanofiller-based composites.

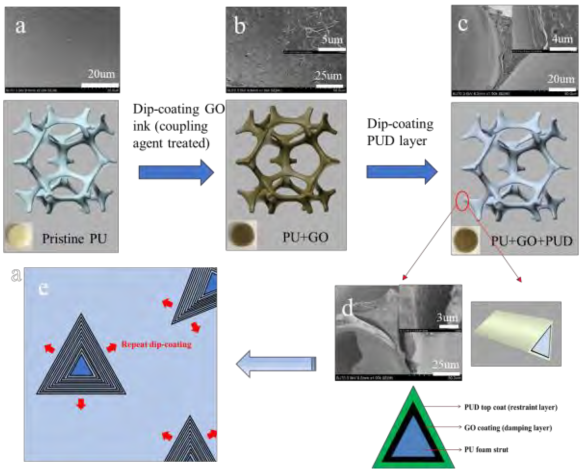

Fig.1 Preparation of sandwich structure foams.

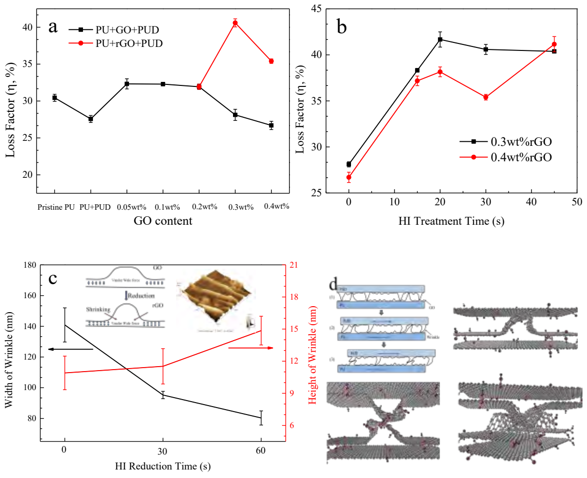

Fig.2 Damping performance of designed composites and the energy dissipation mechanism of wrinkles.

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Carbon nanotube-cellulose paper as scaffold of nano-silicon for Li-Si battery

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Silicon-based anodic materials have the highest theoretic capacity of 4200mAh/g among the known anodic materials. It was considered as one of potential anodic materials to replace graphite for lithium ion battery. The main obstacle of silicon as anode is the huge volume change of a 400% during the charge-discharge process which resulted in the pulverization of silicon and big irreversible capacity. The silicon-carbon composite anode was considered as a potential resolution to improve cycle performance and reduce irreversible capacity. In this work, nano-silicon and multiwalled carbon nanotubes(MWCNTs) composite anodes were prepared. Highly conductive carbon nanotubes paper(CNTP) with porous structure and interconnected channel was used as host to replace the copper foil current collector. The CNTP exhibited high conduction and excellent absorptivity of electrolyte. Nano-Si penetrated into the network of CNTP to achieve a low interface resistance which contributed to the high rate performance of the battery. The porous CNTP with interconnected channel can absorb an amount of electrolyte and was wetted fully by electrolyte. All those help to the excellent electronchemical performance of CNTP electrode. As is shown in Fig.1, CNTP electrode exhibited a 1000mAh/g, 900mAh/g, 500 mAh/g and 200mAh/g at a current density of 80mA/g, 200 mA/g,1000 mA/g and 2000 mA/g, respectively(Fig.1a). And CNTP electrode obtained a reversible capacity of as high as 900mAh/g at a current density of 200mA/g after 200 charge-discharge cycles and Coulomb efficiency kept up to about 99%(Fig.1a). Therefore, it was believed that CNTP has a useful application prospect as current collector for high performance silicon-based lithium ion batteries.

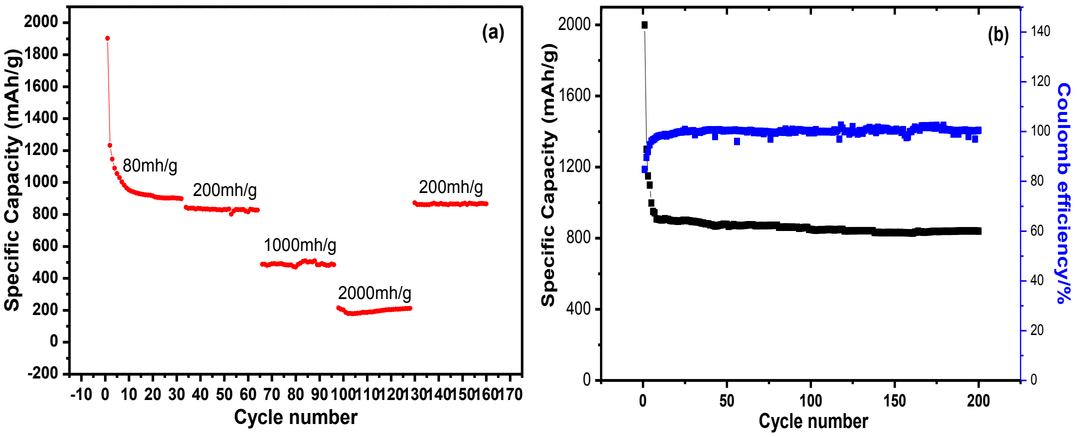

Fig.1 Cycle performance in different rate of copper foil cell and CNT paper cell

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DTT doped MWCNTs coating for checking shuttle effect of Lithium-sulfur battery

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Lithium-sulfur (Li-S) battery was considered to next generation of rechargeable lithium batteries [1]. Sulfur behave the advantages of low cost, natural abundance and environmental friendliness [2]. But the long-chain lithium polysulfides (LiPSs) are easily dissolved in the electrolyte and deposited on anode lithium foil to form short-chain lithium polysulfides. The process caused shuttle effect and resulted in self-discharge and loss of sulfur, poor cycle performance and low coulombic efficiency [3].In order to improve the rate and reversible capacity of lithium-sulfur (Li-S) battery. A reagent of dithiothreitol (DTT) was utilized to check the dissolution and shuttle of long-chain LiPSs by cutting the disulfide bond (-S-S- bonds) in them. The slurry of DTT doped MWCNTs was coated on the surface of sulfur cathode as a shield to slice the long-chain LiPSs to short-chain ones for checking the dissolution and migration of LiPSs to lithium anode. The initial discharge capacity of S-DTT-CNTP electrode reached 1670 mAh/g and 949 mAh/g at 0.05 C and 2 C respectively with a Coulombic efficiency of over 99%. This suggested that the DTT doped MWCNT coating can restrain shuttle effect and improve the rate and capacity of Li-S battery.

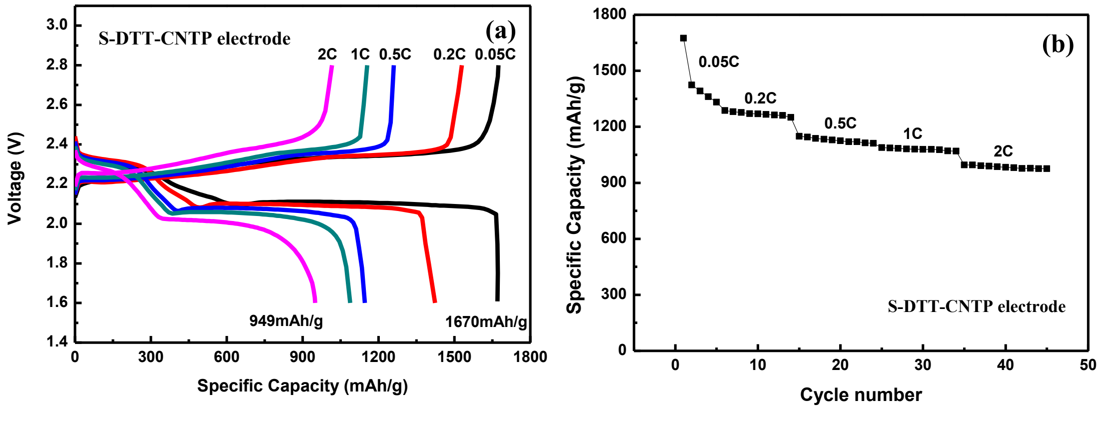

Fig.1 Charge-discharge and rate performance S-DTT-CNTP electrode

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Performance of lithium-ion capacitors using pre-lithiated multiwalled carbon nanotubes/graphite composite as negative electrode

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Lithium-ion capacitors (LICs), which combine the Faraday chemical reaction of the lithium-ion batteries and the physical adsorption and desorption reaction of electric double layer capacitors, are a new type of energy storage device that bridge the gap between the lithium-ion battery and electrical double layer capacitor[1, 2]. Multiwalled carbon nanotubes have been synthesized by floating reactant method in a vertical tubular reactor. An internal short approach process was developed to achieve the pre-lithiated multiwalled carbon nanotube MWCNTs/graphite composite anodes. Lithium ion capacitors (LICs) were composed of a pre-lithiated multiwalled carbon nanotubes/graphite composite anode and an activated carbon (AC) cathode. The electrochemical performance of LICs with different MWCNTs content was investigated through galvanostatic charge/discharge and electrochemical impedance. The results show that the charge‑discharge performance of LICs was greatly improved with the addition of MWCNTs in anodes. LIC25 (25 wt% MWCNTs) was found to achieve the optimal electrochemical performance. The LIC25 hold a specific capacitance of 58.2 F/g at the current density of 100 mA/g. The maximum energy density and power density were up to 96 Wh/kg and 10.1 kW/kg, respectively, in the current range of 100*8000 mA/g. The continuous galvanostatic charge‑discharge cycling tests revealed that the LIC25 maintained excellent capacity retention of 86% after 3000 cycles.

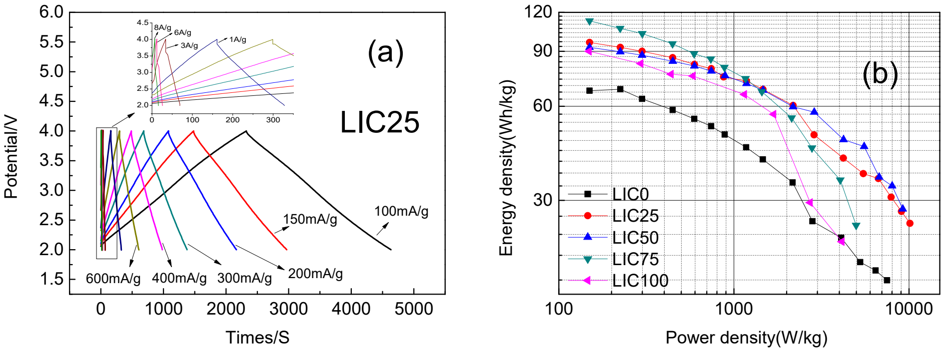

Fig.1 Galvanostatic charge-discharge curves and Ragone plots for LIC25

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Single-walled carbon-nanotube/graphene hybrid structure for all-carbon multifunctional sensors

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Sensors are of paramount importance to detect external conventional signals, but most of sensors can only monitor single signal. So recent researches have been focusing on the development of the multifunctional sensors, which can detect simultaneously multiple stimuli [1]. Single-walled carbon-nanotube (SWCNT) has been extensively investigated as a promising active material for sensors due to its high carrier mobility, large absorption coefficient, high specific surface area, etc.[2]. However, the sensitivity is limited by ultrafast recombination of carriers and poor exciton hopping ability between SWCNTs [3]. Herein, we report a new all-carbon hybrid structure based on SWCNTs and graphene. The device exhibits broadband photoresponse (405~1064 nm) with a maximum responsivity of 1.02 A/W. Meanwhile, obvious humidity responses with good stablity can also be observed when a finger (the source of humidity) was located 8 cm away from the device, and the response time is as fast as 154 ms. The all-carbon multifunctional sensors show a promising potential in future environment sensing and health monitoring.

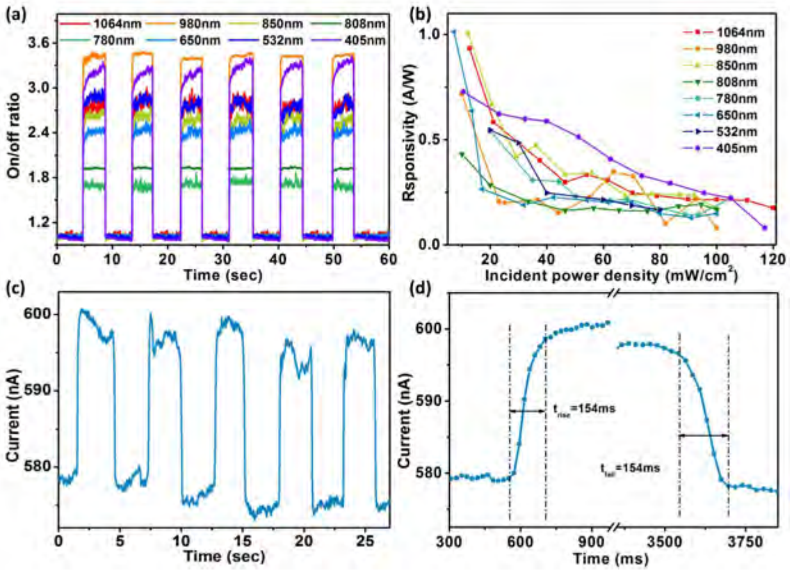

Fig.1 (a) Time-dependent photoresponse of the device operating at 0.5V (100mW/cm^2) (b) Photoresponsivity as a function of incident power density operating at 0.5V under illuminations with different wavelength. (c) Time-dependent humidity response of the device operating at -1mV and (d) One cycle measured when a finger was located 8 cm away for estimating rise time and fall time.

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Detection of Off-Resonance Single-Walled Carbon Nanotubes by Enormous Surface-Enhanced Raman Scattering

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The resonant Raman spectroscopy can only detect on-resonance single-walled carbon nanotubes (SWNTs) within the laser resonance window [1,2]. In principle, surface-enhanced Raman scattering (SERS) spectroscopy can expand the resonance window [3]. However, detection of off-resonance SWNTs by SERS remains challenging due to the difficulties in locating the SWNTs exactly at the hot spots with enormous SERS enhancements [4,5]. Here, we report a facile design of a ultrasonic spray pyrolysis method to in-situ form closely spaced polyhedral gold nanocrystals (AuNCs) on one-dimensional SWNTs [6]. The fact that the edges of the AuNCs attach to the SWNTs ensures the location of SWNTs at the hot spots. Consequently, we achieve enormous enhancements of the Raman signal of the SWNTs that are two orders of magnitude higher than any previous values. The enormous enhancements not only enable the detection of many off-resonance SWNTs but also allow the detection of several Raman bands of the SWNTs that have not been reported previously.

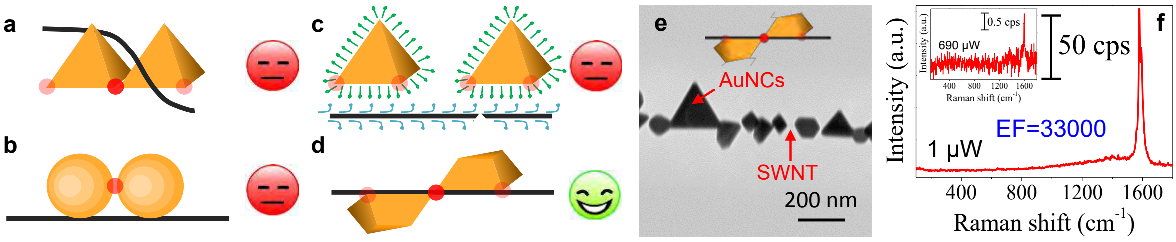

Fig.1 Schematics of SERS enhancements of SWNTs in various cases, the maximum EF and the corresponding morphology of AuNCs-SWNT.

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Photon antibunching in single-walled carbon nanotubes at telecommunication wavelengths and room temperature

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Quantum light sources, which can operate at room temperature and telecommunication wavelength band, are required for future applications of the quantum information technology. In this study, we demonstrated the quantum light generation at room temperature and telecommunication wavelength [1]. We measured the photoluminescence (PL) of individual air-suspended SWNTs over the telecommunication wavelength range and a range of temperatures. Air suspended SWNTs were grown on a line-and-space patterned silicon substrate, and the PL was measured from 6 to 300 K. We carried out photon correlation measurements with a Hanbury-Brown-Twiss setup, and observed the first photon antibunching in the telecommunication wavelength range at room temperature. This high-temperature photon antibunching can be explained by the exciton diffusion in a suspended SWNT taking into account exciton-exciton annihilation (EEA) and end quenching investigated by Monte Carlo simulation, which was recently reported [2]. We also measured spatial resolution PL mapping, photoluminescence excitation (PLE) mapping, time-resolved PL. SWNTs can open new routes for the high-efficiency single photon sources at room temperature and telecommunication wavelength [3,4].

This work was partially supported by PRESTO and A-STEP from JST, KAKENHI and Core-to-Core program from JSPS, SCOPE from MIC, the Cooperative Research Program of “Network Joint Research Center for Materials and Devices”, Spintronics Research Network of Japan, and NIMS Nanofabrication Platform in Nanotechnology Platform Project by MEXT.

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Valley Polarization of Trions and Magnetoresistance in MoS_2/YIG Heterostructures

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Abstract: Manipulation of spin degree of freedom (DOF) of electrons is the fundamental to spintronic and valleytronic devices. Two-dimensional transition metal dichalcogenides (2-D TMDCs) exhibit an emerging valley pseudospin. This valley polarization gives a DOF for spintronic and valleytronic devices. Recently, magnetic exchange interactions between graphene and magnetic insulator Yttrium Iron Garnet (YIG) have been exploited. However, the physics of 2-D TMDCs with YIG have not been shown before. Here we demonstrate strong many-body effects in a heterostructure geometry comprising MoS_2 monolayer and YIG. The electron doping density is up to ~10^{13} cm^{-2}, resulting in a large splitting of ~40 meV between trion and exciton. The trions exhibit a high circular polarization of ~80% under optical pumping by circularly polarized light at ~1.96 eV; it is confirmed experimentally that both phonon scattering and electron-hole exchange interaction to contribute to the valley depolarization with temperature; importantly, a magnetoresistance (MR) behavior in MoS_2 monolayer were observed, and a giant MR ratio of ~30% is achieved. Our experimental results confirm that the giant MR behaviors are attributed to the interfacial spin accumulation due to YIG substrates. Our work provides an insight into spin manipulation in a heterostructure of monolayer materials and magnetic substrates.

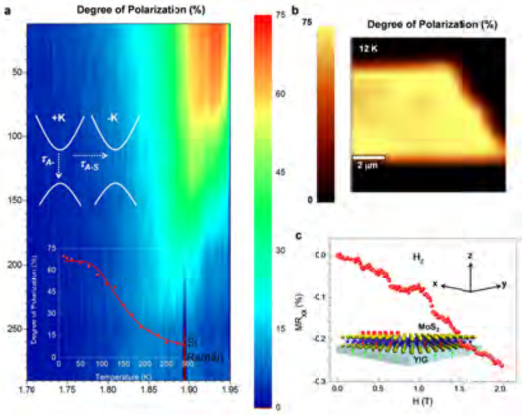

Fig 1: (a) Degree of circular polarization η as a function of temperature in the range of 1.70-1.96 eV. The insets represent the temperature dependence of η of trion and the spin relaxation. (b) The two-dimensional image of degree of circular polarization at 12 K, (c) Magnetoresistance behaviors of MoS_2 monolayer on YIG and SiO_2/Si substrates.

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Intrinsic hydrophilic character of carbon nanotube ensembles

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Carbon nanotubes (CNTs) have revealed many exciting electrical, thermal, optical and other properties. Pristine CNTs also demonstrated surprisingly high stability against the action of high temperature [1] or corrosive environments [2], which is advantageous, but becomes highly unwanted under certain circumstances. The lack of compatibility with common polymer matrices means that CNTs have to be grafted with functional groups, which often involves harsh chemicals to overcome the problem of its relatively inert surface. Is it really necessary?

We demonstrate that CNTs can be made hydrophilic for a prolonged amount of time without introducing functionalization, which can disrupt their delicate properties [3,4]. One of the steps of a recently developed method of formation of free-standing CNT ensembles [5] removes hydrocarbon contamination present on the surface, which is responsible for apparently hydrophobic character of the surface. Once it is annealed, the surface becomes very hydrophilic. With quasi-permanent water contact angle of about 30° our material is very promising for a wide range of composite applications.

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Fast metrology of floating-catalyst carbon nanotubes using array of transistors

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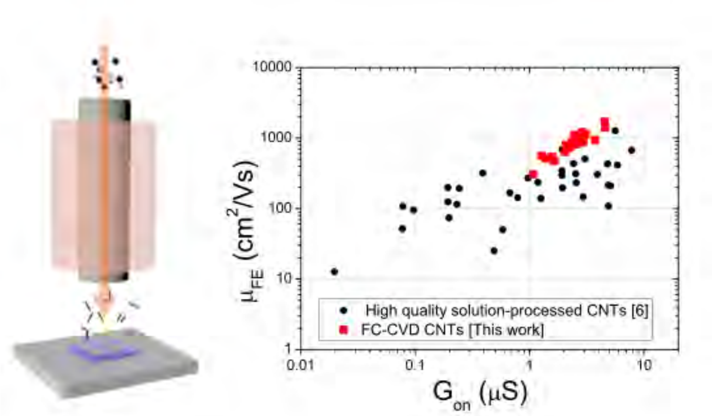

Figure 1 FCCVD CNT mobility

Carbon nanotubes (CNTs) grown by the floating-catalyst chemical vapor deposition (FC-CVD) are known to make fast thin-film transistors [1,2], however, the electronic quality of individual FC-CVD CNTs has not been clearly understood, as compared solution-processed and substrate-grown CNTs [3-5]. Here, we introduce a dry method for fabricating a statistically significant number of ultraclean single CNT field-effect transistors using FC-CVD CNTs, revealing the quality of FC-CVD CNTs with a mean field-effect mobility 3.3 times higher than that of high-quality solution-processed CNTs [6] and on-off current ratios higher than $10^{7.5}$. This method enables a fast, reliable and fine-grained inspection of FC-CVD CNT population, and provided a strong direct evidence about their near-perfect electronic quality.[7] This new understanding explains the good performance of FC-CVD CNT films and TFTs, and the obtained large number of ultraclean single-walled CNT transistors provide new possibilities to study the properties of pristine CNTs.

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Moiré pattern in encapsulated 2D materials

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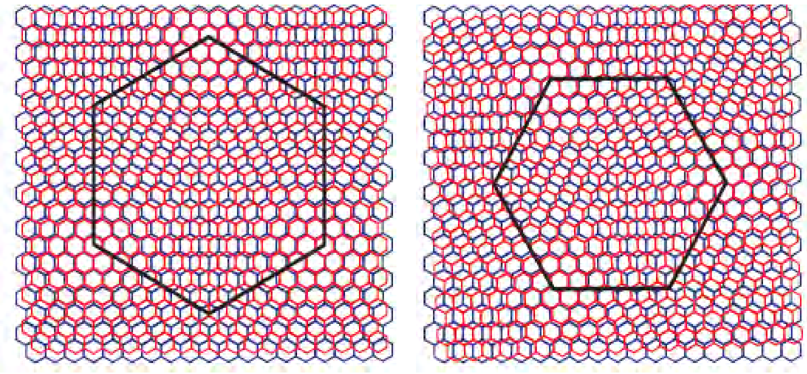
Over the last few years, graphene deposited on hexagonal boron nitride (hBN) has gained a great level of attention thanks to the unique physical properties of such heterostructures. In particular, due to the comparable lattice constants of graphene and hBN, the latter two can be aligned with respect to each, that results in the formation of a superlattice potential, also known as a Moiré pattern. Such a potential drastically affects the band structure of graphene enabling the observation of many spectacular phenomena, i.e. second generation of Dirac points[1], Hofstadter butterflies[2], Brown-Zak high temperature oscillations[3], etc.

In this work, we will present an approach that allows characterization of graphene-hBN superlattices by the atomic force microscopy (AFM). We will show that the AFM operating in the peak-force mode accompanied by the Raman measurements provides a clear visualization of the Moire potential enabling the measurements of its period and strain distribution[4,5]. Last, we will discuss dual-alignment of graphene with respect to two thick slabs of surrounding hBN as well as with an hBN monolayer.



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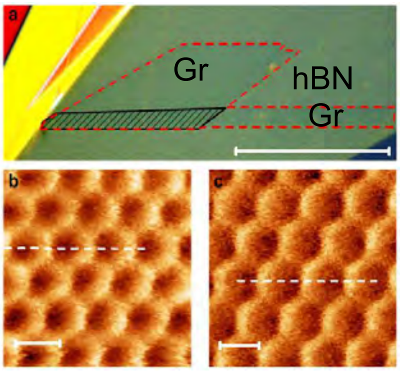

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Study of the charge transfer between molecular fillers and SWCNTs via optical methods

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Single walled carbon nanotubes (SWCNTs) have been widely investigated as platforms for sensing applications due to their high surface to bulk ratio. However, a major problem in this context is that the SWCNTs themselves are relatively inert. This explains why a considerable amount of literature has been published on increasing their reactivity and changing their physical properties in a controlled manner. Most of these studies focus on the functionalization of the outer wall of the tubes rather than using the hollow core, especially when changing the optical properties sought. Thus far, previous studies from our group have confirmed the effectiveness of filling SWCNTs with molecules such as ferrocene, nickelocene, etc, and molecular nanostructures like metallofullerenes. Molecular filling can induce a charge transfer between molecule and SWCNT, which changes the tube’s optical properties. However, this interaction is far from fully understood and the advantages or disadvantages of using certain fillers actually induce unexpected changes in the optical properties of pristine materials. In this work we have inspected hybrid nanotubes materials with different fillers via optical absorption, Raman and photoluminescence spectroscopy, since these methods are sensitive to the charging of the SWCNTs.

Observing evolution of low-energy band structure in Bernal stacked multilayer graphene: from 1 to 7 layers

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Multilayer graphene is expected to have variety of band structure depending on its number of layers and stacking structure. However, only a few of them have been studied to date. In this work we present systematic study of low-energy band structure of Bernal stacked graphene with number of layers from one to seven, by using high mobility samples. Samples are consisted of graphene which is encapsulated with a couple of thin h-BN flakes or is transferred on a thin h-BN flake. Landau level structure showed systematic evolution with increasing layer numbers as shown in Fig. 1, a mapping plot of derivative of resistance with respect to magnetic field. An even-odd layer number effect in terms of presence of monolayer band was clearly observed; a monolayer band is present only in odd layer numbers. Moreover, in more than 4 layer graphene, formations of the semi-metallic band structures are observed as Landau level crossings near the charge neutrality point. Further analysis of periodicity of the oscillation in the 1/B dependence of the resistance by using FFT, indicated that detailed feature of the even-odd layer number effect; there are n bilayer bands in $2n$ (n=1,2,3) layer graphene, and in $2n$-1 (n=0, 1, 2) layer graphene there are n bilayer bands and a monolayer band. Ratio of the carrier density in each band to the total carrier density can be uniquely determined from the band structure in principle. However, experimentally observed ratios were significantly different from those expected from the band calculations using the SWMcC parameters of graphite. The experiment was explained by calculations including potential of each layer, which is due to distribution of gate-induced carriers with screening length of about one layer. This is a direct evidence of screening effect in the multilayer graphene.

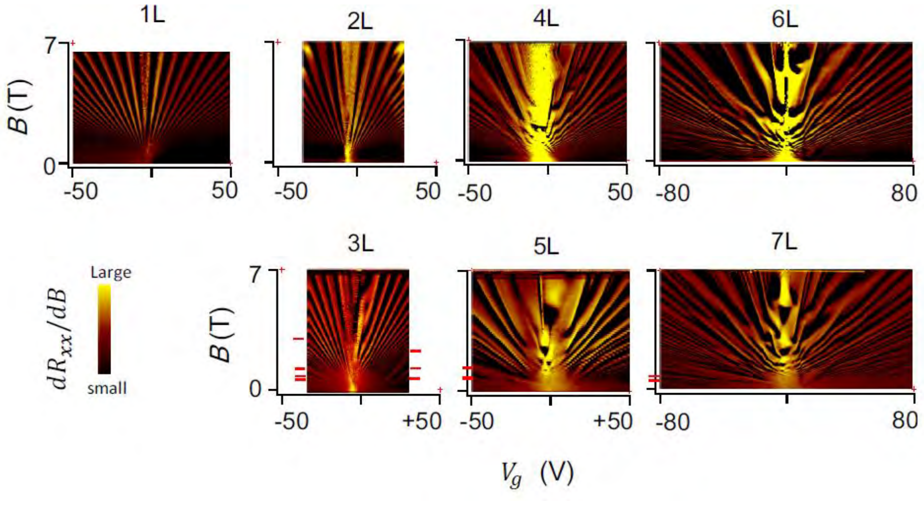

Fig 1. Mapping plot of dR_{xx}/dB of Bernal stacked graphene.

Observation of Band structure effect in carrier density dependence of dual-gated 4-layer graphene sample at zero magnetic field

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It is widely accepted that bilayer-like bands in graphene show energy gaps by perpendicular electric field, and it can been observed by spectroscopy measurements. However, in transport measurement, there has been no other methods to access this issue other than by observing insulating behavior of resistance. In this work, we show that resistivity measurement of top and bottom gate voltage dependence can clearly exhibit splitting of energy band, at zero magnetic field by using tetra-layer graphene sample which was encapsulated by using hexagonal boron nitride and dual-gated. Mapping plot of zero-field resistance with respect to top and bottom gate voltage showed clear ridge structures due to resistance peaks (Fig. 1). It is seen that a single peak at zero perpendicular electric field $(D_{\perp} = 0)$ splits into two peaks and two ridges are formed by the vertical electric field. The peaks originate from bottoms of conduction and valence bands; the splitting of the resistance peak is due to formation of energy gap. This was verified by detailed measurements of magnetoresistance. Zeromode Landau levels appeared at the same carrier densities as those of the resistance peaks at zero-field. Similar peak splittings were observed for the heavy mass bilayer band in negative carrier densities. The presently observed features generally appear in graphene with more number of layers; we have observed similar peak structures in six-layer graphene but at different carrier densities.

At the charge neutrality point of the same tetra-layer graphene sample, we also observed that the resistance grows with increasing the perpendicular electric field. This might be a precursor of the insulating behavior due to formation of energy gap by electron-electron interactions associated asymmetric potential.

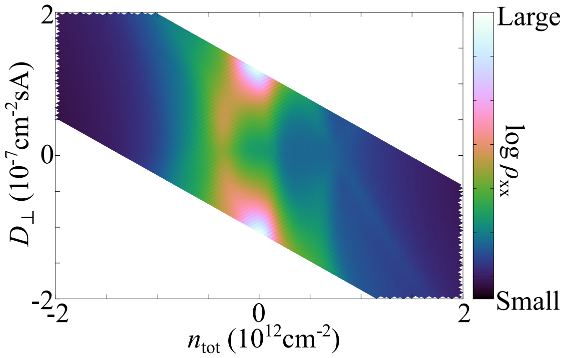

Fig. 1 Mapping plot of resistance as a function of perpendicular electric field and carrier density.

Interlayer Shear Behaviors of Bilayer Graphene

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The outstanding electrical and mechanical properties of graphene have attracted broad interests in the next-generation electronics including high-performance semiconductor technologies and flexible applications.[1] For such flexible applications that require large-area graphene films, the interfacial behavior of graphene synthesized by chemical vapor deposition (CVD) method on the supporting polymer substrates will be of most interest, such as sliding, buckling and inhomogeneous strain field that can directly influence the performance and reliability of the devices.[2,3] Here we investigate the interlayer shear behaviors of as-synthesized bilayer graphene (BLG) on flexible substrates with a reinforced interface using Raman spectroscopy. To identify the two layers for Raman detection, we used isotope labeling of 13C for the substitution of atoms in one of them, so that feature peaks from the two layers are easy to analyze. We found that AB-stacked BLG exhibits a strong interfacial stress transfer to achieve a maximum strain for the top layer is larger than 1%, whereas for the twisted BLG such interfacial stress transfer is much smaller. The interfacial shear stress of BLG was also calculated using modified shear-lag model. [3] Transferred BLG as well as other 2D material heterojunctions are also investigated. This work can provide new insight into the mechanical behaviors of graphene as well as valuable guidance for designing graphene-based flexible electronics.

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Synthesis of highly electrical conductive SWCNT Fiber by a simple and scalable wet-spinning method

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Single-wall carbon nanotubes (SWCNTs) have ultrahigh strength, high electrical conductivities, high thermal conductivities and mechanical property, and high specific areas which allow for a wide range of potential applications such as multifunctional fabrics, composites, structural fibers, and devices[1-2]. The fabrication of SWCNTs into a continuous multifunctional CNT yarn is an important step towards these macroscopic applications. However, how to obtain highly conductive SWCNT yarns with a simple and scalable method still remains a big challenge. In this work, we prepared a highly conductive SWCNT fiber using a scalable and simple wet-spinning method [3] by selection high quality SWCNTs synthesized by a floating catalyst chemical vapor deposition method as raw material [4]. The obtained fiber exhibit excellent electrical conductivity of 1.36×10^5 S/m conductivity, which can reach to 2.30×10^5 S/m after annealing at temperature of 100-350℃. The electrical conductivity of the SWCNT fiber further increase to 4.22×10^5 S/m by immersing the fiber in 0.5mM iodine solution.

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Multifunctional graphene aerogel-poly (methyl methacrylate) composites: Experiments and modeling

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Graphene aerogel (GA)-poly(methyl methacrylate) (PMMA) composites are developed by infiltrating PMMA precursor into the pores of the GAs. Due to the pre-formed porous network of GAs, the as-prepared GA-PMMA composites possess uniform distribution of multilayered reduced graphene oxide (rGO) in the PMMA matrix. Electrical, mechanical and thermal properties of the GA-PMMA composites are comprehensively studied by two-probe, microindentation and comparative infrared techniques, respectively. As graphene loadings increase from 0.67 to 2.50 vol.%, the composites exhibit significant enhancements in their electrical conductivity (0.16-0.859 S m^{-1}), microhardness (303.6-462.5 MPa) and thermal conductivity (0.35-0.70 W m^{-1} K^{-1}), which are superior compared to that of the neat PMMA matrix and the graphene-PMMA composites prepared *via* traditional dispersion methods [1-2]. Thermal boundary resistance (TBR) between rGO and PMMA is estimated to be 1.906×10^{-8} m^2 K W^{-1} by an off-lattice Monte Carlo algorithm [3]. This novel fabrication method for the GA–PMMA composites may effectively solve the dispersion issue of graphene (or CNTs) in polymer matrix, and also offer a facile approach for the preparation of various filler-matrix composites with multifunctional capabilities. This developed model offers an easily accessible approach to accurately predict the thermal conductivity of the graphene–polymer composites and effectively estimate the TBR at the graphene–polymer interfaces.

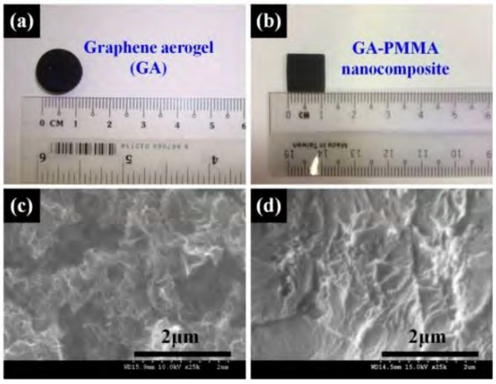

Fig.1 Digital images and SEM images of (a, c) the unfilled GA and (b, d) the GA-PMMA composite.

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Electrical Characterization of Ion Gel and Its Application on MoS_2 Field Effect Transistors

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Ion liquid has attracted much interest as a gate stack since high carrier density can be induced with relatively small operating voltages as it forms electric double layer on the interface. Ion gels prepared by mixing a host polymer and ionic liquid are garnering interests as an effective gate stack, especially for flexible devices thanks to its mechanical stability.

In this study, electrical properties of an ion gel consisting of Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide([EMIM][TFSI]) as a candidate for a gate stack for MoS_2 field effect transistors (FETs) are investigated. Ion gels with different ratio of the host polymer and ionic liquid are prepared and their capacitance and impedance in the side gate geometry are measured to assess the optimal condition for a gate stack. An equivalent circuit model is also developed, which fits the experimentally obtained frequency-dependent impedance well. The ion gel is utilized as a gate stack for FETs based on mono to few layer MoS_2 which are grown by chemical vapor deposition. The high carrier density induced by low operating voltages using an ion gel gate stack makes it possible to investigate both hole and electron transports of MoS_2 FETs with different number of layers. The response and stability of FETs with ion gels are also investigated for possible flexible electronics applications.

Synthesis and Optoelectronic Characterizations of MoS_2-Single Walled Carbon Nanotube Hybrids

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The nanostructure hybrids of low dimensional nanomaterials have attracted great attention as they offer new or improved functionalities for future optoelectronic applications. In this study, we focus on the hybrids of two-dimensional transition metal dichalcogenide (2D-TMDC) and one dimensional (1D) materials, in particular, MoS_2 with single walled carbon nanotubes (SWCNTs). The hybrids are obtained by either *in situ* chemical vapor deposition or transfer of MoS_2 on individual SWCNTs. The morphology and quality of as-synthesized hybrids were examined by atomic force microscopy (AFM) and Raman measurements. The devices based on the hybrids reveal different transfer characteristics depending on the formation of MoS_2 conduction channels along SWCNTs. Upon exposure to visible light, negative photoresponse originating from charge transfer from MoS_2 to SWCNT is observed while common positive photoresponse is observed in MoS_2 conduction channels, leading to ambipolar photoresponse in devices with both SWCNT and MoS_2 channels. In addition, the devices also exhibit high responsivity (~1000 AW^{-1}) at low bias voltages (0.1V) at visible range by combining high mobility conduction channel (SWCNT) with efficient light absorbing material (MoS_2). Temporal response of photoresponse and its improvements will be also discussed.

Relationship between mobility and Raman spectra for CVD Graphene on exfoliated h-BN

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Kenji Watanabe[2], and Masataka Hasegawa[1]

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Extremely high mobility of exfoliated graphene on h-BN was reported [1,2]. From the application point of view, it is considered that CVD graphene is appropriate material [3]. However, scatter in mobility of CVD graphene is one of the remaining problems [4]. In order to realize applications using CVD graphene, it is necessary to understand the origin of scatter in mobility of CVD graphene. In this study, we fabricated the four terminal devices of CVD graphene on exfoliated h-BN and evaluate the relationship between field effect mobility and Raman spectra.

Thermal CVD graphene on Cu foils were transferred on the exfoliated h-BN using PMMA as a support material [5]. Then, four terminal devices with back gate were fabricated using electron beam lithography. Electrical properties were measured at room temperature in vacuum (under 10^{-2} Pa), and field effect mobility was calculated from transconductance from I_D-V_{GS} characteristics. Intensity ratios between 2D and G (I_{2D}/I_G) were obtained from the Raman spectra of the graphene channels. Figure 1 shows relationship between calculated electron mobility and I_{2D}/I_G. An increase in I_{2D}/I_G corresponds to an increase in electron mobility, in which electron mobility excesses 20,000 cm^2/Vs with high I_{2D}/I_G (~8). To understand these results, we are currently investigating the surface morphologies of graphene channels since the surface morphologies affect the electrical properties was reported [6].

This report is partially founded by the New Energy and Industrial Technology Development Organization (Grant No. 16010). The four terminal devices were fabricated at the AIST Nano-Processing Facility, which is supported by the IBEC Innovation Platform.

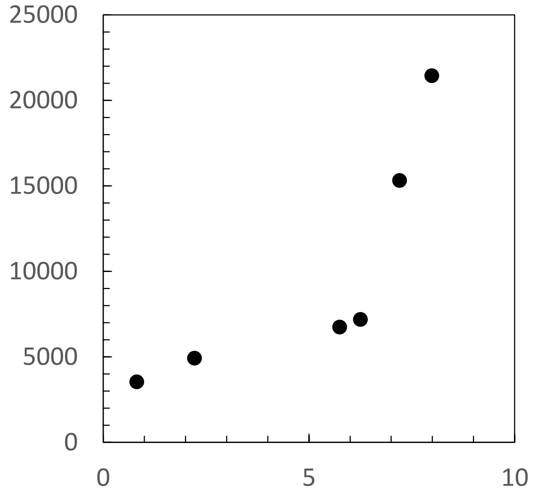

Fig.1. Field effect mobility vs I_{2D}/I_G

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Optical Actuator Made by Single Carbon Nanocoil

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Carbon nanocoils (CNCs), with unique helical morphology and chiral features, are considered as super nanosprings with excellent mechanical [1], electrical [2] and thermal properties [3]. CNCs have been studied for force measurement sensor [4] and wearable devices [5].

Traditional understanding of nanowire mechanics comes from attaching nanowires to the probes used in atomic force microscopy for direct force measurements. However, such progress has been hampered with one-at-a-time device fabrication and the inability to exert arbitrary controlled forces. Optical manipulation on those micro/nano scale structures opens up new possibilities for assembly and control of micro/nano electromechanical systems without direct mechanical contact and damage. A single CNC cantilever was stimulated to vibrate steadily under a periodic square wave laser in air, as shown in Fig.1. A fitting formula to describe the frequency response of the laser-induced vibration was deduced based on a classical continuum model, from which the resonance frequency of the CNC can be determined directly and accurately. This laser-induced vibration method could be widely used in stimulating quasi-1D micro/nano rod-like materials, and has potential applications in micro/nano opto-electromechanical systems.

This study was supported by the National Natural Science Foundation of China (No. 51661145025, 11274055).

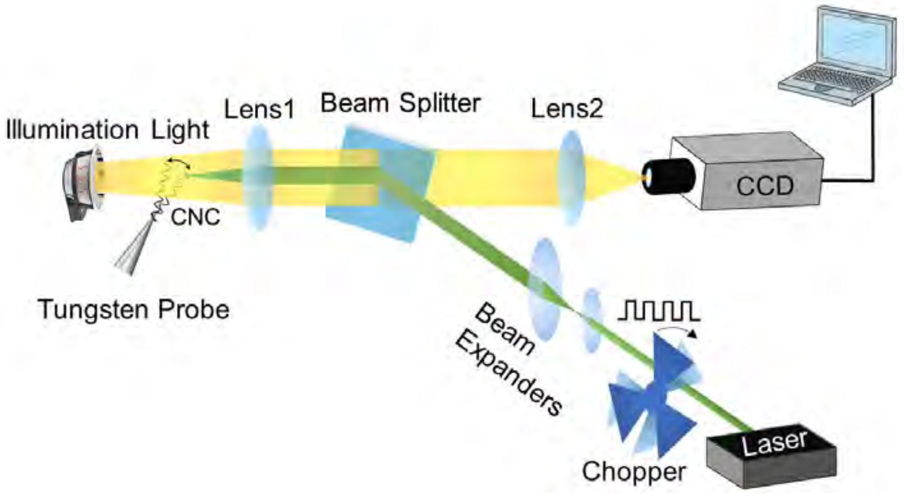

Fig.1 Experimental schematic for observing, stimulating and measuring the CNC vibration.

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Ampacity and Failure Mechanisms of CVD-spun CNT Fibres and PAN-based Carbon Fibres

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Fibres made of carbon nanotubes are materializing as a viable technology to produce lightweight, flexible, and chemically resistant electrical conductors. These “wires” would potentially carry higher current loads than copper, on a per weight basis, and would be particularly suited for applications in harsh environments such as overhead and undersea power transmission lines.

We used a cyclic current ramping protocol to determine the maximum electric current density that CNT fibres, produced from different carbon sources by a continuous floating-catalyst CVD method [1], can withstand before undergoing permanent damage – a parameter broadly known as ampacity but more precisely named specific failure current density (SFCD) – in air and vacuum. For comparison purposes, we carried the same experiments on commercially available PAN-based carbon fibres. The failure points of the fibres were thoroughly examined with a scanning electron microscope (SEM) and a simple finite-element multiphysics model was used to predict the temperature profiles of the samples.

Qualitatively, resistance vs current behavior of the CNT fibres is strongly dependent on the atmosphere in which they are tested and (almost) independent on the carbon precursor used to spin them. Contrary to the wet-spun fibres studied by other groups [2], our fibres exhibit higher SFCDs in vacuum than in air. Despite being more resistive than either material, direct-spun CVD fibres have higher SFCDs than wet-spun fibres and copper. Our results suggest that, with some improvement on the specific conductivity, our material may be an ideal replacement for copper in applications requiring high ampacity, mechanical strength, and corrosion resistance.

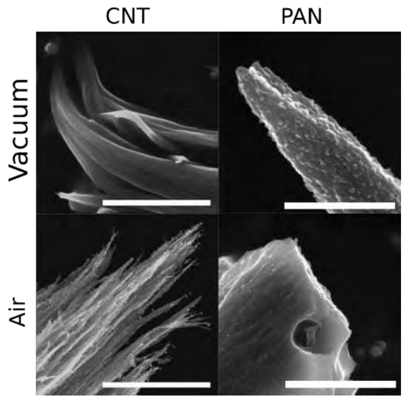

Fig.1 Comparison of the failure surfaces of CNT and PAN after current overload in vacuum and air. All scale bars represent 1 μm.

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Tuning of the Thermoelectric Properties of High-Purity Single-Chirality (6,5) Single-Walled Carbon Nanotubes by Electrolyte Gating

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One-dimensional materials have potential to exhibit extremely high thermoelectric performance [1]. One of suggested approaches to achieve the high thermoelectric performance is to tune the Fermi level of the 1D materials with sharp van Hove singularity (vHS). Single-walled carbon nanotubes (SWCNTs) are a model for 1D system with sharp vHS, and thus we can investigate how the location of Fermi level influences their thermoelectric properties. Previously, we have investigated the thermoelectric properties of SWCNTs as a function of Fermi-level using an electrolyte gating technique [2]. However, the observed relationships between the Fermi level and the Seebeck coefficients of semiconducting SWCNTs were not in agreement with theoretical predictions. It is suggested that even a small amount of impurities (~1%) affects the thermoelectric properties [3]. Recently, we established a separating technique, which controls pH of solutions using CO2 bubbling in gel-column chromatography, to obtain extremely high-purity single-chirality SWCNTs (6,5) with purity of more than 99% (Fig.1) [4]. Therefore, in this study, we investigated the relationships between thermoelectric properties and location of Fermi levels of high-purity single-chirality SWCNTs.

As shown in Fig.2, we found very large Seebeck coefficient (above 1mV/K), which is about 10 times larger than previous reported values. We found that the improvement of semiconducting SWCNTs purity strongly enhances the film thermoelectric properties.

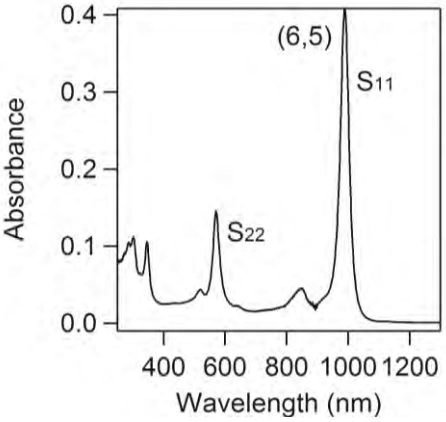

Fig.1 Optical absorption spectrum of (6,5) SWCNTs.

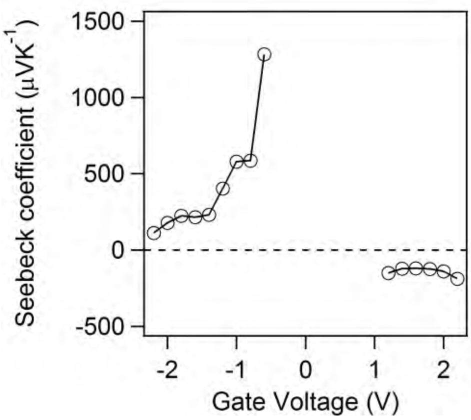

Fig.2 Seebeck coefficient of (6,5) using electrolyte gating.

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Evaluation of electrical conductivity in turbostratic multilayer graphene thin films synthesized from CVD graphene

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Turbostratic multilayer graphene with the relatively weak interlayer coupling between layers preserve both high mobility and conductivity because the band structure of the turbostratic multilayer graphene shows linear dispersion similar with a monolayer graphene. Therefore, this material is a promising candidate for electrical devices. In previous publication, we demonstrated that the additional graphene layers were grown on the mechanically exfoliated graphene template using the chemical vapor deposition (CVD) method with ethanol [1]. Unfortunately, the typical size of the graphene template is limited to several tens of nanometers, and it is an important subject to scale-up for the evaluation and device application of synthesized multilayer graphene. In this work, turbostratic multilayer graphene was grown on large area synthesized CVD graphene template.

The monolayer graphene used as template was synthesized on copper by CVD method and then was transferred to fused quartz. The growing temperature is 1300ºC using the infrared heating furnace. Figures 1(a) and 1(b) show the Raman spectra observed from grown multilayer graphene. The peak shape in the 2D-band region associated with stacking structure can be fitted by one large and two small Lorentz functions. The large Lorentz function indicates the formation of turbostratic structure in synthesized multilayer graphene [2]. Figures 2(a) and 2(b) show an optical and atomic force microscope (AFM) images of the synthesized multilayer graphene channel fabricated by the conventional lithographic method. From the height profile analysis along L-L’, the film thickness of synthesized multilayer graphene is known to be about 8 nm, which indicates about 22 graphene layers. The sheet resistance of our samples is evaluated to be around 200 Ω/□. As a comparison, non-defect monolayer graphene’s sheet resistance is around 360-1,000 Ω/□ [3]. This result means that the electrical performance of graphene sheet is improved by multilayer stacking using our growth method.

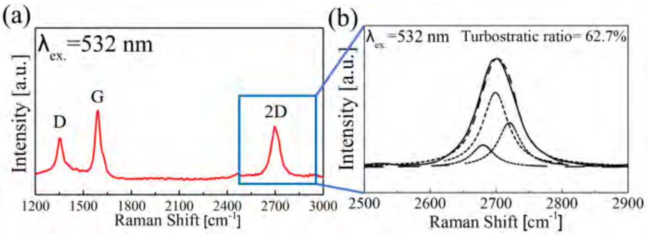

Fig.1 (a) Raman spectrum of the multilayer graphene grown on CVD graphene template. (b) Analysis of the stacking structure of the multilayer graphene. The solid and dash lines indicate the experiment and fitting curve using Lorentz functions, respectively.

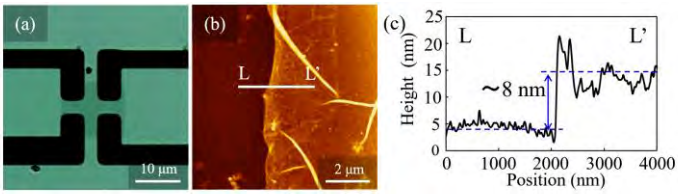

Fig.2 (a) Optical image of graphene with electrodes. (b) AFM image of the edge of graphene channel. (c) Height profile along L-L’ line.

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Photon Reabsorption Effect on Resonance Raman Spectra of Single-Wall Carbon Nanotubes

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Photon reabsorption effects are well known and commonly observed in photoluminescence measurements for many kinds of materials. In the case of single-wall carbon nanotubes (SWCNTs), however, this effect is very important because of their very small Stokes shift between E_{11} absorption and emission wavelength. This effect often leads to an unexpected underestimation in intrinsic spectral intensity because the experimentally observed intensity does not correspond to the intrinsic intensity [1]. Recently, we have reported photon reabsorption effects on the photoluminescence quantum yields using chirality sorted SWCNTs. In this work, we investigated the photon reabsorption effect on the resonance Raman spectra of chirality sorted SWCNTs.

In the case of photoluminescence, we observed nonlinear decrease of the apparent emission intensity with increasing SWCNT concentration, which could be fully explained by the reabsorption effects. In the case of resonance Raman measurement, because frequency shifts of radial breathing mode (RBM) and G-band are largely different, we observed a vibration mode dependent photon reabsorption effects in the resonance Raman intensity. This effect is relatively weaker than that for photoluminescence but is more complicated due to the vibrational mode dependent nature. Importantly, RBM/G intensity ratio varies as a function of concentration of SWCNTs. This effect strongly affects the quantitative evaluation of the specific (n,m) species abundance in the as-grown mixture or even (n,m)-sorted samples. Detailed results will be given in the presentation.

This work was supported by KAKENHI No. JP25220602, the National Natural Science Foundation of China (Grant No. 11634014), and “100 talents project” of Institute of Physics.

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Experimental and Theoretical Study of the Surface State of Carbon Nanopot

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Carbon nanopot, a novel material developed recently [1], is a pot-shaped material composed with multi-layered graphene sheets, and is produced in series to form fibers (nanopot fibers). The typical size of carbon nanopot is 20-40 nm in diameter and 100-200 nm in length. Its narrow and deep mesopore is closed on one end, which suggests that this material could be applied as nano-container. It has been revealed through high-resolution TEM studies that carbon nanopot consists of several parts including a multi-wall CNT like part and a tapered part where graphene edges are exposed and distributed densely. We expect that the densely localized graphene edges could be a distinguished feature of carbon nanopot from the viewpoints of the study of its fundamental properties and the development of its applications.

In this study, we have conducted XPS, KFM, electric transport measurements, and ab initio calculations to investigate the surface state of carbon nanopot. XPS studies suggested that the graphene edges may be terminated by hydroxyl groups. In KFM observations, the surface potential varied by about 7 mV between the ends of nanopot and the middle of the tapered part. DFT calculations for simplified nanopot-like structure models clarified that the partial charge densities corresponding to HOMO levels in zigzag-edged structures with OH-termination were in line with the surface potential distribution mentioned above, in contrast to those with unterminated or H-terminated ends, or any armchair-edged structures examined. These results suggest consistently that the graphene edges in carbon nanopot are dominantly the zigzag-type with OH-termination, and exposed in the tapered part densely. In the transport measurements, we observed that the resistance of carbon nanopot decreased by 30% approximately through evacuation from the atmosphere. This behavior implies that the surface state could be not only modified by the physisorption of molecules largely but also related to the electronic property of carbon nanopot itself firmly.

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Charge transport through graphene-like conjugated molecules at the single-molecule scale

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Molecular electronics targets the application of functionalized molecules as novel building blocks in electronics circuits. To reach this goal, understanding of charge-transport through the single molecule comprises an essential prerequisite. Due to the unique electric performance, the π-conjugated molecules is valuable for the molecular electronic. We present the mechanical controllable break junction (MCBJ) technique to collect the charge transport information of the single molecules.

The graphene-like molecules, anthanthrene owns a fused π-system with an intense molar extinction coefficient and a high photoluminescence quantum yield, which is an excellent component in photoelectric device. We prepared the graphene-like aromatic molecules (1 and 2), and studied the charge transport though the molecular. Both the experimental and theoretical studies demonstrate a new magic ratio rule, clarifying the correlation between the connection points and the electric conductance. The conductance rule would provide reference for the molecular design based on targeted application in nanoelectronic devices.[1]

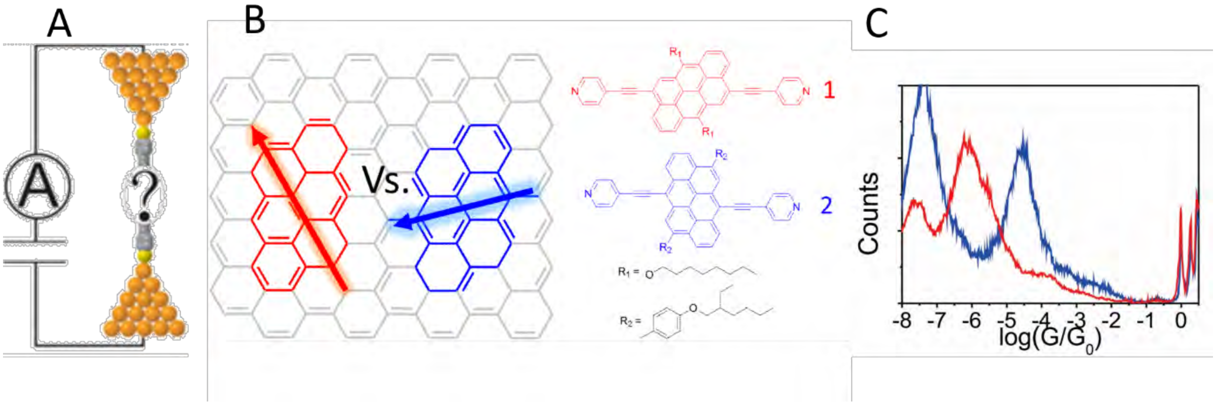

Fig.1 A) graphic of the molecular junction in MCBJ; B) graphene-like molecules with different charge transport pathways; C) conductivity of the molecules, blue is for molecule 2 and red for molecule 1. G_0 is the quantum conduction.

[1] C. Huang et al. *J. Am. Chem. Soc,* 137(35):11425–11431 (**2015**)

Shaping a single electron in a nanotube with a parallel magnetic field

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Transport measurements on single wall carbon nanotubes allow fascinating insights into the interplay of molecular structure and electronic wave functions. Here, we analyze the magnetic field behaviour of quantum states in the limit of a single electron strongly confined to a quantum dot [1]. An axial magnetic field (in the experiment up to 17T) exposes a very distinct behaviour of the two valleys. K' valley states experience an increase of the tunnel coupling at low field, followed by subsequent decoupling. In contrast, K valley states decouple from the leads monotonically.

We show that this phenomenon stems from the unique combination of cylindrical topology and bipartite atomic lattice. Longitudinal and transversal momentum are coupled, allowing manipulation of the longitudinal electronic wave function via the Aharonov-Bohm phase. At zero field, the nanotube acts similar to a “quarter wavelength resonator”, where a wave function amplitude is finite near one of the contacts. A large magnetic field restores quantum box behaviour comparable to a “half wavelength resonator”, where the amplitude vanishes on both sides. This is directly reflected in the tunnel rates.

As the impact of wave function tuning is not limited to tunnel rates and the conductance, but affects all electronic parameters, an axial magnetic field proves to be an even more versatile tool than already known.

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Rotation of Polarization by Aligned Multiwall Carbon Nanotubes

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Oriented carbon nanotube (CNT) sheets absorb polarized light anisotropically. The highest absorption is when light is polarized parallel to the CNT alignment direction and it is minimum for perpendicular polarization and the difference between the absorptions along the two directions gives the anisotropic absorption (ΔA) of the CNT sheets, related to the orientational order of the nanotubes [1]. Oriented multi-walled carbon nanotubes (MWNT) sheets created by dry-drawing of spinnable CNT forests [2] have been shown to be transparent electrode and alignment layer for liquid crystal display devices [3]. In the study of the integration of CNTs in liquid crystal display (LCDs) cells, it is important as first step to investigate the interaction between CNTs and polarized light, used in the ordinary LCDs operations. In our experiments we observed that light, after travelling through the aligned CNT sheets, rotates its polarization as shown in figure 1. For a single layer of CNT sheets, deposited on glass substrate, ~4° rotation of polarization was measured. We believe that this phenomenon is mainly due to the anisotropic absorption of CNTs. Our theoretical model based on the principal absorption values also supports that the rotation of polarization is induced by the anisotropic absorption of CNTs. The results of this study help gaining a better understanding of the optical properties of CNTs on substrate for potential applications in optical systems.

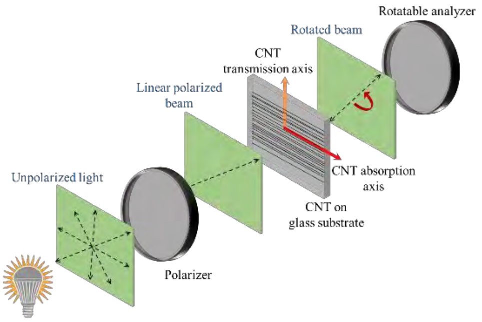

Fig. 1 Schematic of rotation of polarization of light by aligned CNT sheets

[1] M. A. Rahman *et al.* Photonics Lett Of Pol, **9**, 26-28 (2017).

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Exciton Energy Transfer between Different (*n*, *m*) Single-Wall Carbon Nanotubes Probed by Photoluminescence

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Exciton energy transfer often occurs in the photoluminescence of semiconducting single-wall carbon nanotubes (SWCNTs) if the individual nanotubes are existing as bundles [1, 2]. However, it is unclear that whether exciton energy transfer occurs in the photoluminescence of structure-sorted semiconducting SWCNT solution, in which most of nanotubes are usually considered to be highly suspended. This is very important for quantitatively evaluating the abundance and the content rate of specific (*n*, *m*) species.

In this work, we investigated the exciton energy transfer between different (*n*, *m*) SWCNTs using (*n*, *m*)-sorted samples by gel chromatography method [3-5]. To reduce the tube-tube distance and thus induce the exciton energy transfer, we added an equal amount of solution with high SWCNT concentration of (9, 4) SWCNTs (E_{11} absorbance is about 2 for optical path length of 10 mm) into the target (6, 5) solutions with the same but low SWCNT concentration (E_{11} absorbance is about 0.1). After measuring the photoluminescence of each mixed solution, we found that the photoluminescence intensity derived from (6, 5) SWCNTs for the mixed solutions significantly decreased compared with the (6, 5) reference solution with the same concentration. This decrease could be explained by the exciton energy transfer of (6, 5) SWCNTs in solution. Importantly, we replaced (9, 4) solution by (10, 3) solution with the same E_{11} absorbance, and then observed a more significant decease for (6, 5) photoluminescence intensity. One of the possible explanations is that the excitons are easier to transfer from (6, 5) to (10, 3) SWCNTs because the difference in the band gap between (6, 5) to (10, 3) is larger. Detailed results and analysis will be given in the presentation.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51472264, 11634014), the Key Research Program of Frontier Sciences, CAS, Grant No. QYZDB-SSW-SYS028, and “100 talents project” of Institute of Physics.

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[3] H. Liu *et al.*, *Nature Commun.* **2**, 309 (2011).

[4] Y. Yomogida *et al.*, *Nature Commun.* **7**, 12056 (2016).

[5] X. Wei *et al.*, *Nature Commun.* **7**, 12899 (2016).

Electrochemical properties of graphene aerogels loaded in nickel foam

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Graphene aerogel (GA) and the composite of graphene aerogel/nickel foam (GA/NF) were prepared by an improved hydrothermal procedure[1,2] followed by freeze drying, respectively. The electrochemical capacitance performance of GA/NF and GA was investigated with cyclic voltammetry and galvanostatic charge/discharge measurements. GA/NF exhibited a specific capacitance of 217 F/g at 1.0 A/g and 191 F/g at 10.0 A/g. In contrast, GA exhibited a specific capacitance of 168 F/g at 1.0 A/g and 148 F/g at 10.0 A/g. After cycling 2000 times in 6 mol / L KOH electrolyte, the cycle performance of GA / NF and GA maintained 92% and 88% of the original capacitance. Therefore, GA/NF has advantages over GA in much higher specific capacitance and in better recycling stability.

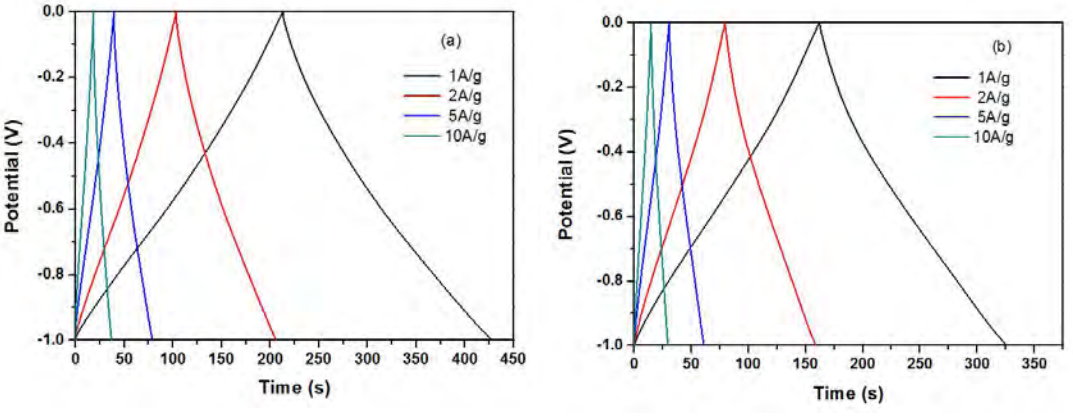

Fig.1 The charge/discharge curves of GA/NF (a) and GA(b) electrodes at current densities of 1, 2, 5, and 10 A/g, respectively.

[1] Wan, Wenchao; Zhang, Fei; Yu, Shan, et al. New Journal of Chemistry, 40,3040(2016)

[2] Gigot, Arnaud; Fontana, Marco; Pirri, Candido Fabrizio, et al. Materials 11, 57 (2018)

High-harmonic generation of THz light in single-wall carbon nanotubes

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High-power laser source in terahertz (THz) region enables us to investigate high-harmonic generation (HHG), which is one of the unique phenomena in extreme nonlinear optics [1]. HHG of intense THz light has been observed in various kinds of materials, such as semiconductor crystals (ZnO [2], etc.) and two-dimensional materials (graphene [3], MoS_2 [4], etc.) But the essential feature of HHG in solid has still been elusive, while that of HHG in atomic gases is well-known, because of the presence of various physical parameters in solids affecting nonlinear processes.

To tackle with this problem, we try to investigate HHG in single-wall carbon nanotubes (SWCNTs) for the following reasons. SWCNTs have the unique one-dimensional structure and are mechanically and chemically very stable for strong THz light, and we can systematically change electronic structure of SWCNTs from gap-less metallic to semiconductor with different band-gap. Therefore, we assumed we can clarify how the electronic structure of SWCNTs influences HHG.

We prepared SWCNT thin films with systematically different electronic structures and investigated HHG of 62.5 THz laser. The type of SWCNTs is metal, semiconductor (diameter is 1.4nm), semiconductor (diameter is 1.0nm), and single-chirality (6,5).

The results are shown in Fig.1. We observed HHG from (6,5) and semi. (1.0 nm), and slight 5th HHG from semi. (1.4 nm), but didn't find any HHG from metal. These results indicate that electronic structure of samples strongly influences on HHG. In this poster, the physical background of HHG from SWCNTs will be discussed.

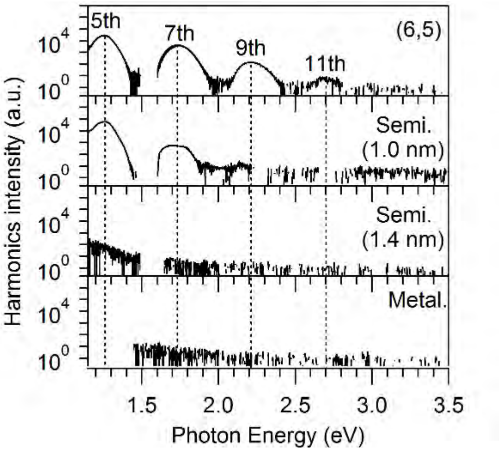

Fig.1 HHG spectra in a series of SWCNTs

[1] K. Tanaka, Hikaribussei kenkyukai tutorial (2017)
[2] S. Ghimire *et al.,* Nature Physics, **7**, 138 (2010)
[3] N. Yoshikawa *et al.*, Science **356**, 736 (2017)
[4] H. Liu *et al.,* Nature Physics, **13**, 262 (2016)

K.Y. acknowledges support by JSPS KAKENHI through Grant Numbers JP17H01069.

Photo irradiation effects on luminescence dynamics in graphene oxide

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Graphene oxide (GO) is a one of attractive material for new electronic and optical device. In this study, we have studied luminescence dynamics and its photo irradiation efects.

Figure 1 shows the luminescence spectra of GO before and after photo irradiation. Broad luminescence bands are observed for both samples. This luminescence band is considered from the electronic transition of the nanodisk like graphene region in GO[1]. After photo irradiation the luminescence intensity decreases, and the peak energy shifts to the lower energy side. It is well known that the photo irradiation makes reduction of GO, and it causes the increase of graphene region. The energy shift to lower energy side can be explained by the increase of nanodisk size.

Time-resolved photo luminescence (PL) measurements were carried out using streak camera. Decay behavior of PL could be reproduced with two component exponential function. Figure 2 shows photon energy dependence of luminescence decay time of GO before and after photo irradiation. The decay time becomes shorter with higher energy side. After photo irradiation, the decay time is shortened and photon energy dependence is decreased as indicated by open triangles in Fig. 2. These results suggest that the photo irradiation makes the increase of both nanodisk size and defects in graphene region as trapping sites for excited carriers.

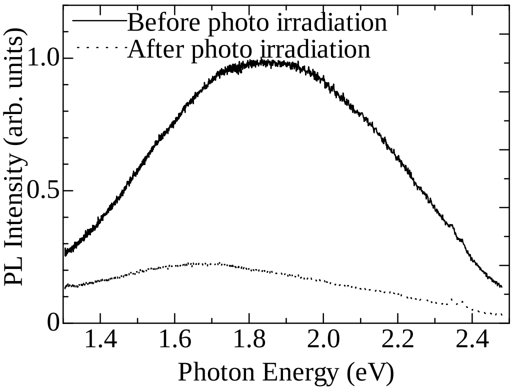

Fig.1 luminescence spectra of graphene oxide

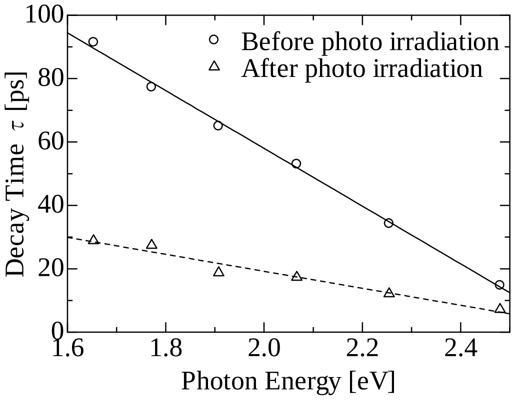

Fig.2 Photon energy dependence of luminescence decay time of graphene oxide

[1] D. Kozawa *et al.*, J. Phys. Chem. Lett. 5, 1754 (2014).

Imaging Local Conductance Changes in Nanomaterials using Electrostatic Force Microscopy

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Electrostatic force microscopy (EFM) can be used to investigate local conducting state of nanomaterials and monitor its evolution with high spatial resolution. In this study, we applied EFM to study evolution of local conducting states in graphene oxide (GO) and VO_2 nanorods. For many applications, GO is typically reduced thermally or chemically to recover electrical conductivity. With EFM, we identify isolated conducting regions in the initial GO and monitor the reduction process at different temperatures. In the same way, we also monitor the metal-insulator transition (MIT) of VO_2 nanorods and thin films. Unlike previous studies using Kelvin Probe Force microscopy (KPFM) which measures local work functions, EFM signals can be directly correlated with the local conductance. Therefore, we could observe the MIT of the VO_2 nanorods at the transition temperature as a function of time, which shows the growth of metallic domains at the phase transition temperature. These local changes will also be compared with the global conductance changes in IV measurements.

Temperature-dependent electroluminescence of carbon nanotubes

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2. Technical University of Darmstadt

Electrically-driven semiconducting carbon nanotubes (CNTs) can be scalably integrated into versatile nanophotonic circuits and demonstrate narrow-line, ultra-fast emission at adjustable wavelength in the telecom band [1]. Moreover, at cryogenic conditions CNTs can act as non-classical light emitters with electrical drive [2]. However, the spectral characterization of electroluminescent CNT-emitters was performed so far only at room temperature. Here, we present the first electroluminescent studies on individual CNTs in the broad temperature range from 4K to 400K. At cryogenic conditions, electroluminescent CNTs show the narrowest emission and the highest device efficiency observed so far [3].

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[2] S. Khasminskaya, F. Pyatkov, *et al.* Nature Photonics **10**, 727 (2016).
[3] M. Gaulke, F. Pyatkov, *et al.* (in preparation).

Highly Conductive and Transparent Single-walled Carbon Nanotube Film Fabricated by Floating Catalyst Chemical Vapor Deposition using Ethanol as Carbon Source

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Single-walled carbon nanotube (SWCNT) films have a great potential to replace indium tin oxide films for applications in transparent and conductive electronics. Here we report SWCNT transparent conducting films (TCFs) fabricated by floating catalyst chemical vapor deposition method (CVD) using ethanol as carbon source. Ethanol [1,2] is selected as carbon source since it has not been employed for the direct fabrication of SWCNT TCFs from a floating catalyst CVD reactor. The fabricated SWCNT TCFs exhibit low sheet resistances of 78 Ω/sq. at 90% transmittance (Fig. 1). Meanwhile, various characterizations, including diameter and length of SWCNT bundles, are performed to elucidate the causes of the excellent optoelectronic performance of our SWCNT TCFs. It turns out that clean, long and narrow bundled SWCNTs are synthesized. Depicting chirality maps of SWCNTs by analyzing statistically counted electron diffraction patterns is the most significant part, which fills the gap in chirality distribution of SWCNTs. Our study provides fundamental basis to SWCNT research, and highlights the potential of SWCNT TCFs to be extensively applied in high performance flexible electronics.

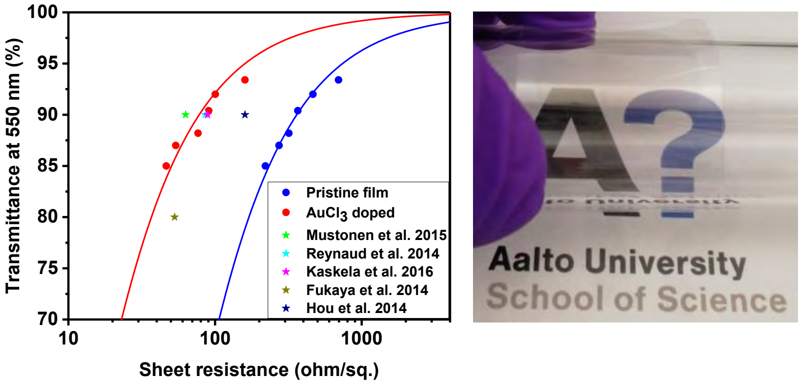

Fig. 1 Comparison of optoelectronic performance of our SWCNT TCFs and other recently reported TCFs produced using the same method.

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Experimental and computational study of interlayer interaction effects on the high-frequency Raman features of double-walled carbon nanotubes

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In this communication, we report on the experimental and computational study of the effect of interlayer interactions on the high-frequency Raman features (G and 2D modes) in individual index-identified free-standing double-walled carbon nanotubes with different electronic configurations (SC@SC, SC@M, M@SC, M@M). The interactions between the layers of DWCNTs induce a measurable shift of the G bands relative to the isolated layers, which has been previously reported experimentally [1,2]. Here we present the computational study of this G-band shift as a function of the semiconducting inner layer radius and interlayer separation (Fig. 1) [3]. We find that with increasing interlayer separation, the G band shift decreases, passes through zero and becomes negative, and further increases in absolute value for the wide range of considered inner layer radii. The theoretical predictions are shown to agree with the available experimental data within the experimental uncertainty. The prediction of this shift is important for supporting the assignment of the measured double-walled nanotubes to particular nanotube types. Finally, we present the first experimental investigation of the resonance behavior of 2D-modes in individual DWCNTs and demonstrate their dependence on the tube diameter and interlayer distance. DL gratefully acknowledges support from RFBR Grant 18-32-00397 mol_a.

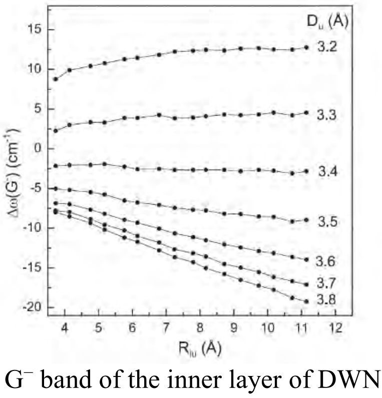

Fig.1 Total shift (solid circles) of the G^- band of the inner layer of DWNTs as a function of unrelaxed isolated layers radii R_{iu}, calculated directly from (n,m), for different unrelaxed interlayer distance D_u. The lines are guides for the eye.

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Thermoelectric Properties of Aligned Single-Wall Carbon Nanotube Films

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Since the seminal study by Hicks and Dresselhaus [1], it has been of great importance to experimentally clarify how the dimensionality of a material influences its thermoelectric properties and whether reduced dimensionality can enhance thermoelectric performance. Single-wall carbon nanotubes (SWCNTs) are one-dimensional materials with sharp van Hove singularities, and their thermoelectric properties have been intensively studied. However, we still do not understand the relationships between thermoelectric performance, current, and thermal flow directions with respect to the tube axis. For example, electrical conductivity along the axis is evidently higher than that in the perpendicular direction, but it is not clear whether thermoelectric performance in the parallel direction should be higher than that in the perpendicular direction. Since thermoelectric properties are strongly dependent on the location of the Fermi level [2], it is crucial to evaluate thermoelectric properties in particular current and thermal flow directions as a function of Fermi level in order to correctly answer the above question. In this study, as a first step, we investigated Seebeck coefficients and electrical conductivities of aligned SWCNT films as a function of Fermi level using electrolyte gating techniques. We fabricated large-area films of aligned SWCNTs, a mixture of metallic and semiconducting types, using the slow filtration method reported by He et al. [3]. Then we investigated how the thermoelectric properties are influenced by current and thermal flow directions as a function of Fermi level.

We found that, although the electrical conductivity in the direction parallel to the tube axis is higher than that in the perpendicular direction, there is no significant difference in their Seebeck coefficients between the parallel and perpendicular directions. This fact indicates a unique an-isotropy of thermoelectric properties in aligned SWCNT films.

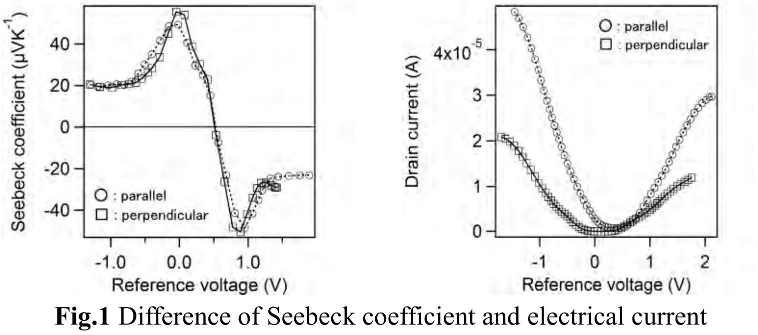

Fig.1 Difference of Seebeck coefficient and electrical current between parallel and perpendicular directions along the tube axis as a function of shift of the gate voltage.

[1] Hicks & Dresselhaus, PRB **47**, 16631 (1993)   [2] Yanagi *et al.*, Nano Lett. **14**, 6437 (2014)
[3] He *et al.*, Nat. Nanotechnol. **11**, 1 (2016)

"K.Y. acknowledges support by JST CREST through Grant Number JPMJCR17I5, Japan"

Dynamics of the Radial Deformation Recovery Process of Single Wall Carbon Nanotubes

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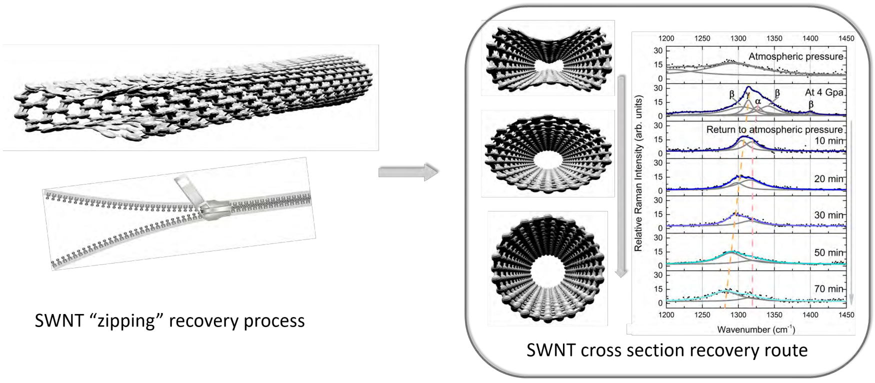
Carbon nanotubes, and more specifically single walled carbon nanotubes (SWNTs), possess unusual properties which are valuable for nanotechnology and other fields of materials science and technology, owing to their extraordinary thermal, electrical, and in particular mechanical properties. Most of the desirable mechanical properties, including a high tensile strength, result from the covalent sp^2-bonds formed between individual carbon atoms. However, SWNTs are much softer in their radial compared to their axial direction, [1] which results in a reversible elastic deformation of the cross section when applying sufficiently strong hydrostatic pressures. [2, 3] This article provides further evidence, via time dependent Raman spectroscopy, that a stable deformed state exists as a result of van-der-Waals-interactions within individual tubes and specifically that these tubes can fully recover from this deformed state on surprisingly long time scales on the order of tens of minutes.[4] In order to distinguish inter-tube from intra-tube effects, all experiments have been performed with densely packed, vertically aligned, free-standing SWNT arrays in comparison to individual, de bundled SWNTs.[5] These insights lead to far reaching conclusions regarding the mechanical properties and binding energies of the found stable state and, via a detailed analysis of D-mode, enable the distinction of fully reversible deformations from defect induced states.



SWNT “zipping” recovery process

SWNT cross section recovery route

Fig.1 SWNT cross section “zipping” recovery process.

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Electro-Optic switching of graphene oxide and reduced-graphene oxide liquid crystals

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Graphene oxide (GO) in water forms liquid crystal (LC) phases, that means phase in which the flakes spontaneously form macroscopic domains with orientational order thanks to their high aspect ratio and the dispersability in water. Interestingly, the optical properties of GO LC can be tuned by small electric fields due to an extremely large Kerr coefficient [1]. However, the response to electric fields is strongly affected by the flake dimension but also by the electrode types and the flake characteristics. Reduction of graphene oxide is usually performed for recovering the pristine properties of graphene but for GO LC this results in lost of suspension character due to the flake aggregation. By aid of surfactants GO LC could be turned into an LC reduced-GO suspension that was also responsive to electric fields [2, 3]. Interestingly, the response to electric fields was even much lager than for GO suspensions with the same concentration and at the same field strength. The higher conductivity of graphene compared to graphene oxide signify a larger response to electric fields that in the LC case results in larger reorientation to electric fields thus in higher electro-optic modulation.

Reduced-GO LC is not only giving higher response to electric fields but it shows also higher time stability than GO LC. Graphene based suspensions are showing to be very interesting new types of LC with very attractive electro-optic performance.

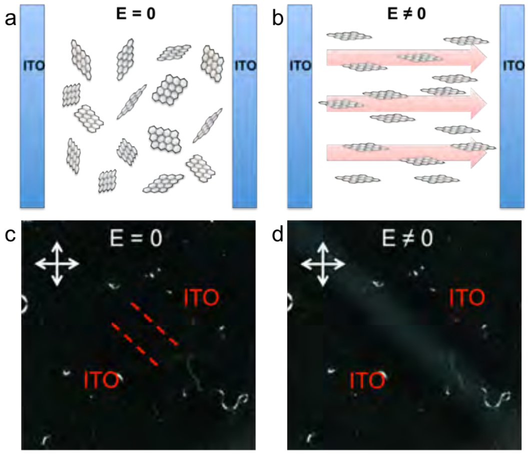

Fig. 1 a) and b) schematic of the field free and reorientation under field of the flakes, respectively: c) and d) real images of the cell between crossed polarizers

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The Exterior of Single-Walled Carbon Nanotubes as a Millimeter-Long Cation-Preferring Nanochannel

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In this study, the exterior of single-walled carbon nanotubes is shown to preferentially migrate cations over a millimeter length scale. Applying an electrical bias across droplets of NaCl placed at both ends of the nanotubes causes the formation of bright and dark lines along the nanotubes in scanning electron microscopy. Kelvin probe force microscopy and mass spectrometry imaging of individual nanotubes suggest that such a phenomenon corresponds to the transport of a cation-enriched solution along the nanotubes, while the anion-enriched solution counter-migrates along the adjacent substrate. Blocking the exterior of the nanotubes prevents both the bright/dark lines and flow of current through the nanotubes, confirming the absence of interior ion transport and electron current. The cation-preferring transport results in the formation of positively charged salt crystals along the nanotubes (with a cation-to-anion ratio >1.5 for KCl) followed by the subsequent migration of crystals in the direction of cation flux. Molecular dynamics simulation shows that cation–π interaction is responsible for such cation-preference observed during transport. The loss of cation-preference upon covalent functionalization of the nanotubes further supports this mechanism. Utilizing the short-range cation–π interaction as a transport mechanism suggests broader applications in areas where charge-specific transport is desired.

High-efficiency arrangement of oriented SWCNTs for high-performance transistors

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As one-dimensional structure, single-wall carbon nanotubes (SWCNTs) possess extremely high carrier mobility and structure-tunable bandgaps, and have great potential applications in micro-nano photonic, electronic and optoelectronic devices. In order to fabricate high-performance SWCNT-based devices, both structure control and orientation arrangement of carbon nanotubes are critical. Recently, the gel chromatography technique has been developed for the separation of the synthetic SWCNT mixture. With this technique, we achieved the separation of metallic and semiconducting SWCNTs, and even the production of single-chirality SWCNTs with identical properties [1-2]. Achieving the structure separation of SWCNTs provides high-quality SWCNT electronic inks for the fabrication of devices. However, high-efficiency arrangement of oriented SWCNTs by printing still remains a challenge. In this presentation, we will report the orientation printing of structure-sorted SWCNT ink for fabricating high-performance SWCNT-based transistors.

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Properties of doped single-walled carbon nanotube based heterojunction cells

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Since the high carrier mobility, single-walled carbon nanotubes(SWNTs) are expected to the application to the various kinds of the electronic devices. Especially, semiconducting SWNTs(S-SWNTs) are direct and tunable band-gap materials with strong photoabsorption from infrared to ultraviolet, and expected to be useful for photovoltaic material. The S-SWNTs are reported to show unipolar p-type behavior under ambient conditions and various chemical doping have been reported to convert from p-type to n-type. Recently, many research groups reported on the fabrication and properties of S-SWNTs based heterojunction solar cells using as photoactive layer. Many S-SWNTs based heterojunction cells reported were mainly fabricated by using intrinsic p-type SWNT films on n-type Si for p-n junction formation. On the other hands, LittThis type of heterojunction photovoltaic cells showed a high power conversion efficiency of 17 %. There are few reports on the heterojunction cells of doped n-type SWNTs and p-type semiconductors because the control of the doping level of n-type SWNTs is difficult and that their low stability. Establishing a stable n-type SWNTs thin film with precisely controlling the doping level is indispensable for the development of next generation carbon nanotubes based photovoltaic cells.

In this study, we fabricated the several kinds of n-type SWNTs based heterojunction cells by using some fabrication procedures and characterized their diode and photovoltaic properties systematically. We also investigated the effect of several types of gas exposure on their electric and photovoltaic properties. The detailed results and discussion will be presented in the coming conference.

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Origin and Control of Spectral Diversity from sp^3 Defect States of Single Wall Carbon Nanotubes

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Low-level covalent functionalization of single wall carbon nanotubes (SWCNTs) introduces new photoluminescent defect states appearing 100-300 meV to lower energy than the normal band-edge E_{11} exciton emission.[1,2] Exciton localization at the defect sites gives rise to new functionality, including single photon emission at room-temperature and at telecom wavelengths.[3,4] One challenge in harnessing the defect-state emission is that, even for single chirality samples, emission over a broad spectral window (~100-200 nm range) is observed. A better understanding of the origins of this spectral diversity is required to arrive at strategies for narrowing the emission window. We present a single-tube low-temperature spectroscopic study paired with TD-DFT modeling of defect-state behavior for aryl diazonium sp^3 functionalized SWCNTs. We show that the spectral diversity arises from the potential for 6 different aryl binding configurations to occur on the nanotube structure. Each configuration is a chemically distinct species, with its own defined electronic structure and emitting behavior.[5,6] We further explore the structural dependence of this behavior and show that chirality may be used as a parameter for limiting emission wavelengths. Furthermore, TD-DFT modeling paired with kinetic studies shows that aryl diazonium binding is limited to ortho-only configurations.[7]

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Pressure-induced charge transfer between single-wall carbon nanotubes and encapsulated quaterthiophene

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We performed high-pressure resonance Raman experiments on hybrid system composed by quaterthiophene (4T) confined in single-wall carbon nanotubes (SWCNTs), named 4T@SWCNTs [1], simultaneously with empty SWCNTs. For laser excitation energies 2.33 and 2.41 eV, close to optical absorption of the oligomer, we observed a quick attenuation of the RBM modes of the host SWCNTs from the composite 4T@SWCNTs, explained here through of pressure-induced charge transfer between nanotube and 4T molecule. This assumption is supported by the slow attenuation of the RBM modes intensity of empty SWCNTs, which are expected to have no charge transfer. Besides, a discontinuity in ω_{4T} vs. pressure plot around 0.8 GPa for modes lying in 650-1300 cm^{-1}, concomitant with the disappearance of the lowest RBM frequency from the host SWCNTs, were attributed as being another indicative of pressure-induced charge transfer. Furthermore, a fast detuning of the G-band of the host SWCNTs emphasizes the strong charge transfer. Aiming to probe how the charge transfer evolves with pressure for energy excitation far from 4T resonance, we performed a high pressure experiment using a laser excitation energy of 1.96 eV. Our results revealed a much slower decreasing of the G-band intensity, evidencing a less pronounced pressure-induced charge transferred from the 4T molecules to SWCNT. Finally, in order to verify the influence of the 4T ordering into SWCNTs, we carried out more three high pressure experiment using the 2.41 eV energy excitation varying the host tube diameters (0.8, 1.4 and 1.7 nm). The results showed an optimized pressure-induced charge transfer for the SWCNT diameter of 1.4 nm, where two 4T molecules are encaged closer two to tube walls along the tube axis [2].

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Atomic-layered MoS_2 on SiO_2 under high pressure: Bimodal adhesion and biaxial strain effects

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The stacking effect on the E^1_{2g} and A_{1g} vibrational modes of mechanically exfoliated MoS_2 samples supported on SiO2 was investigated by nonresonant Raman spectroscopy at high-pressure conditions. The split of E^1_{2g} and A_{1g} modes were observed for single- and bilayered samples whereas such splitting disappears for higher numbers of layers. The differences on the E^1_{2g} pressure coefficients allowed us to interpret the observed splitting as due to the presence of two types of regions corresponding to a high and a low conformation of MoS_2 to the substrate roughness. The difference in the pressure coefficient appears then as due to the biaxial stress introduced via the substrate compression. Such effects were not observed for the A_{1g} mode due to its vibration symmetry. This out-of-plane vibration is mainly affected by the normal stress that corresponds to pressure transmitted by the pressure-transmitting medium.

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Thermionic electron emission and hysteresis conductivity of h-BN at high temperature

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Abstract: In this paper, with a coaxial h-BN/CNT cable synthesized by chemical vapor deposition (CVD) epitaxial growth h-BN on CNT yarn, we have studied the thermionic electron emission and measured the work function of h-BN. The result shows the work function of h-BN ranges from 4.215 eV to 4.873 eV in the measured temperature range 1306-1787 K. The insulating h-BN becomes conductive at the temperature above 1300K around. The conductivity shows hysteresis with temperature and can be divided into different range according to their behavior characteristics. The reason is attributed to the thermo-generated electron injection and re-arrangement inside the h-BN. For the conductive state of h-BN at high temperature (above ~1300K), we measured the resistivity variation with temperature and find that it follows the Ohmic conduction model of insulator. Based on Schottky junction model, we have brought up an energy band model of the coaxial h-BN/CNT cable system. After taking into the well-established data of CNT yarn work function and h-BN bandgap, the calculated "electron activation energy" (from the Fermi level of CNT yarn to the conduction band of h-BN) and the work function of h-BN are well accordance with the experiment measured results.

Chirality engineering and metal-to-semiconductor transition of individual SWCNTs by in situ TEM

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Chirality is a unique intrinsic structure for the carbon nanotubes (CNTs), determining the electronic, physical and chemical properties. Controlling the chirality is one of the ultimate goals for nanotube science. In recent years, progresses have been made by designing the catalyst seeds for growing CNTs and chirality-specific growth has been realized by using the symmetry matched stable solid catalysts.[1-3]

In the current work, we propose to use a new strategy to control the chirality of CNTs. Instead of controlling the chirality of the whole nanotube, we are aiming at engineering the chirality of the nanotube segment. For example, by changing one segment of the metallic nanotube into semiconducting, the whole nanotube will behave as a semiconductor.

As shown in Fig. 1a, we use a special in situ TEM-STM holder, on which two STM probes are available, so that electrical pulses could be applied and electrical properties of transistors could be measured.[4-8] The structure changes including the chirality could be monitored in real-time (Fig. 1b-c). An interesting pattern of the chirality transitions has been unveiled that the chirality favors changing by continuous (1, 0) dislocations. Importantly, metal-to-semiconductor transition has been realized (Fig. 1d), and an intramolecular Schottky junction is fabricated. Our work not only provides insights to the fundamental chirality dynamics but also offers implications for the CNT based molecular electronic devices.

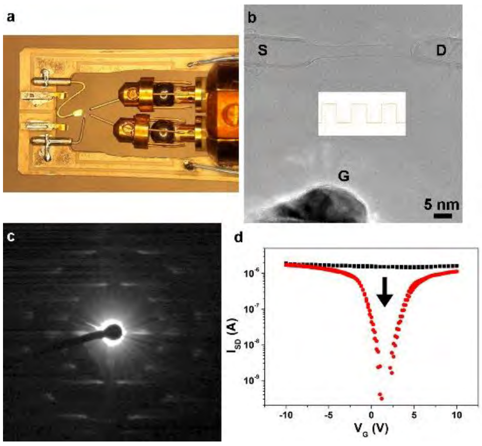

Fig.1 Chirality engineering of individual CNT by in situ TEM probing. (a) Twin-probe TEM-STM holder. (b) TEM image of an engineered SWCNT transistor. (c) Electron diffraction of individual CNT. (d) Transfer curve of a CNT transistor demonstrating metal-to-semiconductor transition.

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Subwavelength-Structure-Induced Hot Electron Effect and Relative Phenomena in the Carbon Aerogels

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Owing to its diverse chemical compositions and unique properties, aerogels could be regarded as a state of matter.[1] Much work discussed the influence of density on the physical properties, but rare work talks clearly about the microstructure/properties relationship. Recently, we found that subwavelength microstructure obviously affect the diffuse reflectivity of the carbon aerogels.[2] There was a roughly positive correlation between reflectivity and density (42~328 mg/cm^3) of the carbon aerogels. Moreover, subwavelength structure including primary skeleton and micropores significantly the reflectivity. By tuning their nanostructure, we got the minimum diffusing reflectance of about 0.19 % which approached the measuring limit of our equipment. We attribute this behavior to the indirect interactions including electromagnetic-electron interaction and electron-microstructure interaction. The subwavelength structure of the conductor strongly decreases the mean free path of the electrons, leading to an extra hot electron absorption besides considering the Joule's heating. Thus we designed an experiment to study the photoelectric effect of the ultra-black carbon aerogels. The visible light could induce strong light current, while the infrared could not. The light current is in direct proportion to the intensity of the lights but saturated when the light power is higher than ~80 mW. The saturated current has been demonstrated to be induced by the producing of plasmas. We designed another experiment to and find that carbon aerogel could obviously enhance the photocatalysis efficiency, indicating a strong tunneling/coupling effect between carbon aerogels and photocatalyst.[3] We further found that both the real permittivity and real permeability of carbon aerogel are negative in the wavelength ranged from 600 to 1000 MHz, which could be regarded as a nanoscale metamaterials with a single component.[4] We believe that the strong hot electron effect will lead to various novel physical phenomena.

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Consecutively Strong Microwave to Terahertz Absorption Performance of 3D Fe3O4/Graphene Bulk Material

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With the booming microwave and terahertz technology for communication and detection, the consequent increasingly complicated electromagnetic environment is in urgent need of high-performance microwave and terahertz absorption materials [1]. However, it's still a huge challenge to achieve consecutively strong absorption both in microwave and terahertz regimes [2]. Here, an ultra-broadband and highly efficient absorber for both microwave and terahertz waves based on 3D cross-linked Fe_3O_4/graphene bulk material (3DFG) is first reported. Its incredible qualified absorption bandwidth (3.4 GHz to 2.5 THz, reflection loss (RL) less than -10 dB) covers 99.9% of the entire measured frequency range. Furthermore, the excellent elasticity renders it stable performance even after 50 compression cycles. And its excellent absorption performance at oblique incidence is also demonstrated. The designed highly porous structure for minimizing surface reflection combined with high lossy 3DFG network results in the remarkable performance, as proved by terahertz time-domain spectroscopy technique. Eventually, the specific average microwave and terahertz absorption value of 3DFG in measured frequency realm is over two orders of magnitude higher than other kinds of materials. The lightweight 3DFG with strong absorption in both microwave and terahertz bands really opens up the opportunity for increasingly complex electromagnetic environment in life and military detection technology in the future.

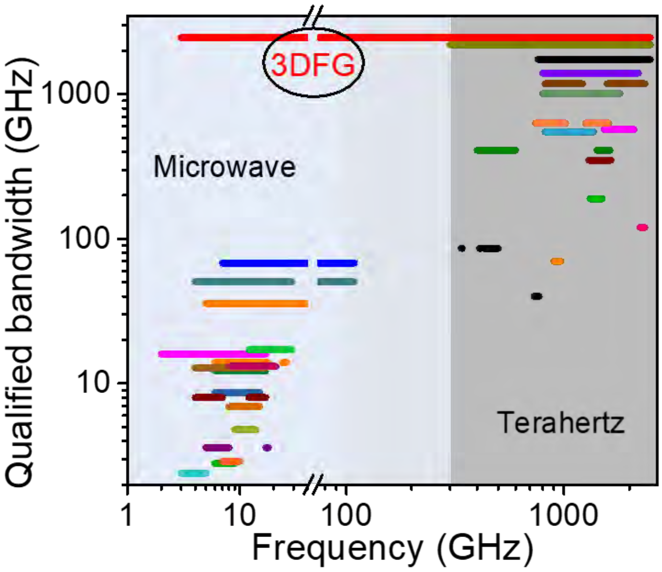

Fig.1 Comparison of electromagnetic wave absorption performance of widely reported materials: Qualified absorption bandwidth of represented materials in microwave and terahertz bands. Each color bar with the same qualified bandwidth represents a material.

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Intra-band and Inter-band Carrier Dynamics in a Few Layer ReS$_2$

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Atomically-thin layered materials including graphene and transition metal dichalcogenides possess intriguing physical properties originating from the two dimensional honeycomb structure. ReS$_2$ is a new class of the layered material with reduced symmetry because of the distorted *1T* structure, which imparts highly anisotropic one dimensionarity to optical and electronic properties [1]. The early study reported that ReS$_2$ remains direct bandgap semiconductor from bulk to monolayer [2], while the other reported that the band structure depends on the layer number [3]. The understandings of electronic and optical properties including the optically excited carrier dynamics are still controversial, and are not fully understood. Here we described the ultrafast spectroscopy of 3-layer ReS$_2$ using ultrafast spectroscopy to obtain the insight of band structure and carrier dynamics.

The sample was prepared by mechanically exfoliation onto a quartz substrate. Figure 1(a) shows the spectrally integrated PL decay profiles. The instrumental response function (IRF) is also shown with a black solid line. The profile of transient PL decay exhibits a very fast response, and the PL decay profile is almost identical to IRF, which is evaluated as less than 10 ps from the analysis of convolution procedure. Figure 1(b) shows pump-probe differential reflectivity. The transient differential reflectivity shows decay times of around 100 ps. The different time scales in the transient differential reflectivity and PL spectroscopy provide the information on the intra-band and inter-band photocarrier dynamics. Figure 1(c) shows the schematic of energy band structure of 3L ReS$_2$ around the conduction band minimum (CBM) and valence band maximum (VBM). The CBM is at Γ point, and VBM at slightly displaced from Γ to X point in the momentum space, which suggests that the 3L ReS$_2$ is indirect band gap semiconductor with close direct band gap near Γ point. The band structure could strongly affect the intra- and inter-band carrier dynamics in 3L ReS$_2$.

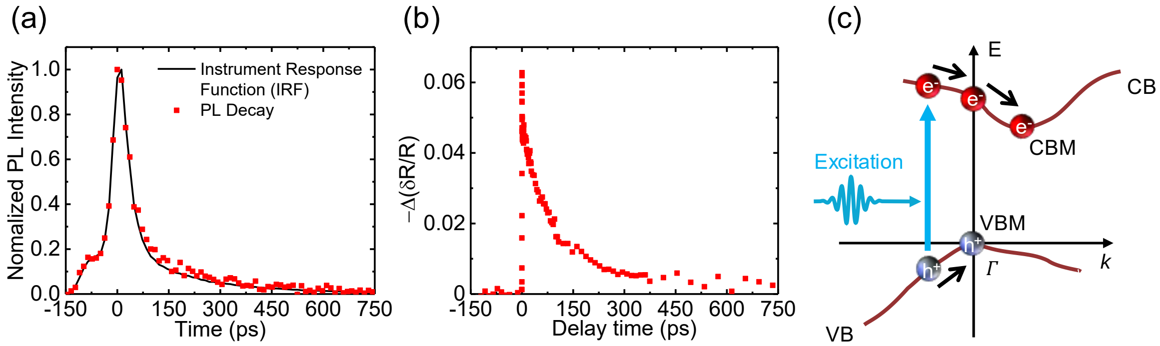

Fig.1 (a) Transient PL decay profiles of 3L ReS$_2$ measured at 10 K. The black lines indicate the IRF of the experimental setup. (b) Decay profile of transient differential reflectance spectra of 3L ReS$_2$ at 5 K. (c) Schematic of energy band structure of 3L ReS$_2$ and intra-band dynamics. The photocarrier relaxation dynamics at the initial stage of photoexcitation are shown.

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Optical characterization of BN-wrapped Single-walled carbon nanotubes

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A conceptually new structure, in which mono or few boron nitride (BN) layers seamlessly wrap around a single-walled carbon nanotube (SWNT) was demonstrated recently. Ammonia borane (BH_3NH_3) as the precursor was directly used to form the BN nanotubes on SWNTs by chemical vapor deposition (CVD). This heterostucture of coaxial SWNTs with BN nanotubes will be promising for application in many fields and enriching 1D material system.

In this work, quality and diameter controlled SWNTs synthesized by extended alcohol zeolite-supported catalytic CVD [1] is employed as the starting material and a template. Optical properties of BN nanotubes wrapping on this bulk SWNTs was observed by Raman, absorption and photoluminescence (PL). Compare to pristine SWNTs, the differences in Raman spectra and the shift of predominant SWNTs observed by PL are clarified in Fig.1. The effect of starting SWNTs and the preferred BN wrapping trend on SWNTs will be discussed and demonstrated. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are also employed to examine the morphology of coaxial structure.

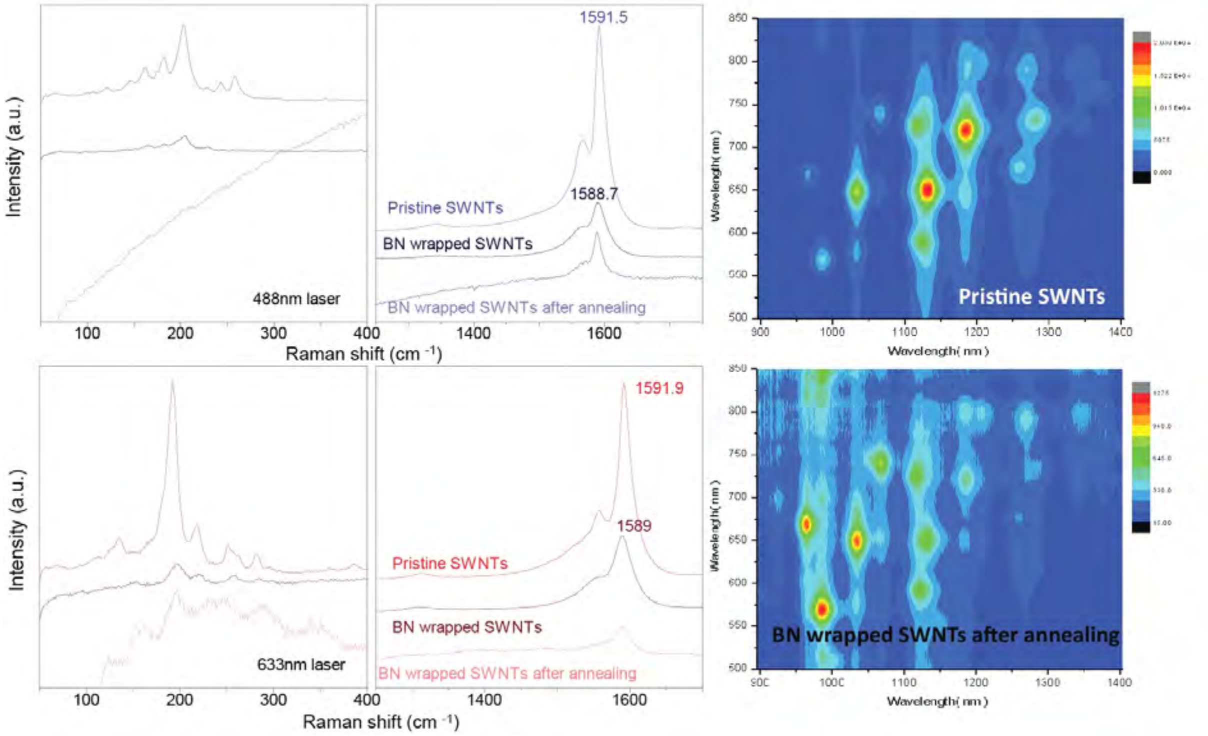

Fig.1 Raman and PL spectra of pristine SWNTs and annealed BN-wrapped SWNTs.

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Observation of Electronic Raman Scattering in Suspended Semiconducting Carbon Nanotubes

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Recently, the Electronic Raman Scattering (ERS) is reported to be a particular Raman feature arising from the inelastic scattering of the photoexcited electrons by a continuum of low-lying electron-hole (*e-h*) pairs across the linear electronic subbands near the Fermi level of the metallic single-walled carbon nanotubes (M-SWNTs) [1-4]. However, such process has not been predicted and observed in semiconducting (S-) SWNTs previously due to the absence of those low-lying *e-h* pairs. In this work, we report that the ERS spectra are not only applicable to M-SWNTs, but also can be observed in S-SWNTs. Although S-SWNTs do not possess the low-energy *e-h* pairs across the linear electronic subbands near the Fermi level like the M-SWNTs do, S-SWNTs have high-energy *e-h* pairs that can also contribute to the ERS processes (Fig. 1). Similar to the case for M-SWNTs, the ERS process reveals a wealth of information about the electronic structures for S-SWNTs, which are of great importance to nanotube-related science and technology.

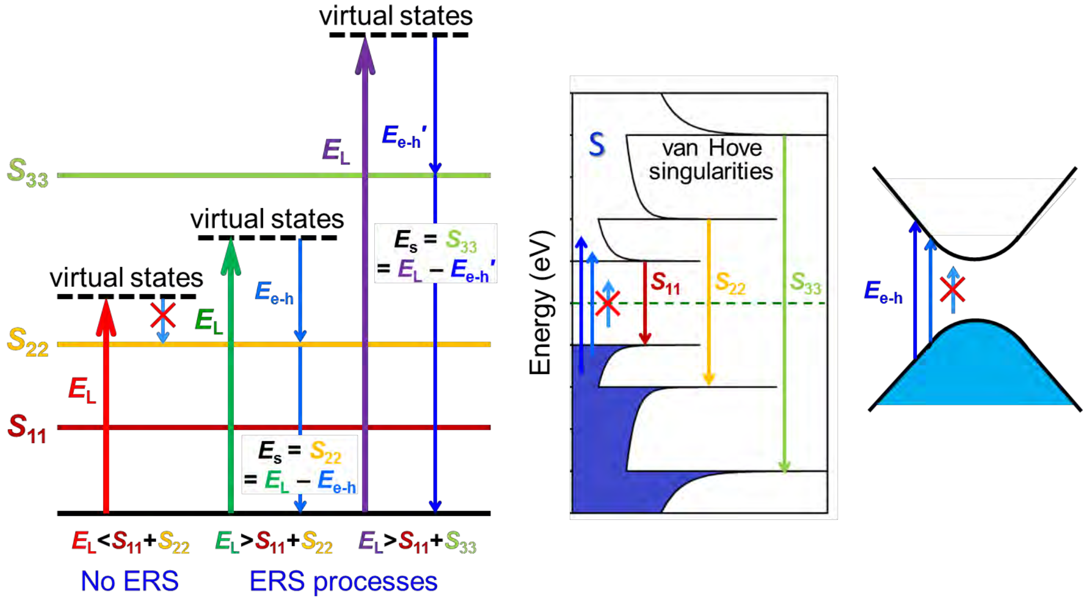

Fig.1 The ERS processes in S-SWNTs.

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Thermal transport of $^{12}C/^{13}C$ graphene phononic crystals

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Since the main heat carrier in graphene is phonon, graphene isotopic heterostructures effectively block phonon propagation, thereby reducing its thermal conductivity [1]. To further reduce the thermal conductivity, coherent effect such as phonon wave interference is required. It is predicted that the reduction in the thermal conductivity can be further achieved by creating energy bandgaps for thermal phonon using periodic nanostructures [2]. In this study, we synthesize isotopic graphene heterostructure superlattices and investigate the thermal transport properties of graphene across the heterointerfaces.

Graphene was synthesized by low-pressure chemical vapor deposition (CVD) on copper foils using CH_4 as carbon sources, where graphene isotopic heterostructures were synthesized by flowing $^{12}CH_4$ and $^{13}CH_4$ alternately. With this method, graphene is grown by single CVD process without breaking vacuum during growth; clear heterointerfaces can be produced in hexagonal graphene single crystals. Figures 1(a) and 1(b) show the typical optical and Raman 2D band intensity mapping images of heterostructures, respectively. Grown graphene was clearly composed of ^{12}C graphene and ^{13}C graphene superlattices. Figure 1(c) shows the laser power dependence of the 2D Raman peak shift using two types of graphene single crystals (^{12}C graphene and $^{12}C/^{13}C$ graphene). As the laser irradiation induces heat into the center of each graphene, we can estimate the temperature rise at the center of graphene from the dependences. The peak position shift of $^{12}C/^{13}C$ graphene by the laser irradiation is approximately 1.6 times larger than that of ^{12}C graphene, indicating that the temperature rise of $^{12}C/^{13}C$ graphene is also 1.6 times higher. This suggests that heterointerfaces block phonon transport and suppress heat dissipation. Further reduction in the thermal conductivity without modifying the electrical property can be expected using $^{12}C/^{13}C$ graphene periodic heterostructures with shorter widths.

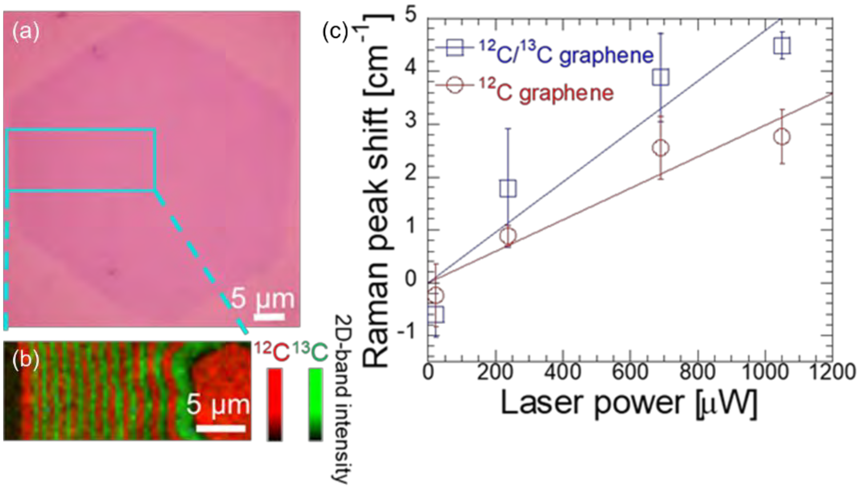

Fig.1 (a) Optical microscope image of a hexagonal graphene single crystal. (b) Raman 2D band mapping showing clear periodicity of ^{12}C-graphene at 2685cms^{-1} (red) and ^{13}C-graphene at 2585 cm^{-1} (green). (c) Laser power dependence of 2D peak position shift of ^{12}C graphene and $^{12}C/^{13}C$ graphene.

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Transverse thermoelectric voltage in isotopic graphene heterostructures

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Due to its high career mobility and power factor, graphene is expected as thermoelectric conversion elements. However, the figure of merit (ZT) of graphene is low because of the extremely high thermal conductivity. Recently, the introduction of isotopes or defects has been reported to reduce the thermal conductivity for enhancing ZT value [1-3]. In this study, we focus on transverse thermoelectric effect to enhance thermoelectric conversion performance using graphene. The transverse thermoelectric effect is expected in materials which have anisotropic electrical and thermal properties. In this type of materials, thermoelectric voltage appears in the direction perpendicular to the temperature difference. As graphene is basically isotropic material, isotopic graphene heterostructures composed of ^{12}C and ^{13}C are used to investigate the transverse thermoelectric effect.

Transverse thermoelectric voltage is expressed as

$$|\Delta V| = \left| \frac{\Delta T}{2} \frac{l}{d} \left(S_{\parallel} - S_{\perp} \right) \sin 2\theta \right|, \qquad (1)$$

where ΔT, l/d, θ, $S_{//}$, and $S_{\perp}$ are the temperature difference, aspect ratio of the device, tilt angle of the isotopic interface, and Seebeck coefficient of graphene heterostructures in the parallel and perpendicular directions to the interface, respectively. Fig. 1(a) shows optical microscope and Raman mapping images of isotopic graphene heterostructures. Red and green colors represent 2D band intensity of graphene composed of ^{12}C and ^{12}C/^{13}C (50%/50%). Fig. 1(b) shows the interface tilt angle dependence of transverse thermoelectric voltage, which well fits the transverse voltage as in Eq. 1. The aspect ratio dependence of the thermovolatge was also confirmed. The transverse thermoelectric effect was successfully observed by introducing anisotropicity into graphene.

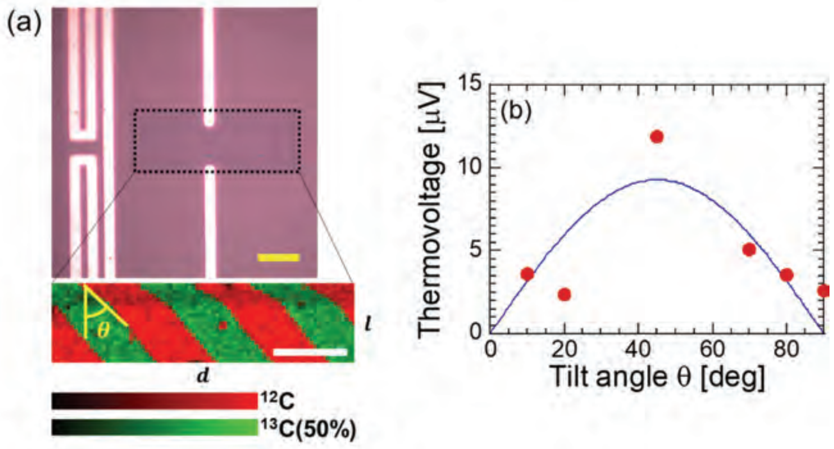

Fig.1 (a) Optical and Raman mapping images of isotopic graphene heterostructures Bars in the images represent 10 μm. (b) The interface tilt angle dependence of transverse thermoelectric voltage.

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Local structures and electronic properties of metal halide encapsulated single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) have a hollow space in the nanometer size that can be encapsulated various functional molecules. The confined molecular assemblies exhibit unique low-dimensional structures and solid state properties that can not be realized in the bulk states. Synthesis and structures of ionic metal halide crystals encapsulated SWNTs have been reported [1-9]. However, tube diameter, chirality or temperature dependence on the local structure and properties of metal halide crystals encapsulated SWNTs have not been systematically investigated. In this study, we report the effects of the diameter and chirality of SWNTs on the local structures and the electronic states of the encapsulated several kinds of metal halide by using molecular dynamics (MD) and first-principles density functional theory (DFT) simulations.

In the MD simulation, we used the Born-Mayer-Huggins-Tosi-Fumi intermolecular potential between the alkali halide ions and the Dreiding potential between carbon atoms in SWNT. We have designed on the armchair and zigzag nanotubes with diameters ranging from 1.1 to 1.6 nm. One SWNT and any number of metal halide ion pairs around SWNT were set in a rectangular cell as initial configuration. Stable structure at 300 K was calculated with the NVT ensemble after the relaxation calculation at 1000 K.

In the DFT calculation, we used a code package PWscf and GIPAW in Quantum ESPRESSO. We also made claculations of NMR chemical sift and Electric field gradient (EFG) tensors.

The detailed results and discussion will be presented in the coming conference.

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Enhancing the Infrared Response of Carbon Nanotubes From Dye interactions

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Middle infrared response on a carbon nanotube is very weak because this homonuclear allotrope of carbon does not bear permanent dipoles. Nevertheless, a significant number of infrared phonons are predicted by the group theory. Encapsulating molecules inside nanotubes (called hybrid nanotubes in the following) is a common strategy to add new functionalities. The one-dimensional nature of single-walled carbon nanotubes (SWCNT) internal channels has been exploited here to induce a molecular order and specific interactions which are dependent of the size of the nano container (figure).

Here we report the discovery of a strong dependence on the infrared response of the hybrid nanotube due to confinement effect when dimethylquaterthiophenes are encapsulated inside SWCNTs[1]. Results are compared to experiments performed on nanotubes where dyes are π-stacked at the outer surface. Surprisingly, the confinement properties lead to an exaltation of the infrared absorption response in the carbon nanotubes from dye molecule interactions. Thanks to the comparison between the experimental investigations and DFT calculations, we elucidate the origin of the large enhancement of this infrared absorption and demonstrate that interactions between conjugated oligomers and nanotubes can be probed.

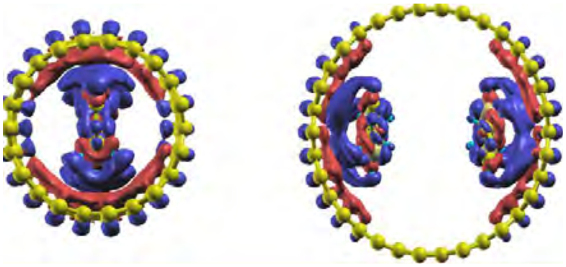

Figure: Electronic charge density as the function of size of the nano container controlling the molecular order

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Single-Walled Carbon Nanotubes Individually Dispersed by a Low-Cost Natural Product Solution

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The individual dispersion of single-walled carbon nanotubes (SWNTs)[1] is important for the applications in electronics[2], optics[3] and nanodivices[4]. Here, we report a low-cost dispersion of SWNTs using a natural product baicalin (BC) solution. The well resolved absorption and photoluminescence (PL) spectra indicate that the SWNTs are dispersed individually by BC. Moreover, we observe significantly enhanced PL intensities after adding La^{3+} into the dispersion whereas the absorption intensity does not change, suggesting a significantly enhanced quantum yield of SWNTs.

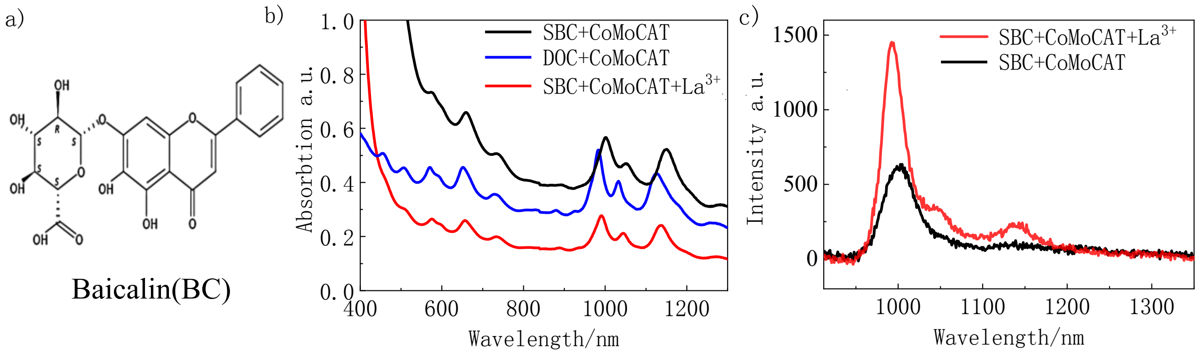

Fig.1 a) Structure of baicalin (BC).b) Absorption spectra of CoMoCAT dispersed by sodium baicalin (SBC, NaOH:BC=1:1), sodium deoxycholate (DOC) and SBC+La^{3+}. c) Photoluminescence emission spectra of CoMoCAT dispersed by SBC and SBC+La^{3+}, excited at 575 nm.

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Helical conformation of poly(3,5-disubstituted phenylacetylene)s tuned by nanomaterials

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The novel poly(phenylacetylene)s (PPAs) substituted at the *meta* position(s) by chiral alkylamide group, R-I and S-I, were used. The dependence of the screw sense of helical polyene backbone on the structure influenced by different kinds of nanomaterials, i.e., HiPCO SWNTs, graphene, C_{60}, Au NPs, SiO_2 NPs, was systematically investigated in organic solution. The chain structures and helical transitions were mainly characterized by UV-vis absorption and circular dichroism (CD). The CD spectra shows that R-I and S-I's CD signal changes after the above-mentioned nanomaterials were added. We propose that the helical transitions of the polyene backbone is related to the spatial configuration of pyrene group, which is dependent on the nanomaterials.

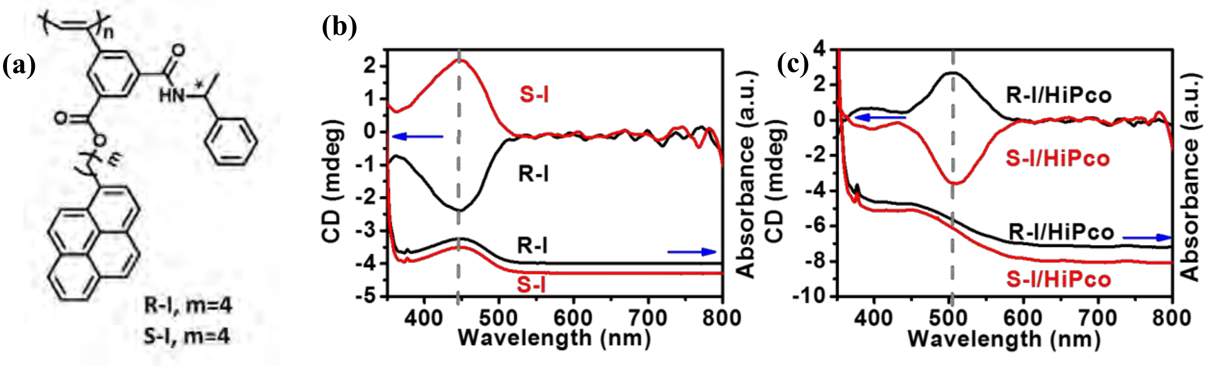

Figure: (a) Suctures of **R-I** and **S-I**; (b,c) CD spectra of 0.01mg/mL R-I/S-I in NMP (b) and 0.05mg/mL **R-I/S-I** HiPCO in NMP (c)

One-second Formation of Graphene Functionalized Nano-Tips for Nano-electrical Measuremtns

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Nano-material tailored tips, which meet the requirements of researchers to probe and manipulate materials down to nanoscale, have been adopted for various applications. Graphene functionalized nanotips are expected to possess promising potentials based on the outstanding electrical and mechanical properties of graphene. However, current methods, e.g. Chemical Vapor Deposition (CVD), are suitable for growing graphene on a flat surface at a high temperature (usually > 900 °C). It still remains a big challenge to directly grow graphene on a convex surface and fabricate functionalized tips with high quality graphene at the nano-sized tip apex.

In this work, we succssfully grew high quality graphene on Ni tips with an apex size around 30 nm within 1~2 sec. for the first time. A novel ultrafast annealing method, which featured in the superfast ramping/cooling rate (> 1000 °C/s), was developed for growing graphene at an instantaneous high temperature but avoiding the melting or oxidation of the tips. Further, we obtained direct evidence to support a new growth route that graphene was formed at the high temperature (higher than the decomposition T of nickel carbide) via the direct conversion of surface carbide, instead of the conventional segregation mechanism.

Moreover, thus-produced graphene nanotips possessed an outstanding conductivity, exhibiting their potential for nano-electrical measurements. The electrical tests on a graphene sheet down to a nanoscale range were performed using two graphene nanotips installed on a micro-manipulator/SEM system, which will be discussed in details in the presentation.

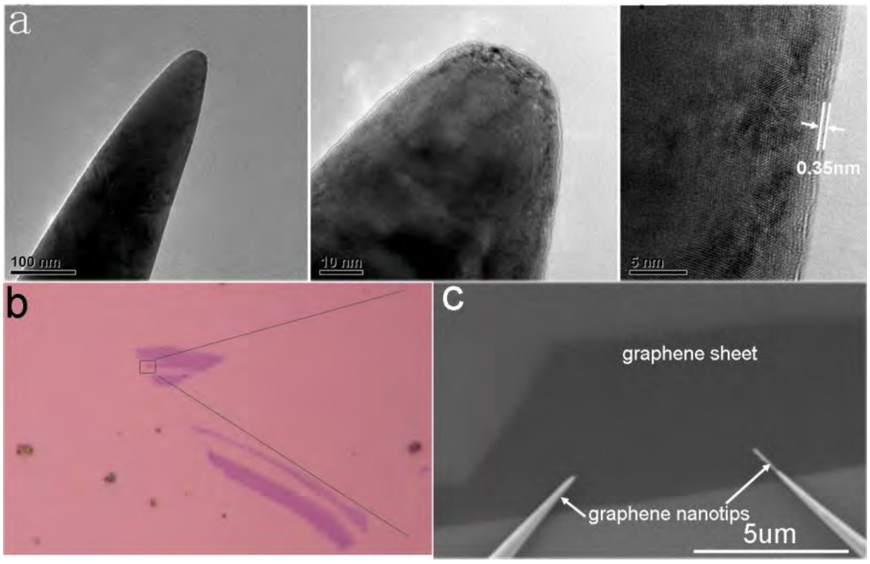

Fig.1 (a) TEM images of a graphene nanotip. (b, c) Optical and SEM images of a few-layered graphene sheet investigated by two graphene nanotips controlled by micro-manipulators.

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Scalable fabrication of monolithic solid supercapacitors based on graphene-carbon nanotube ink

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Among the various available energy storage devices, supercapacitor is an attractive potential candidate due to its high power performance, excellent coulombic efficiency, extremely long cycle life and variable working temperature range. [1, 2] The ever-growing demand of smart electronic devices require continuous development in supercapacitors that are sufficiently compact and can potentially be integrated on a chip with other electronic components. [3]

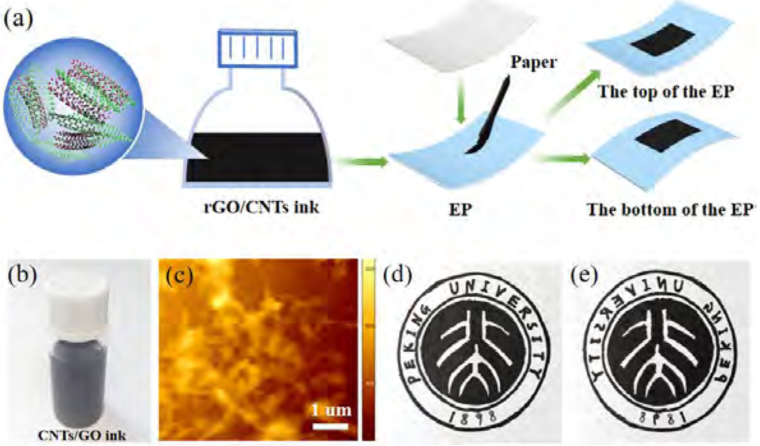

Fig 1. (a) Illustration of the formation process for monolithic paper SCs. (b) Photograph of MWCNTs/rGO ink. (c) AFM image of the ink dropped on silicon wafer. (d) and (e) Optical photographs of the school badge of PKU drawn by MWCNTs/rGO ink.

We fabricated solid paper-ink SCs with a sandwich structure, in which all the components are monolithically integrated into an on-chip paper substrate. The electrodes with mirror symmetry were obtained by directly writing with the ink containing multi-walled carbon nanotubes (MWCNT) and reduced graphene oxide (rGO). The non-introduction of surfactants and harsh chemical processes contribute to the excellent mechanical, electrical, and electrochemical performance of MWCNT/rGO electrode. The energy densities of the full paper supercapacitor reached 0.80 mWh cm^{-2} while the power densities could achieve 22.5 W cm^{-2} during the charge and discharge process.

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Stacking effects on the electronic properties of janus WSSe multilayers: a first-principles study

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There exists the mirror symmetry breaking and the intrinsic out-of-plane electric field in janus monolayers of transition metal dichalcogenides MXY (M = Mo, W; X ≠ Y = S, Se, Te), that have been concerned experimentally[1] and theoretically[2-4]. Taking WSSe as an example, we present a first-principles investigation of the electronic structures of multilayer janus MXY. The most stable stacking pattern in energy is the AA′ type, but it can be obviously affected by the order of the chalcogen atomic layers. Various energy valleys are contributed by different chalcogen atomic orbitals, leading to the varying degrees of energy splitting in different stacking patterns. Due to the net dipole moment and the symmetry breaking in the vertical direction, the electronic structures of the Se-S-Se-S-… systems are similar to that of the Type-II heterojunctions, which can be well applied in the field of photoelectric conversion. The layer dependent Rashba splitting exists in the asymmetric stacked WSSe multilayers, and the splitting energy has a positive correlation with the difference of potential energy in the vertical direction, which is linear in monolayer but not in multilayers. The electronic structures and spin splitting can be easily modulated by controlling the stacking structures of WSSe multilayers.

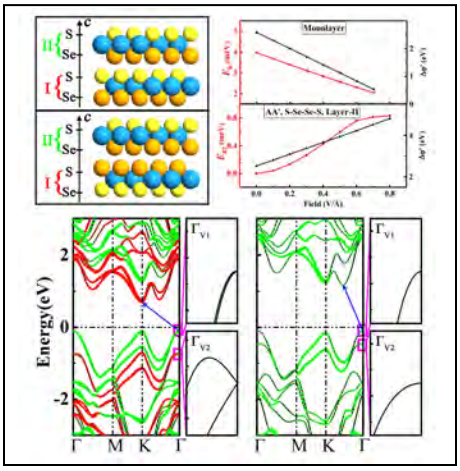

Fig.1 Atomic and band structures of AA′ stacked WSSe bilayers, and the potential difference and Rashba splitting energy in the vertical electric field.

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Enhancement thermal stability of single-walled carbon nanotubes by co-axially wrapping with boron nitride nanotubes

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New materials technology presents a great opportunity to push beyond the performance limits of single materials by combining with distinctive physicochemical properties from other new ones. Boron nitride nanotubes (BNNTs) display different chemical properties from carbon nanotubes (CNTs) owing to their partial ionic bonding character. They exhibit an extraordinary heat resistance up to 900 °C in air [1], which shows great potential to combining these two materials to enhance thermal stability of single-walled carbon nanotubes.

We synthesis SWCNT@BN structure by chemical vapor deposition. From in-situ Raman experiment, we find that the outer BN layer could effectively protect the inner CNT to avoid burning in air below 650°C. It is expected to be helpful to broaden the application of carbon nanotubes at higher temperature.

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Fabrication of Super-strong Carbon Nanotube Bundles with Tensile Strength over 80 GPa

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Carbon nanotubes (CNTs), one of the strongest materials ever known, are the most promising materials to help us realize the space elevator dream. Additionally, many future applications, such as rackets, ballistic armors and space vehicles also need fibers which are both light and superstrong. When CNTs assemble into fibers, however, the strength of fibers are usually impaired by defects, impurities, random orientations and discontinuous lengths of CNTs. Fabricating CNT fibers with strength reaching that of single CNTs has been a challenge for decades. Herein, centimeters long CNT bundles (CNTBs) with defect-free, neat, uniform oriented and continuous structure were in-situ synthesized using a gas flow focusing method. It was revealed that the tensile strength of CNTBs was controlled by the Daniels effect due to the nonuniformity of the initial strains in the components. A synchronous tightening and relaxing (STR) strategy is proposed to release the nonuniform initial strains of the CNTB components. Consequently, the tensile strength of the bundles can be improved to over 80 GPa, which is far higher than that of any other strong fibers ever fabricated. According to our study, the strength of CNTBs consisting of a large number of components with parallel alignment, defect-free structures, continuous lengths and uniform initial strains won't change much with the number of components increasing. Our results provide a new approach for fabricating ultrahigh-strength CNT-based materials.

Strengthening Carbon Nanotube Fibers through Graphene-Oxide Nano-Patching

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Last decade has witnessed the great research efforts in the design, fabrication and characterization of microfibers based on carbon nanotubes (CNTs). The mechanical and physical properties of CNT fibers reported so far are comparable to these of existing high performance fibers, such as carbon fibers, glass fibers, aramid fibers, and some other polymeric fibers. However, CNT fibers exhibit far lower mechanical and physical properties than individual CNTs, which is mainly due to the weak interfacial load transfer between adjacent nanotubes. To enhance the interactions of CNTs in the fiber, in this study, 2D graphene oxide (GO) sheets, which possess similar atomistic structures and properties with CNTs, were introduced into the CNT fibers to establish more connections between CNTs. The hybrid fiber was further heated to reduce the GO and enhance the CNT/graphene interaction. The effects of the GO size, GO concentration, as well as the annealing temperature on the fiber performance were investigated. It has been found that the tensile strength of the hybrid fibers can be 100% higher than that of the pure CNT fibers. Atomistic simulations were also implemented to reveal the underlying mechanism of such enhancement. This study would extend our understanding of the structure-property relation of CNT fibers, and promote their engineering applications.

Graphene glass with superior hemocompatibility makes it a candidate for biomedical application

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Biomedical materials with superior hemocompatibility are of great significance in the treatment of cardiovascular disease. However, there is still not a kind of material's quantity like the vascular wall could preserve the blood for a long time. Most blood compatible materials depend on surface modification and their permanency is worthy of scrutiny. Graphene is a single atom layer material with chemical inertness, anti-inflammatory ability, anti-cytotoxic, low coefficient of friction, high electrical conductivity and transparency which favors its biomedical application. In this study, graphene was grown on the quartz slide and quartz tube using chemical vapor deposition. It shows excellent hemocompatibility both in vitro and ex-vivo tests compared with positive control-quartz and negative control-high density polyethylene. This work may be beneficial to those quartz-based biomedical applications such as optical fiber sensor in vessel and angioscopic. Also, Transferring graphene to other functional materials with thrombofenicity will endow the materials with hemocompatibility, which greatly expands the use of graphene in biomedical application field.

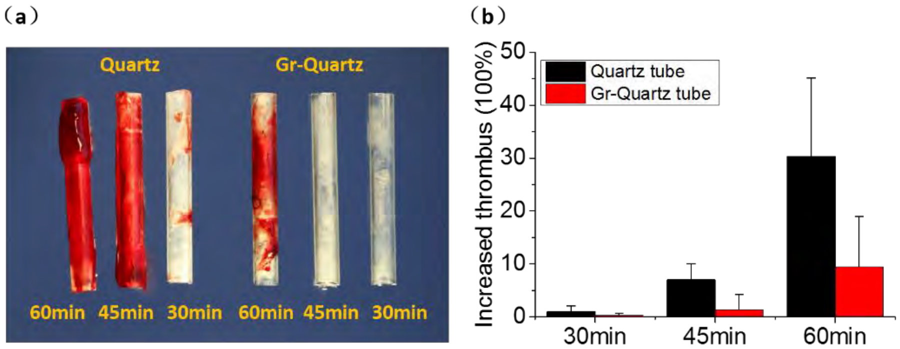

Fig.1 Image of thrombus on the quartz tubes and Gr-quartz tubes through ex vivo blood circulation using a rabbit (a). Increased thrombus percentage on the tubes at different time (b).

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Experimental observation of chiral phonons in monolayer WSe$_2$

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Chirality is a fundamental property of an object not identical to its mirror image. In condensed matter physics, Fermions have been demonstrated to obtain chirality in many platforms with unconventional electronic transport phenomena, such as the quantum Hall effect and Weyl semimetals. Electron chirality was also found in two-dimensional systems such as graphene with pseudospin, and monolayer transition metal dichalcogenides showing optical helicity and valley degree of freedom. On the other hand, for bosonic collective excitations in atomic lattices, chirality was only theoretically discussed but never observed, including the recent prediction of chiral phonons in 2D hexagonal lattices [1]. We experimentally show that phonons can exhibit intrinsic chirality in monolayer tungsten diselenide [2]. The broken inversion symmetry of the lattice lifts the degeneracy of clockwise and counterclockwise phonon modes at the corners of the Brillouin zone. We identified the phonons by the intervalley transfer of holes through hole-phonon interactions during the indirect infrared absorption. Their chirality was confirmed by the infrared circular dichroism (CD) arising from pseudo-angular momentum (PAM) conservation. From the spectrum we further deduce the energy transferred to the phonons, which agrees with both the first principle calculation and the double-resonance Raman spectroscopy. The chiral phonons are important for electron-phonon coupling in solids, lattice-driven topological states, and energy-efficient information processing.

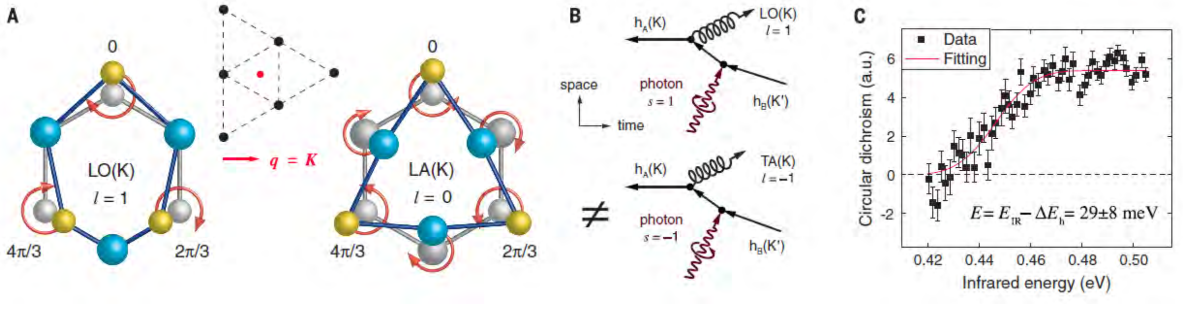

Fig.1 Nondegenerate chiral phonons in monolayer WSe$_2$ and the selection rule of hole-phonon interactions. (A) The atomic motion of W and Se atoms (blue and yellow spheres, respectively) in the real space is intrinsically circular for the chiral phonons residing at the K point (red dot) in the reciprocal lattice (array of black dots), due to the threefold rotational symmetry. Because the momentum vector determines the relative phase of the Se motion, opposite rotations correspond to completely different modes. The two modes have distinct PAM with respect to the center of the hexagon. (B) The phonons participating in the indirect optical transition are different for the left- and right-circular polarized IR photons because of the conservation of linear and angular momentum. Their distinct electron-phonon scattering strength dictates that the two processes have different amplitudes, leading to polarized IR absorption. $h_A(K)$, hole at the valence band edge of the K valley; $h_B(K')$, hole in the spin-split band of the K' valley. (C) The spectrum of the transient CD shows a photonic energy threshold of 0.448 ± 0.002 eV. Subtracting the energy difference between the initial and final hole states, a phonon energy of 29 ± 8 meV is deduced, in agreement with that of the LO mode.

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Toughening CNT-based composites via non-covalent interactions

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The increasing demands for light-weight, high-modulus and tough materials call for the large research interest in developing high performance nano-composites. Carbon nanotubes(CNTs) and their composites are promising materials for these demands, according to their superb mechanical and physical properties. However, the performance of CNT based micro- or macro-assemblies are still far lower than that of single CNT, which is because of the weak interactions between tubes or bundles inside the assemblies. In this work, two different kinds of polymers were applied to CNT suspension and functionalized the CNTs via π-π interactions. The strong interactions between CNTs and polymers endow the CNT-based composites both improved strength and toughness, increasing by 350% and 219%, respectively, which were always a trade-off in the mechanical properties of composites. The mechanism of the striking improvements were investigated through the chemical structure of the polymers and the structures of the as-prepared CNT-based composites.

Key Words: CNT, composites, π-π interactions

TEMPERATURE EFFECT ON THE INTERFACIAL SHEAR STRESS TRANSFER IN CARBON NANOTUBE FIBER/EPOXY RESIN COMPOSITES

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Keywords: Interfacial shear stress, carbon nanotube fiber, epoxy resin, temperature effect

ABSTRACT

Carbon nanotubes (CNTs) have been of interest as reinforcement for polymer composites owing to their extraordinary mechanical and electrical properties. Structure and properties of the fiber/matrix interface play a major role in controlling the mechanical and physical properties of composite materials. In particular, the interfacial shear strength (IFSS) is one of the most important parameters in determining the strength and the toughness of a composite, since the load applied to the composite is transmitted from the matrix to the fiber through the interface.[1]Aiming at predicting the fiber/matrix interface mechanical properties, many authors have investigated and discussed the role played by matrix and interphase properties, especially surface treatment in normal temperature[2]. In consideration of composites complicated application, it’s meaningful to research their interfacial properties under high temperature condition.

In this article, the interfacial shear strength has been determined in an CNT fiber/epoxy system by using a microdroplet test. Experiments were conducted from 20 to 140℃ in order to investigate how temperature affect the transfer of shear stress at the interface. Schematic of test set-up and the CNT fiber/epoxy droplet before interfacial debonding could be seen in Fig.1. This was followed by a quasi-static plateau in which relative sliding was maintained between the fiber and the droplet as a result of the movement of the droplet along the fiber pushed by the knives.[3] Besides, IFSS between the fiber and its surrounding matrix can be calculated according to the following equation:

$$IFSS = \frac{F_d}{\pi d_f L_e} \tag{1}$$

Here, F_d is the maximum fiber axial force recorded at the onset of microdroplet debonding, d_f is the fiber diameter, L_e is the embedded fiber length and $\pi d_f L_e$ is the embedment area.

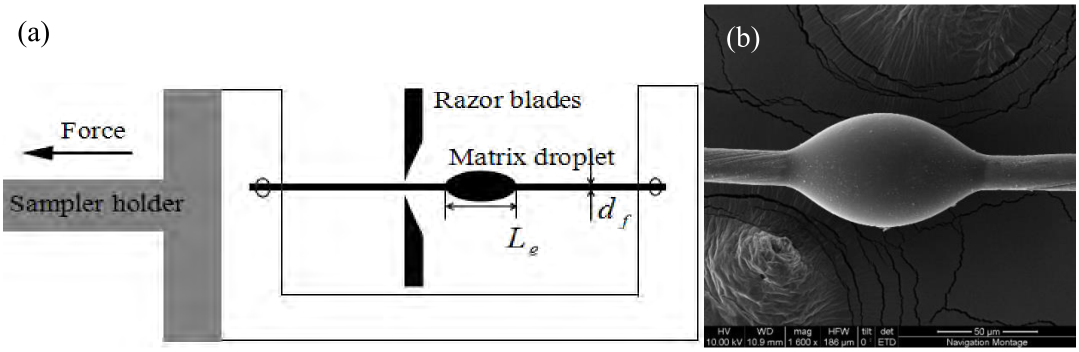

Fig. 1 Microdroplet test to evalute the IFSS between a CNT fiber and epoxy matrix. (a) Schematic of test set-up. (b) SEM images of the CNT fiber/epoxy droplet before interfacial debonding.

On the basis of evaluation of fiber/resin composite interface properties by microdroplet tests, the experimental relationship between IFSS and temperature effect is given in Fig.2. The IFSS for pure and composite CNT fiber range from 11.06 to 38.65MPa and 18.98 to 49.73MPa under the variation in temperature respectively. The values of composite CNT fiber are much higher than the pure one.

According to the SEM observation of the fiber surface (Fig.3) after interfacial debonding occurred as a result of interfical sliding of CNT bundles within the fiber. As suggested by some authors, the epoxy resin could be affected by the presence of the fiber, which absorbs part of the curing amine on its surface, so causing a stoichiometric imbalance of the epoxy resin in proximity of the fiber and lower crosslinking density, therefore, to lower resin Tg.[4] In this case, aiming at improving the high temperature shear strength, we adopted the method of infiltration of the fiber. The infiltration of unsaturated polyester resin can reduce the stoichiometric imbalance to enlarge the thermal expansion coefficient of composite fiber. As shown in Fig.4, the matrix droplet debonded as a whole from the surface of the composite CNT fiber through A to D, which is different from the pure one debonded from A to B in Fig.3. The infiltration strengthen the interface bonding force between fiber and resin.

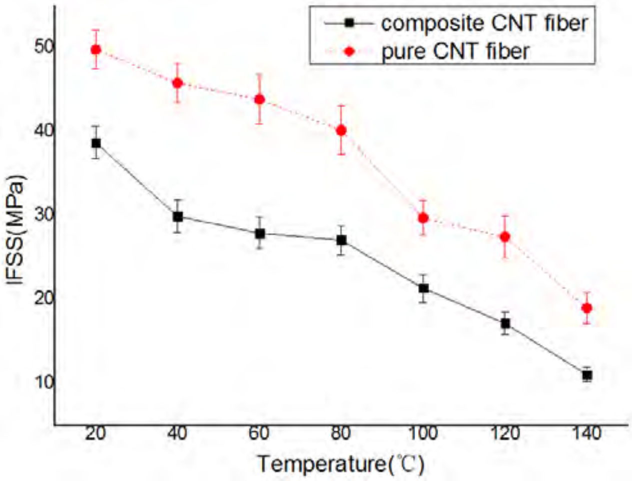

Fig.2 Effect of temperature on interfacial shear strength values in pure and composite CNT fiber.

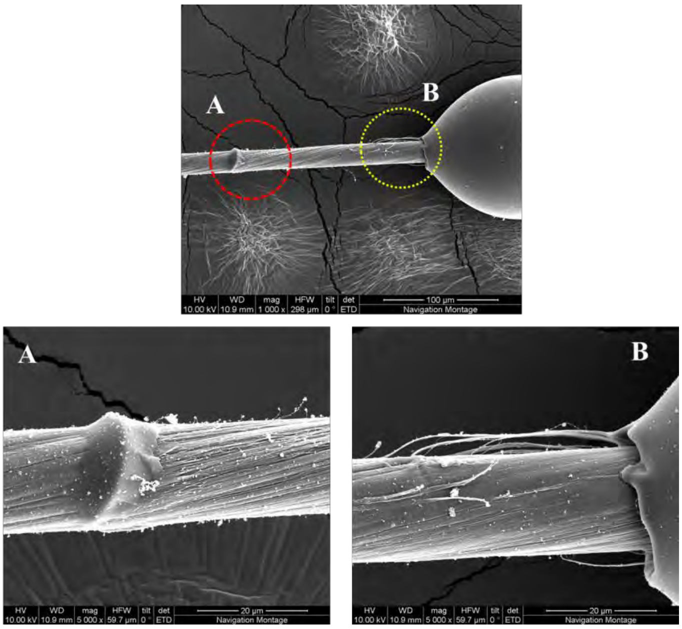

Fig.3 SEM images showing that the matrix droplet debonded as a whole from the surface of the pure CNT fiber.

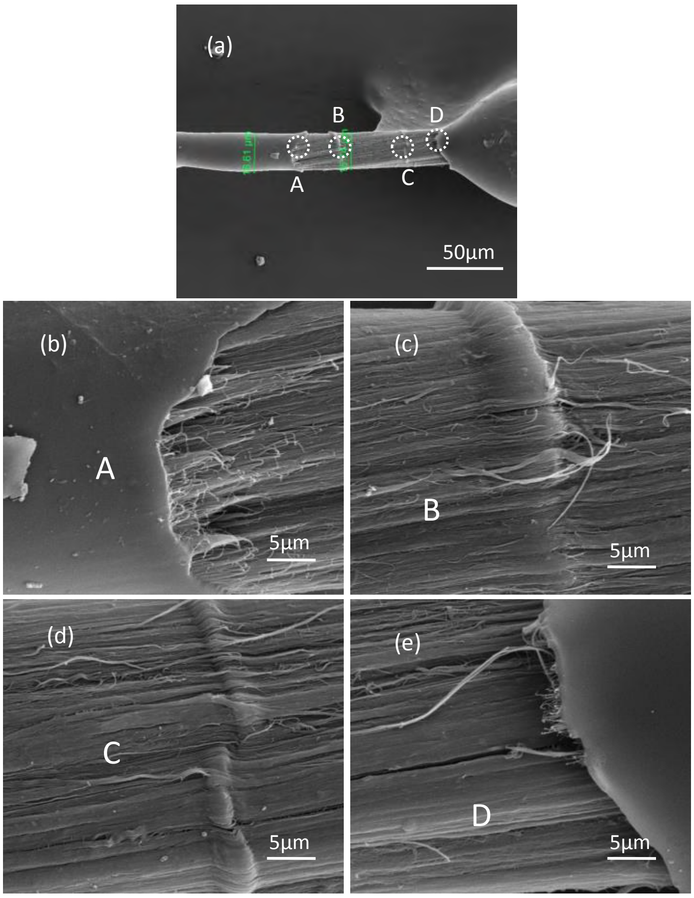

Figure 4. SEM images showing that the matrix droplet debonded as a whole from the surface of the composite CNT fiber.

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Monitoring Local Strain Vector in Atomic-layered $MoSe_2$ by Second-Harmonic Generation

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ABSTRACT: Strain serves as a powerful freedom to effectively, reversibly and continuously engineer the physical and chemical properties of two-dimensional (2D) materials, such as bandgap, phase diagram and reaction activity. Although it is highly desirable to fully characterize strain vector at local points, both amplitude and direction, a technique is very challenging experimentally. Here we report a novel approach to monitor the local strain vector in 2D molybdenum diselenide ($MoSe_2$) by polarization-dependent optical second-harmonic generation (SHG). The strain amplitude can be evaluated from the SHG intensity in a sensitive way (-49% relative change per 1% strain); while the strain direction can be directly indicated by the evolution of polarization-dependent SHG pattern. In addition, we employ this technique to investigate the interlayer locking effect in 2H $MoSe_2$ bilayers when the bottom layer is under stretching but the top layer is free. Our observation, combined with ab-initio calculations, demonstrates that the non-covalent interlayer interaction in 2H $MoSe_2$ bilayers is strong enough to transfer the strain of at least ~1.4% between the bottom and top layers to prevent interlayer sliding. Our results establish that SHG is an effective approach for in-situ, sensitive and noninvasive measurement of local strain vector in non-centrosymmetric 2D materials.

KEYWORDS: strain, $MoSe_2$, second-harmonic generation, 2D materials

Effect of surface of carbon nanotubes on deposition of CdS nanoparticles

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At present, the development of novel light-emitting elements is necessary to create compact energy-saving full-color light devices. The hybrid materials from CdS nanoparticles and carbon nanotubes (CdS/CNTs) possess a combination of high electrical conductivity of CNTs and size-tunable optical properties of CdS nanoparticles, and have attracted the attention of many researchers due to the wide potential of application in photovoltaics and optoelectronics. Interfacial interactions between CdS species and CNTs determine the architecture and optical characteristics of CdS/MWCNT hybrids. The effect of surface of CNT on the decoration with CdS nanoparticles from an ammonia solution of cadmium(II) chloride and thiourea was studied. Here we study ability of the single-walled and multi-walled carbon nanotubes to be decorated by CdS nanoparticles under high-temperature solvothermal conditions. The CdS nanoparticles were also grown on the CNTs with surface modified by fluorine atoms or hafnium oxide. The morphology and structure of the hybrid structures were studied by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy. A detailed study of the phenomenon of electroluminescence and photoluminescence in hybrid structures was carried out. It was shown that the photoluminescence of the CdS/CNT hybrid structures depends not only on the structure, morphology and density of CdS nanoparticles, but also on the chemical state of carbon nanotubes.

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Retrieving the exit-wave phase from a single HRTEM image of two-dimensional lattice

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High-resolution transmission electron microscopes (HRTEM) is one of the most powerful tool to characterize the lattice structure at the atomic scale. Although with the aid of the hardware spherical aberration (Cs) correctors, the atoms on the two-dimensional lattice could be almost observed directly. However, the influence of the residual spherical aberrations and astigmatisms become prominent. On the other hand, the exit-wave function can be reconstructed from a focal series of HRTEM images, on which the residual aberrations could be retrieved completely by using a numerical method. But, in this method, it typically requires 20~30 images. Some two-dimensional materials face the challenge of electron-beams damage.

Recently, a numerical method has been proposed to efficiently remove the contribution of the aberrations for a weakly scattering object, but it is only effective for anti-symmetric geometric aberrations [1]. In this work, we propose a new method to retrieve the phase of the exit-wave function from only one single HRTEM image. Specially, all geometric aberrations can be removed. Fig 1(a) show one experimental HRTEM image of graphene. If only the powerful filter tool of the BM3D algorithm is used, the image is not very clear to distinguish each atom, especially on the defect region. By employing our proposed algorithm, atoms are directly observed, which is benefit from the remove of all geometric aberrations.

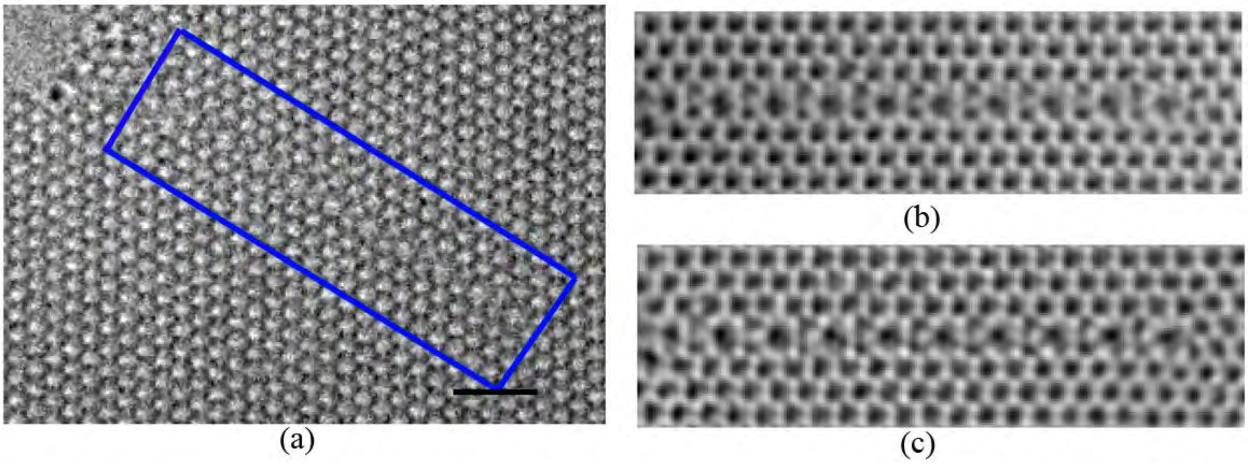

Fig.1 (a) Experimental HRTEM image of graphene. The scale bar is 1 nm. (b) The interesting region in (a) is filtered by the BM3D algorithm and its contrast is inversed. (c) The phase of exit-wave is retrieved by our proposed method and filtered by the BM3D algorithm.

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nano-FTIR spectroscopy: nanoscale resolved infrared spectroscopy of self-assembled polymer monolayer

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nano-FTIR is an emerging new optical super resolution microscopy technique that enables IR spectroscopy and chemical mapping with down to 10nm spatial resolution. Utilizing broadband laser sources like a mid-IR supercontinuum laser for tip illumination and interferometric light detection analogous to classical FTIR spectroscopy enables near-field spectroscopic measurements at nanometer scale spatial resolution with unprecedented signal quality.

Owing to its order of magnitude higher detection sensitivity compared to standard FTIR spectroscopy and extremely high spatial resolution nano-FTIR has been successfully employed for determining the chemical composition of multicomponent thin film polymer blends, probing the local secondary structure in individual insulin and collagen fibers and determining the molecular orientation and cluster size in ultrathin polymer brush layers.

We demonstrate for the first time nano-FTIR spectroscopy and infrared mapping of a thin self-assembled polymer film with a thickness of only 7nm. nano-FTIR spectra are reproducible and are in good agreement with standard FTIR spectra from similar, yet bulk materials. This first study opens a whole new perspective and opportunities towards nano-chemistry and nano-biology and. Several applications will be presented.

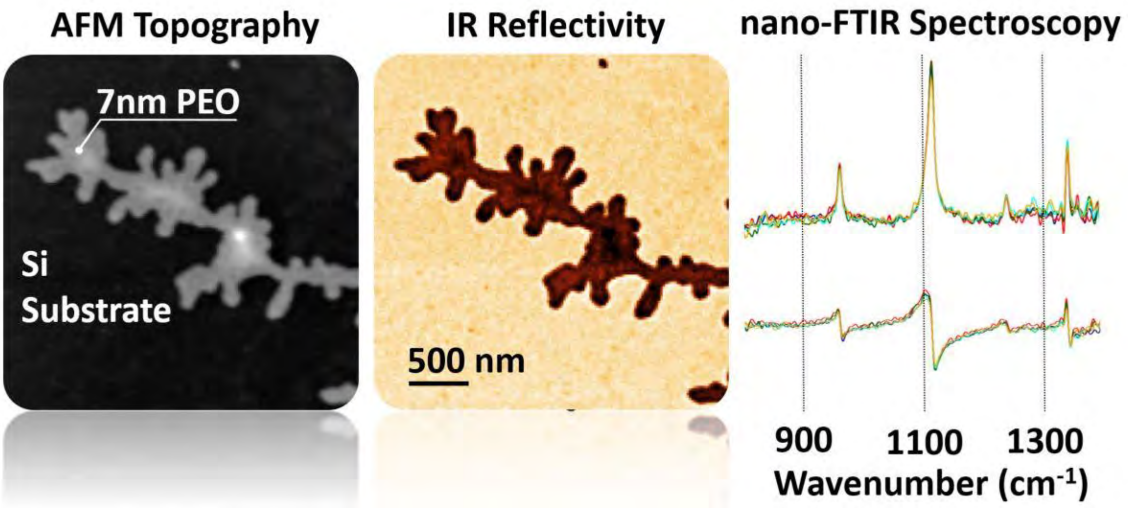

Fig.1 World first infrared visualization and spectral characterization of self-assembled polymer monolayer.

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Frequency-domain Raman Optothermal Method to Measure Thermal and Optical Properties of 2D Materials and Heterostructures

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Heat conduction properties of individual low-dimensional materials is of fundamental interest for understanding nanoscale physics and developing applications like thermal management and thermoelectric energy conversion, but the existing methods for nanoscale thermal measurements are very limited [1],[2]. Here, we present a frequency-domain Raman optothermal method to *in-situ* measure the in-plane and out-of-plane thermal properties as well as the laser absorption coefficients of 2D materials and the van der Waals heterostructure with arbitrary atomic layers. The extracted thermal properties include the in-plane thermal conductivity and specific heat of each layer, and interfacial thermal conductance between every two adjacent layers. A train of tightly focused laser pulses (on/off duration ratio = 1:1) is used to heat the atomic layers, while the temperature of each layer is detected from their distinct Raman band shifts that are linearly dependent on the local temperature. We change the laser spot sizes and the frequency of the laser pulse train to generate multiple temperature rise curves as a function of the pulse frequency at varied spot sizes. By multi-response multi-parameter fitting of the measured temperatures into a three-dimensional heat conduction model, we can simultaneously obtain all the unknown thermal properties as well as the laser absorption with high accuracy.

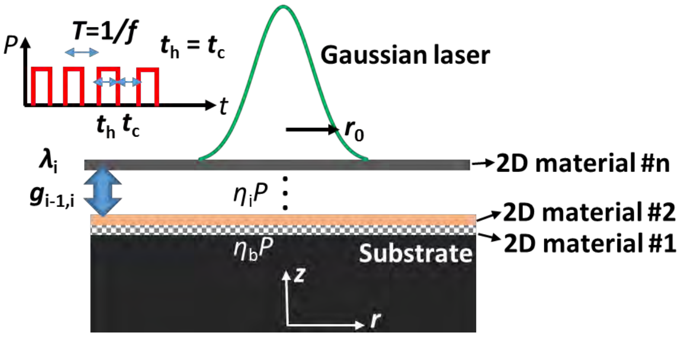

Fig.1 Schematic of the frequency-domain Raman method.

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Directly observing carbon nanotubes liquid behavior via liquid cell transmission electron microscopy

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Understanding the behavior of carbon nanotubes (CNTs) in liquid is important to the solution-based investigation on chemical functionalization[1] and dispersion[2-3] of CNTs. In this research, we directly observed the attachment between CNTs in water via the emerging liquid cell transmission electron microscopy (liquid cell TEM). The observed results revealed that there existed local CNTs attachment, rotation and bending during the attachment processes. What's more, we also observed the degradation of CNTs caused by the hydroxyl radicals[4] which were generated from the interaction between electron beam and water[5]. Degradation could happened along the radial and axial direction of CNTs, and additionally on some preferred sites leading to the formation of holes on CNTs, respectively.

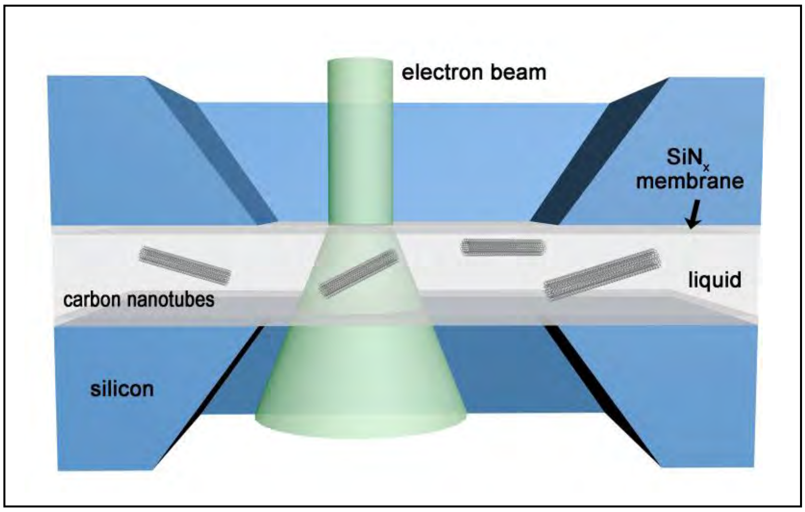

Fig.1 The schematic of liquid cell.

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Ultrafast time-resolved electron diffraction: nanoscopic phenomena occurring in bulk-scaled carbon nanotubes during annealing

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Ultralight bulk-scaled materials with excellent electrical, thermal, and mechanical properties are on demand for broad applications in automobiles, aircrafts and outer-space developments. CNTs is one of the desirable materials, which exhibits extremely high tensile strength, electric and thermal conductivities. However, these physical properties are valid only within the single CNT or on the nanometer-scale, and they decrease by several orders of magnitude when the CNTs are assembled as bulk-scaled devices. CNTs are bound up via van der Waals force in the CNT assemblies, and the amorphous carbon and impurities in the interface among the CNTs bottleneck the mechanical strength as well as hamper the electric and thermal conductions. Annealing of CNT assembly under noble gas atmosphere is prospective to control the interface among the CNTs. The electric and thermal conductions are improved through annealing process at extremely high temperature. However, this process often induces surface damage and graphitization of the CNTs, resulting in impairing the flexibility of CNT assemblies. In this study, we performed ultrafast time-resolved electron diffraction [1,2] on CNT webs and analyzed the nanoscopic phenomena occurring at the interface among the CNTs (Fig. 1). According to the analyses, the CNT assemblies after moderate annealing conditions in vacuum gain three times higher thermal conductivity without impairing their mechanical strength and flexibility.

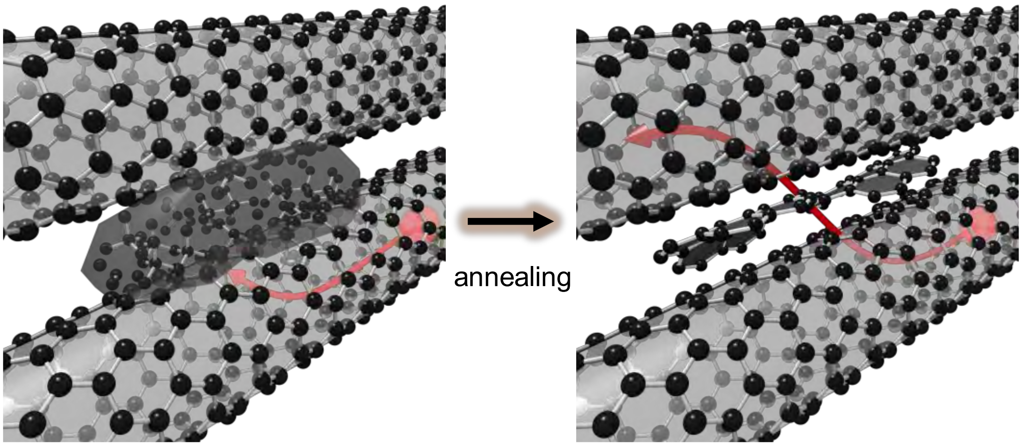

Fig. 1 Schematic of CNT assemblies during annealing. The red arrows in the figures indicate the phononic transport.

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Direct correlation of carbon nanotube nucleation and growth with the atomic structure of Re nanocatalyst

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The atomistic pathways of chemical transformations facilitated by nanocatalysts remain largely unknown due to uncertainties associated with the highly labile structures of the metal nanoclusters, changing during the reaction significantly, affecting the reaction pathways. In this study, we directly image the parasitic growth of SWNT catalysed by Re metal nanoclusters, in real time and with atomic resolution.[1,2] The reaction is performed by a FEI Titan 80-300 at 80 keV. In contrast to environment TEM and liquid cell TEM where the impact of the e-beam is treated as an undesirable and unavoidable side effect, our approach directly harnesses the energy transfer from the e-beam to the atoms to initiate specific chemical reactions. Time-series imaging reveals that nanotube growth on Re nanoclusters promoted by the e-beam has remarkable similarities to catalytic CVD processes. The symbiotic relationship between the nanocatalyst and nanotube, resembling a mechanism predicted in the theoretical studies, demonstrates directly that the efficiency of nanotube formation depends on the crystalline order of the metal atoms in the nanocatalyst, which, along with the observation of catalytically active single atoms in our study, improves the mechanistic understanding of nanotube nucleation and growth.

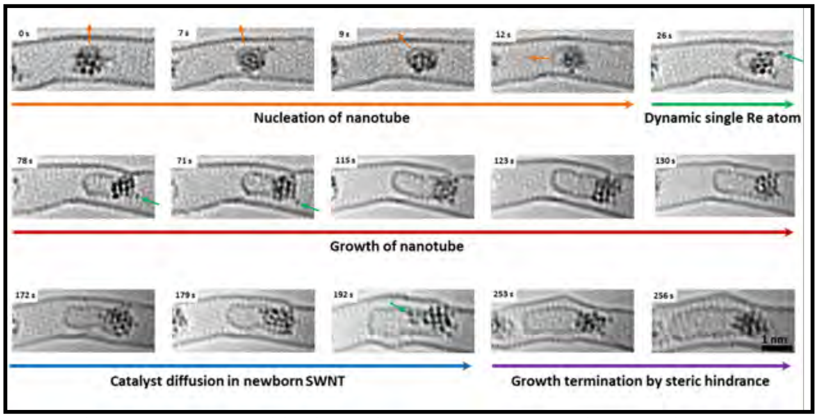

Fig.1 Time-series aberration-corrected high resolution TEM images showing the parasitic growth of SWNT catalysed by Re metal nanoclusters under electron beam irradiation.

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Chirality Identification and Quantification of Carbon Nanotubes on Substrates

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The characterization of the chiral structure of single-walled carbon nanotubes (SWNTs) is a crucial issue for the chirality-specific growth and has been a great challenge [1]. The selection of suitable techniques is important for obtaining accurate identification and reliable quantification of the chirality of SWNTs on substrate. Normally, a combination of multiple techniques is needed to acquire a reasonable result.

Here, we developed a systematic method by using optical spectroscopy including Raman, photoluminescence, absorption combined with electron diffraction (ED) to identify the chiral index (*n*, *m*) of tubes grown on substrates. We used the multiple techniques such as Raman, AFM/SEM combined with Raman, UV–Vis–NIR absorption to provide the quantitative chirality assessment of SWNTs with specific charities, such as (12,6), (16,0), and (14,4) [2–5]. Recently, we also show the quantitative chirality assessment of large diameter aligned tubes with specific chirality by using Raman, ED, polarized optical absorption, and scalable Rayleigh scattering based methods. It will be a practical pathway to provide the comprehensive structure information of different SWNT samples.

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Non-Blinking Single-Molecule Detection in A Carbon Nanotube by Surface-Enhanced Raman Scattering

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The study of single-molecule (SM) behaviour can provide fundamental physical and chemical information otherwise obscured by the ensemble averaging due to the existence of vast molecules and accessible microstates. Large efforts have been made to immobilize the single molecules in order to in-situ study the SM behaviour[1-4]. Here, we propose a strategy to encapsulate and immobilize single molecules inside a single-walled carbon nanotube (SWNT), the interior of which can serve as a nanoscale confined space with definite and uniform environments to facilitate the SM study. We utilize surface-enhanced Raman spectroscopy (SERS) to achieve the ultrasensitivity that can detect the SM signals and to provide the chemical specificity that can distinguish different molecular moieties via the vibrational fingerprints. We show that a single molecule located inside the SWNT and exactly at the SERS hot spot can not only be unambiguously detected, but also provide non-blinking and stable SERS signals with little spectral wandering, whereas signal fluctuations including temporal blinking, intensity variation, and spectral wandering are widely considered as the characteristic behaviour of single molecules in the SERS community. This approach opens new possibilities toward SM chemistry and physics in nanoscale confined space.

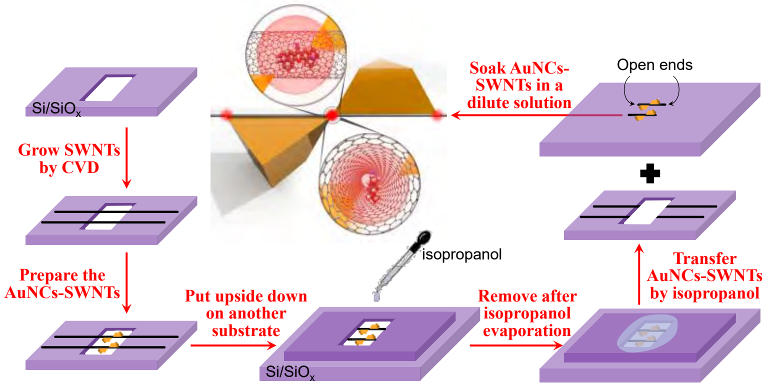

Fig.1 Schematics of the experimental procedures to prepare the AuNCs-SWNTs with open ends for molecules to be encapsulated and schematics of the AuNCs-SWNTs with a single molecule encapsulating inside the SWNT and locating exactly at the hot spot.

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Bilayer Plots for Accurately Determining the Chirality of Single-Walled Carbon Nanotubes Under Complex Environments

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The chirality (n,m) determines all structures and properties of a single-walled carbon nanotube (SWNT), therefore, accurate and convenient (n,m) assignments are vital in nanotube-related science and technology. Previously, a so-called Kataura plot that protracts the excitonic transition energies (Eii's) of SWNTs with various (n,m) with respect to the tube diameter (dt) has been widely utilized by researchers in the nanotube community for all (n,m)-related studies[1-3]. However, the facts that both Eii and the calculated dt are subject to interactions with the environments make it inconvenient to accurately determine the (n,m) under complex environments. Here, we propose a series of bilayer plots that take into account the interactions between the SWNTs and the environments so that the (n,m) of SWNTs can be accurately determined. These plots have more advantages than the Kataura plot in concision, less data overlapping, and the suitability to be used in complex environments. We strongly encourage the researchers in the carbon nanotube community to utilize the bilayer plots for all (n,m)-related studies, especially for accurate and convenient (n,m) determination.

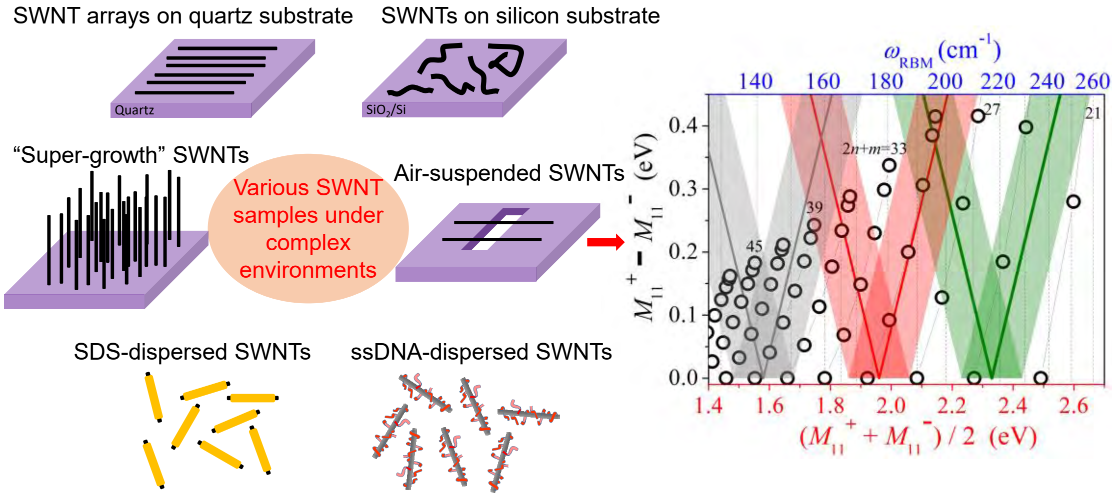

Fig.1 Accurate (n,m) assignments under 6 different environments.

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Understanding the superlubricity of freestanding carbon nanotubes and graphene

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Understanding the superlubricity of carbon nanotubes and graphene is crucial for their NEMS and ultralow-friction applications. Here we study superlubricity of freestanding carbon nanotubes and graphene using molecular dynamics [1-4]. We demonstrate that asymmetric lateral deformation is the key to stable superlubric sliding between freestanding carbon nanomaterials. The breakdown of superlubricity is found to be caused by a competition between the energy gain associated with friction and that of elastic deformation. Moreover, the tensile deformation is found to be beneficial for achieving low friction in samples with thermally-treated periodic ripples.

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Gauge Invariance of Linear and Nonlinear Optical Response

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Recently, the interest in the optical response has grown due to the large response and exotic phenomena observed in two-dimensional materials such as graphene, hexagonal boron nitride (hBN), and transition-metal dichalcogenides, which can have many possible applications. From a theoretical point of view, the perturbative calculations of optical response are performed routinely. However, it is well-known various methods for calculation, e.g., the choice between length and velocity gauges, frequently generate different results [1-3].

Here, we present a comprehensive review of the differences that arise from the choice of method on the linear and nonlinear optical responses. The responses obtained by using four different methods are compared. The methods stem from the combinations of gauges, i.e., length and velocity, and two ways of evaluating the current density response: directly and indirectly via the polarization density. The invariance of response functions is investigated in two levels of modeling: by including or excluding the electron-hole interaction, i.e. excitonic effect. We derive the expressions for the conductivity tensors by adapting a density matrix approach with and without excitons. As a case study, the linear and nonlinear response functions of hBN monolayers are studied numerically. Our results show that when the electron-hole interaction is ignored, the response functions obtained using the length and velocity gauge methods converge toward an identical result by increasing the number of bands in the calculations. Nonetheless, the length gauge calculations are the most accurate results among all methods for any number of bands [2]. Including the excitonic effects changes the linear and nonlinear responses of hBN monolayers dramatically due to the reduced screening. More importantly, the optical responses obtained by the conventional velocity gauge method do not agree with the length gauge results as shown in Fig. 1 for second-harmonic generation (SHG) of hBN monolayers. Nonetheless, by rewriting the interaction Hamiltonian in the velocity gauge as a series of commutators, a fully gauge invariant response is obtained, c.f. Fig. 1 [3]. More details will be discussed in the presentation.

This work was supported by the QUSCOPE center sponsored by the Villum Foundation and the CNG center under the Danish National Research Foundation, project DNRF103.

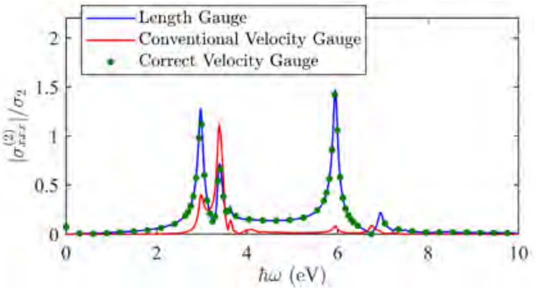

Fig.1 Excitonic SHG spectrum of hBN monolayer obtained by different methods ($\sigma_2 = 3.28 \times 10^{-15}$ Sm/V).

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Mechanisms of BNNT Nucleation and Growth during CVD: Non-Equilibrium MD Simulations

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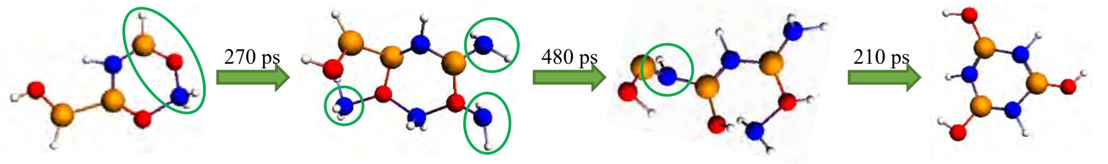
Boron Nitride Nanotubes (BNNTs) can be synthesised effectively via boron oxide chemical vapour deposition (BOCVD).[1-3] This method involves heating solid B and a metal oxide such as MgO, FeO or Li_2O, producing B_2O_2 to react with a flow of NH_3 to form BNNTs on the walls of the reactor or on catalyst surfaces such as MgO, Fe and Ni:[4]

$$B_2O_{2(s)} + NH_{3(s)} \rightarrow 2BN_{(s)} + 2H_2O_{(s)} + H_{2(s)}$$

The mechanism explaining this self-assembly process remains essentially unexplored, and the above equation is proposed from experimental findings without insight from theoretical work.[5] Here we investigate nucleation and growth of BNNTs and the early stages of BNNT growth, using nonequilibrium ReaxFF molecular dynamics simulations.[6] The $\mathrm{ReaxFF_{HBN}}$ force field[7] was employed with a timestep of 0.25 fs. An NPT ensemble was enforced on a periodic unit cell initially containing 125 B_2O_2 and 250 NH_3 molecules via the Berendsen barostat with a target temperature of 1100 °C and a target pressure of 1 atm. These simulations reveal, for the first time, the fundamental steps towards BNNT nucleation from B_2O_2 and NH_3 precursors during CVD including borazine ring self-assembly (Fig. 1). We also elucidate the role of pertinent experimental parameters (temperature, pressure, H_2O and H_2 partial pressures, and the presence of solid-phase boron nanoparticle catalysts) on this self-assembly process.



B-N and N-O bonds form | NH_x group additions | Rearrangement, B-N bonds form | Borazine Ring Formation

Fig.1 Atomistic formation mechanism of borazine rings during BOCVD as calculated by ReaxFF NPT MD simulations with B_2O_2 and NH_3 precursors at 1100 °C.

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Analytical Modeling of Single-Walled Carbon Nanotube Energies

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To fully utilize the properties of single-walled carbon nanotubes (SWCNTs) for future materials and devices one would require uniform SWCNT products. However, current SWCNT production methods tend to give non-uniform products with a distribution of chiralities. The origin of this “distribution of chiralities” have long been a puzzling question, but in recent years several breakthroughs have been made [1-5]. These advances rely on having accurate energies for SWCNTs with different chiralities, lengths and terminations. Such energies are usually calculated using density functional theory (DFT) which gives very accurate energies, but the calculations are time and resource intensive. This limits the size of the systems, chiralities, lengths and terminations that can be studied. Here we present a new analytical model, derived from DFT results, for calculating total energies of SWCNTs. This new model consists of wall, edge and termination energies and can quickly and accurately determine total energies for hydrogen terminated SWCNTs with any chirality and length. Tests against previously published total energies calculated by DFT show the model having excellent accuracy, with a mean absolute error in the total energy below 1.5 meV per atom. The model can also be expanded on to include other terminations such as catalytic metals, by fitting model parameters to DFT results (ongoing work). Our model can calculate total energies of SWCNTs with good accuracy and negligible time consumption, which allows for probing of larger parameter spaces, in order to understand the distribution of SWCNT chiralities found in experimental products.

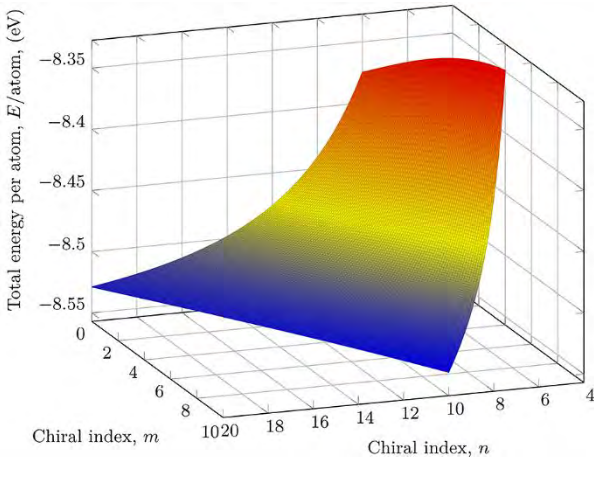

Fig.1 Total energy per atom as a function of chiral indices (n,m) for SWCNTs of length S=8 layers.

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Uncovering the Mechanism of the Improved Stability of Two-Dimensional Organic-Inorganic hybrid Perovskite

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Organic-inorganic hybrid perovskites (OIHP) have been recently demonstrated to exhibit outstanding potential on light harvesting devices, and many investigations have been sparked from the synthesis and applications[1-5]. The poor long-term stability of the materials is an intractable issue to hinder the large-scale commercial applications. Two-dimensional (2D) OIHP is a promising material to resolve the problem, however, the underlying mechanism is still unclear. Here, we employed first-principle calculations to investigate the enhanced stability of 2D OIHP comparing with the bulk structures. Two factors can be attributed to the enhanced stability. First, the intrinsic stability can be improved due to the non-restrictions of perpendicular distortion induced by the reductions of dimension. Second, the 2D OIHP exhibited enhanced humidity stability by comparing with the bulk OIHP. By uncovering the mechanism, we designed several new 2D OIHP with excellent stability and comparable electronic properties. Our findings should improve the applications of OIHP in solar cell industry.

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Effect of growth species on the onset of CNT growth

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The choice of carbon precursors is considered as one of the important parameters in CVD-based CNT growth toward chirality control. Despite various simulation studies [1,2], the effect of precursor on the onset of CNT growth has not yet been theoretically investigated.

We therefore studied the role of adsorbed carbon species during the CNT nucleation/growth from C_x (C and C_2), C_xH_y (CH_4, C_2H_2 and C_6H_6) and $C_xH_yO_z$ (CH_2O and C_2H_6O) species, by means of hybrid (reactive) MD and (force-bias) MC simulations. In all simulations, a Ni_{55} nanocluster virtually adsorbs on Al substrate at 2000 K.

We analyzed all C atoms in the CNT growth, dividing into five types (see Fig. 1), i.e., (i) dissolved C atoms (dis-C) into the Ni nanocluster, (ii) CH_nO_m species on the cluster surface, (iii) surface $C_kH_nO_m$ species, including carbon polyyne chains, (iv) C atoms in the carbon network (ring-C), including carbon cap or graphene-like patches [2], and (v) gas-phase carbon species (gas-C), including desorbed carbon species [3]. We found that precursors dissolve completely into the Ni cluster, despite of their different sticking probabilities [4] and consequently the concentration of dis-C species increases, before saturation occurs. Simultaneously, H_nO_m species, including H_2 or H_2O, desorb from the catalyst surface. After the saturation, other C-species appear and make specific contributions for building the nascent carbon nanostructures on the cluster surface, depending on type of carbon precursors used in growth process. The overall results indicate that the understanding of the nature of C-supply to a growing carbon network, after adsorption/dissociation of the growth precursors, is also important, in addition to the study of the role of catalyst and temperature in CVD growth technique.

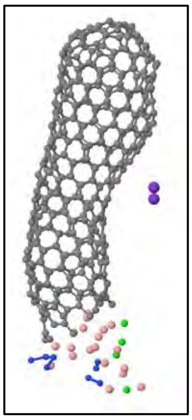

Fig.1 C species in SWNT growth: dis-C (pink), CH_nO_m (green), $C_kH_nO_m$ (blue), ring-C (grey) and gas-C (purple). For the sake of clarity, Ni, H and O atoms are not shown in the figure.

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Plasma-assisted etching of nascent CNTs

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In spite of numerous experimental and simulation studies, the precise etching mechanism in the early stage of plasma-based CNT growth is still not fully understood.

We thus studied the effect of H atoms to the grown CNT in CH_4 plasma, using hybrid (reactive) MD and (force-bias) MC simulations. Prior to hydrogenation, CNT structures (i.e., carbon caps, small and long CNTs) were base-grown on either on Ni_{55} or Ni_{148} nanoclusters, physisorbed virtually on Al substrate at 2000 K. During the simulations, the amount of H atoms in the gas-phase is kept constant.

During the hydrogenation process, the carbon cap converts to a carbon nanosheet/carbon nanowall and subsequently to carbon rings or short polyyne chains, before the removal of all carbon nanostructures from the catalyst surface (see Fig.1) [1]. We found, however, that the etching onset of long CNTs is not similar to the etching character of a carbon cap or nascent CNT [1,2]. During the hydrogenation, ortho H pairs play an important role in initiating the etching process on the tube side-wall, whereas most H-atoms are found on the tube cap, similar to the cases of the carbon cap and short CNT [1,3]. During the etching process, the occurrence of various gas-phase C_xH_y species is also analyzed in order to understand the effects after their re-adsorption [1]. We also analyzed CNTs, which adsorb either on small (Ni_{55}) or large clusters (Ni_{148}) to clarify the etching behavior of CNTs found in tangential and perpendicular growth modes [4]. Overall, this investigation leads to a better understanding of the nanoscale etching mechanisms of CNTs in plasma environment.

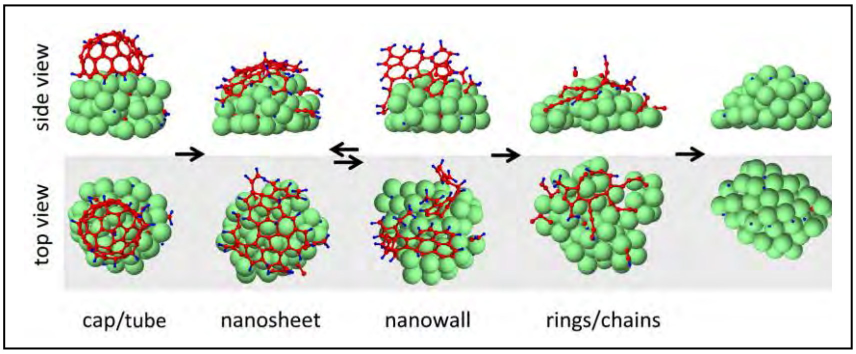

Fig.1 Sequential transformation of a carbon cap or small CNT into nanosheet, nanowall and initial carbon structures prior to cap/tube elimination from the catalyst surface in the hydrogenation/etching process.

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Charge enhancement in layered MoS2 predicted by an atomistic electrostatic model

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We present an atomistic model for predicting distributing behaviors of doped electrical charges in layered MoS2. This model mimics the net charge on each atom as an induced dipole plus a net charge Gaussian-spacial-distributed, and is able to predict the charge distribution on layered MoS2 in an external electrostatic field in a self-consistent scheme. The charge distributions in monolayer MoS2 flakes computed by the charge-dipole model is found to be in excellent agreement with those obtained by density-functional-theory calculations. Using this model, we predict the charge enhancement effect in MoS2 monolayer nanoribbons.

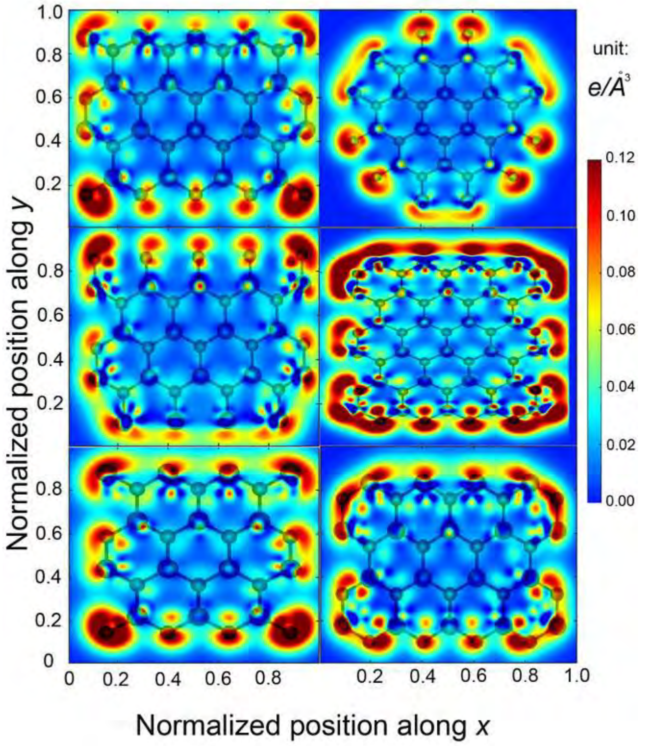

Fig.1 DFT-calculated distributions of a doped electron in MoS2 monolayer flakes of different dimensions.

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Twisting phonons in carbon nanotubes

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Precise control of the thermal transport properties of carbon nanomaterials is of great significance for its applications in many fields[1]. In this work, we use torsional deformation[2] to turn the lattice thermal conductivity of carbon nanotubes. We use a traditional phonon transport model combined with molecular dynamics simulations [3-6] to study the effects of length, tube diameter, temperature, and torsional deformation on heat transfer in carbon nanotubes. We reveal the dependence of the lattice thermal conductivity of carbon nanotubes on the torsion angle at different temperatures. Comparing with the relevant experimental results, we found that tube length, diameter and temperature affect the lattice thermal conductivity of twisted carbon nanotubes. Based on these results, we propose a model for adjusting the lattice thermal conductivity of carbon nanotubes by torsional deformation.

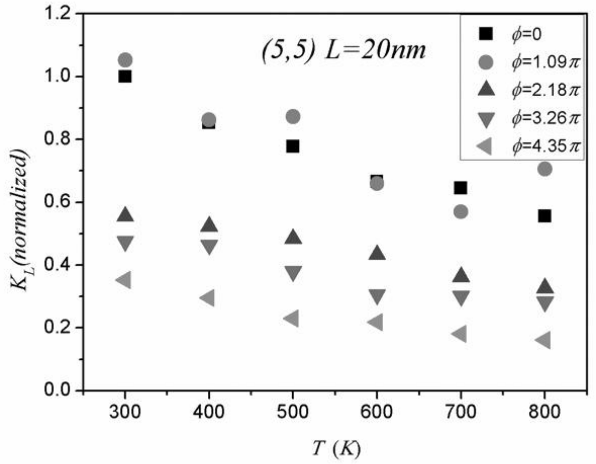

Fig.1 Relationship between lattice thermal conductivity of carbon nanotubes with different torsional angles and temperature.

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Superlubricity of graphene nanoribbons

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We report on simulations in which a graphene nanoribbon (GNR) is manipulated on another GNR substrate [1-4]. We find certain discrete orientations in which the lateral force of manipulation dramatically increases as we move the GNR in the graphene plane. The symmetry of these discrete orientations indicates commensurate contact between the GNRs. We observe that the transmission between these two GNRs is orientation-dependent and exhibits superlubric nature.

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Model calculations for superlubricity of Molybdenum disulfide

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Molybdenum disulfide is a well-known lamellar solid lubricant with a hexagonal lattice structure. The friction between a nanometer-sized molybdenum disulfide flake and a molybdenum disulfide surface is analyzed within the Tomlinson model combined with molecular-dynamics simulations [1-4]. The flake is coupled to a support by springs in the x, y and z directions while it is pulled on a periodic potential surface. The simulation results predict the underlying mechanism for the superlubricity of molybdenum disulfide.

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Improving thermoelectric performance of monolayer semiconductors beyond the confinement effect

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Thermoelectric research has been significantly activated during the past two decades by the quantum confinement effect, a characteristic of low-dimensional materials, thanks to the pioneering work of Hicks and Dresselhaus [1]. The confinement effect leads to a modification of the density of states and enhance thermoelectric power factor (PF) of low-dimensional materials. We showed that the PF is enhanced only when the confinement length or thickness in the two-dimensional (2D) material is smaller than the thermal de Broglie wavelength [2]. Thus 2D monolayer semiconductors naturally satisfy this condition so that they are a good candidate as a thermoelectric material. *However*, the thermoelectric performance of monolayer materials still need to improve for the industrial applications. In this work, we offer several possible strategies to improve the thermoelectric performance beyond the confinement effect. Firstly, we show that the figure of merit (ZT) of the low-dimensional semiconductors is set by a universal function of a dimensionless parameter α [3], which can be experimentally measured. Obtaining as large α as possible will give better ZT of 2D semiconductors. Next, we show how to improve the PF and ZT of the 2D semiconductors by means of the convergence of multivalley electronic bands, in which some distinct valleys become degenerate. This technique is possible to realize, for example, by applying mechanical strain. Monolayer InSe could be a good example material whose thermoelectric properties are greatly improved by the band convergence [4]. We find that the PF of monolayer InSe can be enhanced by nearly a factor of 3 through the band convergence under a biaxial compressive stress of about 1.16 GPa. Finally, we show that the presence of nonparabolic Kane bands and large anharmonicity in the 2D semiconductors could lead to better thermoelectric performance. The example materials are monolayer Bi_2Te_2S and Bi_2Te_2Se, in which the best ZT value could be more than 2 at 500 K.

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"Divide-and-Couple" mechanism of Dirac cone formation in 2D binary materials

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Two-dimensional (2D) materials with Dirac cone band structures possess exceptional electronic properties such as high electron velocity. Compared with the unitary monolayers graphene or silicene, 2D binary materials exhibit more varied configurations, some of which have DC electronic structures. However, there are still lack of through understanding of origins of DC formation. Combining density functional theory and tight-binding method, we studied the DC formation of 2D binary graphene-like and graphyne materials (e.g. AB, A_3B, or AB_3 systems where A/B= C, Si, or Ge). We proposed a "divide-and-couple" mechanism to elucidate the DC formation (Figure 1): First, we coupled the electronic states of the selected atoms who are paired atoms in AB system[1], triple atoms in graphyne[2], and six-membered ring atoms in A_3B or AB_3 systems[3], refereed to "pair coupling", "triple coupling", and "ring coupling" mechanisms, respectively; Second, we divide all electronic states into the groups so that the intragroup coupling make the band structures degenerated at the DC points but the states from different groups does not couple at the DC points; Finally, the intergroup coupling enlarged the band gaps except at the DC points where the energy bands remain touched due to little couplings. Understanding the origins of DC formation helps to design novel Fermi-Dirac systems.

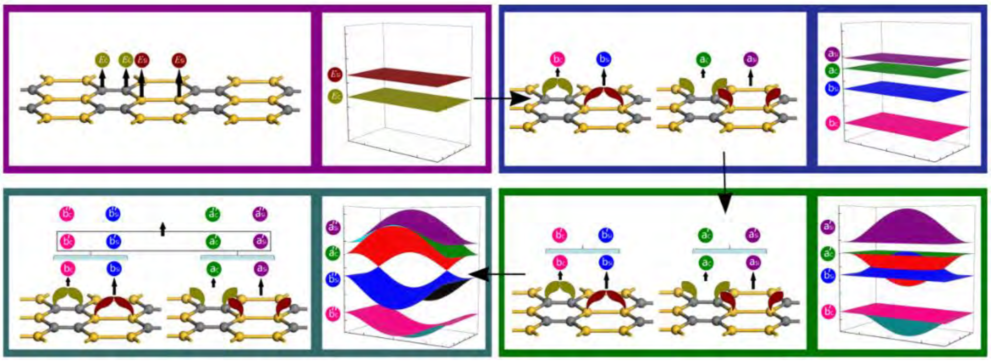

Figure 1 Schematic illustration of Dirac cone formation in the band structures of t1-SiC.

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Optical properties of multilayer dielectric stacks: Hidden symmetries and application to graphene

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Abstract: Graphene is a candidate for THz optics, especially for photonic devices. Photonics is a branch of science that studies how the light propagates through the material and how to modify its propagation, such as how to prevent the propagation or to localize the light, which can be useful to amplify the electric field at a specified position of material. To achieve this, one can use a system containing N layers of varying dielectric media in one dimension, which is called multilayer dielectric stacks. By manipulating the sequence of dielectric media within the multilayer system, one can control the light propagation through it. In this work, we will show that the number of transmission probability of light (T) for the 2^N possible sequence of the general N layers is not 2^N, however, there are either (N/2 + 1) or (N + 1) discrete values of T for even or odd number N, respectively. This high degeneracy implies the existence of hidden symmetries within the multilayer, which we will explain in this presentation [1]. We then apply the multilayer system for calculating the absorption of light in undoped graphene suspended inside the specially designed multi-layer structure. We found that the absorption is enhanced up to 50%, which is much larger than the conventional 2.3% absorption of undoped graphene without the multi-layer structure [2]. The reason for the absorption enhancement is because that the electric field is enhanced by interference occurring inside the multi-layer structure. We will show that the absorption depends on the number of layer and also the ratio of refractive indices of the dielectric media of the structure. For more quantum mechanical understanding of optical absorption, we also discuss the optical absorption in doped graphene by the contribution of single particle excitation and the collective excitation of electron.

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Electronic Property of the Composite of Carbon Nanotube and Carbon Nanobelt

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Carbon nanotube (CNT) is a one dimensional nano material with some good electrical characteristics and is expected to be applied to some electronics devices. In order to use CNTs as semiconductor devices, it is necessary to control the energy band structure of it.

In this study, we propose a necklace-like structure, which is composite of carbon nanobelt (CNB) and single wall carbon nanotube (SWCNT), as shown in Figure 1. The main purposes of this structure is local control of the band structure of SWCNT. We expect that this one dimensional heterostructure can form quantum well in SWCNT and works like heterojunction semiconducter.

We studied about this structure by computer calculation. First, we confirmed CNB and SWCNT form this structure by molecular dynamics calculation. After that, we calculated the energy band structure of these composites by density functional theory (DFT) under periodic boundary condition (PBC). We calculated some combinations of CNB and SWCNT by changing chirality of CNB, meanwhile the chirality of SWCNT was fixed to (7,0). The result of calculation suggests that the value of SWCNT's energy band gap will change about 1~30 meV because of the influence of CNB. How the gap changes mainly depends on the distance between CNB and SWCNT and probably positional relationship of the two. The result also show energy level of CNB will appear in band gap of SWCNT with the appropriate charity combination of the two. This imply that this technique might be able to be applied for local carrier doping.

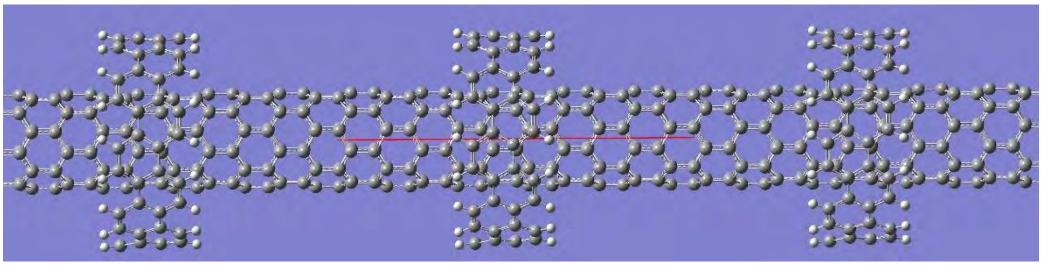

Figure 1. Structure of composite researched in this study. Red line shows length of unit cell of PBC.

Interlayer excitons in $MoSe_2$/WSe_2 heterostructures from first principles

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Novel two-dimensional materials from the group of layered transition metal dichalcogenides (TMDC) have recently attracted scientific interest for their unusual physical properties, such as their strong optical response. Two possible ways to tailor the electronic and optical properties are (i) the combination of different TMDCs to form lateral and stacked heterostructures and (ii) creation of alloys containing different metal or chalcogen atoms. Recent experiments have found the occurence of additional photo- luminescence signals that have been attributed to long-lived interlayer excitons in stacked heterostructures, with spatial separation of electrons and holes across the layers, possibly allowing for exploitation in solar cells.

We computed the theoretical absorption spectra of bilayer $MoSe_2$-WSe_2 heterostructures by solution of the excitonic Bethe-Salpeter equation with GW quasiparticle corrections [1] and inclusion of spin-orbit-coupling for three different stacking orders. Our calculations strongly suggest two qualitatively different contributions to the observed additional photoluminescence peaks: We find two spin-orbit split Rydberg series of low oscillation strength below the absorption onset of the monolayer materials, which arise from momentum-direct and spatially indirect excitations at the K point of the hexagonal Brillouin zone with a binding energy on the order of 250 meV.

Additionally, our calculations firmly establish that the fundamental band gap of $MoSe_2$-WSe_2 heterostructures is indirect and has a distinct interlayer nature, possibly giving rise to a momentum- and spatially indirect contribution [2]. These results confirm the recent experimental observation of a doublet nature of the interlayer photoluminescence [3]. We further show that the local stacking order leads to small variations in the hybridization between the $MoSe_2$ and WSe_2 bands and has a decisive effect on the polarization dependence of the interlayer excitonic absorption [2].

Our results motivate detailed studies of electron-phonon coupling effects and exciton dynamics in TMDC heterostructures by time-resolved optical experiments and *ab initio* methods.

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A Linear Model for Learning Ground State Electron Densities – An Alternative Machine Learning Route to Total Energies for Carbon

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Traditional attempts to learn the potential energy surface (PES) of molecular and crystalline materials are centered on mapping a local description of the chemical environment of each atom directly to a total energy contribution. For crystals like few layer graphene and carbon nanotubes these atom-centered environments are highly anisotropic but can nonetheless be exactly represented by descriptors that remain invariant to the translation and rotation of atoms.

Motivated by the ubiquitous success of density functional theory (DFT), recent interest has been shown in an alternative paradigm whereby first a local description of chemical environment is mapped to an electron density value and next, the inferred electorn density field is mapped to a total energy [1]. This two-stage inference process side steps the issue of approximating accurate first order derivatives to empirical kinetic energy functionals in orbital free DFT by providing an empirical ground state density directly [2].

We present a real space linear model for mapping local chemical environment descriptors to an electron density field and apply our model to a range of high symmetry molecular and crystalline structures including transition metals and strongly covalent stystems such as graphite and carbon nanotubes [3].

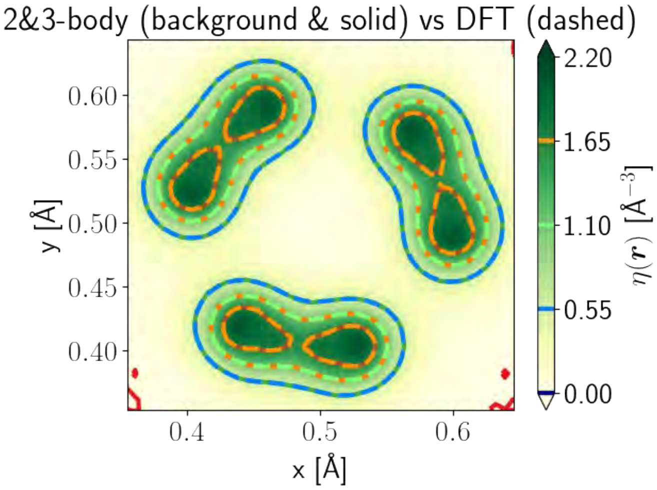

Fig.1 Our linear model (background and solid) accurately reproduces the ground state electron density (dashed) for this primitive cell carbon nanotube with lattice constants close to the linear model training set.

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Proximity spin-orbit coupling in graphene on transition-metal dichalcogenides stacked with general rotation angles.

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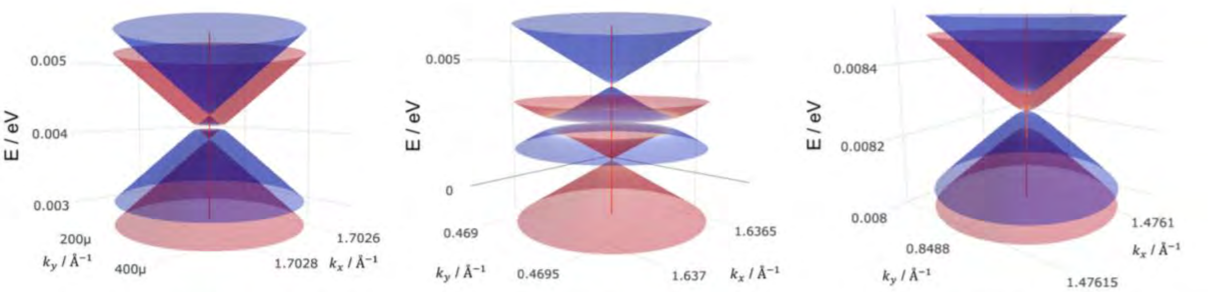
We theoretically study the proximity spin-orbit coupling (SOC) of graphene on transition-metal dichalcogenide(TMDC) stacked with arbitrary rotation angles. We derive the effective Hamiltonian for graphene using the continuum model, and estimate the spin-splitting energy as a function of the rotation angle. We find that the SOC splitting can be enhanced by 10 times by rotation.

Whereas a wide variety of potential applications have been proposed for graphene using its unusual physical properties, the lack of SOC limits its utilization for spintronics. To overcome this drawback, various strategies to enhance the SOC have been developed [2]. Using the proximity effect is one of the promising methods. Experimentally, monolayer graphene can be efficiently grown on the surface of TMDC, and there the strong SOC of TMDC induces a spin splitting on graphene. This approach is further supported by the first principles studies [4–6] of graphene stacked on various TMDCs, where the SOC splitting increases from the intrinsic value of order 10^{-3} meV to 0.5 - 20 meV. However, since the first principles method only works for the commensurate systems, all the previous studies are limited to the non-rotated geometries where the lattice orientations of graphene and TMDC are aligned. The rotated geometries with arbitrary orientation angles have not yet been investigated.

In this work, we develop a theoretical method to describe the graphene-TMDC hybrid system with arbitraty rotation angles, to systematically study the angle dependence of the proximity SOC effect. Starting from the general treatment of incommensurate interfaces [1], we derive the effective continuum Hamiltonian of graphene on MoS_2, $MoSe_2$, WS_2 and WSe_2. The band structures of graphene-MoS_2 with 0°, 16° and 30° are illustrated in Fig 1a, 1b and 1c, respectively. Noticeably, the splitting can be increased to about 3 meV for 16° [Fig 1b], while it is around 0.3 meV for 0° [Fig 1a].



(a) 0° (b) 16° (c) 30°

FIG. 1. (a), (b) and (c) show the band structures of graphene stacked on MoS2 with 0°, 16° and 30° respectively.

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Ab Initio Study of Sodium Dodecyl Sulfate (SDS) and Related Surfactants on Single-Wall Carbon Nanotubes

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How differently sodium dodecyl sulfate (SDS) surfactants behave on metallic and semiconducting single wall carbon nanotubes (SWCNTs) is one of the fundamental questions in the science and application of SWCNTs. Gel chromatography experiments [1], which brought about metal/semiconductor separation of SWCNTs, proposed a separation mechanism, where metallic (M-)SWCNTs having higher-density surfactant SDS on the surface pass through the gel, whereas semiconducting (S-)SWCNTs with lower-density SDS adsorb onto the gel. In recent times the subject of separation has been extended not only to the electronic type but to the chirality of SWCNTs. Aqueous two-phase extraction (ATPE) [2] separates SWCNTs by their electronic type, diameter, or chirality. The amount of SDS on SWCNTs also plays an important role in controlling their hydrophobicity in combination with other surfactants and salt. In spite of such progress in separation experiments, the fundamental origin causing the difference between M- and S-SWCNTs in the adsorption of SDS surfactants was not clear. Recently we showed that the adsorption energy of sodium dodecyl (DS) ions for M-SWCNTs is much stronger than those for S-SWCNTs, which is considered to be attributable to the difference in the band energy of M- and S-SWCNTs, using ab initio methods [3]. As shown in Fig. 1, dodecyl sulfate (DS) ions are more likely to adsorb onto SWCNTs than sodium (Na) ions or SDS molecules. Whereas the adsorption energy of SDS molecules becomes stronger as the diameter of the SWCNTs increases, the adsorption energy of DS ions for metallic (5, 5) nanotubes is much stronger than those for semiconducting (6, 5) or (10, 3) nanotubes. This causes a larger aggregation number of DS ions on M-SWCNTs, and also a separation of SWCNTs by the electronic type. This result is also consistent with the results of the multi-column gel chromatography where (10, 3) CNTs are obtained after (5, 6) CNTs.

In this study we perform density functional theory (DFT) calculations on the adsorption of several surfactants related to SDS onto SWCNTs and investigate the effect of the tail length and the head part of surfactants. This study, we believe, provides a fundamental understanding of separation of SWCNTs from a microscopic point of view, and will be applied to further investigation of the interaction between large molecules and nanocarbon materials.

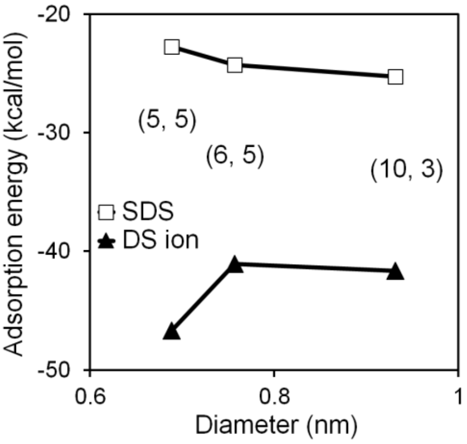

Fig.1 Dependence of the adsorption energy of SDS molecules and DS ions on the diameter of CNTs.

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Two-dimensional Phosphorus Carbide: Competition between sp^2 and sp^3 Bonding

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We propose previously unknown allotropes of phosphorus carbide (PC) in the stable shape of an atomically thin layer, as shown in Fig. 1. Different stable geometries, which result from the competition between sp^2 bonding found in graphitic C and sp^3 bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. Depending on the category, we identify 2D-PC structures that can be metallic, semi-metallic with an anisotropic Dirac cone, or direct-gap semiconductors with their gap tunable by in-layer strain.

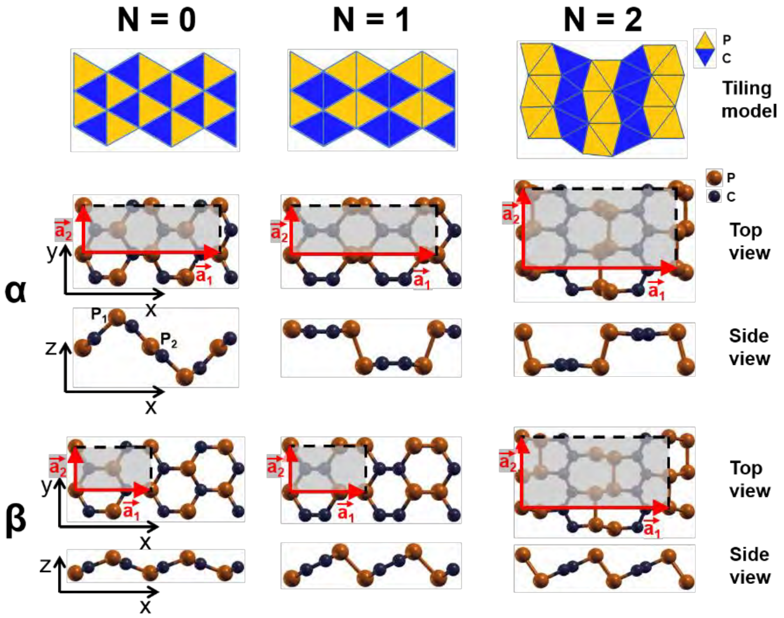

Fig.1 Tiling pattern and ball-and-stick model of atomically thin PC monolayers

Vibrational spectra of methylated forms of cytosine and adenine in the graphene nanopore and for regions of hydrogen binding

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In the human genome, DNA methylation is an epigenetic mechanism involving the transfer of a methyl group onto the cytosine to form 5-methylcytosine and 5-hydroxymethylcytosine that regulate, as a signaling tool, gene expression and silencing and control such medical conditions as oncology. With development of single-molecule resolution in the tip-enhanced and surface-enhanced Raman spectroscopy, (TERS & SERS) [1-3], identification of methylated forms of cytosine and adenine by their vibrational spectra in the DNA strands will soon become possible and can be incorporated into DNA sequencing to analyze methylated nucleotide positions. Therefore, knowledge of corresponding vibrational spectra is required. Spectral maps of the methylated nucleotides were investigated by molecular dynamics (MD) simulation. Fourier transfer of the density of states (DOS) was performed to obtain the spectra of various bonds in reaction coordinates for DNA nucleotides during transport through the 1.5nm graphene nanopore [4]. The vibrational frequencies were acquired for the C5'methylated cytosine and N6'methylated adenine vs. unmethylated nucleotides at the range 400-2000 cm^{-1} at a numerical resolution 20 to 40 cm^{-1}. The frequencies that can serve as markers of the corresponding base methylation status have been evaluated. To confirm obtained MD results, calculation of DFT based Raman frequencies of the cytosine nucleobase methylation have been carried out.

The signature frequencies of the methylated forms of a molecule are defined by hydrogen bonding at the frequency region 2500-4000 cm^{-1}. MD vibrational spectra of the methylated forms of cytosine were obtained at the H-X (X=C, N, O) bond stretching range. The calculated frequencies were compared for C5'methylated and hydroxymethylated cytosine. We were able to distinguish the modes that can mark the different forms of methylated cytosine. Our MD results were confirmed by DFT calculations of the Raman spectra of methylated forms of cytosine (DNA/RNA nucleotide configuration). Number of correlating frequencies corresponding to different type of methylation was found in MD and DFT spectra.

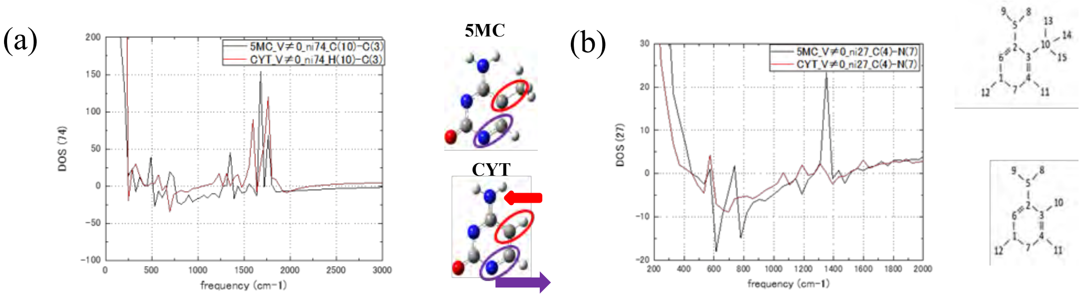

Fig.1 Spectra of cytosine and 5methylcytosine for the (a) H(10)-C(3), (b) C(4)-N(7) atoms of the base part.

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Photothermoelectric effect in a mixture of metallic and semiconducting carbon nanotubes

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Carbon nanotubes (CNTs) can absorb electromagnetic waves in a wide spectral range, including THz regime. Recently, aligned CNTs in THz detectors are shown by some researchers to be useful due to the intrinsic polarization sensitivity of the CNTs as light absorbers [1]. The THz signal in the detectors is understood to originate from photothermoelectric effect [2]. However, the reported thermoelectric performance is quite low (about a thousand times less efficient than commercial thermoelectric generator) because the detailed structure of the CNTs are not considered. In this work, we theoretically investigate the photothermoelectric effect in a mixture of semiconducting and metallic CNTs under illumination of THz light. We propose that, in an aligned CNT system, the metallic and semiconducting CNTs play independent roles for the photothermoelectric effect. The metallic CNTs are responsible for absorbing THz light and convert it into heat, which results in a temperature distribution along the device. On the other hand, the semiconducting CNTs are responsible for generating voltage difference from the temperature distribution due to Seebeck's effect. We find that large-diameter metallic CNTs absorb more THz light than the small-diameter ones, while from our previous work it is known that small-diameter semiconducting CNTs have larger Seebeck coefficients than the large-diameter ones [3]. Thus, combining large-diameter metallic CNTs with small-diameter semiconducting CNTs may be important to obtain better CNT photothermoelectric devices. It should also be necessary for us to consider the ratio of the metallic and semiconducting CNTs in the mixture for optimizing the thermoelectric performance.

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Crystallographic Selectivity in Growth of Graphene and Nanotubes

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The two carbon champions among nanomaterials, graphene and nanotubes (CNT) have not yet raised to an industrial use, in part due to the limited scalability and quality of their growth. Recent achievement in growing large graphene films [1] which are not only monocrystals but also display selective crystallographic orientation, resembles in an important way the chiral-selective CNT growth [2]. We will focus on the different fundamental factors in play of essentially "pure" crystalline nanomaterial synthesis. First, we will discuss the theoretical origins and quantitative kinetics underlying the success with monocrystalline graphene films [1, 3], obtained by CVD without substrate epitaxy but instead by guiding the distribution of feedstock or imposing other condition-gradients, Fig. 1. Deeper exploration of the "evolutionary selection" concept and how it operates in 2D will be discussed. The grains forming a polycrystalline front compete to survive and only the ones that have the fastest propagation vector aligned with the growth direction eventually dominate, becoming the monocrystalline growth front. It is particularly important for possible extension to other, non-graphene, materials of lower symmetries [4]. In contrast to graphene grains, fusing and competing, the well-isolated individual CNTs lack the basic means for similar "evolutionary selection": each one is on its own. Yet recent observations do show high selectivity towards the (12,6) CNTs when a solid Co_7W_6 catalyst is used [2]. Second then, we discuss how these experiments can be understood within the framework of our theory of CNT helicity [5], customized for the specific catalyst facets. Based on large-scale DFT calculations, we provide first-principles evidence that the CNT edge in contact with Co-W catalysts, as well as Ni and Co, can undergo an armchair-zigzag "phase segregation" [6], leading to an asymmetric edge, which largely suppresses the pronounced chiral-angle dependence of the interface energy typical for the conventional, circular CNT edge. Kinetic Monte Carlo simulations reveal that such segregation substantially alters the carbon insertion kinetics and the edge growth mode, and allow us to identify conditions resulting in overall preference for (12,6) tubes.

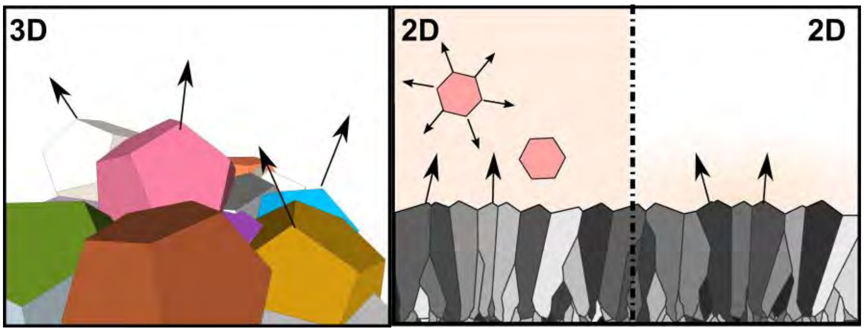

Fig.1 Growth by evolutionary selection for a 3D vs 2D crystalline material, especially since in 2D additional considerations such as suppression of secondary nucleation become important.

[1] I. Vlassiouk *et al*. *Nat. Mater.* **17**, 318 (2018).
[2] F. Yang, *et al.* *Nature* **510**, 522 (2014).
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[4] N. Gupta, K. Bets and B. I. Yakobson (in preparation).
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Enhanced Laser Field by Planar and Curved Graphitic Materials Applied for Water Decomposition: A TDDFT Study

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Strong and short pulse laser is applied as manufacturing tools. Currently available laser equipment can decompose water molecules that opens a way to producing hydrogen fuel alternative to conventional fossil fuel. By performing the time-dependent density functional theory (TDDFT) simulation, we propose that the necessary laser power for water decomposition is reduced by using 2-dimensional sheets and tubule form of graphitic materials. By assuming the full-width-of-half-maximum 10fs for wavelength 800 nm, we have studied decomposition of a water molecule being isolated or being located near 2-dimensional sheets or carbon nanotubes. The computed power threshold for water decomposition can be reduced by factor 2 by using the 2-dimensional sheet, and by factor 4 by using the carbon nanotubes compared to the power for decomposing pure water.

By computing the modulated optical field by TDDFT calculation, field enhancement near 2D sheet [1] as well as near carbon nanotube [2] was observed that is consistent with factor of threshold power reduction for water decomposition. The cause of reduction is optical field enhancement near 2 dimensional sheet as well as carbon nanotube. Especially for carbon nanotube, the field enhancement is not only coming from polarization but also by curvature of the wall of the tube that helps field concentration [2].

Figure 1 demonstrates present TDDFT-MD simulation of mono-layer water molecules above graphene sheet tested for the three different initial atomic configurations that give the same threshold power for the decomposition. Practical estimation of yield of water decomposition compared to the reported value obtained by using photo-catalysis with ordinary light will be discussed.

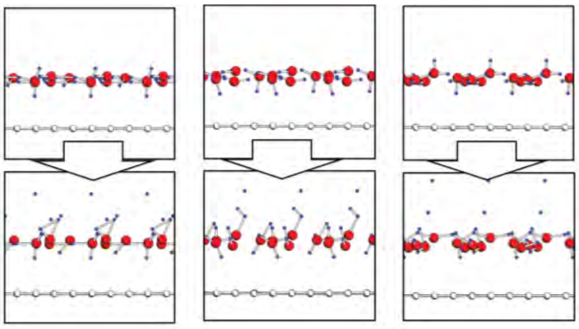

Fig.1 Snapshot of decomposition for one mono layer water molecules above graphene sheet. Three different initial atomic configurations were tested giving the same power threshold of the decomposition.

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The growth mechanism of two-dimensional materials

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Two-dimensional (2D) materials have attracted extensive attention for many years due to their extraordinary properties. In order to get large-area and high-quality 2D materials aimed for practical applications, many synthesis methods for 2D materials have been established. To improve the synthesis route of 2D materials, it is necessary to understand the growth mechanism during the growth process of 2D materials. In this talk, I'm going to present our recent theoretical studies on the precursor decomposition[1] and nucleation[2,3] of graphene. and coexist phases[4] of stanene on metal catalysts.

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Thermal Stability and Flexibility of Hydrogen Terminated Phosphorene Nanoflakes

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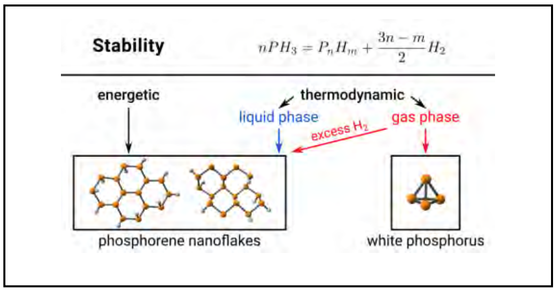
Formal cut of lower dimensional structures from 2D phosphorene layers is one of the most promising ways to tune their properties.[1] Recently, nanoflakes attracted considerable attention among the lower dimensional phosphorene-based nanostructures as, their tunable properties (e.g. size-dependent band gap) induce a wide range of possible applications, like solar cells[2] or photocatalytic water splitting[3].

While stability and flexibility of phosphorene nanoflakes is crucial for several applications, there is only limited information available. We present the flexibility and stability of hydrogen terminated phosphorene nanoflakes with diameters ranging from the molecular size (0.2-0.6 nm) to nano-size (1-2 nm) using quantum chemical computations, ab-initio molecular dynamics as well as using the External Force is Explicitly Included (EFEI) method.

Our computations [4] showed that while the flexibility of hydrogen terminated phosphorene nanoflakes depends on their geometry, they keep their quasi-planar structure up to at least 500K, while at more elevated temperatures they distort and decompose. Hydrogen terminated phosphorene nanoflakes are energetically more stable than the white phosphorus, however the investigation of the gas phase free energies showed the opposite trend. In the gas phase the temperature and the pressure have great effects on the stability of phosphorene nanoflakes. Our computations showed that during gas phase synthesis from phosphine the formation of white phosphorus is preferred over the due to the change of the entropy. This highlights the importance of the precursor for the gas phase synthesis. Larger phosphorene nanoflakes may also be synthesized in the gas phase from phosphine. Also, the solvation computations showed that in the liquid phase the formation of phosphorene nanoflakes is preferred.



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Growth by crystallographic selection of graphene and carbon nanotubes

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Growth by crystallographic selection of graphene and carbon nanotubes

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Scalable growth of high quality carbon nanomaterials, both graphene and nanotubes (CNT), seems only possible by precise control of chemical vapor deposition (CVD) conditions. At present, growth of these materials suffers from issues of quality such as polycrystallinity in the case of graphene, and inseparable mixtures of differently chiral nanotubes. Synthesis of these materials in their "pure" crystalline phases, which means monocrystalline graphene, and chiral-selective CNTs, has been a longtime goal in the research community. Recent achievements in the growth of large single-crystal graphene films [1] by evolutionary selection mechanism parallels with the experimentally observed high chiral-selectivity of (12,6) nanotubes on solid catalyst [2], since both lead to selectivity of a specific crystalline phase among several other similar phases.

In this poster, we explain these parallels and their fundamental aspects. First, we explore the concept of "evolutionary selection growth" in the context of 2D materials and how it is the underlying mechanism in the success of growing large monocrystalline graphene by local control of feedstock distribution and no substrate epitaxy [1,3]. Briefly, it describes the evolution of a polycrystalline front as a competition between neighboring grains, where the fastest one eventually dominates becoming the monocrystalline growth front. In the case of low-symmetry materials, its significance is more prominent [4]. Next, we explain the experimental observations of high (12,6) selectivity for solid Co_7W_6 catalysts within the framework of our theory of CNT helicity [5], customized for the specific catalyst facets. We demonstrate using large-scale DFT calculations, that a CNT edge in contact with a solid metal catalyst can undergo an armchair-zigzag "phase segregation", thereby forming an asymmetric edge, and suppresses the dependence of the tube interface energy on its chiral angle, as is typically known for the "conventional" CNT edge. Kinetic Monte Carlo simulations were used to study the carbon insertion kinetics, which allowed us to identify conditions that show preference for selectivity of (12,6) tubes.

[1] I. Vlassiouk *et al. Nat. Mater.* **17**, 318 (2018).
[2] F. Yang, *et al. Nature* **510**, 522 (2014).
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[5] V. I. Artyukhov, E. S. Penev, and B. I. Yakobson, *Nat. Commun.* **5**, 4892 (2014).
[6] K. Bets, N. Gupta, E. S. Penev, and B. I. Yakobson (submitted).

Electron emission properties of graphene edges under an external electric field

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Graphene acts as an excellent field emission source with remarkable emission efficiency, owing to its high structural aspect ratio, high mechanical stiffness, high chemical stability, and high electron conductivity arising from its sp^2 covalent network. The field emission from graphene edge strongly depends on the detailed atomic structure and termination of its edge where the emission occurs. In this work, we investigated the electrostatic properties of graphene under an external electric field, using density functional theory with effective screening medium method. To investigate how the field emission properties depend on the detailed edge shape and termination, we consider the graphene nanoribbons (GNRs) with the edge angles of 0º(armchair), 8º, 16º, 24º, or 30º(zigzag) and with functionalized edges by functional group R (H, O, NH, COH, COOH, or OH). (Fig. 1).

Our calculation showed that the electrostatic properties of GNR depend on the edge shape. The armchair edge possesses lower potential barrier and larger field emission current than edges with other shapes. Furthermore, hydrogenation decreases the potential barrier by introducing a dipole, causing an increase in the field emission current. In addition, for chiral GNRs, the electron emission is primarily attributed to the zigzag portion of edges because of the concentration of electrons arising from either the dangling bond state or the edge state [1]. On the other hand, the potential barrier for electron emission and field emission current are sensitive to the functional group attached GNR edge. The termination of O increases the potential barrier, causing the decrease in the emission current, while other functional groups decrease the potential barrier, causing the increase in the emission current. Interestingly, all cases show the decrease in the potential barrier with increase in the electric field, except the case of OH. The anomalous phenomenon for the case of OH is caused by the electrons in the nearly free electron state in the vacuum [2].

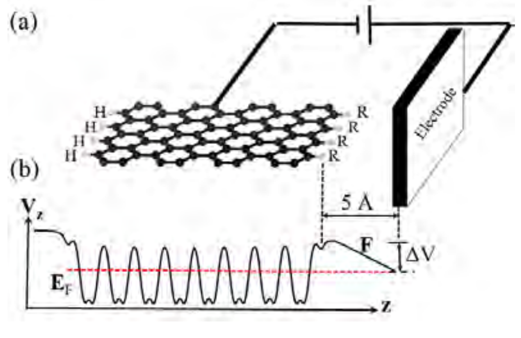

Fig.1 (a) A structural model and (b) schematic diagram of the electrostatic potential for GNR under an electric field.

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[2] Y. Gao and S.Okada, Appl. Phys. Express **10**, 055104 (2017).

Properties and growing processes of the border between h-BN/graphene

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Recently two-dimensional in-plane heterogeneous structure of graphene and h-BN with bulk grain boundaries has been experimentally synthesized, because of their small lattice mismatch. The experiments revealed that the BC heterobonds are preferentially generated at the zigzag border between graphene and h-BN. From the theoretical studies, it has been predicted that the h-BN domain perfectly terminates the π states of graphene at the border. Despite the experiments and theories have been elucidating fundamental aspects of the in-plane heterostructures consisting of graphene and h-BN, the energetics and formation mechanism of the heterostructures with regard to the border structure are unclear and are highly demanded for their synthesis and practical applications. Thus, in this work, we aim to investigate the energetics and formation mechanism of in-plane heterostructures of graphene and h-BN with respect to their border shapes and hetero-bonds, using the density functional theory (DFT) with the generalized gradient approximation (GGA).

To calculate energetics of border between graphene and h-BN, we considered the BNC nanoribbons consisting of h-BN and graphene nanostrips with various edge conformations. Figure 1 shows the total energy of the BNC heteroribbons with the border between h-BN and graphene as a function of the border angles. The total energy has an energy minimum at the border angle of 8 degree where the BC heterobond is dominant, because of the competition between the energy gain upon the formation of BC heterobond and the energy loss arising from the polarity at the border. We also demonstrated that the adsorption energy of B to graphene edges is larger than that of N, indicating that the preferential growth of h-BN from the zigzag edge of graphene with BC heterobonds.

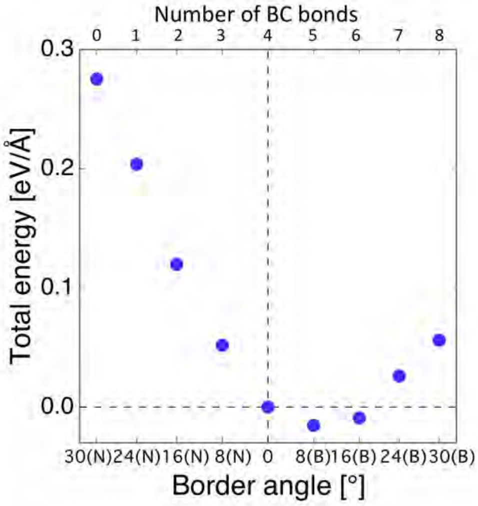

Fig.1 Total energy of the heterostructures as a function of border angle.

Energetics and electronic structure of graphene adsorbing CO$_x$ under an external electric field

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Graphene has been attracting much attention in the fields of fundamental and applied sciences for these decades, because of its unique physical properties. The energetics and electronic properties of graphene are found to be sensitive to the external environments such as molecular adsorbates and an external electric field. Despite the electronic structure of graphene with foreign materials having been well studied to date, little is known about the structural properties of graphene hybrids under external perturbations, such as the external electric field and mechanical deformations. Such studies may advance the application of graphene in sensing devices because adsorption phenomena are influenced by charge density distributions on graphene and adsorbates. Thus, in the present work, we aim to give theoretical insight into the energetics and electronic properties of graphene adsorbing CO and CO_2 molecules in the field effect transistor in terms of the molecular arrangements and carrier concentration, using the density functional theory with generalized gradient approximation combined with the van der Waals correction and the effective screening medium method.

Our calculations show that the optimum spacing of CO and CO_2 molecules to graphene monotonically decrease with increasing hole and electron concentrations, indicating that the molecules are tightly bound to graphene under the electric field. The increase of molecular binding to graphene occurs regardless of the molecular conformations to graphene and the counter electrode. This fact indicates that the electric field controls the binding properties of molecules, thereby enhancing the molecular sensing capability of graphene. Furthermore, the stable molecular orientation strongly depends on the carrier concentration for both molecules: The lying conformation to graphene is the ground state under neutral conditions, whereas the standing conformation is the ground state under either electron or hole injection (Fig.1).

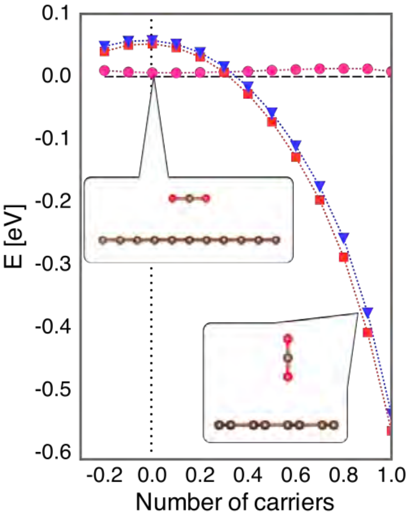

Fig.1 Relative total energy of CO_2 on graphene as a function of the carrier concentration.

Electronic structure and magnetic-state tuning of h-BN nanoflakes by hole doping

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Thin films of h-BN are attracted much attention as a flat substrate for other 2D materials, because of its mechanically stable hexagonal covalent network and an insulating electronic structure. Chemical vapor deposition technique has realized large-area and high quality h-BN films, which mostly possess triangular shape with N edges. In the topological view, hexagonally bonded flakes with the triangular shape possess numbers of non-bonding states at or near the Fermi level. For instance, hydrocarbon molecules with the triangular shape possess zero modes at the Fermi level making them unstable under ambient condition. In contrast, for the h-BN nanoflakes, the experiments corroborated that the triangular shape is the most energetically stable conformation. The fact implies that h-BN nanoflakes can possess the high-spin states under the carrier injection using the appropriate procedure, if they possess highly degenerate electron states near the Fermi level. Therefore, in this work, we aim to investigate electronic and magnetic properties of h-BN nanoflakes with the triangular shape in terms of the hole injection using the density functional theory with the effective screening medium method.

Our calculations show that H-terminated h-BN nanoflakes with the triangular shape possess highly degenerated states just below or above the Fermi level for N and B edges, respectively. The degeneracy of these states corresponds with the sublattice imbalance between N and B atomic sites as the case of hydrocarbon molecules with the triangular shape. By injecting the hole, the H-terminated h-BN triangular flakes with N edge possess various spin states depending on the hole concentration (Fig.1). The polarized electron spins are ferromagnetically aligned throughout the N atomic sites, in contrast to the hydrocarbons with triangular shape.

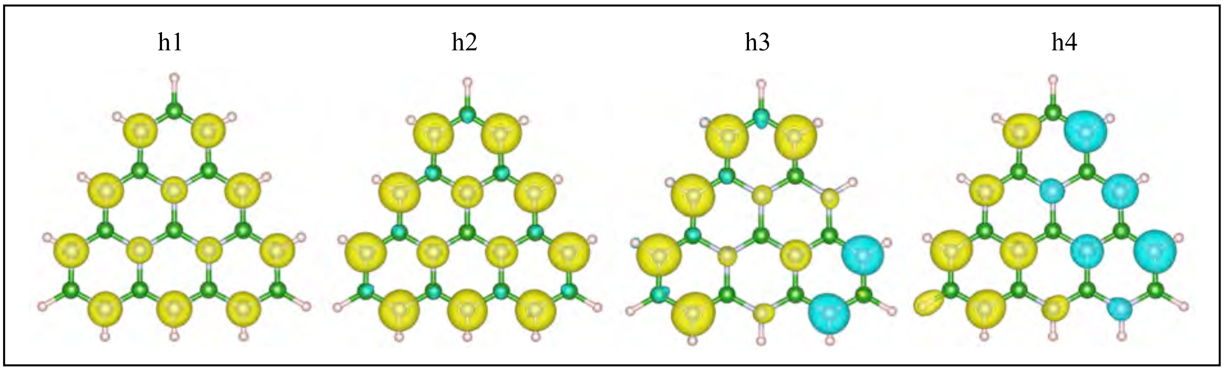

Fig.1 Spin densities of H-terminated h-BN nanoflake with N edges.

The mechanism of the preferential growth of (6, 5) SWNTs

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The enrichment of (6, 5) single-walled carbon nanotubes (SWNTs) was broadly observed in chemical vapor deposition (CVD) experiments, especially by in those performed at a low temperature and using Fe, Co, Ni or their alloys as catalyst since 2003[1]. While, until now, although our understanding on SWNT growth becomes deeper and deeper, the related underlying mechanism about the preferential growth of the (6,5) SWNTs has never been revealed. Here, based on our current study on the mechanism of SWNT growth from solid catalysts, we proposed theoretical model to understand the experimental selection of the (6, 5) SWNTs. Firstly, the symmetry matching between a SWNT cap and the catalyst surface with three- or six-fold symmetry allows abundance of the (6, 6) caps at the nucleation stage.[2]-[3] While, without any kink at the rim of the (6, 6) SWNT, its fast growth is prohibited until a topological defect, a pentagon-heptagon pair, turns it into a chiral one, which could be (6, 5), (7, 6) and (7, 5). Among the three possible chirality evolution routes, the one towards the (6, 5) SWNT has the lowest energy barrier. By applying thermodynamics in SWNT nucleation stage and the kinetics in growth stage, we successfully explained the abundance of (6,5) SWNTs in various experiments and such a mechanism also explains the dominating of (9, 8), (12, 11) SWNTs observed in other experiments.

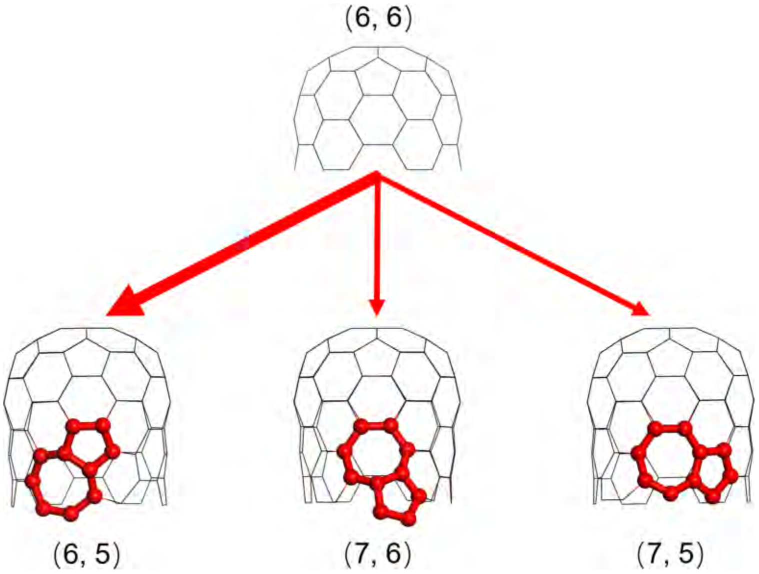

Fig.1 chirality evolution of the (6, 6) SWNT.

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The Role of Alloy Catalyst in Carbon Nanotube Growth

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Metal catalyst plays an important role in the synthesis of carbon nanotube (CNT) such as catalyzing the decomposition of carbon precursors, controlling carbon diffusion and maintaining the reactivity of the CNT, etc. While recently many experimental evidences indicate that bimetal or alloy catalyst could facilitate the growth of CNT as well as increase the selectivity of the as-grown tubes. In this paper, *via* density functional theory molecular dynamic (DFT-MD) simulation, we observed, for the first time, that the alloy particle underwent a phase separation during the CNT growth due to the difference in carbon affinity of these two kinds of metals in the alloy. This CNT induced phase separation would lead to the accumulation of the relatively active metal in the alloy at the CNT open end. Thus the other metal would be pushed to the other side of the alloy particle. Further investigation showed that the phase separated alloy benefits for the CNT growth by: attracting the dissolved carbon atoms to quickly diffuse to the tube end, and therefore facilitate the CNT growth; preventing the dissolved carbon atoms to aggregate on the particle surface, which may result in the poisoning of the catalyst and the termination of the tube growth.

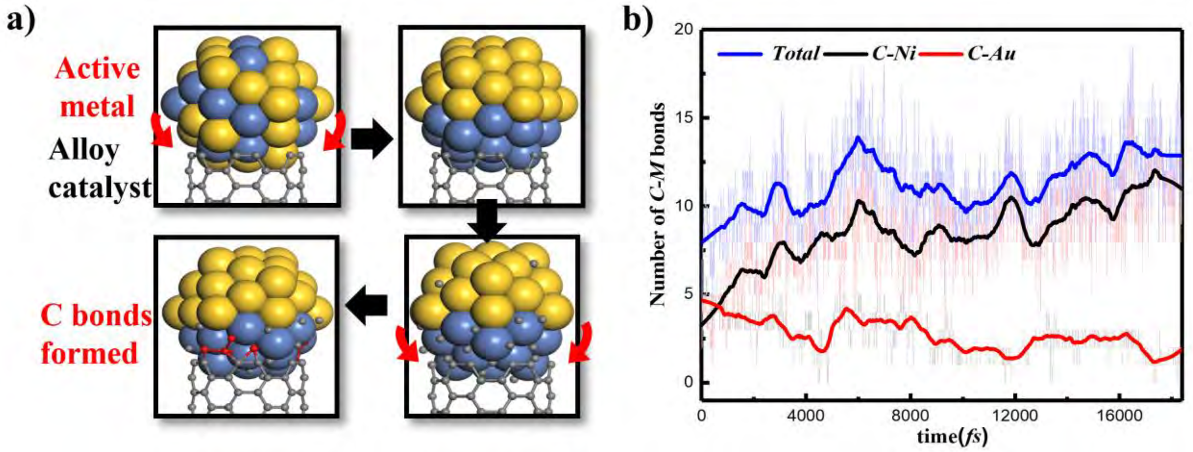

Fig.1 a) CNT growth with alloy catalyst undergoes a process including: i) the CNT induced phase separation; ii) phase separation induced carbon diffusion, and iii) phase separation facilitated growth of CNT. b) The number of the carbon-metal bonds during the DFT-MD simulation.

Electronic properties of in-plane 2H/1T′ monolayer MoTe2 interfaces

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Very recently, experimentalists have made great efforts on the preparation of 2H/1T′-MoTe2 coplanar structures, aiming to achieve low-resistance contacts and functional devices. Using first-principles calculations, we report on the stability and electronic properties of these coplanar phase interfaces. Twelve types of interfaces in total are considered, and two of them are calculated to be the possible best stable structures depending on chemical potential. All the interfaces possess quite small and localized mid-gap states, however, which still lead to strong Fermi level pinning on the interfaces. We also observed polarization-induced band offsets in the 2H-MoTe2 sides of the interfaces, and which can be reserved when connected with 1T'-MoTe2 on both sides. These phase interfaces show great potential in high-performance photoelectric devices and logic devices.

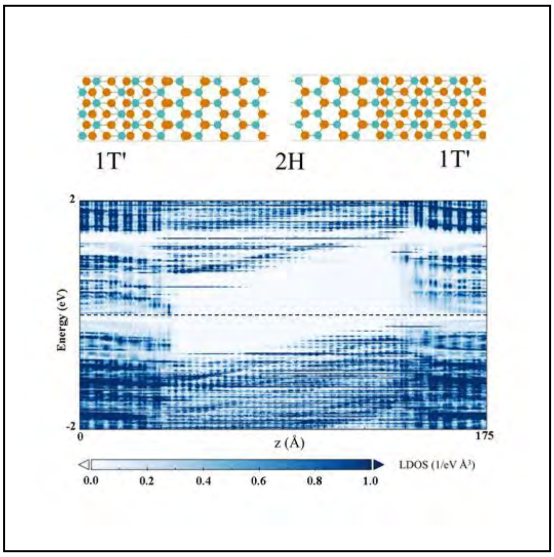

Fig.1 One of the 1T'-2H-1T' coplanar structures and its projected local density of states (PLDOS). The polar discontinuities on the interfaces cause built-in field in the monolayer 2H-MoTe2.

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Influence of self-consistent screening and polarizability contractions on interlayer sliding behavior of hexagonal boron nitride

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The interlayer sliding behaviors of hexagonal boron nitride (h-BN) were investigated via a density functional theory approach with dispersion interaction included. It was found that the self-consistent screening effect (SCS) and the polarizability contractions had significant influences on London dispersion forces, which are responsible for not only the stacking modes but also for the sliding behaviors of h-BN. In consideration of the ionic characteristics of h-BN, surprisingly, the calculated dispersion force was found to dominate the electrostatic interaction along a minimum-energy sliding pathway and make a pronounced contribution (~ 35%) to the barrier during the constrained sliding. This study demonstrates that the SCS and polarizability contractions play important roles in the sliding behaviors of h-BN and that the long-range dispersion interaction should be carefully treated, even in systems with ionic characteristics.

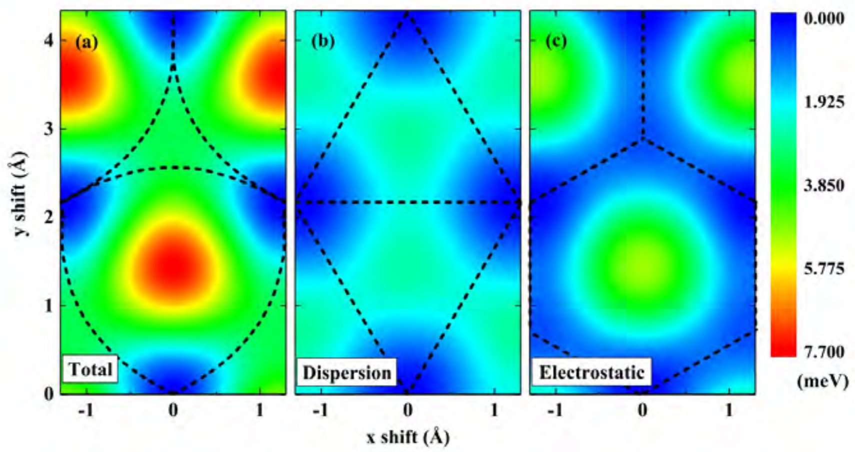

Figure 1 Energy surfaces calculated with respect to the most stable stacking mode for (a) total, (b) dispersion, and (c) electrostatic interactions. The dashed lines indicate different minimum-energy sliding pathways for corresponding interactions.

Modulation of CVD Carbon Nanomaterial Nucleation and Growth Mechanisms via Chemical Etchants

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Graphene and carbon nanotube growth begin with the precipitation/aggregation of carbon atoms on a catalyst surface to form extended carbon chains, which quickly combine and oligomerise to form "islands" of sp^2-hybridized carbon. Larger nanostructures then form *via* the coalescence of these structures on the catalyst surface, which are stabilised through strong carbon-catalyst σ-bonding [1-3]. Herein I will discuss how these mechanisms are influenced by the presence of chemical "etchants", such as H_2 [4], NH_3 [5,6], CH_3CN (acetonitrile) and H_2O [7]. Such etchants have been shown to be linked to chirality [8] and diameter [9] control during growth.

Our simulations demonstrate how each of these parameters can potentially be exploited towards controlling the growth of graphene and carbon nanotubes. For instance, the presence of trace levels of NH_3 during methane CVD on Fe and Ni nanoparticle catalysts leads to efficient etching of small carbon species and the formation of hydrogen (iso)-cyanide (Figure 1). This is driven by the selective activation of the N-H bond by the catalyst surface. Ultimately however this impedes carbon ring formation during the early stages of carbon nanotube growth, leading to a greater degree of control during synthesis. By contrast, the presence of acetonitrile during methane CVD on Fe and Ni nanoparticle has the opposite effect; rather than reducing carbon it effectively oxidises it via hydrogen abstraction to form hydrogen (iso)-cyanide. This increases the rate of carbon chain oligomerisation and ring formation. It also increases the rate of carbon removal from the catalyst surface, consistent with experimental observations.

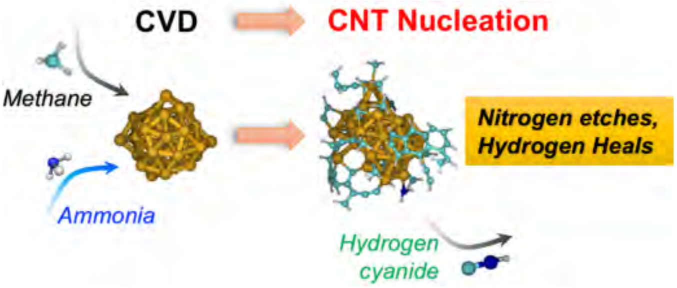

Fig. 1. (a) Quantum Chemical simulations reveal how nitrogeneous etchants such as ammonia and acetonitrile influence CVD synthesis mechanisms of carbon nanotubes.

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Thermal Bubble Inkjet Printing of Water-based Graphene Oxide and Graphene Inks on Heated Substrate

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Printed electronics is emerging as the next fast growing market with great potential for the electronics industry by enabling low-cost, large area, flexible devices [1, 2]. Since inkjet print technology is a non-contact, digital, multi-materials, modular and scalable technology [3], it is very suitable for printed electronics, especially for printing 2D materials [4-12].Stable jetting water-based graphene oxide (GO) and graphene (GR) inks without any surfactant or stabilizer are prepared from an unstable jetting starting water-based solvent with many satellite drops for thermal bubble inkjet by simply increasing the materials concentration. The concentration dependent thermal bubble inkjet droplet generation processes are studied in details. To overcome the low concentration properties of the water-based inks for thermal bubble inkjet, the substrate temperature is tuned below 60 ℃ to achieve high quality print lines. Due to the difference of hydrophilicity and hydrophobicity of the 2D materials, the printed GO lines show different forming mechanism from that of the GR lines. The printed GO lines are reduced by thermal annealing and by ascorbic acid, respectively. The reduced GO lines exhibit electrical conductivities with the same order of magnitude as that of the GR lines.

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Silk-Sheathed Carbon Nanotube Wires for Wearable Electronic Textiles

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Keywords: silk fibroin, carbon nanotube fibers, flexible wire, wearable electronics, smart textile

Abstract

Silk, which has outstanding mechanical properties, biocompatibility, and large-scale production, has been used for the fabrication of traditional textiles for thousands of years. It is significant if this traditional material could be applied in modern smart textiles. However, silk is not electrically conductive, limiting its applications in electronics. Moreover, regenerated silk is usually rigid and brittle, putting obstacles for post processing. Herein, we report the fabrication of conductive silk wires by electrospinning fluffy and highly flexible silk nanofibers on the outside of carbon nanotube (CNT) yarns. The silk-sheathed CNT (CNT@Silk) wires have an insulating sheath, protecting the human body from electrical shock. At the same time, the wire has good electrical conductivity, high mechanical strength and excellent flexibility, which owe to the CNT yarns. The wire shows good resistance to humidity and can even be treated to be splash-resistant, enabling its wide applications. In addition, stretchable wires can be fabricated by combining the CNT@Silk wire with elastic fibers. Based on the above features, we further demonstrated the applications of the CNT@Silk wire in smart clothes, including electrochromism and near field communication, showing its high potential applications in smart textiles.

Paper-based pressure sensors utilized by a peculiar interface of liquid metal and carbon nanotube network

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Flexible and lightweight pressure sensors are expected to be applied for living body surfaces, man-machine interfaces, and artificial intelligent robots[1]. In general, applied pressure can be detected by mechanical deformation of sensing materials in the sensor systems. The mechanical deformation changes the piezo electricity, piezo resistive, and capacitance of the materials. For wide range applications that require various sensitivities and dynamic ranges, appropriate materials that are suitable for each application should be chosen.

In this study, we propose a novel pressure sensor, of which sensitivity and sensing range can be easily controlled without changing sensing materials[2,3]. Our sensor is composed of multi walled carbon nanotube (MWNT) networks and a droplet of liquid metal (eutectic Ga-In (EGaIn) alloy) (Fig.1(a)). EGaIn droplet, which is a sensing material, is sandwiched with a MWNT network-deposited paper and a copy paper. By changing the gap of these papers, the shape of EGaIn droplet can be changed. Namely, contact area of MWNT network and the droplet can be tuned. As a result, it is possible to detect the applied pressure by monitoring the resistance change of the MWNT network. In principal, we can control the sensitivity and sensing range by changing the shape of MWNT network and type of spacer in the device, respectively.

Figure 1(b) shows a typical sensing property: resistant change vs applied load. We have confirmed that the resistance of MWNT network decreases with decreasing the gap (i.e., increasing the pressure). Sensitivity and resistance change $\Delta R/R_0$ were approximately 3.9 mm^{-1} and over 80%, respectively. Because of high lyophobic of EGaIn against both the MWNT network and the copy paper, this sensor can be repeatedly used. Furthermore, we have calculated the spatial current distribution in the MWNT network attached with EGaIn by using finite element method.

In the presentation, we will introduce detailed experimental results of lyophobicity and sensing properties including simulation results.

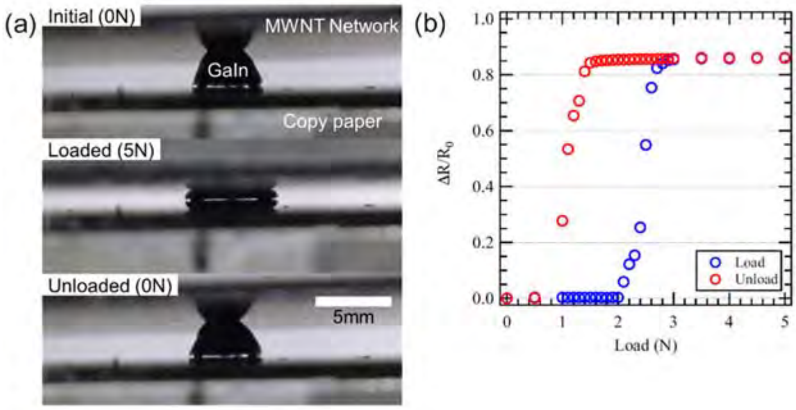

Fig.1 (a) Photograph of deformation of an EGaIn droplet and (b) resistance change as a function of applied load.

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Colloidal Electronic Cells Based on 2D Materials

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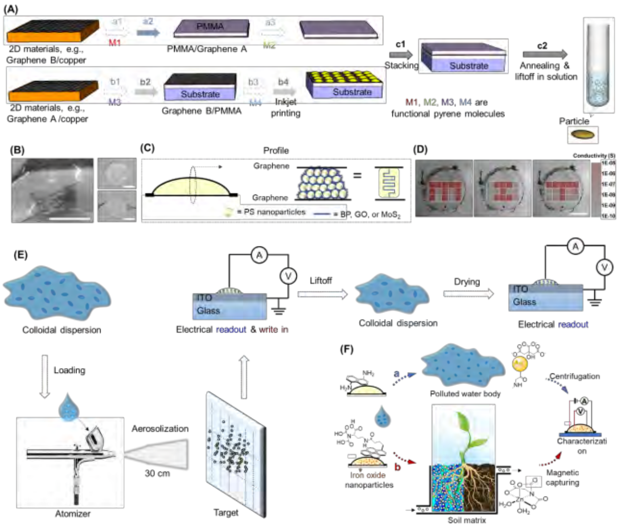
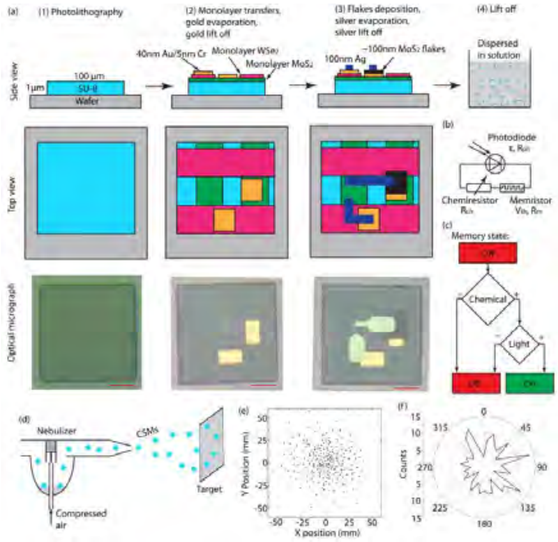
Abstract:

Graphene and other 2D materials possess desirable mechanical and functional properties for incorporation into or onto novel colloidal particles, potentially granting them unique electronic and optical functions. A here-to-fore unexplored property of 2D electronic materials such as graphene, hexagonal boron nitride and MoS2 is the ability to build electronic circuits, transistors, memory and sensors onto or into colloidal particles. Such particles can access local hydrodynamics in fluids to impart mobility and can otherwise enter spaces inaccessible to larger electronic systems. In this talk, I will present our recent work on the fabrication and application 2D materials-based colloidal electronic cells from two aspects: (1) We developed an "*autoperforation*" technology providing a means of spontaneous assembly for colloidal microparticles comprised of 2D molecular surfaces at scale. Such particles demonstrate remarkable chemical, mechanical and thermal stability. They can function as aerosolizable electronic tattoo capable of storing and transferring digital information, and recoverable microprobes for sensing and recording chemical information in water and soil. (2) We further demonstrated the design and fabrication of fully autonomous state machines built onto a SU-8 particle powered by a p-n heterojunction of MoS2 and WSe2 operating as a photodiode. These colloidal state machines enable new functions, such as the detection and storage of information after aerosolization and hydrodynamic propulsion to targets over 0.6 m away. The systems are texted in a variety of constrained conduit environments and are also shown to enable large area surface detection of triethylamine, ammonia and aerosolized soot in otherwise inaccessible locations. Such two different types of synthetic electronic cells, enabled by 2D nanoelectronics, may find widespread application as probes in confined environments such as the human digestive tract, oil and gas conduits, chemical and biosynthetic reactors, and as autonomous environmental sensors.

Colloidal Electronic Cell - I



Colloidal Electronic Cell - II



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A flying balloon based on carbon nanotube freestanding films

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Unmanned Aerial Vehicles(UAVs) with multirotors are used in outdoor environments. Especially, they are suitable for monitoring in harsh environments such as disaster areas. On the other hand, flying monitoring systems in constructions are required for crime control in doors. However, it is difficult to use the conventional UAVs [1] because they make loud noise and strong wind. In addition there are safety issues such as collision due to falling them down.

In this study, to resolve the issue, we propose a light-weight flying object without any sound noise and wind. The flying object proposed here is a balloon based on carbon nanotube (CNT) composites.

Our flying object is composed of a CNT freestanding films (CNT-FSFs). [2] This is able to absorbing electromagnetic wave effectively, and the internal space of the balloon is heated. It can be levitated by the difference of gas densities between inside and outside the balloon. The CNT balloons were prepared by the following procedure. First, a multi walled CNT (MWNT) ink containing cellulose nanofibers was spray-coated on a substrate, and the CNT-FSF was carefully peeled from the substrate. Second, a balloon was formed using the CNT-FSFs. Finally, the balloon was annealed in the atmospheric environment at 250°C. We characterized the surface morphologies, the gas permeabilities, the mechanical strength, and crystallinity of CNT-FSFs, and the balloon's surface temperature and levitation motion were observed while light irradiation. The thickness, film density, gas permeability, and tensile strength of typical CNT-FNFs were approximately 8 μm, 0.50 mg/cm^2, 2.0×10^{-12} m^4/Ns, and 32.7 MPa, respectively. When the prepared CNT balloon was irradiated with light, the balloon was radiatively heated. Then we confirmed that the balloon is levitated and the levitated height was about 20 cm.

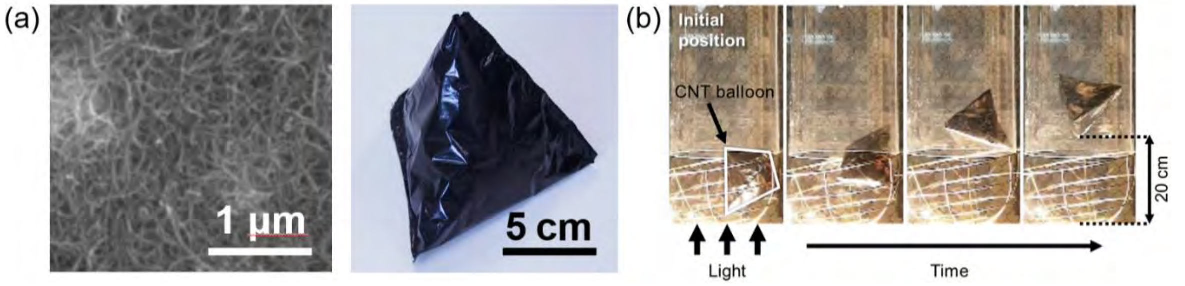

Fig. (a) SEM image of a typical CNT freestanding film and photograph of a triangular pyramid-shaped CNT balloon. (b) levitation of the CNT balloon by light irradiation.

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Radiative heating simulation of CNT balloons for improvement of the levitation

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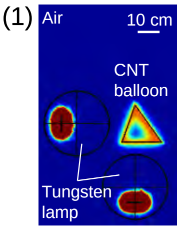
Unmanned aerial vehicles (UAVs), which generate no noise and no wind, are expected to be indoor type monitoring devices [1]. Among various UAVs, from viewpoints of noise and wind by wings, conventional UAVs with wings are inappropriate for indoor type devices. These UAVs have extra issues such as short flight time and injury risks due to falling.

We focus on balloon type UAVs that are suitable for the indoor use because these are light and generate no noise and no wind. Therefore, using carbon nanotubes (CNTs) free-standing films (CNT FSFs) have high light absorption coefficient, we fabricated a novel balloon (CNT balloon) that can levitate by light irradiation [2]. As a result of the levitation experiment, the balloon was found to be levitated for 10 s at a maximum height of 20 cm by light irradiation. However, the detailed mechanism of levitation has not been fully elucidated. In addition levitation properties of the balloon are insufficient.

In this study, we tried to elucidate the levitation mechanism in terms of thermal conduction by finite element method simulation, and to improve levitation properties of the balloon by changing films properties [3].

We simulated time evolution of the spatial temperature distribution by radiative heating (Fig.1). We revealed found out that the temperature of CNT FSFs steeply increased over 200°C within 0.4 s and air in the balloon is heated by heat transfer from the heated film within 10 s. For further improvement of levitation properties, we improved films (thickness 5 μm, film density 0.6 mg/cm^2) of the balloon. Consequently, the new CNT balloon levitated for 20 s at a maximum height of 30 cm by light irradiation (λ=1.3 μm) and showed repeatable levitation (Fig.2).



CNT

Property	Value
Thermal conductivity	6600 (W/m•K)
Heat capacity	8.5 (J/mol•K)
Density	720 (mg/cm^3)

Geometries

Object	Scale
Air (Cube)	one side 100 cm
CNT balloon (RTE)	one side 11 cm
Tungsten lamp (Sphere)	radius 8 cm

RTE: Regular tetrahedron

Fig.1 Simulation model of radiative heating

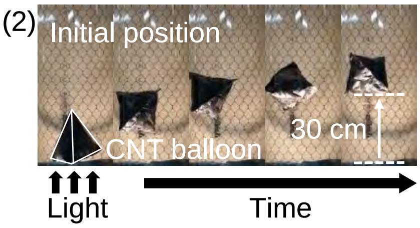


Fig.2 Levitation of the new CNT balloon

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Laser scribed graphene carbon “grass” forming a highly sensitive, selective and low-detection-limit dopamine sensor

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A range of novel carbon nanomaterials, including 0D fullerene, 1D carbon nanotubes, 1D carbon nanofibers, 2D graphene and graphene oxide, and 3D carbon aerogels, has attracted considerable interest and investments from across the scientific society. Due to their excellent performance, the carbon nanomaterials have contributed significantly towards the development of miniaturized integrated point-of-care biological and chemical sensors. Graphene, as a sensing and signal transducing material is well established, and the recently developed method of “laser scribing” has already been demonstrated as a facile approach for manufacturing graphene electronics for highly selective, sensitive biological sensing devices [1, 2]. Inspired by the different morphologies and derivatives of the carbon nanomaterials that have been fabricated, including carbon nanowalls, graphene nanoribbons, vertically aligned CNTs and laser induced graphene fibers, we first fabricated laser scribed graphene (LSG carbon grass) with a novel 3D vertical aligned tree-like morphology. We have then used the LSG carbon grass in the application of dopamine detection by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrochemical anodic peaks of dopamine (DA), ascorbic acid (AA) and uric acid (UA) using LSG carbon grass electrode were investigated, where UA and AA were considered as common interferences. The sensitivity of LSG carbon grass for DA sensing was highly improved compared to normal LSG. The fabricated LSG carbon grass sensor exhibits a sensitivity of 0.299 μA/μM and detection limit of 1 μM. The outstanding performance for dopamine detection using LSG carbon grass is a reflection of the promising future of carbon nanomaterials with interesting high surface area morphologies.

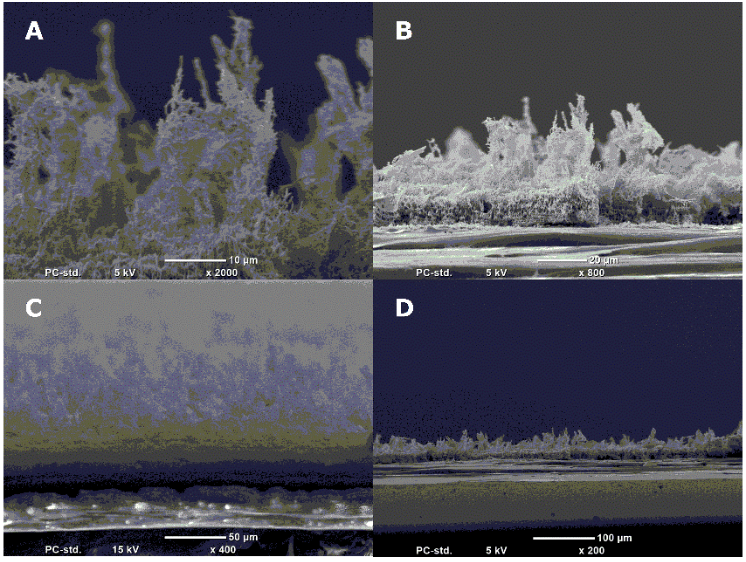

Figure. 1. Cross-sectional SEM images of LSG carbon-grass electrode (A) magnification × 2000, (B) magnification × 800, (C) magnification × 400, and (D) magnification × 200. The materials was formed with the power set at 20 %, speed 30 % and PPI of 500.

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Carbon Nanotube-Coated Carbonized Silk Fabric for Highly Sensitive Textile Airflow Sensor

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Recent years have witnessed the explosive development of electronic skin and smart textiles, which aim to imitate or even exceed the functions of human skin. Various flexible sensors, such as strain sensors and pressure sensors, have been extensively studied. However, flexible airflow sensors, which can detect the external airflow, have been paid much less attentions. To date, most of the reported airflow sensors are rigid, bulky, and expensive, limiting their potential in flexible electronics. Herein, inspired by the slender fluff (trichobothrium) of spider, we report a textile airflow sensor based on carbonized silk fabric coated with fluffy carbon nanotubes. Due to the unique structure of the fabric, the airflow sensors shows high sensitivity, low detection limit, fast response and good flexibility. In addition, we demonstrate the all-textile airflow sensor can be directly integrated in clothing without sacrifice of comfort, indicating its great potential for applications in smart textiles or wearable electronics.

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High-Speed and on-Chip Blackbody Emitters based on nanocarbon materials

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High-speed light emitters integrated on silicon chips can enable novel architectures for silicon-based optoelectronics, such as on-chip optical interconnects, and silicon photonics. However, because of their large footprints, the low crystallinity of the compound semiconductors grown directly on Si wafers, the integrated light sources face significant challenges with respect to their integration with silicon-based electronics, photonics. Here we report ultra-high-speed, highly-integrated, on-silicon-chip blackbody emitters based on nanocarbon materials in the near-infrared region including telecommunication wavelength [1-4]. We fabricated the blackbody emitters with carbon nanotube films and observed high-speed blackbody emission with the response speed of 1 Gbps, which is > 10^6 times higher than that of a conventional incandescent emitter with a filament and is higher or comparable to a light-emitting diode and a laser diode. This high-speed response is explained by the extremely fast temperature response of the CNT film, which is dominated by the small heat capacity of the CNT film and its high heat dissipation to the substrate. We also demonstrated the high-speed blackbody emitters with graphene on silicon chips. The emission responses of the graphene emitters are strongly affected by the graphene contact with the substrate depending on the number of graphene layers. The observed ultra-high-speed emission can be understood by remote quantum thermal transport via surface polar phonons of the substrates. By using these blackbody emitters with nanocarbon materials, we demonstrated short-pulsed light generation, real-time optical communications, integrated two-dimensional array emitters, capped emitters operable in air, and the direct coupling of optical fibers to the emitters. These emitters can open new routes to on-Si-chip, small footprint and high-speed emitters for highly integrated optoelectronics and silicon photonics.

This work was partially supported by PRESTO and A-STEP from JST, KAKENHI and Core-to-Core program from JSPS, SCOPE from MIC, KISTEC project, the Cooperative Research Program of "Network Joint Research Center for Materials and Devices", Spintronics Research Network of Japan, and NIMS Nanofabrication Platform in Nanotechnology Platform Project by MEXT.

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Highly conductive and transparent films of HAuCl$_4$-doped single-walled carbon nanotubes for flexible applications

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The rapid development of flexible and transparent electronics imposes growing demands on new highly conductive, optically transparent and mechanically robust materials. Single-walled carbon nanotubes (SWCNTs) are a unique material with diverse exceptional properties, which could be utilized in many fields of science and technology. We have synthesized high quality SWCNTs using an aerosol CVD method and examined doping technique to enhance their optoelectronic performance for transparent and conducting applications [1]. We empirically selected the most effective dopant, HAuCl$_4$, dissolved in various solvents (ethanol, acetonitrile, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and n-methyl-2-pyrrolidone). We optimized the doping conditions and obtained the state-of-the-art sheet resistance value of as low as 40 Ω/□ at the transmittance of 90% at the wavelength of 550 nm (Fig. 1). This work was supported by the Russian Science Foundation (No. 17-19-01787).

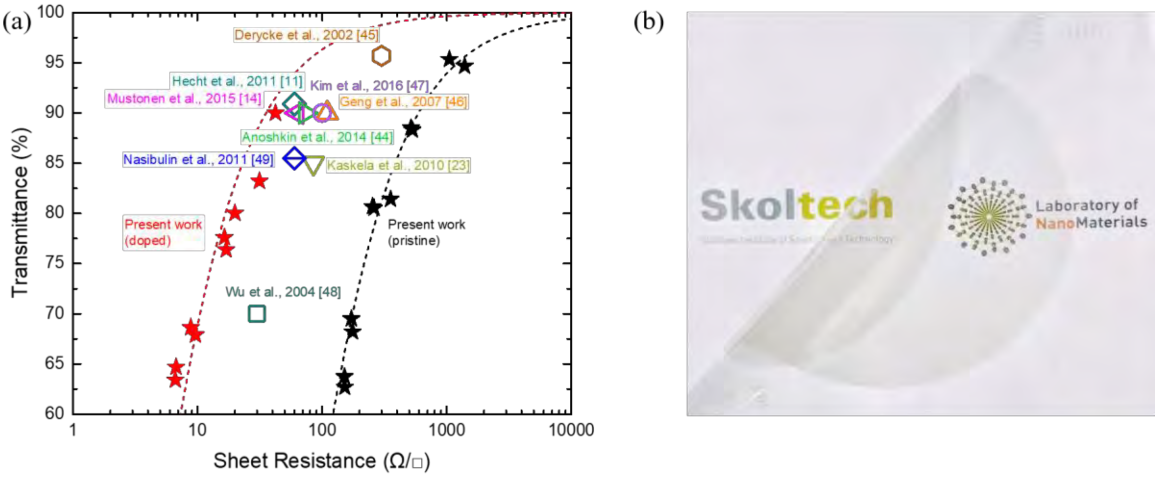

Fig.1 Comparison of the performance of SWCNT-based TCFs after p-type doping: sheet resistance vs. optical transparency at 550 nm. Dashed lines indicated theoretical relationship between transmittance and sheet resistance of pristine (black) and HAuCl$_4$-doped (using ethanol as a solvent) SWCNT films (red) obtained in this work. (b) A photograph of an HAuCl$_4$-doped SWCNT film on a flexible PET substrate.

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Printed graphene-based sensors for air quality monitoring

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Rapidly increasing air pollution has been recognized as a major concern for human health, and the real-time identification of pollution sources has become a priority task for prevention of hazard exposure and control of emission.

We present scalable fabrication and platform technologies to realize a printed air-quality sensor network capable of detecting nitrogen dioxide (NO_2) for potential implementations in portable devices.

We demonstrate a cost-effective solution-processing approach to synthesize polymer-free graphene-based nano-composite sensing element based on graphene/α-Fe_2O_3, where the metal-oxide nanoparticles are uniformly decorated in a network of graphene flakes. The approaches involve liquid phase exfoliation of graphite and hydrothermal growth of Fe_2O_3 onto graphene in alcoholic solvents for film deposition by inkjet printing.

We deposit our sensing material on a CMOS micro-hotplate platform *via* inkjet printing. The sensors are capable of detecting NO_2 at room temperature with sensitivity of 18% at 1 ppm. Thanks to precisely-controlled thin-film deposition technologies, we achieve consistent readings among the fabricated devices (<5% variation), and minimal baseline drift. Furthermore, due to room temperature operation, power consumption of sub-micro Watts level is achievable, offering potential for operation in portable devices or remote sensing.

Tailoring kinetic behavior of graphene-based sensors via chemical modification

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Gas sensors are devices that able to detect combustible, flammable, toxic gases and widely used in industry or in firefighting. Graphene among large number of materials has been kept key place as a platform for gas sensor due to its combination of electronic and structural features, such as tunable conductivity and high specific surface area and 2D structure [1]. Additionally, unsaturated carbon-carbon bonds in graphene are available for modification with functional groups, which allow tailoring electronic properties in wide range, improve reactivity of graphene and change its charge state [2]. Depending on the type of functional group it is possible to manage energy and charge transfer of interaction with adsorbed molecules, as well as an adsorption equilibrium.

In the present work, we investigate sensor properties of covalently modified graphene films, namely fluorinated (FG) and oxyfluorinated (OFG) graphene. Fluorination was performed by reaction of natural graphite with bromine trifluoride/bromine mixture (BrF_3/Br_2) at room temperature, which allows controlling chemical composition. Oxyfluorination of graphene was obtained by one-pot synthesis using chromium oxide in the anhydrous hydrofloride. The gas sensor properties of these materials were investigated toward electron-donor (ammonia) and electron-acceptor (nitrogen dioxide) gases. The kinetics and thermodynamics of gas adsorption were evaluated from electric response of the sensor. The obtained results pointed out that functional groups form specific adsorption site for molecule, while adsorption and activation depend on the nature of functional groups and its configuration. It was shown that both material had similar sensitivity, however FG shows lower adsorption energy and adsorption/desorption times at room temperature comparing to oxyfluorinated graphene [3]. Notably, at higher temperatures OFG sensor kept it high performance and kinetic characteristics improved several times. At the operating temperature of 75 ^{o}C, OFG is usable for reversible adsorption of NO_2 with sensitivity of 9.5%/ppm. The operating temperature for OFG sensor is much lower than it for graphene oxide (150^{o}C) [4] or carbon nanotube (100-350^{o}C) [5] gas sensor materials. In conclusion, this work has demonstrated that fluorination of graphene is more perspective for gas sensing as compared to oxygenation due to its higher chemical stability and weaker interactions with the adsorbed molecules.

This research was supported by the Russian Science Foundation (Grant #18-33-00760)

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Study on electrical conductivities and mechanical strengths of different types of CNT fibers

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Carbon nanotube (CNT) fibers and yarns have been extensively studied because of their potential abilities to replace conventional electrical and mechanical wires. Although some CNT fibers show very high performances in conductivity and mechanical strength [1], however, the number of laboratories which can fabricate such fine CNT fibers are limited. Further, the understanding of the detailed mechanism between the fiber structures and the properties is still needed. Hence, in this presentation, we characterize various commercially available CNT fibers and try to clarify the relation between the fiber structures and the physical properties.

Figure 1 shows (a) the specific conductivities and (b) specific strengths of three multi-walled (MW), one few-walled (FW) and two single-walled (SW) CNT fibers as a function of the fiber bulk density. Specific conductivity does not show strong dependences to bulk density among these fibers, in contrast, specific strength showed clear density dependences. These results indicate that i) the electric property is less sensitive to bulk density and it should be sensitive to other properties, for example, CNT lengths, and ii) the specific strength depends on bulk density strongly.

In the presentation, the other properties of fibers such as fiber structure, CNT length, crystallinity and wall number will be reported and their relationship to the fiber properties will be discussed.

This presentation is based on results obtained from a project (P16010) commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

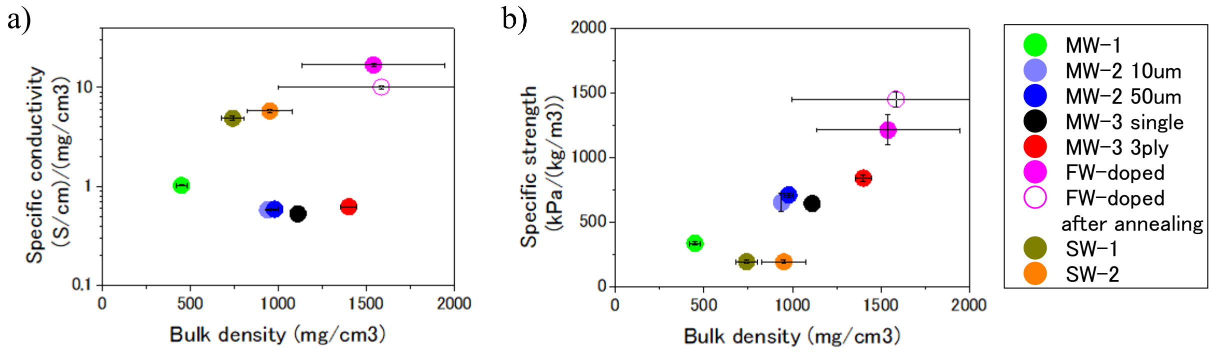

Fig.1 a) The specific conductivities and b) specific strengths of the commercialized CNT fibers as a function of the fiber density.

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A novel straightforward wet pulling technique to fabricate carbon nanotube fibers

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The growing demand for wearable electronics requires flexible and stretchable conductive materials. Among them, carbon nanotubes are recognized for their outstanding mechanical, electrical, optical properties and chemical stability. In this paper, we introduce a novel technique of carbon nanotube fiber fabrication, which we named Wet Pulling. The method allows straightforward fiber production out of carbon nanotube thin films, collected on a filter after the synthesis or deposited onto any substrate. It relies on a combination of film properties and self-assembly due to capillary forces. The wet pulling technique has prominent advantages that make it a promising candidate for both small and large-scale production of CNT fibers with desired properties. The method is also easily adaptive to different kinds of carbon nanotubes and allows rapid fabrication of both active and passive flexible electronic components (Fig.1). A tactile sensor, a pulsometer and an electrical circuit are fabricated for the demonstration of their applicability. We expect this new approach to simplify the production of functional carbon nanotube fibers and to enlarge their usage in diverse applications. This work was supported by the Russian Science Foundation (No. 17-19-01787).

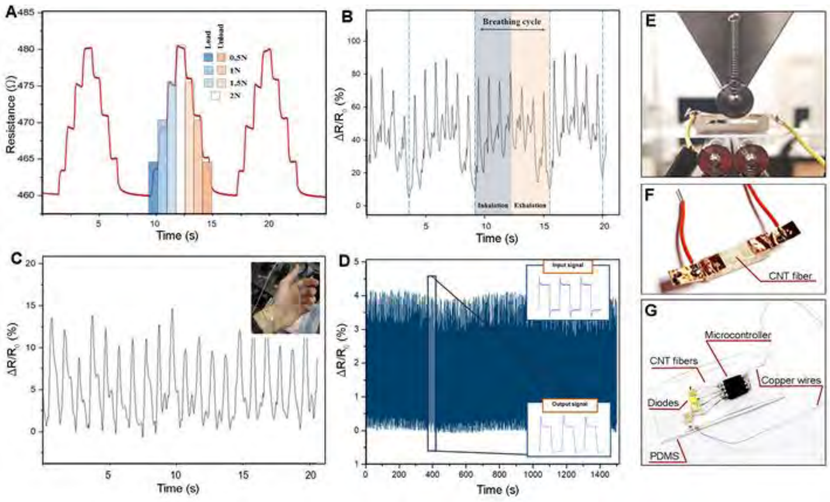

Fig.1 A) The resistance of the fiber during three-point bending test, stepped load. B) Relative resistance change during pulse measurements on a neck also demonstrating the possibility for the breath detection. C) Relative resistance variation during pulse measurements on a wrist. D) Fatigue test relative resistance demonstrating the durability of the WP produced fibers for 1500 cycles. E) Force sensor under tapper load (three-point bending test with wires attached). F) A force sensor with encapsulated SWCNT fibers. G) Stretchable electrical circuit made of SWCNTs on a PDMS substrate.

Anti-proximity effect in superconducting NbN nanowires based on suspended carbon nanotubes

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Superconducting nanowires, which have a quasi-one-dimensional structure of about several tens nanometers in diameter, have attracted attention due to quantum-mechanical properties such as phase-slips (PSs) and studied for application such as qubits. PSs correspond to tunneling of magnetic vortex across nanowires, resulting from thermal (tPS) or quantum (qPS) fluctuations.

In this study, we fabricated superconducting nanowires by coating suspended carbon nanotubes with a thin NbN film. In the resistance-temperature characteristic curves, the residual resistance in the nanowire of 17 nm width and 1.8 μm length remains due to PSs well below the superconducting transition temperature. In addition, we observed the t-qPS crossover at 8 K which is the transition temperature of the electrode. This is because of the suppression of QPS caused by the anti-proximity effect (APE): the density of cooper-pairs in nanowires is varied by electrons from the normal conductive electrode. Moreover, in shorter nanowires of 350 nm length, we observed the resistance dip due to the strong APE. We believe that our results could be useful for next-generation quantum nanodevices.

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Fabrication of NiO Decorated SWCNTs Buckypaper for Electrochemical Detection of Glucose

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Single-walled carbon nanotubes (SWCNTs) are considered to be ideal catalyst carrier for electrochemical sensors owing to their high chemical stability, large surface area and excellent electrical conductivity. Recently, the so-called flexible buckypaper from carbon nanotubes has shown significant application in many areas such as bioelectrocatalytics [1]. Herein, iron loaded SWCNTs were fabricated by hydrogen arc discharge method using iron as catalyst [2]. After removing iron nanoparticles in concentrated hydrochloric acid, purified SWCNTs (p-SWCNTs) were acquired. Nickel loaded SWCNTs were synthesized by helium arc discharge using nickel as catalyst [3]. Heating treatment was conducted to oxidize the nickel nanoparticles and remove amorphous carbon. The two kinds of SWCNTs were dispersed in deionized water and vacuum filtrated layer by layer to form NiO decorated buckypaper (NiO-BP). The NiO-BP consists of two layers, in which NiO loaded SWCNTs (NiO-SWCNTs) and p-SWCNTs function as catalyst layer and conductive support layer, respectively. A typical TEM image of NiO-SWCNTs is shown in Fig.1 (a). Electrochemical method was adopted to examine its performance in glucose detection, in which the NiO-BP, platinum foil and Hg/HgO (1 M KOH) were used as working electrode, counter electrode and reference electrode, respectively. At potential of 0.55 V in 0.5 M NaOH, the sensor performed a high sensitivity of 1824.8 μA mM^{-1} cm^{-2} to glucose and a linear range of the detection up to 8 mM.

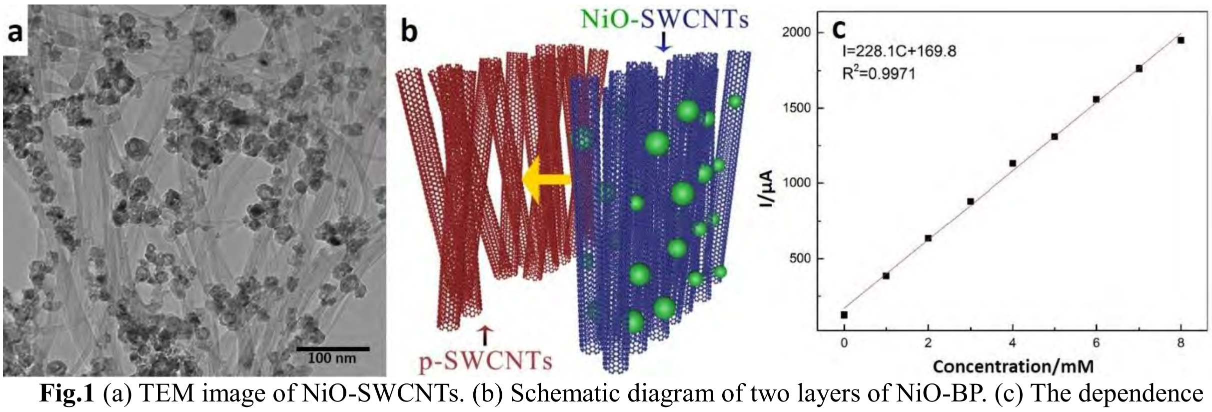

Fig.1 (a) TEM image of NiO-SWCNTs. (b) Schematic diagram of two layers of NiO-BP. (c) The dependence of response current vs. glucose concentration and the linear fitting result.

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Holey single-walled carbon nanotubes for ultra-fast broadband bolometers

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The development of new materials for sensitive and fast broadband photodetectors remains actual problem in the fields of IR vision and spectroscopy. Carbon nanotubes have already been demonstrated as a promising material for bolometers [1]. However, the sensitivity enhancement of such bolometers while maintaining the speed of operation is still a great challenge. Here, we present a new material, holey carbon nanotube network, designed to improve the temperature coefficient of resistance (TCR), the key parameter that determine the sensitivity of bolometers [2]. Fine treatment with low frequency oxygen plasma allows to control the conductive properties of the material. The temperature coefficient of resistance of our films is much higher than reported values for pristine carbon nanotubes in wide temperature range up to 3 % K^{-1} in absolute value at liquid nitrogen temperature which is much higher than reported values for carbon nanotubes and comparable with vanadium oxides. The bolometer prototypes made of free-standing plasma treated SWCNT films possess high sensitivity in wide IR range (3-50 μm), smooth spectral characteristics of IR absorption, ultrafast (3 ms) response time and relatively low noise level comparing to similar devices made of carbon nanotubes.

This work was supported by the Russian Science Foundation (No. 17-19-01787)

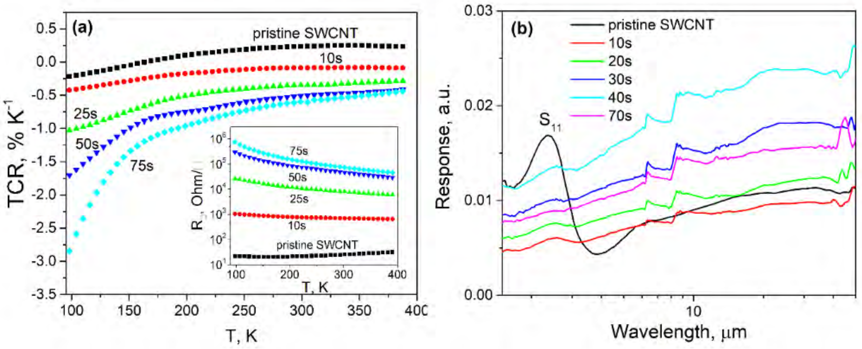

Fig.1 The plasma treatment effect on TCR of SWCNT films and bolometers response (a) TCR of pristine SWCNT films and the ones treated in oxygen plasma at different exposure time, inset: temperature dependence of film sheet resistance. (b) Spectral characteristics of bolometric samples made of 100 nm thick free-standing SWCNT film, pristine and oxygen plasma treated with different time of treatment.

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The Effects of Semiconducting SWCNT Film Thickness on their Hydrogen Sensing Performance at Room Temperature

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Although hydrogen gas is thought to be a green and renewable energy source for various applications, hydrogen gas could be extremely dangerous due to the flammable and explosive nature [1-2]. Therefore, the accurate measurement of the H_2 level is crucial for safety. Previous works have demonstrated that the pure carbon nanotube(CNT)-based gas sensors have poor sensitivity of H_2 at room temperature because of both the weak adsorption of the electron-neutrality gas and high activation energy barrier between H_2 molecules and CNTs [3]. In this work, flexible and transparent hydrogen gas sensors with different film thickness were fabricated using 2D semiconducting and metallic single-wall CNT networks synthesized by a floating catalyst vapor deposition method. It was found that the film thickness plays an important role in the sensing performance, which indicated the importance of the formation of the CNT connecting-network. The sensors based on semiconducting SWCNTs demonstrated both a fast response time (serval seconds) and a fast recovery capability (in minutes) at a low detection concentration of 5vol% hydrogen gas in dry air. In addition, the sensing performance of the semiconducting SWNCTs based sensors is better than that of metallic SWCNTs based sensors, indicating the superiority of semiconducting SWCNTs to be used in sensors.

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Conformal printing of graphene inks and multilayered devices onto arbitrarily shaped 3D objects

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Printing has drawn a lot of attention as a means of low per-unit cost, high throughput and additive patterning of graphene inks for scaled-up functional thin-form factor device manufacturing. However, the traditional printing processes typically require a flat surface and hence the current graphene printing methods are incapable of achieving patterning onto arbitrarily-shaped objects such as 3D printed parts and even on human skin.

Here, we present a conformal printing method to deliver conductive graphene patterns on to arbitrarily-shaped 3D objects using a sacrificial layer. We first formulate a water-insoluble conductive graphene ink and print it on to an ultrathin polyvinyl alcohol (PVA) film using conventional printing processes. The printed graphene patterns are then floated onto water, allowing the dissolution of PVA, while retaining the graphene patterns. This allows transfer of the conductive graphene patterns directly onto arbitrarily-shaped 3D objects with high resolution (Fig 1). I will present the formulation process and the parameters vital to achieving this and demonstrate this process onto a variety of irregularly-shaped 3D objects. Using this approach, I will also demonstrate multilayered device fabrication/transfer, including simple 2D material based electric circuits and components as well as resistive and capacitive strain sensors, without requiring post deposition processing.

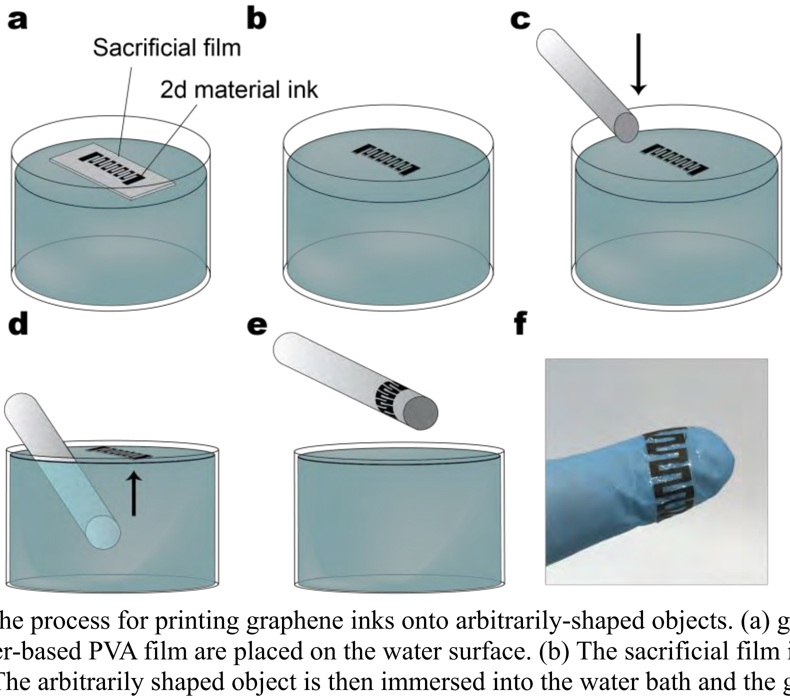

Fig. 1 Schematic of the process for printing graphene inks onto arbitrarily-shaped objects. (a) graphene inks printed on sacrificial, water-based PVA film are placed on the water surface. (b) The sacrificial film is then allowed to dissolve. (c, d, e) The arbitrarily shaped object is then immersed into the water bath and the graphene is transferred onto the object *via* a wet transfer process. (f) Printed graphene strain sensor on a finger.

Lowering Internal Friction of 0D-1D-2D Ternary Nanocomposite-based Strain Sensor by Fullerene to Boost the Sensing Performance

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The development of strain sensors with both large strain range (>50%) and high gauge factor (>100) is a grand challenge. High sensitivity requires material to perform considerable structural deformation under tiny strain, whereas high stretchability demands structural connection or morphological integrity for materials upon large deformation, yet both features are hard to be achieved in one thin film. Herein, we develop a new 0D-1D-2D ternary nanocomposite-based strain sensor that possesses high sensitivity in broad working strain range (gauge factor 2392.9 at 62%), low hysteresis, good linearity, and long-term durability. The skin-mountable strain sensor, fabricated through one-step screen-printing process, is made of 1D silver nanowire offering high electrical conductivity, 2D graphene oxide offering brittle layered structure, and 0D fullerene offering lubricity. The fullerene constitutes a critical component that lowers the friction between graphene oxide-based layers and facilitates the sliding between adjacent layers without hurting the brittle nature of the nanocomposite film. When stretching, layer slippage induced by fullerene can accommodate partial applied stress and boost the strain, while cracks originating and propagating in the brittle nanocomposite film ensure large resistance change over the whole working strain range. Such high comprehensive performance renders the strain sensor applicable to full-spectrum human motion detection.

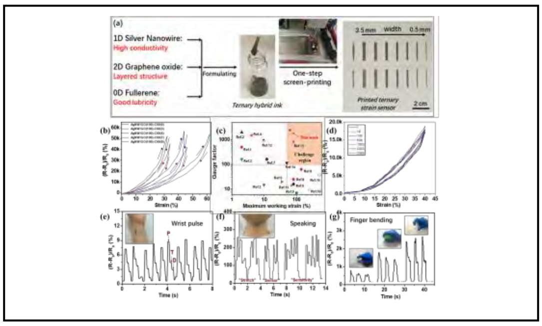

Fig.1 (a) Schematic of the screen-printing process for fabricating 0D-1D-2D ternary nanocomposite-based strain sensors. (b) Typical relative resistance change-applied strain curves under one stretch/release cycle for GO-AgNW-C60$_{\text{(different fraction)}}$ strain sensors. (c) Comparison of the GF and maximum working strain range of the present GO-AgNW-C60 strain sensor with various recent published results. (d) Typical relative resistance change-applied strain curves under specific stretch/release cycle of stretching and releasing between 0 and 40% strain for the GO-AgNW-C60 strain sensor. Monitoring of human motion using GO-AgNW-C60 strain sensor. Relative resistance change of (e) wrist pulse, (f) speaking and (g) finger bending to different degree.

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Flexible Carbon Nanocoil Network Based Strain Sensor with Ultrahigh Sensitivity

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In recent years, with increasing demand for intelligent devices, flexible strain sensors have become an essential component in wearable devices [1-5]. The strain sensor in this research has been fabricated, which uses PDMS as flexible substrate, a pair of gold thin film with the distance of 100 μm on the flexible substrate as electrodes, and a carbon nanocoil network deposited by an electrophoretic method as sensing medium. The morphology of carbon nanocoil network is shown in Fig. 1(a).

The strain sensor owns a gauge factor close to 10000 for tensile strain (Fig. 1(b)). A high stability and reproducibility of more than 5000 cycles and a fast response time of approximately 50 ms have been achieved. It also has a high sensitivity for bending strain. Due to these advantages, it has a good performance in the application of high sensitive detection, such as breath (Fig. 1(c)), wrist pulse and vibration.

This strain sensor can be fabricated with a simple technology and low cost, suggesting great potential applications in micro-nano electromechanical systems, wearable devices and electronic skins.

This study was supported by the National Natural Science Foundation of China (No. 51661145025, 11274055).

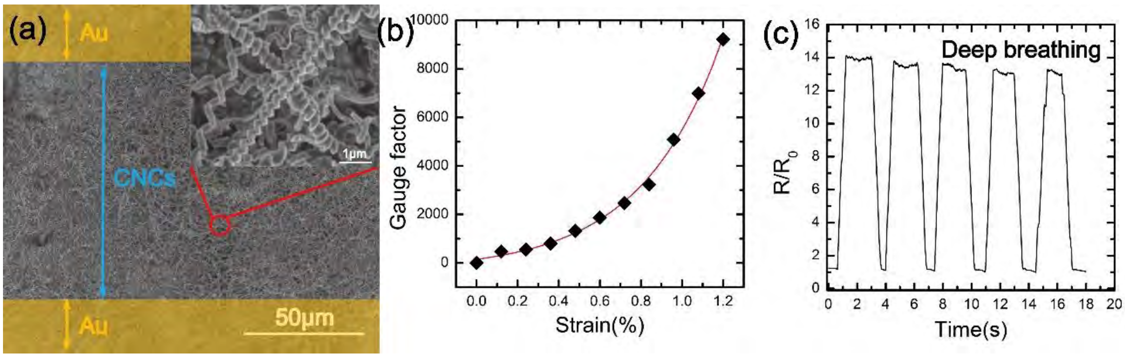

Fig.1 (a) SEM image, (b) strain sensing performance and (c) application of the strain sensor based on carbon nanocoil network.

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Flexible, all-inorganic actuators based on vanadium dioxide and carbon nanotube bimorphs

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Flexible actuators responsive to multiple stimuli are much desired in wearable electronics. However, general designs containing organic materials are usually subject to slow response and limited lifetime, or high triggering threshold. In this study, we develop flexible, all-inorganic actuators based on bimorph structures comprised of vanadium dioxide (VO2) and carbon nanotube (CNT) thin films. The drastic, reversible phase transition of VO2 drives the actuators to deliver giant amplitude, fast response up to ~100 Hz, and long lifetime more than 1,000,000 actuation cycles. The excellent electrical conductivity and light absorption of CNT thin films enable the actuators to be highly responsive to multiple stimuli including light, electric, and heat. The power consumption of the actuators can be much reduced by doping VO2 to lower its phase transition temperature. These flexible bimorph actuators find applications in biomimetic inspect wings, millimeter-scale fingers, and physiological-temperature driven switches.

Effects of heat-generation and transport in coil-shaped soft-actuators consisting of polymer threads and carbon nanotube yarns

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As an alternative type of motor, the motions generated by soft-actuators have attracted considerable attention because they are not only lightweight and inexpensive, but they also realize human-mimetic mechanical motions that are strongly demanded in the field of robotics. One of the important challenges presented by coil-shaped soft-actuators resides in their thermal absorption and extraction design. One of the ideas is that using metal-wires or silver-paste for resistive heating to soft-actuators [1,2]. However, the use of metal materials increases the weight of the soft-actuators and suppresses their flexibility. In addition, the difference in the thermal expansion coefficients between the polymer-thread and accompanying metal frame may cause the performance of the soft-actuators to decrease.

In this study, we fabricated metal-free soft-actuators using poly(ethylene terephthalate) (PET) threads and heat-introducing CNT yarns in several different designs. We analyzed the effects of thermal absorbance and extraction on their performance with respect to their mechanical force. Figure 1 shows the schematic of three type designs of soft-actuator and peak force of these samples at same induced electric power per one CNT yarn. Figure 2 shows the results of calculations based on the heat diffusion equations in monofilament and multifilament soft-actuators. From these results, we found that homogenous thermal distribution in the soft-actuators, *i.e.*, the use of the multifilament structure, provides the highest performance in terms of mechanical force because inhomogeneous heat generation in the soft-actuator causes parts of the actuator to remain unheated and this interferes with the mechanical motions.

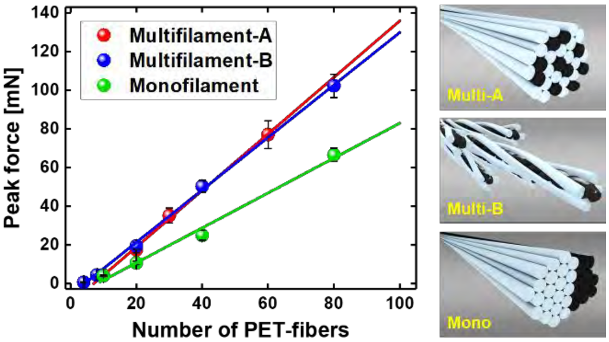

Fig. 1 Peak force of three types of coil-shaped soft-actuators.

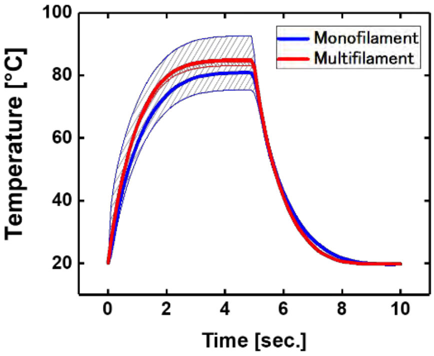

Fig. 2 Simulated thermal distributions in the soft-actuators.

[1] C. S. Haines *et al.*, *Science* **343** (6173), 868–872 (2014).
[2] M. Hiraoka *et al.*, *Sci. Rep.* **6**, 36358 (2016).

Noise reduction in sensor response of carbon nanotube thin film biosensor using HfO_2 layer as protective film

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Carbon nanotube thin film transistor (CNT-TFT) is a promising candidate for rapid and highly sensitive monitoring of biomolecules because CNT has excellent electric properties, a large surface and stability against chemical reactions [1]. In general, in the biosensing, the buffer solution including target biomolecules is directly injected onto the channel surface of the CNT thin film. The injection of the solution leads to the occurrence of the physical fluctuation of CNT, resulting in increasing noise. In this study, we examined noise change during the sensing by introducing a protective thin film onto the CNT surface.

CNTs were synthesized on a SiO_2(300 nm)/Si substrate from nanodiamond particles as growth seeds using chemical vapor deposition [2]. The thrombin and thrombin aptamer were used as antibody and antigen, respectively. After the aptamers were modified onto the CNT surface, HfO_2 thin films as a protective layer are deposited by atomic layer deposition method. Figure 1(a) shows the scanning electron microscope image of the CNT thin film channel. Figures 1(b) are an optical image of the CNT-TFT after the deposition of HfO_2 layer. The HfO_2 layer of 20 nm is uniformity deposited on overall CNT thin film. Figure 2 shows the specific detection of thrombin molecules using the aptamer-modified CNT-TFT with (a) no-HfO_2 layer and (b) HfO_2 layer. Here, we prepared the phosphate buffer solutions (PBS, pH 6). Thrombin with an isoelectric point of pH 5.2-5.8 is positively charged in the PBS solution. In this case, the gate characteristic of the TFT shifts in the negative direction due to inducing electron on the channel surface. When the gate voltage is kept at p-type region, the source-drain current (I_{sd}) increases stepwise [1]. However, the change in the sensor response of the CNT-TFT with no-HfO_2 layer as shown in Fig. 2(a) is unstable. On the other hand, the sensor response of the CNT-TFT with HfO_2 layer increases stepwise and shows a lower noise. This result indicates that the protective treatment using HfO_2 layers is useful for suppressing the fluctuation of CNT when injecting the solution onto the sensor device.

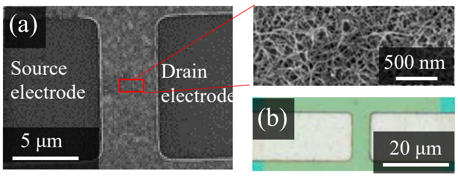

Fig. 1 (a) SEM images of the CNT thin film channel. (b) Optical image of the CNT-TFT with HfO_2 layer.

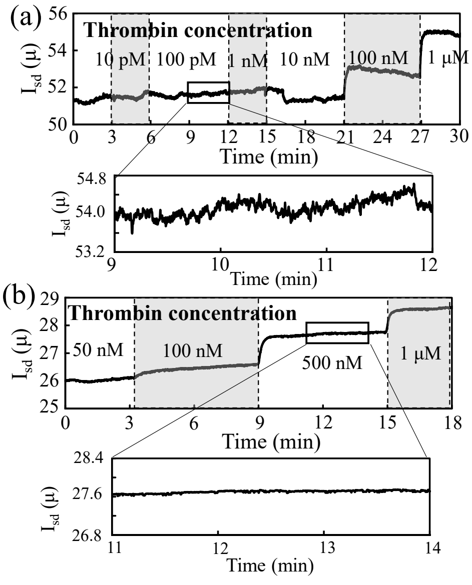

Fig. 2 Sensor response in the CNT-TFT biosensors with (a) no-protective layer and (b) HfO_2 layer.

[1] K. Maehashi, *et al.*, Anal. Chem. **79**, 782 (2007).

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Carbon-Nanotube-based Flash-evaporation printing methodology for perovskite thin films

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Printing solutions have attracted wide attention from various research fields, but thin films made by printing technologies still cannot match the quality of the films made by conventional thin-film deposition methods. In this study, a flash-evaporation printing (FEP) technology, which employed a freestanding carbon nanotube (CNT) flash evaporator, was developed to address this issue and to achieve a compact physical vapor deposition geometry. The target material precoated on the CNT flash evaporator was printed onto a substrate by gas-phase transportation. The FEP methodology presented a printable solution for hybrid perovskite thin films. The as-fabricated photovoltaic devices exhibit a champion power conversion efficiency of ~16.8%, and the thin films were also utilized as potential photodetectors. In addition, this technology can also be used to print patterns and a wide variety of materials on large panels. The environmentally friendly and cost-effective FEP technology will be of significant benefit to printed electronics, organic electronics and future flexible electronics.

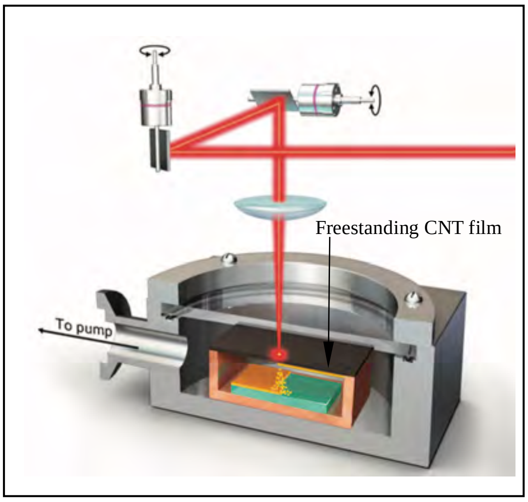

Fig.1 FEP technology based on freestanding CNT evaporator.

[1] H. Wei, X. Zhao, Y. Wei, *et al*. NPG Asia Materials **9**, e395 (2017).
[2] H. Wei, H. Ma, M. Tai, *et al*. RSC Adv. **7**, 34795 (2017).
[3] M. Tai, X. Zhao, H. Wei, *et al*. Submitted (2018).

General and Reversible Strategy of Water Monitoring Aimed at Amphiphilic Pollutants

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For monitoring diverse pollutants in a complicated water environment, the design and improvement of various detection strategies are necessary. Here, we introduce a general strategy of water monitoring aimed at amphiphilic pollutants based on carbon nanotube (CNT) film. The key of this monitor strategy is that the pollutant or additive is able to effectively change the wetting behavior between the CNTs and water. It results in the change in the interface resistance of the CNT film, further the body resistance of the film[1]. The experimental results demonstrate that the change ratio of the film resistance is related to the concentration of pollutants in solution. This monitoring strategy is general for the detection of amphiphilic materials in mixed solution, such as surfactants and some organic solvent. The ability to achieve a sensitive and repeatable change in film resistance has potential applications in high-sensitivity, real-time, long-lasting, and multiple water monitoring[2].

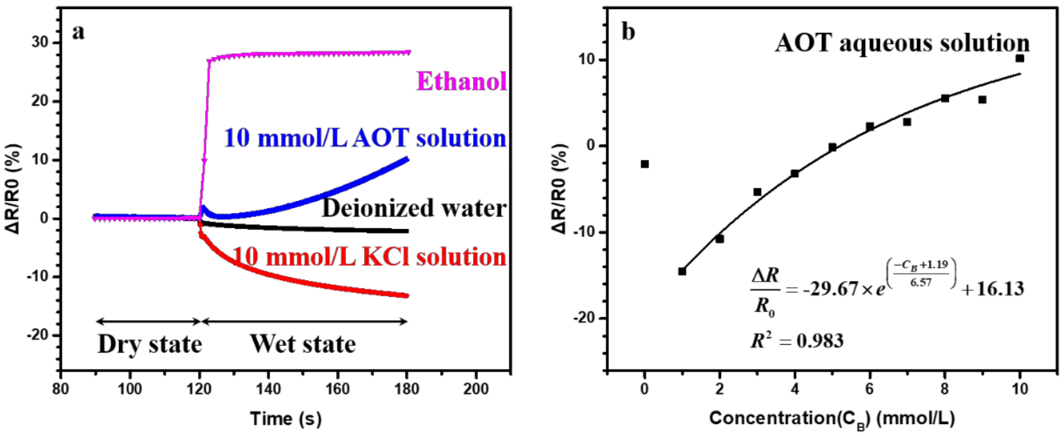

Fig.1 (a) Time-resolved ΔR/R0 plots of film immersed in water, 10 mmol/L KCl aqueous solution, 10 mmol/L AOT aqueous solution, and ethanol. (b) Change ratios of CNT film immersed in AOT aqueous solution.

[1] Zhang Q, Meng P, Zheng R, et al. Langmuir **33(47)**, 13496-13503 (2017).

[2] Zhang Q, Meng P, Wu Y, et al. ACS Applied Materials & Interfaces **10(3)**, 3106-3111 (2018).

Interdigitated electrode with high mass density carbon nanotube forests for electrochemical biosensors

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Electrochemical label-free sensing using redox reactions is powerful and feasible method to detect biomolecules with high sensitivity. Among several geometries of electrodes, interdigitated electrode (IDE) has an advantage for high sensitivity because the current by redox reactions is amplified by shuttling of analytes. As a candidate material for the electrodes in IDE, carbon materials are widely studied due to their fast electron transfer kinetics and wide potential windows.[1] Among others, carbon nanotubes (CNTs) have several advantages such as high aspect ratio with large surface area and high electrical conductivity. Direct growth of CNTs on substrates by chemical vapor deposition (CVD) is especially a suitable way to integrate the CNTs into the IDE. We have engineered the catalyst design and achieved low temperature growth (450 °C) of ultra-high mass density CNT forests (1.6 g cm^{-3}) on conductive supports.[2,3] They are suitable for the electrode material in IDE as the CNTs and supports have an ohmic contact which is different from the conventional CNT forests on insulators (e.g. SiO_2 or Al_2O_3).

We applied the dense CNT forests to the IDE by combining the UV lithography and the CVD process (Fig. 1a and 1b). By optimizing the geometry of the electrodes (width and gap), the performance of the IDE was significantly improved. The cyclic voltammetry (CV) measurements of $K_4Fe(CN)_6$ showed that the current of IDE with CNTs (CNTF-IDE) reached to the steady-state current much more rapidly compared to that of conventional gold IDE (Au-IDE) (Fig. 1c and 1d). By the shuttling of the analytes, the current of the redox reaction was amplified by a factor of ~18. As a model case of the biomolecules, dopamine (DA) was measured under coexistence of ascorbic acid (100 μM). The selective detection of DA was achieved with the linear range of 100 nM – 100 μM and the limit of detection (LOD, S/N=3) of 42 nM. Compared to the conventional carbon electrodes, the CNTF-IDE showed superior anti-fouling property with a negligible shift of half-wave potential ($\Delta E_{1/2}$< 1.4 mV) for 30-times repeated CV measurement of DA at high concentration (100 μM).

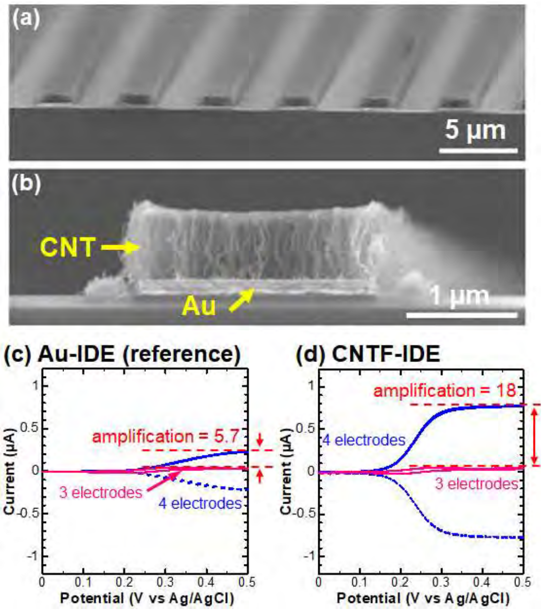

Fig. 1: (a) Oblique-view and (b) side-view SEM images of the CNT forests on Au electrodes. CV results of (c) Au-IDE (reference) and (d) CNTF-IDE with the $K_4[Fe(CN)_6]$ (100 μM) in KCl (100 mM) at the scan rate of 10 mV/s.

[1] Niwa et al., *Anal. Chem.* **66**, 285 (1994). [2] Sugime et al., *Appl. Phys. Lett.* **103**, 073116 (2013). [3] Sugime et al., *ACS Appl. Mater. Interfaces* **6**, 15440 (2014).

Carbon nanotube-based mechanical sensors for motion detection and health monitoring

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Abstract:

With the fast development of wearable devices, flexible sensors have attracted much attention in the recent years. Many breakthroughs have been made in mechanical sensors which allow as to monitor human motions detection and biological signals. However, the fabrication process of many mechanical sensors is too complicated and diffcult to integrate with traditional silicon-based Micro-Electro-Mechanical System(MEMS). Besides, stretchability and sensitivity are very difficult to be combined in one sensor, due to the opposite requirements in the structure of conductive networks.

Here, we demonstrate a carbon nanotube-based pressure sensor with high sensitivity (95.5 kPa−1), low sensing threshold (16 Pa), fast response speed (<16 ms), and zero power consumption when without loading pressure. With a carbon nanotubes/photoresist/carbon nanotubes sandwich-like structure, sensitivity of the pressure sensor can be altered easily by changing the structure of photoresist insulation layer. On the other hand, we found that the sensitivity and stretchability of carbon nanotube-based strain sensor depend significantly on the structure of carbon nanotubes. Random arrangement carbon nanotubes can increase the sensitivity of strain sensor, while well aligned carbon nanotubes can enlarge the stretchability. Therefore, by combining these two structures into one continuous structure we have fabricated a gradient carbon nanotubes strain sensor which can maintain high sensitivity (GF = 13.5) even under extremely large applied strain (570%).

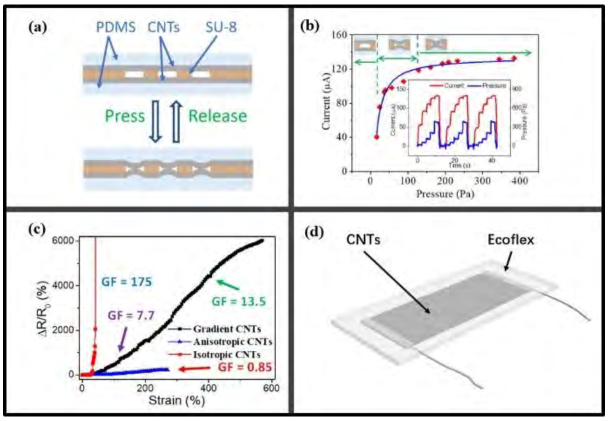

Fig.1 Structure and performance of carbon nanotube-based mechanical sensors.

[1] **B. Liang**, W. Chen, Z. He, Z. Tang* and X. Gui*, *et al*. Small **13**, 1702422 (2017).

Non-contact Remote Imaging by Multi-array Carbon Nanotube Terahertz Scanners

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1. Introduction: Terahertz (THz)-based imaging technologies have proved to be useful as novel inspection tools in diverse fields such as security, organic/inorganic materials characterization, agriculture, medical and biological examinations [1,2]. Among various promising materials for THz devices, we demonstrated that carbon nanotubes (CNTs) exhibit high performance as thermoelectric THz sensors and imagers [3,4]. Here, we present a non-contact remote imaging system based on a multi-element CNT THz scanner.

2. Results: We fabricated a THz scanner consisting of multi-element array of CNT detectors, in which detection mechanism is based on the photothermoelectric effect of the CNTs. The size of each CNT detector was 5mm in length and 1mm in width. We here used this scanner to remotely sense the existence of water drop by irradiating 90-GHz oscillator beam. As depicted in Fig. 1 (a), the water drop was put on an aluminum plate. The metal almost perfectly reflects the THz wave whereas the water absorbs the THz wave well. This means that our THz scanner can work as a sensitive probe for water detection by mapping out the intensity profile of the reflected THz wave. Figure 2 (b) clearly displays that the obtained THz image successfully revealed the existence of the water. This result thus provides an interesting possibility of non-contact and non-destructive determination and analysis of water contents in various materials, bio-samples, and industrial products.

This work was supported in part by the JST-Mirai Program from the Japan Science and Technology Agency.

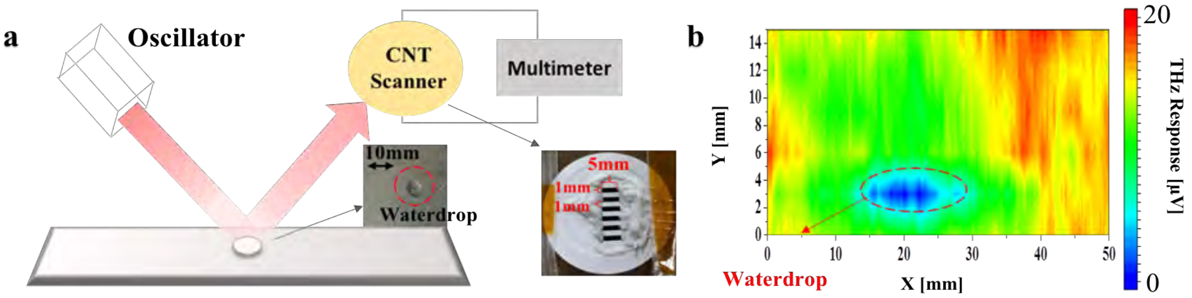

Fig. 1 (a) Schematic of the remote inspection system with multi-array CNT THz scanner. (b) Reflected THz intensity map of the water drop on the aluminum plate.

[1] M. Tonouchi, Nature Photonics, 1, pp. 97-105 (2007)
[2] Y. Kawano, Contemp. Phys, 54, pp. 143-165 (2013)
[3] D. Suzuki, S. Oda, and Y. Kawano, Nature Photonics, 10, pp. 809-814 (2016)
[4] D. Suzuki, Y. Ochiai, Y. Kawano, ACS Omega, 3, pp. 3540–3547 (2018)

Thermoelectric Device Design of Carbon Nanotube Terahertz Imagers for Sensitivity Enhancement

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I. Introduction: Despite of the fact that terahertz (THz) imaging has much possibilities for useful applications including in-line nondestructive examinations [1], existing unbendable THz imagers have a difficulty in adapting to three-dimensional surface imaging. We previously developed a flexible THz camera by using macroscopically bendable single-walled carbon nanotube (SWNT) films and demonstrated multi-view THz imaging [2,3]. In this work, we found key parameters that are directly linked to the sensitivity of THz detection, and proposed a newly designed thermoelectric structure of the SWNT THz device: series combination between the SWNT film and Bi electrode. As a result, we achieved the sensitivity enhancement in THz detection by a factor of about 17, compared to conventional parallel combination.

II. Results: Figure 1 (a) illustrates the conventional SWNT device with parallel combination between SWNT films and Au electrodes. Here, the THz wave was irradiated at the interface between the SWNT film and the Au electrode. Based on the detection mechanism of the photothermoelectric effect, the THz response ΔV is experssed as:

$$\begin{aligned}\Delta V &= |S_{SWNT} - S_{Com}| \times \Delta T \\ &= \left| S_{SWNT} - \frac{\sigma_{Metal} t_{Metal} S_{Metal} + \sigma_{SWNT} t_{SWNT} S_{SWNT}}{\sigma_{Metal} t_{Metal} + \sigma_{SWNT} t_{SWNT}} \right| \times \Delta T \end{aligned} \qquad (1)$$

where S_{Com} is the Seebeck coefficinet of the electrode-SWNT composite material, ΔT is the tempareture gradient generated by the THz irradiation, S_{Metal} and S_{SWNT} are the Seebeck coefficient of the metal and SWNT film, σ_{Metal} and σ_{SWNT} are the electrical conductivity, and t_{Metal} and t_{SWNT} are the film thickness, respectiviely. Equation 1 means that when the SWNT film is much thicker than the electrode, S_{com} is approximated to S_{SWNT}, thereby resulting in the low THz detection sensitivity. To prevent this signal reduction, we formed the electrode metal in series to the SWNT film as shown in Fig.1 (b). The utilization of this structure enables us to use the fundamental Seebeck coefficinet of the metal. Since SWNT films used here are of p-type, the use of Bi with a negative Seebeck coefficinet (-77μV/K) for the series electrode should lead to the sensitivity enhancment. As shown in Fig.1, the THz imager based on such a series-electrode structure exhibited higher performance in THz sensing and imaging.

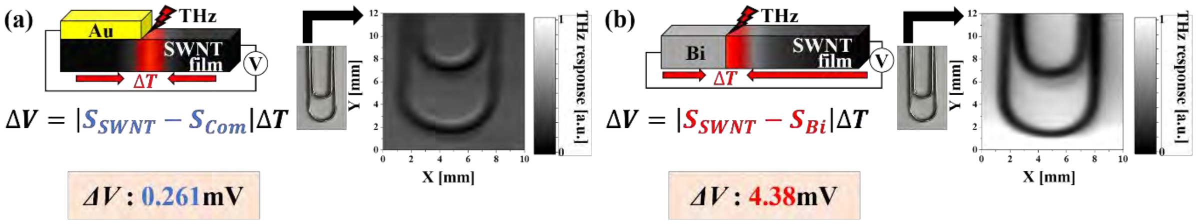

Fig.1 Imaging performances of (a) the conventional parallel-electrode structure (Au 30nm), (b) the present series-electrode structure (Bi 200nm), for the 29THz irradiation at 65.6μW.

[1] M. Tonouchi, Nature Photonics, 1, pp. 97-105 (2007)

[2] D. Suzuki, S. Oda, and Y. Kawano, Nature Photonics, 10, pp. 809-814 (2016)

[3] D. Suzuki, Y. Ochiai, Y. Kawano, ACS Omega, 3, pp. 3540–3547 (2018)

Integration of Carbon Nanotube & Metal Oxide Thin Film Transistors

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Applications of single-walled carbon nanotube (SWCNT)-network in integrated circuits (ICs) and sensors have attracted a lot of attention. In digital ICs, high performance p- and n-channel thin-film transistors (TFTs) are utilized to construct complementary (or referred to as CMOS) circuits with ultra-lower power consumption and high noise margin. SWCNT-TFTs fabricated using ordinary processes show highly stable p-type characteristics under standard ambient conditions. However, air-stable and high-performance n-channel SWCNT-TFTs requires additional treatment. Recently, several approaches have been employed to fabricate n-channel SWCNT-TFTs, mainly through chemical doping of the CNT-channel, passivating the CNT-channel with a high-k dielectric or using low work-function metal contacts. N-channel SWCNT-TFTs suffer from poor stability and high process complexity, thereby hindering optimal operation of integrated SWCNT CMOS circuits.

Wide-bandgap oxide semiconductors are a family of very promising electronic materials for both passive and active device applications. Until now, most of reported high performance metal oxide thin film transistors (TFTs) show n-type characteristics. Although a number of papers have been published for p-type metal oxide TFTs, the performances of p-type metal oxide TFTs are not able to match those of n-type metal oxide TFTs in order to fulfil the requirements of complementary circuits. Another approach is to integrate high performance p-type carbon nanotube (CNT)-TFTs with n-channel metal oxide-TFTs to achieve the functionality of a complementary circuit.

In this presentation, we report on an optoelectrical hybrid inverter, in which a p-type CNT-TFT and an n-type indium-tin-oxide (ITO) TFT are involved. Without light illumination, the device functions as an ordinary inverter. Interestingly, as the conductance of the ultrathin ITO channel in the ITO-TFT is increased by several orders of magnitude under UV light illumination, the logic output does respond to the UV light modulation and the input electrical signal. If UV light illumination and input electrical signal are taken as two logic inputs, the device works as a very good NOR gate. At present, the device is built on a fused quartz substrate and it is of high transmittance of ~90%. The device can, in principle, be implemented on a flexible and transparent substrate for flexible and transparent logic circuits.

This project is financially supported by MOE AcRF Tier1 (MOE 2016-T1-001-197, RG 102/16) and MOE Tier2 (MOE 2013-T2-2-100), Singapore.

Graphene-Base Hot Electron Transistor with Silicon Emitter

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To improve the high-frequency properties of the bipolar junction transistor, the metal-base transistor was once proposed as the best candidate which however encountered both material and fabrication issues [1]-[3]. As a semi-metal, graphene is recognized as the best base material since the nature of ultra-thin thickness and high mobility. A graphene-base hot electron transistor with a Schottky emitter junction is shown in Fig. 1. Simulation works showed even terahertz operation was possible [4]. The feasibility to employ graphene as a base material was also verified by the counterpart devices which emitted carriers via tunneling through oxide layers [5]-[7]. In this study, a silicon-graphene-silicon (Si-Gr-Si) transistor is fabricated by semiconductor membrane transfer. It is expected as one of the most promising devices for ultra-high frequency operation which fully utilizes the supreme nature of graphene and the high efficiency of the Schottky emitter junction.

The fabrication flow for a Si-Gr-Si transistor started from patterning of an n-type Si substrate with a SiO_2 capping layer, leaving a window to the Si substrate. Graphene and n-type Si membrane transfer were then performed one after another [8][9]. Optical and SEM images of the fabricated Si-Gr-Si transistor were shown in Fig. 2. For a typical Si-Gr-Si transistor, the Schottky characteristics of the top Si-Gr and the Gr-bottom Si junctions were shown in Fig. 3 (a). The high on-current is highly needed in the high frequency applications. The characteristics of a typical Si-Gr-Si transistor biased in the common-base mode were shown in Fig. 3 (b) where the top Si was used as the emitter. A clear dependence on V_e of I_c indicated that at the collector a successful collection of the emitted electrons from the emitter was achieved. The current gain excluding the effect of the leakage current of the collector junction was above 10% at biases of V_e=-5 V and V_c=4 V. The current gain increased with increased biases V_c and V_e, which can be understood from the graphene-quantum-capacitance point of view.

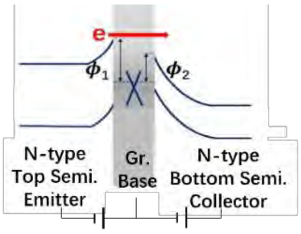

Fig. 1 An illustration of a graphene-base hot electron transistor in the on-state.

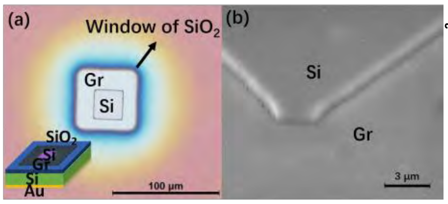

Fig. 2 (a) Optical and (b) SEM images for a Si-Gr-Si transistor. The Si-Gr-Si structure was formed through the window of the SiO_2.

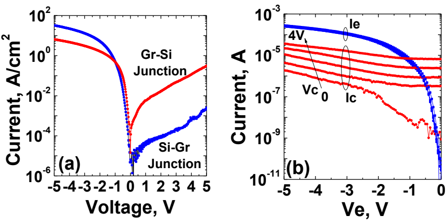

Fig. 3 (a) Characteristics of the Si-Gr junctions (b) Input and transfer characteristics of a typical Si-Gr-Si transistor in the common-base mode.

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Tailoring of thermal stress on resonance frequency shift of atomically thin electromechanical resonators by strain and stack

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Graphene and MoS_2 have unique thermal and mechanical properties. Therefore, the mechanical resonators (MR) made of them are candidate for the oscillator or nonlinear applications with high controllability of the resonance properties by heat [1]. In the case of resonance control utilized by thermal effects, however, we can only tune upward or downward direction depending on the sign of the thermal expansion. Here, we demonstrate tailoring of thermal stress on resonance frequency shift of atomically thin MRs by strain and stack.

We fabricated graphene MR and stacked MoS_2/graphene MR. The resonance properties were measured electrically (Fig. 1(a)). The MRs act as a field effect transistor (FET) and the suspended area of MR corresponds to FET channel. The alternative current source drain voltage V_{sd} is added to the MR, which induces mechanical vibration by periodical electrostatic force. The direct current gate voltage V_g is also applied to the MR. The increase of V_g can add the tension to the resonator and induce strain by electrostatic force. The resonance is detected by amplitude modulation (AM) and output current change, which is down mixed by lock-in-amp. The resonance measurement was performed in vacuum ~ 10^{-3} Pa.

Fig. 1(b) and Fig. 1(c) show temperature dependences of resonance frequency shifts under various V_g on graphene and MoS_2/graphene MR, respectively. In the case of graphene MR, the frequency shift is modulated by increasing V_g. In the range from V_g=2.5 V to 4.0 V, the shift is suppressed with increasing V_g. Then, the shift becomes nearly 0 %/K when V_g=4.5 V. Finally, the slope of the shift changes negative at V_g=5.0 V. These trends indicate that thermal stress is tailored by gate voltage V_g dominantly. In the case of MoS_2/graphene MR, V_g dependence of the shift is weaker than one of graphene MR. In addition, the frequency shift saturates gradually as in creasing temperature change for all V_g. This result means that the temperature dependence of the resonance frequency shift is suppressed. The main cause of the shift is likely to the stacking of the positive and negative thermal expansion coefficients of MoS_2 and graphene.

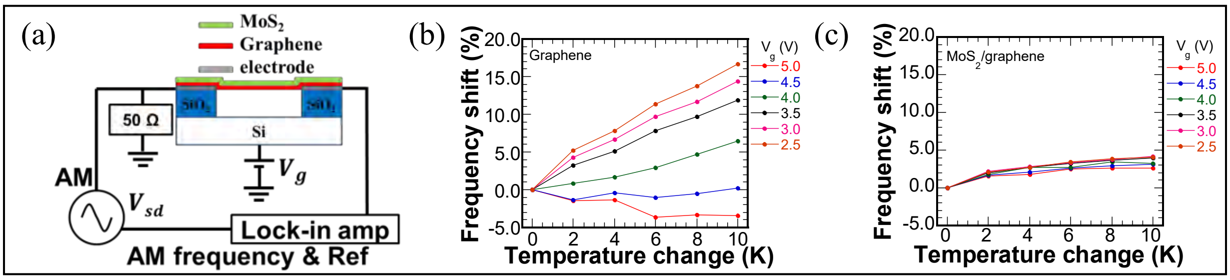

Fig.1 (a) Measurement setup. (b), (c) The gate voltage V_g and temperature change dependence of resonance frequency shift in the case of (b) graphene MR and (c) stacked MoS_2/graphene MR.

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Exploring performance uniformity of thin film transistors based on carbon nanotubes on wafer scale

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Excellent performance uniformity is very important for the practical application of transistors especially in large scale integrated circuit. In this work, we have fabricated top-gated field-effect transistors (FETs) based on solution derived random carbon nanotube (CNT) film on 2-inch wafers, and then investigated their performance uniformity systematically. For CNT FETs with large channel area, the subthreshold voltage (V_{TH}) hysteresis of the FETs could reach as small as 32 mV and the subthreshold swing (SS) could reach near 100 mV/dec and the average of SS have reached 118±7 mV/dec of high uniformity. The on-state current, on/off ratio were all with high uniformity. The coefficient of variation(COV) of the main metrics to characteristic the FETs could be still lower than 20% when the gate length of the transistors scales down to 2 μm. The high uniformity of the FETs constructed with wafer-scale has shown that the CNT film based FETs have the potential in large-scale integrated circuits.

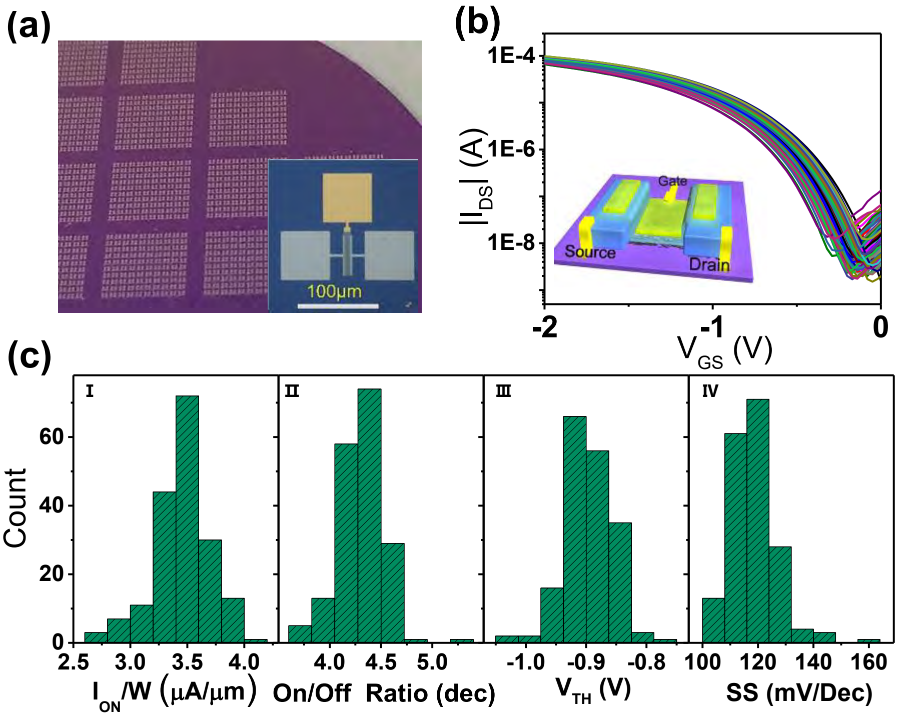

Fig.1 Statistics of key performance for CNT film top-gated field effect transistors with large channel area.

Self-align process with backside exposure to minimize parasitic capacitance of CNT TFTs on transparent flexible film

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Carbon nanotube thin film transistors (CNT TFTs) are promising active component for flexible electronics because of high carrier mobility and excellent mechanical flexibility. In recent years, it has become possible to fabricate CNT TFTs with high yield and uniform characteristics by using purified semiconductor CNTs. This would lead to realizing functional CNT-based integrated circuits (ICs). For flexible electronics applicatoins, devices are fabricated on the plastic substrate, which easily expands or shrinks in size during the fabrication process. Then, a large alignment margin is necessary in the lithography process. This results in the degradation of operation speed of the circuits due to the large orverlap capacitances between the source/drain and the gate electrodes. Self-align process is a key process to eliminate the overlap capacitances. In this study, we have realized a simple self-align prcess with backside exposure for CNT TFTs by utilizing the transparency of the plastic substrate. We have also demonstrated a drastic reduction of the parasitic capacitance and hence switching time of ICs.

Figure 1 shows the schematic structure of the self-aligned CNT TFT fabricated on the transparent and flexible substrate. The device has a bottom gate structure. The source and drain electrodes were self-aligned to the gate electrode by exposing from the backside of the substrate in the lithography process. The overlap capacitance was reduced by a factor of 28 by introducing the self-align process, compared to the conventional process.

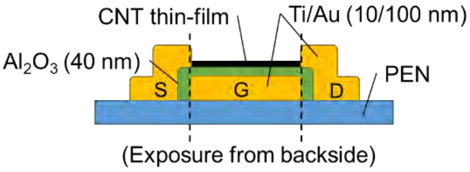

Fig. 1 Schematic device structure of self-aligned CNT TFT.

We fabricated 11-stage ring oscillators to examine the effect of self-align process on operation speed of CNT ICs. The oscillation wave form of an 11-stage ring oscillator is shown in Fig. 2. The switcing time was 16.9 μs/gate for the self-aligned structure, whereas it was 227 μs/gate for conventional structure. The backside-exposure, self-align process is effective to enhance operation speed of CNT ICs, and also easily applicable for large-area plastic devices.

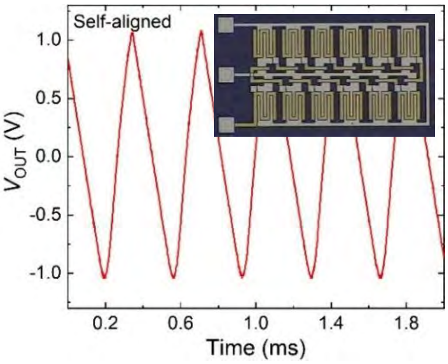

Fig. 2 Oscillation wave form of 11-stage ring oscillator. (Inset) Photomicrograph of the circuit.

Acknowledgments: The semiconducting CNTs were provided by TASC. This work was partially supported by JST/CREST.

Optical modulation of resonance characteristics of cantilevered MoS$_2$ mechanical resonator

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Two-dimensional atomic layer materials are attracting much attention as many useful device applications because of their unique electrical, optical and mechanical properties. Among others, transition metal dichalcogenide such as molybdenum disulfide (MoS$_2$) has a bandgap, so they are expected to be high performance nano-electro-mechanical resonators (NEMR). In addition, Understanding the influence of light on the mechanical resonance is very important to realize novel applications using the unique optical properties of MoS$_2$. Here, we investigate the effect of the light irradiation on the resonance characteristics of a cantilevered MoS$_2$ under electrostatic actuation.

To drive the cantilevered MoS$_2$ NEMR, AC+DC bias (V_{AC}+V_{DC}) was applied to a pair of electrodes on the substrate. To detect the resonance, we irradiated a laser with a wavelength of 521 nm with an intensity of 1 μW to the tip of the MoS$_2$ cantilever. In addition, another laser with the wavelength of 660 or 979 nm was irradiated to the entire MoS$_2$ cantilever, where the laser intensity was changed from 1 to 100 μW. Fig.1 (a) and (b) show laser intensity dependences of resonance characteristics under the irradiation of 660 and 979 nm lasers, respectively. Under the irradiation of the laser with the wavelength of 660 nm, the resonance frequency increases with increasing the laser intensity resulted from the hardening of the effective spring constant of the MoS$_2$ cantilever, while the resonance frequency is almost constant under the irradiation of the 979 nm-laser. This is most likely due to the bandgap of ~1.2 eV of the examined MoS$_2$, where the 660 nm-light was well absorbed than the 979 nm-light. Photothermal effect should be considered for the light induced hardening. Another possible mechanism of laser intensity dependence is that the decrease of the effective dielectric constant may prevent the electrical softening effect by the light irradiation, which results in the inc

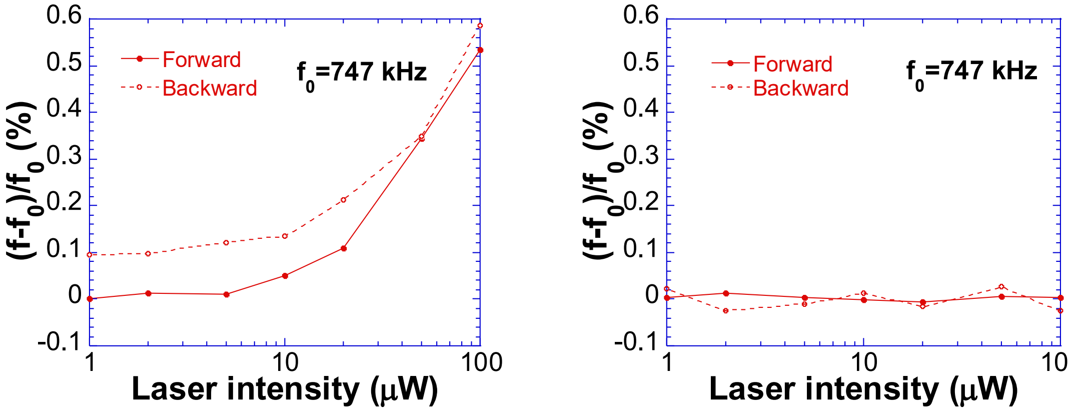

Fig.1 Laser intensity dependence of resonance characteristics (a) 660 nm laser (b) 979 nm laser.

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Carbon nanotube based low-power integrated circuits with bio -integration capability to biological surfaces

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Continuous efforts to develop electronic devices with bio-integration capability are motivated by the increasing demand from clinical and biological applications, aiming to deploy advanced monitoring, diagnosis and therapy. However, as the core unit of electronic systems, low-power integrated circuits (ICs) with simultaneous high complexity capable of in situ biological data computation, operation and analysis in a timely manner are still lacking, hindering the functions and diversity of the system in practical applications. The presentation will detail our work on carbon nanotube-based thin-film transistors and integrated circuits that can be transferred to arbitrary surfaces. The wafer-scale platform can be transferred to biodegradable polymers, plant leaves and a person's wrist, and demonstrate the operation of the transferred devices and circuits on a curved plant leaf. Our nanotube thin-film transistors on biodegradable flexible substrates have ultralow power consumption with an off-state current as low as 0.1 pAμm^{-1}, a subthreshold swing of 62 mVdec^{-1}, and a static power consumption of 2.5×10^{-13} W in an inverter. The thin-film transistors also exhibit highly uniform performance with an 80 mV standard deviation in the threshold voltages. Accordingly, the most complex CNT-based ICs on a flexible substrate, i.e., a full-adder, with rail-to-rail outputs and a read-only memory, were demonstrated driven by a single small supply voltage of 2 V.

Long-Length Removal of Metallic Single-Walled Carbon Nanotubes for Multiple Transistor Fabrication

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Single-walled carbon nanotubes (SWCNTs) are a promising channel material of field-effect transistors (FETs). Highly-miniaturized SWCNT-FETs have realized high current density as well as excellent switching behavior, surpassing silicon-based FETs [1,2]. Also, large scale integration of SWCNT-FETs into logic circuits and sensor arrays has been demonstrated [3]. However, the coexistence of semiconducting and metallic SWCNTs has been still a major obstacle to large-scale integration of high-performance SWCNT-FETs. In this study, we developed a method for selectively removing metallic SWCNTs in long length to obtain semiconducting SWCNT arrays and fabricated multiple FETs along the purified arrays [4,5]. Voltage-induced burning of SWCNTs under various environmental conditions revealed a significant effect of water vapor and polymer layer coating on removed length of metallic SWCNTs. Long-length removal of metallic SWCNTs was found to be initiated from nanogaps on SWCNTs. Based on these findings, we succeeded in removing metallic SWCNTs in a selected area (Fig. 1(a,b)). Multiple FETs were built along the purified semiconducting array (Fig. 1(c)), and all of them showed high on/off current ratio (Fig. 1(d)), confirming complete removal of metallic SWCNTs in the area. This metallic SWCNT removal method would open up a new possibility for robust integration of short-channel SWCNT-FETs.

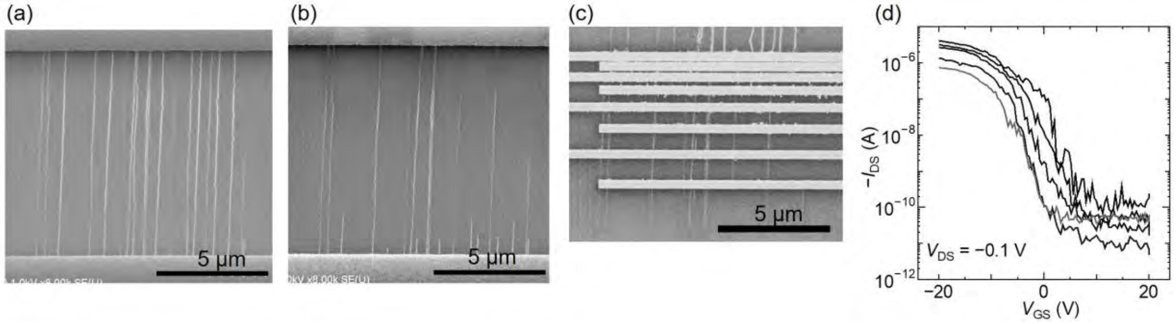

Fig.1 Scanning electron microscopy images of an SWCNT array (a) before metallic SWCNT removal, (b) after metallic SWCNT removal, and (c) after multiple electrode deposition. (d) Current−voltage characteristics of multiple FETs built along the purified semiconducting SWCNT array.

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Optoelectronic and Photovoltaic Properties of Hybrid P3HT Nanofibers on ZTO Nanowires

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The poly(3-hexylthiophene-2,5-diyl) (P3HT) nanofibers and zinc tin oxide (ZTO) nanowires were prepared in solution and on Si wafer, respectively. The ZTO nanowire is moved to a patterned substrate and it is then contacted with Ti/Au source and drain electrode by using the standard electron-beam lithography, followed by thermal evaporation. The heavily doped substrate is used as a back gate electrode. Afterwards, P3HT nanofibers are placed across ZTO nanowires and attached on another two contact pads. The device structure is shown in Fig. 1. In the beginning, we check electrical properties of p-type P3HT nanofibers, n-type ZTO nanowires, and the pn junction between P3HT and ZTO. P3HT nanofibers are photoactive. We thus investigate the role of *p-n* heterojunction playing on the optoelectronic and photovoltaic effects. We discover that the hybrid P3HT/ZTO *p-n* heterojunction assists to increase photocurrents and to enhance photovoltaic effects. Through the controllable gating of the heterojunction, we can discuss the background mechanisms of photocurrent generation and photovoltaic energy harvest.

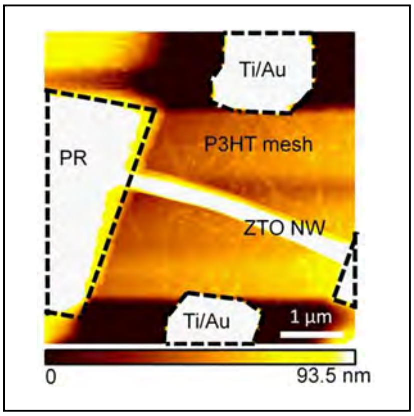

Fig.1 Atomic force microscope image of the device of hybrid P3HT nanofibers on ZTO nanowires.

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Large-area ultrathin graphene films based on Marangoni self-assembly and their applications

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Key Words: Graphene, Self-Assembly, Marangoni Effect, Strain Sensors, Film Heaters

Graphene-based thin films have excellent flexibility, high visible light transparency, and good electrical properties, showing promising potential for the integration of electronic skin applications and the development of wearable/portable devices. The graphene films grown by chemical vapor deposition show superior properties, however, the process difficulty and the product cost are higher due to the high temperature growth and the necessary transfer processes. In contrast, large-area films can be made by spin-coating or screen-printing using graphene nanosheets dispersion, but the drawback is the poor uniformity of the film thickness. In this study, few-nanometer-thick graphene films can be simply formed at the liquid–air interface based on Marangoni self-assembly effect. The films obtained by our process exhibit lower electrical sheet resistance while maintaining high transparency, as compared to other preparation methods. Based on this ultrathin graphene film, we have developed a variety of applications including highly sensitive strain sensors, anticorrosion hybrid coatings, and flexible transparent film heaters.

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Scaling down contact length in complementary carbon nanotube field-effect transistors

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We performed an experimental investigation on contact length (L_c) scaling of carbon nanotube (CNT) complementary field-effect transistors (FETs). Contact resistances of Sc-contacted (for n-type) and Pd-contacted (for p-type) CNT FETs are respectively retrieved based on the experimental data through the transfer length method (TLM). The performance of L_c scaling of Sc/CNT is proved to be comparable to that of the Pd/CNT contact with L_c larger than approximately 40 nm, but it degrades sharply when further scaling down L_c mainly owing to the surface oxidation of the Sc film. After decoupling the effect of oxide thickness, the intrinsic contact scaling behavior of Sc-contacted CNT FETs is found to be as good as that of the Pd-contacted ones, which can further satisfy the requirement of developing complementary CNT FET technology scaled down to the 14 nm node.

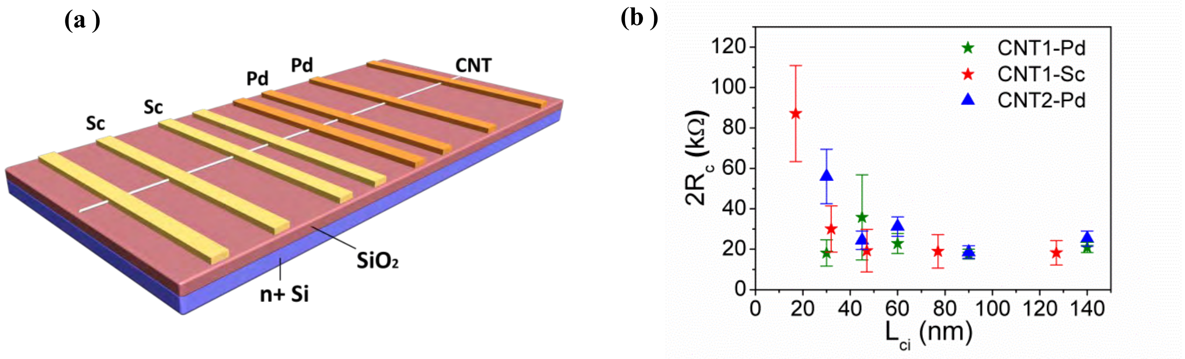

Fig.1 a) Structure diagram of back-gate devices with different gate/contact length and contact type. b) The relationship between the contact resistance and intrinsic contact length after decoupling the oxide thickness of Sc contact.

A METHOD FOR FABRICATING NANO FOUR-POINT PROBES (N4PPs)

Lin Cong, Kaili Jiang

ABSTRACT 2D high temperature superconductors such as single unit-cell FeSe films have attracted much attention because of their scientific and technological importance. Due to the small size of the single domain sample and the possible degradation of the film when exposed to air, there is a discrepancy between the transition temperature measured by in-situ STM tunneling spectroscopy and that measured by ex-situ transport measurement. Scientists are therefore expecting an in-situ transport measurement technique. Now the commercially available micro-4-point-probe (M4PP) is so stiff that usually scratch the single layer film, and of larger size than the single domain of the single layer film. Here we show a method for fabricating nanofour-point probes (N4PPs) by using flexiblecarbon nanotubesas the contact electrodes. The probe chip is made from a 200um thick silicon wafer with SiNx insulating layer and Au electrodes. The tip is composed of 4 streching out CNTs covered by a thin layer of Au, of which the tail end separation is down to 300nm. The microscopic probes are mechinacally flexible and robust enough to do non-destructive measurement and recover their original shape after contacting the sample surface. The N4PP provides an opportunity to investigate and characterise conducting and superconducting thin films with high spatial resolution, facilitating the in-situ transport measurement of 2D superconductors.

High Performance Silicon-Based Photodetectors and Imagers

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In the past few years, our group has been focusing on the exploration of Gr/Si based photodetectors and imagers. In line with the development trend of two-dimensional (2D) applications, we carefully (1) optimize the device structure, based on the Gr/Si shallow junction with tunable Schottky barrier height, and their low capacitance as well as small contact resistance; (2) take the advantage of fast recovering-time induced by majority carriers at Gr/Si Schottky junction; (3) bring the fast separation and high collection efficiency of the photo-excited charge-carriers in the Gr/Si heterostructure into play. [1-9]

Furthermore, to solve the typical problems of silicon-based invisible photodetectors and imagers, we focus on the ultraviolet (UV), infrared (IR) photodetection and their imaging integration system. In recent years, we have achieved the following systematic research outcomes: 1) By proposing a new silicon-graphene synergistic absorption theory and using the silicon-on-insulator (SOI) integrated with graphene structure, we broke the limit of traditional silicon-based UV detection, and fabricated high-speed UV photodetectors and imagers; 2) By proposing a cascade structure combined with plasmon resonant absorption, we fabricated high-performance Silicon-based IR photodetectors and imagers; 3) By integrating large photodetector arrays with signal processing circuits, we established high-performance silicon-based broadband imaging system for potential applications.

We also discussed the engineering issues of critical contact problems between 2D materials and three-dimensional bulk materials into details for high-speed devices. [10,11] Additionally, we outlined the current challenges to develop spin qubits and transports in 2D materials. [12] By taking the interactions between Gr and Si into consideration of device design and fabrication, our work provides theoretical supports and technical guidance for the future development of Gr/Si-based photodetectors and imagers.

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Ultrathin free-standing CNT films for next-generation EUV lithography

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Extreme ultraviolet (EUV) lithography is the next-generation technology for beyond 7 nm nodes. One of the challenges for the introduction of EUV technology for high-volume manufacturing is the need for a transparent mask cover, so-called pellicle, which is suspended above the patterned side of a photomask to keep any fall-on particles out of the focal plane for imaging. Since most materials absorb strongly at the 13.5 nm EUV exposure wavelength, identifying an EUV pellicle solution is difficult. The fundamental challenge is to fabricate a free-standing membrane that is thin enough to limit the imaging impact, while robust enough to survive handling and the elevated temperatures at EUV power levels greater than 250W. We propose an ultrathin, free-standing CNT film as an alternative to the current generation of polysilicon-based films, suitable for EUV source powers of 250W and beyond[1]. We show that a free-standing CNT film possesses very high EUV transmission (up to 99% at 13.5 nm corresponding to >97% at 550 nm) and good transmission uniformity (0.4% half-range), mechanical stability (maximum deflection ~0.08 mm at 2Pa) and thermal stability (no change to the film when exposed at higher than 1 kW EUV source power equivalent in vacuum). The size of such a free-standing CNT film can be scaled to the full pellicle size of 12x15 cm^2. Other important CNT film properties, favourable for the EUV pellicle application, are presented, i.e. low EUV scattering and reflectivity, and high transmission under DUV allowing non-actinic mask inspections through the pellicle. The ability of such a porous CNT film to stop particles is measured and the material is tuned for optimal performance with respect to the CNT density.

The major concern of the CNT material is its instability in the environment of hydrogen radicals/ions within the EUV scanner. The EUV+H_2 resistance of the CNT pellicle when exposed up to 250W EUV source power equivalent using a synchrotron source is shown. The approach to coat free-standing CNTs with inorganic thin films in order to protect the CNTs from hydrogen radicals/ions in the scanner while preserving high EUV transmission and mechanical stability is presented.

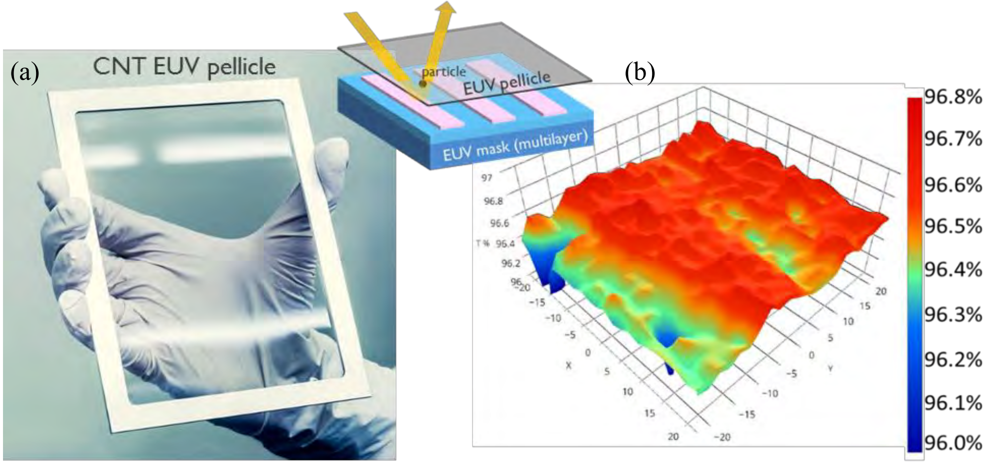

Fig.1 (a) Free-standing CNT film at full pellicle size and schematics of EUV pellicle assembly on the photomask. (b) EUV Transmission uniformity measurements on a 5x5 cm^2 free-standing CNT film.

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Transparent Conductive Single-Walled Carbon Nanotube Films for Human-motion Detection

Yitan Li, [1, 2] *Lu Han,* [1] *Yuguang Chen,* [1] *Yan Li* *[1, 2]

By utilizing the Marangoni flow introduced by the different surface tensions between the basal aqueous solution and the precursor solution, large-scale transparent conductive carbon nanotube films were assembled on the water surface with a tunable transmittance of up to 97%. The films were transferred to various substrates. Carbon nanotube films transferred onto stretchable substrates were then used to build wearable strain sensors to monitor human health parameters such as artery pulses at carotid and wrist, track human voice and detect human motions. Such flexible sensors may act as basic functional components in the interaction between humans and smart systems.

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Gyrification-Inspired Highly Convoluted Graphene Oxide Patterns for Ultralarge Deforming Actuators

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Gyrification in the human brain is driven by the compressive stress induced by the tangential expansion of the cortical layer, while similar topographies can also be induced by the tangential shrinkage of the spherical substrate. Herein we introduce a simple three-dimensional (3D) shrinking method to generate the cortex-like patterns using two-dimensional (2D) graphene oxide (GO) as the building blocks. By rotation-dip-coating a GO film on an air-charged latex balloon and then releasing the air slowly, a highly folded hydrophobic GO surface can be induced.

Wrinkling-to-folding transition was observed and the folding state can be easily regulated by varying the prestrain of the substrate and the thickness of the GO film. Driven by the residue stresses stored in the system, sheet-to-tube actuating occurs rapidly once the bilayer system is cut into slices. In response to some organic solvents, however, the square bilayer actuator exhibits excellent reversible, bidirectional, largedeformational curling properties on wetting and drying. An ultralarge curvature of 2.75 mm^{-1} was observed within 18 s from the original negative bending to the final positive bending in response to tetrahydrofuran (THF). In addition to a mechanical hand, a swimming worm, a smart package, a bionic mimosa, and two bionic flowers, a crude oil collector has been designed and demonstrated, aided by the superhydrophobic and superoleophilic modified GO surface and the solvent-responsive bilayer system.

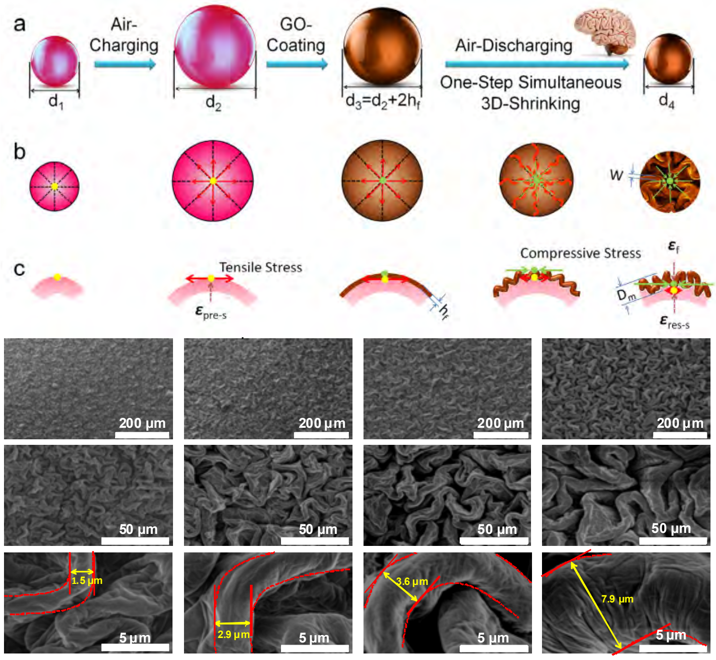

Fig.1 Fabrication process and the highly convoluted graphene oxide patterns.

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MRI compatible neural electrodes for simultaneous deep brain stimulation and fMRI mapping

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Functional magnetic resonance imaging (fMRI) under deep brain stimulation (DBS) provides important insights into understanding the connection of the neural networks. However, such research has been limited by incompatibility of common electrode in the MR environment. To address such issue, we fabricated a novel graphene based neural microelectrode, which exhibited excellent charge storage capacity and MRI compatibility. Using such microelectrode, we successfully demonstrate deep brain stimulation of subthalamic nucleus (STN) evoked robust BOLD activation in cortex and basal ganglia nucleus of the Parkinsonian rats with minimal image artifact. Therefore, MR-compatible graphene microelectrode could provide unique opportunity for simultaneous DBS-fMRI studies.

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Molecular Diffusion-Driven Motion in Two Dimensional Reduced Graphene Film

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We report a new driven mode that the organic molecular filled-reduced graphene film on the water could move, driven by molecular diffusion. Because of ultra-lightweight, micro/nanochannels constructed by interlayered sheets, hydrophobic nature of graphene, one-way 2D diffusion of organic molecules into water results in the induced force/torque for driving the movement of the film. It is worth mentioning that the rectangular film filled with ethanol (1×2 cm^2) shows a high rotational speed of 300 rpm on the water. Importantly, the continuous rotation of the reduced graphene film can be realized by continuously adding the collected ethanol from ethanol–water mixture under visible light irradiation. Moreover, the reduced graphene film filled with ethanol can push the porcelain boat (12 g) with a velocity of 50 mm s^{-1}. Thus, we believe that this phenomenon opens a new driven mode that can be applied in the fields of micro-flow reactors, electric generating device, mini-sensors and actuators.

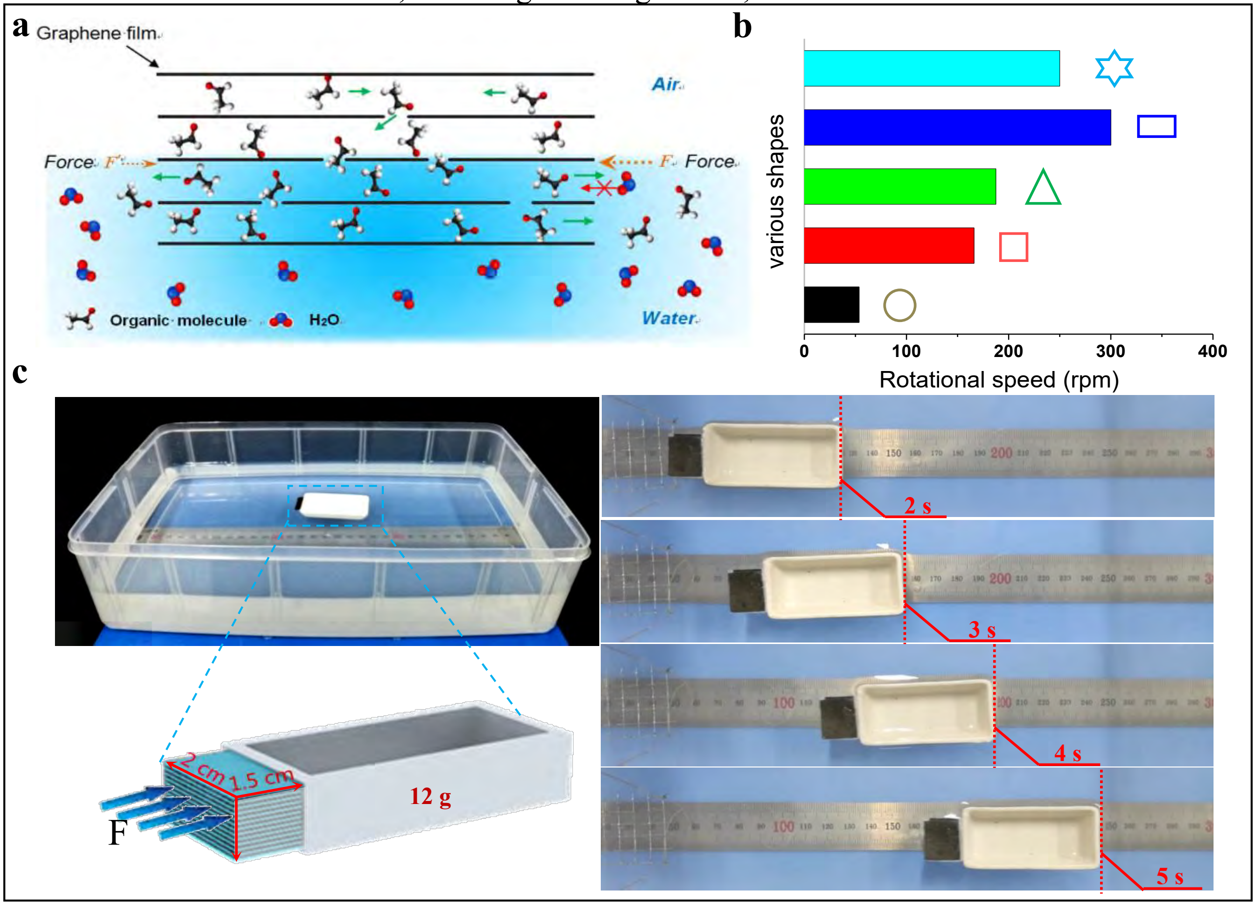

Fig.1 a) Schematic illustration of organic molecules diffusion-driven motion in two dimensional graphene film. b) Rotational speed of RGF-300 with different shapes under the same area (2 cm^2). c) Linear-motion of a porcelain boat (12 g) driven by RGF-300 filled with ethanol by controlling the direction of ethanol diffusion.

Flexible All-Solid-State Supercapacitors Based on MXenes/SWCNTs Paper

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With the development of wearable electronic devices, flexible energy storage equipment are highly desired [1]. Single-wall carbon nanotubes (SWCNTs) are considered as an ideal flexible electrode material due to their high mechanical strength and flexibility. However, the low energy density of SWCNTs hinders their commercial applications. MXenes, a novel family of two-dimensional (2D) metal carbides, have shown great promise as high-rate electrodes for Li-ion batteries and supercapacitors [2-3]. However, the restacking of MXene flakes limits the accessibility of electrolyte ions, hindering the full utilization of their active surfaces. In this work, we propose a simple method for the fabrication of flexible, MXenes/SWCNTs composite paper electrodes through filtration of $Ti_3C_2T_x$ flakes and SWCNTs dispersions. It was found that SWCNT plays a key role in obtaining high strength and flexible composite paper electrodes which not only provide mechanical stabilization for the binder-free electrode, and but also inhibits $Ti_3C_2T_x$ flakes from restacking. As a result, a flexible solid-state supercapacitor assembled from the hybrid paper exhibits a high areal capacitance of 162 mF cm^{-2}, which show great potential in future flexible electronics.

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The direct fabrication, properties and applications of multi-level graphene fiber

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The rapid development of wearable techniques requires that functional materials and devices have better and better properties on flexibility and stretchability. Graphene owes a bright future in fiber-shaped devices and sensors, however, there still exits great challenge in wet-spun graphene fiber on the concerned properties. Here, we report the direct fabrication of multi-level graphene fibers, such as fiber network, helical fiber, spiral fiber and core-shell fiber, via the modulation of the shape, number and movement of the modified spun-net based on a direct writing technique. We further study the principles between the structures and mechanical, electrical properties and the applications on photoelectricity, sensor, and supercapacitors.

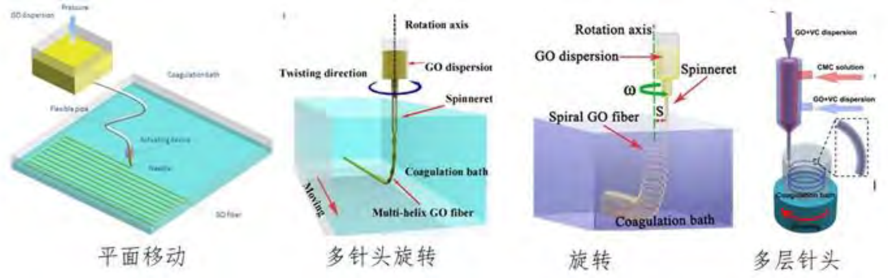

Fig. 1 Schematic illustration of the preparation process for different kind of multi-level graphene fiber

Keywords: graphene fiber; multi-level structure; direct spinning; functional device

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Electrically Sensing Magnetoreception Based on Graphene Field-Effect Transistors

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Biological magnetic sensing, the ability of animals to calibrate motion navigation according to the Earth’s magnetic field, has been widely accepted as a fact but rather controversial for the underlying mechanisms, which were previously proposed to be based on magnetite or chemical magnetoreception. Recently, a protein, *MagR*, mainly comprising iron-sulfur sections and Cry sections was demonstrated to possess capability of patterning itself orderly in the magnetic field due to the inner “biocompass”, which has been attracting more and more attentions into two aspects. One is that such kind of magnetic proteins was expected to promote the deep understanding of magnetic sensing. The other, furthermore, is that magnetic features of the protein might accommodate useful tools to magnetically manipulate bio-molecules with the contribution of magnetogenetics.

Although meaningful, the verification of several critical issues related to the biocompass-protein progresses slowly for the limitation of traditional methods in biological investigation, which can be exemplified by the exploration of the mechanism of light-magnet coupling, transferring of magnetic signals within neuro, essence of Magnetoreception and so on.

Carbon material-based electrical bio-sensors have been developed dramatically, owing to the characteristics of label-free, real-time detection, high sensitivity and good selectivity. The ability of detecting tiny potential changes in the environment and being modified easily enables graphene Field Effect Transistor (G-FET) to identify the biological interactions such as protein-protein, aptamer–protein, DNA-DNA, biotin-streptavidin, etc. For example, the single-molecule lysozyme dynamics has been monitored by Single Wall Nano-Tube electronic circuit.

Here, We take the advantage of G-FETs through fabricating MagR immobilized G-FET devices and detecting the MagR protein motion behavior by monitoring the current changes under magnetic field variation. Preliminary work shows time dependent and memory effect. Light-magnet coupling behavior will further be investigated.

Carbon-Based Memristive Materials and Devices

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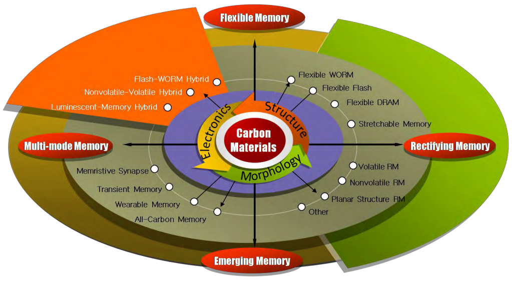
With the rapid development of information technology, scientists are searching for emerging memory devices to make true leaps in sustaining data storage growth. To date, numerous emerging memory devices based on organic and inorganic materials have been reported, such as resistive-switching memories (also named memristors), phase-change memories, ferroelectric memories, and spin memories. In this lecture, issues and challenges facing memory technologies will be introduced briefly. Then our work towards developing flexible memristors fabricated by solution process method will be demonstrated. In particular, several new memristors made from carbon electronic materials will be highlighted, including all-carbon memristors, multimode memristors, self-rectifying memristors and transient memristors, with the function of WORM, Flash and DRAM. It is worth pointing out that the full-solution process enable a low-cost, environment-friendly, and mass-production of carbon-based memristors. Our study not only paves a way to design emerging memristors constructed from nanostructures, but also boosts the development of carbon electronics and flexible electronics.



Acknowledgements

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Lithium-ion battery fiber constructed by diverse-dimensional carbon nanomaterials

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*Weiwei Zuo, Meifang Zhu**

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Learn from Nature, comprehensively high performance has been accomplished for composites consisting of diverse-dimensional nanomaterials, e.g., nacre, leaf and skin. A novel composite fiber is prepared by employing 2D reduced graphene oxides (rGOs) and 1D carbon nanotubes (CNTs). The composite fiber possesses much better electrochemical and mechanical properties simultaneously due to the inside brick-bridge network, in which rGOs serve as the brick and CNTs as the bridge. As a result, a large specific capacity of 522 mAh g^{-1} is obtained for the rGO/CNT fiber, which is 3.2 times that of the rGO fiber. Meantime, tensile strength of the rGO/CNT fiber is 1.6 times that of the rGO fiber. The work reveals superiority of composites composed of diverse-dimensional carbon allotropes, which may be applied in energy storage.

SWCNTs as a universal additive in electrochemical power sources

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As a rule, the electrical conductivity of active electrode materials of electrochemical power sources is insufficient and, therefore, conductive additives are added to the electrodes. These additives do not have an electrochemical capacity and are actually a ballast, which reduces the specific capacity of the system, but increases its conductivity. Conductive carbon black is the most widespread conductive additive in electrodes, which is cheap and is characterized by a high chemical and electrochemical stability. The amount of carbon black in cathodes of Li-ion batteries usually lies within the range from 1 to 4 weight percent (depending on the type of the active material and application of the battery). The loading of carbon black in lead-based materials ranges from 0.5 to 1 weight percent.

The quantity of a conductive additive can be decreased significantly if carbon nanotubes are used as a conductive additive. At present, multi-carbon nanotubes are already actively used as a conductive material in electrochemical power sources. The use of multi-walled carbon nanotubes results in reduction of the conductive additive content by 2-5 times in comparison with the standard recipe with a conductive carbon black. Use of single-walled carbon nanotubes (SWCNT) allows us to reduce the required amount of the conductive additive by another 10 times.

In this report, the data on the use of SWCNTs as a conductive additive in Li-ion batteries are presented. Methods and features of preparing dispersions based on aqueous and organic solvents, the effect of single-walled carbon nanotubes on adhesion and density of electrodes of Li-ion batteries are discussed. The results of the nominal capacity, C-rate, and cycle life tests of the cells of Li-ion batteries are presented. In addition, the results of the studies of the effect of adding nanotubes to the electrodes of lead-acid batteries on their electrical characteristics and cycle life are presented.

Greatly Enhanced Anticorrosion of Cu by Commensurate Graphene Coating

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Metal corrosion is a long-lasting problem in history and the ultrahigh anticorrosion is one of the ultimate pursuits in metal-related industry. Graphene, a monolayer of hexagonal carbon, in principle can be a revolutionary material for anticorrosion due to its excellent impermeability to any molecule or ion (except for proton) and extreme lightness (>2000 m^2/g). However, in real applications, it was found that the metallic graphene may form an electrochemical circuit with the protected metals to accelerate the corrosion once the corrosive fluids leaks into the interface. Therefore, whether graphene can be used as an excellent anticorrosion material is under intense debate now. Here, we employ graphene-coated Cu (Gr/Cu) to investigate the facet-dependent anticorrosion of metals. We demonstrate that a monolayer graphene can protect the Cu(111) surface from oxidation in humid air lasting for more than 2 years, while, in sharp contrast with the accelerated oxidation of graphene coated Cu(100) surface. Further atomic-scale characterization and ab initio calculations reveal that the strong interfacial coupling of the commensurate graphene/Cu(111) prevents H_2O diffusion into the graphene/Cu(111) interface, but the one-dimensional wrinkles formed in the incommensurate graphene on Cu(100) could facilitate the H_2O diffusion at the interface. Our study resolves the contradiction on the anticorrosion capacity of graphene and opens a new opportunity of ultrahigh metal anticorrosion through accurate interfacial engineering between graphene and metals.

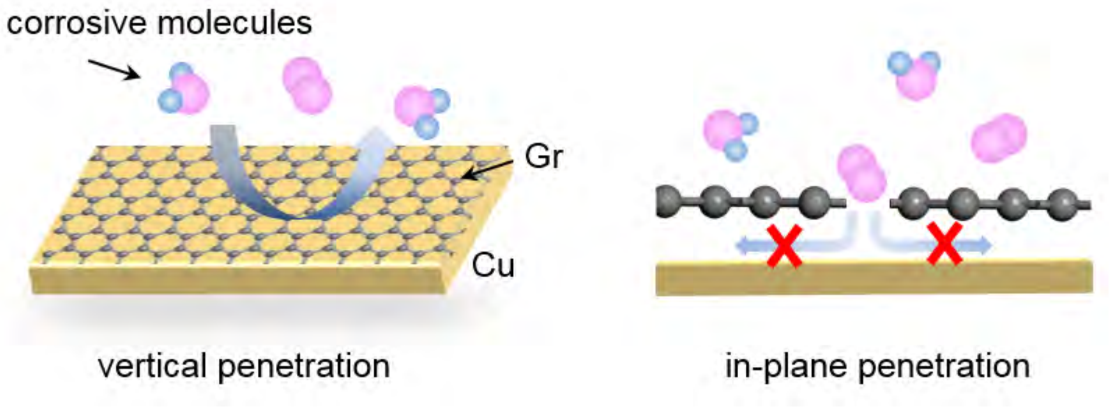

Fig.1 The schematic diagram of two requirements of perfect anticorrosive material.

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Overcoming Efficiency Limits of Carbon Nanotube-Laminated Perovskite Solar Cells

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Owing to the hydrophobicity, abundance, and facile processability, perovskite solar cells (PSCs) with carbon nanotubes (CNTs) demonstrate enhanced stability with low fabrication cost when used as top electrode in PSCs. However, there is still a limit to the efficiency due to 1) the CNT back electrode not being reflective to absorb the reflection of sunlight, and 2) CNTs having lower conductivity than metals.

In this work, we employed a 3D/2D formamidinium lead iodide ($FACsPbI_3$) photo-active layer to maximise the light absorption and trifluoromethanesulfonic acid (TFMS) vapour doping to increase the conductivity of the CNT electrodes. In metal-electrode PSCs, the long-wavelengths of sunlight, which are not fully absorbed by the perovskite layer, get reflected by the metal electrode for further absorption. As CNT electrode are not reflective, the long-wavelength light is wasted in the case of CNT-used PSCs, resulting in low short-circuit current density (J_{SC}). While maximising the light absorption by using low band-gap $FAPbI_3$, is possible, $FAPbI_3$ film has been reported to be extremely unstable. Recently, we developed highly stable $FAPbI_3$ PSCs by harnessing 2D perovskites at the grain boundaries as the protector and obtained a certified efficiency of 19.8%. By integrating this technology into the CNT-based PSC system, we achieved the highest J_{SC} of 24.2 mA cm^{-2}.

To this day, doping carbon top electrode in PSCs has not been reported because application of any dopants damages the layers underneath CNTs. Therefore in this work, we utilised vapour doping of highly effective and durable TFMS to effectively increase the conductivity of CNT electrode without damaging the device. The application of TFMS-doped CNT in 3D/2D $FACsPbI_3$ PSCs produced an efficiency of 17.6% owing to increased hole conductivity and a better energy match between the Fermi level of CNTs and the valence level of $FACsPbI_3$. The obtained efficiency is the record-high efficiency among the reported CNT top electrode-based PSCs.

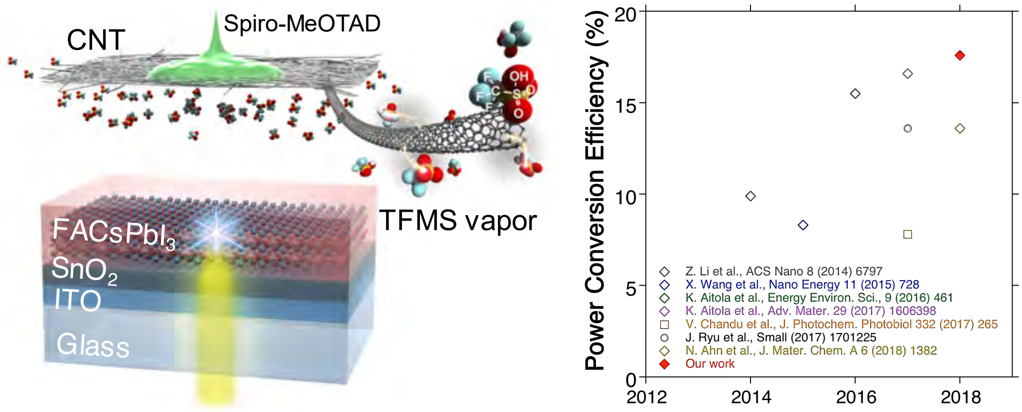

Fig.1 Illustration of our work (left) and efficiency chart of reported CNT-PSCs (right).

Achieving 20% Efficiency Perovskite Solar Cells with High Stability by using Semiconducting Single-walled Carbon Nanotube Grain Bridges

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Since liquid-junction perovskite solar cells (PSCs), the development of organo-lead halide perovskite photovoltaics research has gained momentum with the achievement of the solid-state PSCs in 2012. High absorption coefficient, long-range diffusion length and high defect tolerance of PSCs enable remarkable certified power conversion efficiencies (PCEs) over 20%. Although PSCs are proven to be promising next-generation solar devices, further breakthroughs in terms of efficiency and stability are necessary to supersede conventional silicon solar cells. With regard to the performance and stability of PSCs, perovskite grain boundaries play a significant role. Structural disorders at these boundaries induce shallow trap states and non-radiative recombination of localised charge carriers which serve as limitations to PSC performance. At the same time, these areas are also responsible for the perovskite degradation, as the reaction with moisture in air has been found to initiate from the grain boundaries. Therefore, technologies aiming at passivating the perovskite grains are highly desired.

Over the last two decades, carbon nanotubes (CNTs) with an exceptional charge carrier property with outstanding chemical and mechanical stability have generated a lot of excitement among researchers for their device applicability. Especially, single-walled carbon nanotubes (SWNTs) with a certain chirality possess a wide range of direct bandgap of up to 2 eV, qualifying for a light-harvesting medium with strong absorption and high carrier mobility. Semiconducting SWNTs (s-SWNTs) are highly conductive along the tube axis and therefore can function effectively as a charge-transporter between perovskite grains. While there have been a few reports on phenyl-C61-butyric acid methyl ester (PCBM) as a charge-transporter at the grain boundaries of perovskite films, fullerenes have inherently low carrier mobility and low stability compared to SWNTs. It has also been demonstrated that hydrophobic and air-stable SWNTs can protect the perovskite layer successfully from the oxygen and moisture.

Here, we fabricated PSCs in a configuration of glass/ITO/SnO_2/$CH_3NH_3PbI_3$/spiro-MeOTAD/Au in which the perovskite grains are passivated and connected by s-SWNTs. s-SWNTs here are functioning as a charge-transporter, light-harvester, and protector from the moisture in air. By incorporating a small amount of s-SWNTs in deionised water, 18.0% efficiency of the reference PSCs increased to 20% with reduced hysteresis. due to the increased perovskite grain size arising from favourable vapour pressure of the solvent. Upon addition of s-SWNTs, the PCE further increased beyond 20% with improved hysteresis and air/light stability. Ultimately, s-SWNTs added PSCs showed superior stability over the reference devices.

High-Efficiency SWCNT/Silicon Heterojunction Solar Cells

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Heterojunction solar cells of single-wall carbon nanotubes (SWCNTs) interfaced with silicon have been extensively studied as model devices of photovoltaic applications because of their simple and efficient structures [1]. High transparent SWCNT films with low sheet resistance are highly desired for improving photovoltaic conversion efficiencies and stability [2]. In this work, high-quality, small-bundle SWCNT films synthesized by floating catalyst chemical vapor deposition method (Fig.1a,b), were used to construct SWCNT/Si heterojunction solar cells. Fig. 1c schematically shows the structure of a SWCNT/Si heterojunction solar cell. High power conversion efficiencies of 14.2% and 11.8% were achieved for devices with active areas of 2.3 mm^2 (Fig.1d) and 9.0 mm^2, respectively. This excellent performance is ascribed to the good optical and electrical properties of the SWCNT films originating from their high-quality and small-bundle characteristics. These results demonstrates the superior potential of carbon nanotubes for the next generation of photovoltaic devices.

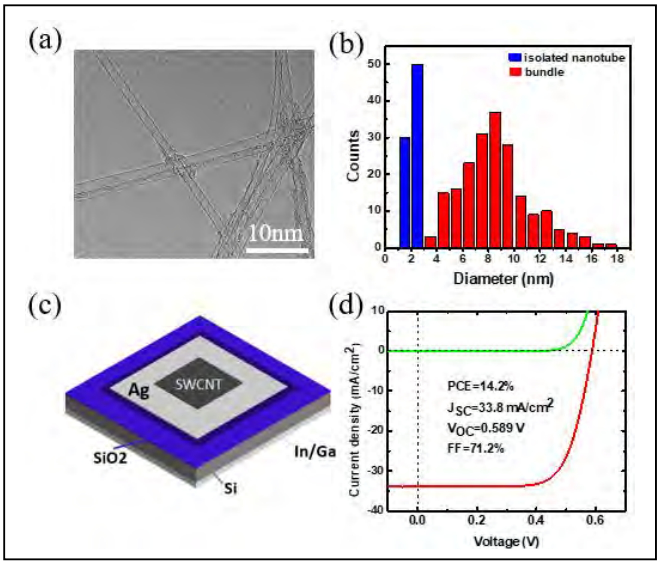

Fig.1 (a) TEM image of a SWCNT film; (b) Diameter distribution of the SWCNT filaments in the network measured from TEM images, showing a high fraction of isolated nanotubes and small bundles; (c) Schematic structure of a SWCNT/Si solar cell; (d) J-V curves of the best SWCNT/Si solar cell with a device area of ～2.3 mm^2.

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Flexible solid-state supercapacitors based on aqueous hydrogel embedded vertically aligned carbon nanotube arrays

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Nowadays flexible solid-state supercapacitors(FSCs) have raised more and more attentions due to the good operability and flexible fabrication process as well as high specific/volumetric energy density. Aligned carbon nanotube (ACNT) arrays are deemed as one of the ideal electrode candidates for energy storage due to their regular pore structure, highly efficient charge transfer rate, excellent rate performance and long cycle life. However the as-grown ACNTs tend to collapse due to the weak interaction between the tubes during the transfer and fabrication process. In this paper we describe a simple and efficient method to fabricate a robust, flexible solid-state super capacitor device by embedding a conductive poly (vinyl alcohol) hydrogel into the ACNT arrays. A total electrochemical capacitance of the device is measured to be 227 mF·cm^{-3} with the maximum energy density of 0.02 mW·h·cm^{-3}, which is dramatically enhanced compared to the similar device composed of unparallel CNTs. Additionally a controllable in-situ electrochemical oxidation greatly improve the compatibility between the hydrophobic CNTs and hydrophilic hydrogel, which decrease the resistance of the device and introduce the extra pseudocapacitance. The energy storage ability then further doubles to 430 mF·cm^{-3} and 0.04 mW·h·cm^{-3} after such oxidation treatment. Besides, the dendified CNT array based FSCs exhibit a much higher volumetric capacitance of 1140 mF·cm^{-3} and a larger energy density of 0.1 mW·h·cm^{-3} with a large power density of 14 mW·cm^{-3}.

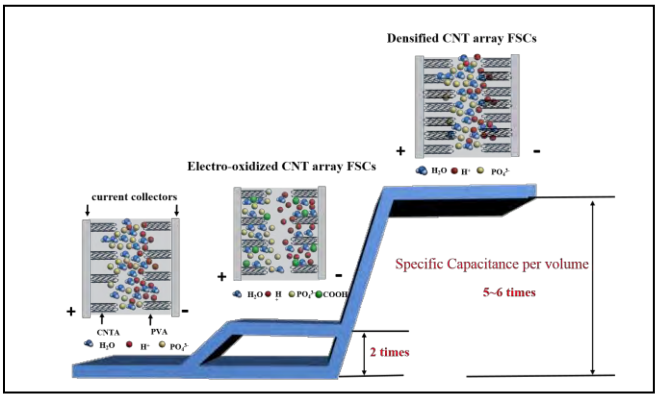

Fig.1 Electrochemical performance of flexible solid-state supercapacitors(FSCs) based on PVA embedded CNT array composites

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Ni@γ-Fe_2O_3 core-shell nanoparticles supported on Nitrogen functionalized carbon nanotubes for the efficient electrocatalytic water oxidation

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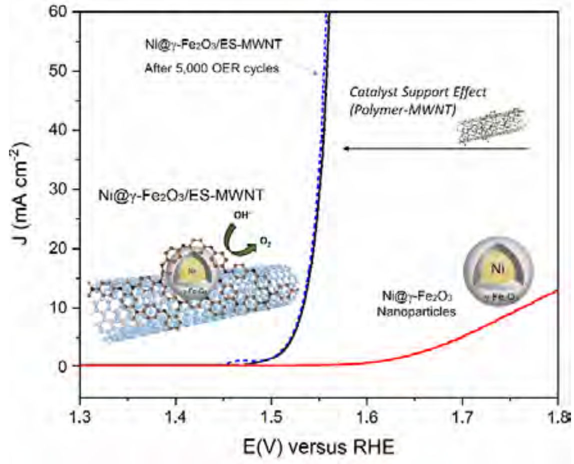
Abstract

This study highlights a novel strategy for one-step synthesis of Ni@γ-Fe_2O_3 core-shell nanoparticles using pulsed laser ablation in liquid. The Ni@γ-Fe_2O_3 NPs have been further supported on functionalized multiwall carbon nanotubes (MWNTs) with nitrogen-rich polymer to develop efficient electrocatalysts for the OER. This type of catalyst support has also shown a good catalytic activity for the OER [1]. It has been observed that the NPs are encapsulated in a C-N shell decorated on the MWNTs to form an active and stable catalyst. Effect of structure on the electrocatalytic activity is investigated by systematically changing the structure of this hybrid material and the roles of the polymer, the nanoparticle composition and the support is clarified. The optimized Ni@γ-Fe_2O_3/ES-MWNT requires only an overpotential of 300 mV and 260 mV to attain a current density of 10 mA cm^{-2} in 0.1 M NaOH and 1 M NaOH, respectively, and shows a stable performance after 5,000 stability cycles.



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Electro-active Carbon Nanotube Filter Technology for Water Treatment

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Development of highly-efficient and cost-effective water treatment techniques is critical to tackle global water crisis and membrane processes are promising among state-of-the-art water treatment technologies. We recently developed a few novel carbon-based electro-active filter technologies that could not only physically adsorb, but also electrochemically oxidize various refractory chemical contaminants.[1] The efficacy and efficiency towards organic compounds electrooxidation were examined by several commonly detected organic pollutants (e.g. antibiotic tetracycline, refractory dyes and phenols).[2,3] The filter materials we are currently working on include graphene, carbon nanotubes and other conductive nanofibers. The energy consumption per volume for our electroc-active filters were calculated to be only <0.1 kW·hr/m3,[3-6] which is better than other recently developed electrochemical systems, as well as other advance oxidation processes for water purification.

In this presentation, we will share some of our recent experimental results that exemplified the advantages of contaminants removal using filters constructed with various nanomaterials integrated with a novel electrochemical approach in a flow-through system. The overall findings demonstrate that this integrated strategy is attractive and useful for both waste water treatment and drinking water purification.

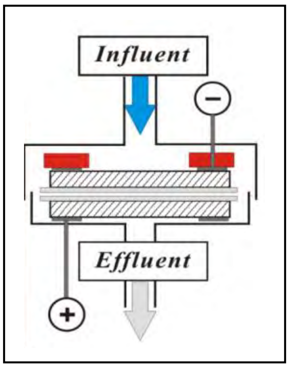

Fig.1 Schematic illustration of the electrochemical carbon nanotube filter technology.

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Single-wall Carbon Nanotubes Decorated With Carbon-encapsulated NiO Nanoparticles for High Performance Flexible Supercapacitor Electrodes

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The advancements in flexible, thin and light-weight electronic devices have categorically increased the demands for equally flexible energy-storage systems that conform to the deformation while retaining their electrochemical performance. Free-standing and binder-free electrodes with outstanding flexibility and excellent electrochemical performance are highly desired for the construction of flexible supercapacitors. In this study, by using a floating catalyst chemical vapor deposition method, we prepared a film in which carbon-encapsulated Ni nanoparticles are anchored on SWCNTs (CENi/SWCNT, Fig. 1a-b). The Ni particles initially acted as the catalyst for SWCNT growth and later as the precursor of the NiO active material. After low-temperature oxidation in air for 11 h to completely transform Ni into NiO while keeping the carbon on the NiO particles and the SWCNT films intact, the obtained CENiO/SWCNT film was used as a binder-free and flexible electrode for supercapacitors. The electrodes were found to exhibit excellent specific capacitance of 1422 F g^{-1} (Fig. 1c) and robust stability (92% capacitance retention after 5000 cycles) [1]. Furthermore, CENiO/SWCNT retained its original specific capacitance (Fig. 1d) even after 500 bending cycles at an angle of 130° showing excellent flexibility.

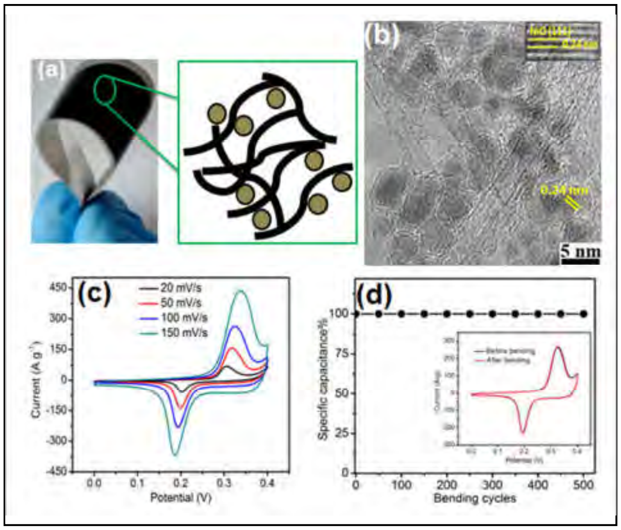

Fig.1 Optical photograph and schematic (a) TEM image (b) cyclic voltammetry curves at different scan rates (c) and specific capacitance after different bending cycles of as-obtained CENiO/SWCNT film.

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Pore Structure Designment for Carbon Nanotube Loaded Porous Carbon Containing Fe-Nx Active Sites and Their Applications in Electrocatalysts

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The oxygen reduction reaction (ORR) is the most important processes in a wide range of renewable energy technologies, such as in fuel cells and metal–air batteries [1]. Fe-N-C has emerged as a promising noble-metal-free catalyst for the ORR, however, to achieve a catalytic activity comparable to that of Pt in acidic medium remains a great challenge [2]. Generally, the ORR performance of a material is determined by the following three crucial factors: 1) the intrinsic nature of the active sites, which is determined by the chemical composition and interactions between different components; 2) the density of effective active sites which are exposed to electrolyte through micropores; 3) the mass transport and electron transfer abilities, which are closely related to the mesoporous structure and crystallinity of the catalyst. Therefore, an ideal electrocatalyst should possess abundant hierarchical micropores and mesopores that provide a large surface area accommodating a high concentration of active sites and efficient mass transport pathways as well as a high electrical conductivity for electron transport. In consequence, we designed and synthesized a series of porous carbon nanotubes containing rich pore structure and exposed Fe-N active sites (Fig. 1). These materials exhibit excellent catalytic activity, and good stability. Recently, we use a simple and scalable atomic isolation technique [3] to load a porous Fe-N-C catalyst on single-wall carbon nanotubes (CNTs) synthesized by a floating catalyst chemical vapor deposition method. The obtained material demonstrates excellent ORR performance under both acidic and alkaline conditions.

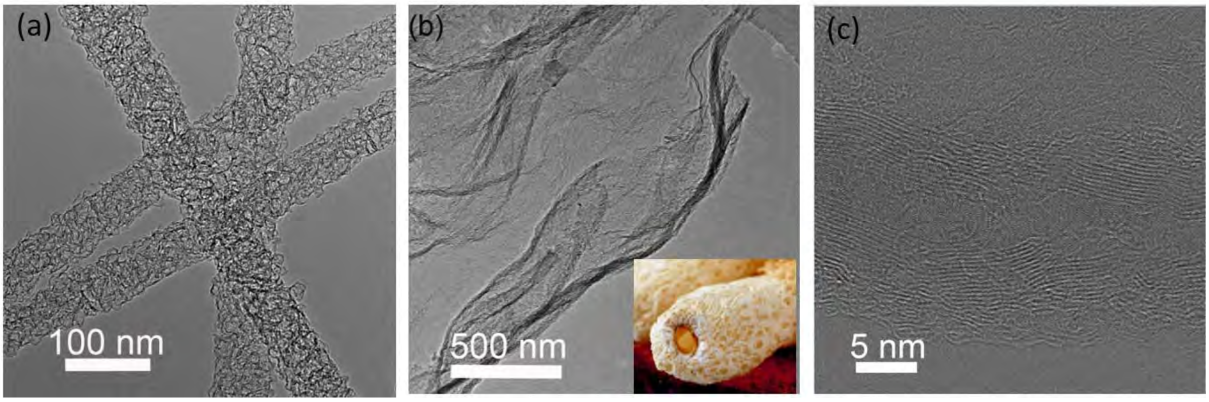

Fig.1 Typical TEM images of hierarchically porous Fe-N-doped CNTs [1] (a), 3D porous N-doped carbon microtube [2] (b), and CNT loaded with porous carbon containing single Fe-Nx active sites [3] (c).

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Simple Method for Removal of Carbon Nanomaterials from Wastewater by Using Hypochlorite

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Carbon nanomaterials (CNM) containing carbon nanotubes (CNTs), carbon nanohorns and graphenes have been applied in a wide range of fields such as materials, electronics, energy storages, and biomedicine. More and more CNMs are produced and CNM-containing products are appearing in our daily life. It is estimated that the annual global market of only CNTs is the order of hundreds of tons now. With the increase of CNM industrialization, more and more CNM-contained wastewater would appear in many institute laboratories and industrial companies. On the other hand, the toxicity of CNM is still unclear and some adverse effects on human health have been reported. CNM-containing wastewater must be purified before being released into the environment and related rules or treatment process need to be urgently established. Unfortunately, no method has been reported so far. In this study, we have developed a simple method to eliminate CNM involved in industrial or laboratory wastewater using sodium hypochlorite. Hypochlorite has been considered to be a key oxidant in enzyme-catalyzed degradation of CNTs [1-2]. We have treated CNTs aqueous dispersions with sodium hypochlorite solution and found that CNTs can be degraded completely into carbon oxides. Since sodium hypochlorite is environmentally friendly and frequently used as a disinfectant or a bleaching agent in household cleaning, the method proposed here would be practically useful in the purification of CNM-contained industrial wastewater.

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Highly efficient carbon nanotube networks in electrodes of Li ion batteries

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Carbon nanotubes (CNTs) with large length-diameter ratios and high conductivity are ideal to fabricate conductive networks in cathodes for Li ion batteries (LIBs). Calculated by a theorecitcal model (Fig. 1), a CNT concentration of only 0.75 wt% is needed for 0.2 μm LFP particles, and 0.12 wt% for 0.5 μm particles [1]. However, good dispersion of CNTs in cathodes still remains great challenge. Here, we demonstrate two approaches to resolving this question.

1) A CNT suspension containing an ultra-low concentration (0.2 wt%) of vertically-aligned CNTs (VACNTs) is used to construct a well-dispersed conductive network in cathodes [1]. The VACNTs exhibit excellent dispersion stability in N-methyl pyrrolidone due to less entangling between CNTs. Significant promotion in specific capacities and low temperature performance have been achieved by adding highly-dispersed VACNTs into LiFePO4 cathodes.

2) In order to solve the problem that CNTs are not able to be dispersed homogeneously in water due to the hydrophobicity of CNTs' side wall, S-doped carbon nanotubes (SCNTs) obtained by a post treatment approach are used as aqueous conductive additive for $LiFePO_4$ (LFP) cathodes in LIBs [2]. The LFP cathode prepared with aqueous SCNT slurry (without using the traditional solvent NMP) exhibits excellent electrochemical performances in terms of capacity (143 mA h g^{-1} at 2 C), rate capability and cycling stability (99.6% of initial capacity after 200 cycles) due to the uniform dispersibility of SCNTs in the bulk of electrodes.

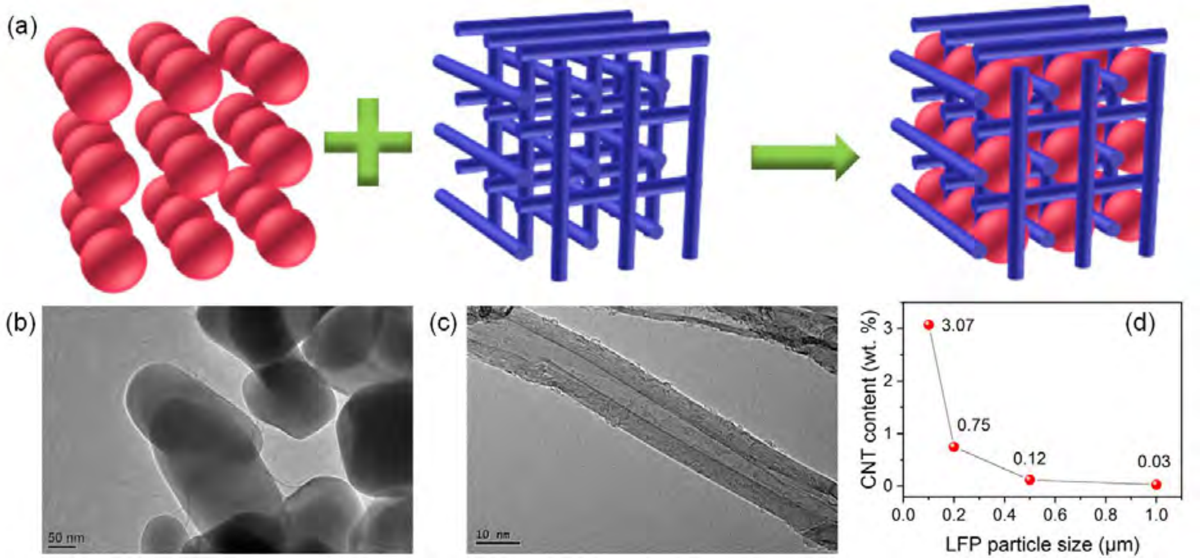

Fig. 1 (a) Model of a 3D CNT conductive network in LIB electrodes. The spheres represent cathode particles, and the cylinders represent CNTs. Typical TEM images of LFP (b) and CNTs (c). (d) The CNT content in the model at different LFP particle size.

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One-step synthesis of Pt-Pd nanoparticles supported on few-layer graphene for methanol oxidation

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Direct methanol fuel cells (DMFCs) have been regarded as prospective devices in transformation of energy for their easy operation, high energy density, and clean production [1] Nowadays, Pt-based nanoparticles supported on carbon-black (Pt/C) are commonly applied as a kind of electrocatalyst in DMFCs [2]. But, in order to obtain better activity and durability, it is necessary to disperse Pt-based catalyst nanoparticles on eligible support. Based on the technique for large-scale production of high-crystallinity SWCNTs and few-layer graphene (FLG) by arc discharge in H_2-inert gas mixtures [3], we have reported the synthesis and electrochemical properties of Pt-Fe/SWCNT and Pt/FLG [4,5].

In this study, Pt-Pd nanoparticles supported on FLG have been firstly prepared by one-step arc discharge evaporation of carbon electrodes containing both Pt and Pd elements. The FLG and Pt-Pd nanoparticles were achieved simultaneously through the evaporation process. After a high-temperature hydrogen treatment, the Pt-Pd/graphene was applied in the study of methanol oxidation in direct methanol fuel cell. The total weight of electrocatalyst keeps 2 wt.% of the electrode. The sample with a mass ratio of Pt:Pd=3:1 (H-Pt_3Pd_1/G) exhibits better electrocatalytic activity (198 $mA•mg^{-1}{}_{pt}$) and better tolerance to carbon monoxide(CO) poisoning (I_f/I_b=1.26). It is noteworthy that the value of I_f/I_b can reach to 1.55 for the sample with the mass ratio of Pt:Pd=2:1 (H-Pt_2Pd_1/G), which implies its excellent ability of CO tolerance. The introduction of Pd element may open a new strategy to improve the CO tolerance by arc discharge evaporation.

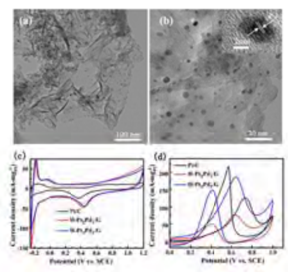

Fig.1 (a) TEM and (b) HRTEM images of H-Pt_3Pd_1/G, (c) Cyclic voltammograms and (d) the mass activity of commercial Pt/C, H-Pt_2Pd_1/G, and H-Pt_3Pd_1/G measured in 0.5 M H_2SO_4 solution with a scan rate 50 mV·s^{-1}, saturated with N_2.

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Direct CVD-derived graphene targeting energy storage applications

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Recent years have witnessed a significantly growing interest in employing graphene materials in the field of energy storages because of its superior electronic conductivity and favorable mechanical flexibility for boosting the device performances [1,2]. As such, graphene can either be utilized as conductive additives for active components in energy storage devices to ensure sufficient electrical contact and buffer the severe volume expansion, or acted as modificators for inactive components, *i.e.*, protective/conductive layers for current collectors and separators. Despite fruitful progress in the rational design of graphene architectures for such aims, it still proves quite challenging thus far to (i) achieve a uniform distribution of a marginal weight content (<3 wt%) of graphene with tailorable defects for electrode materials or (ii) realize highly functional graphene with versatile pore structures and tunable doping levels for modification of inactive parts. In this respect, direct-CVD route serves as a promising solution towards highly-conductive graphene flakes with structural versatility, in sharp contrast to the universal exfoliation approaches that lead to producing reduced graphene oxide (rGO).

In this talk, the speaker will present the state of the art of the emerging direct-CVD routes for the controllable synthesis of graphene targeting energy storage applications, where recent explorations pertaining to this exciting technique would also be covered [3].

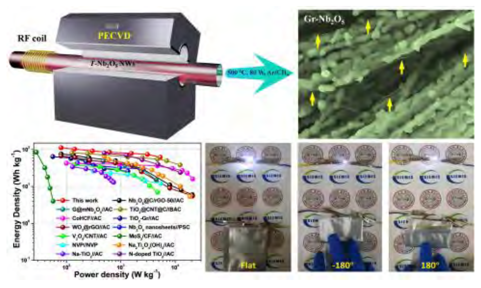

Fig.1 Caging Nb_2O_5 nanowires with CVD-derived graphene towards flexible Na-ion hybrid supercapacitors.

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High-Performance, Transparent and Stretchable Triboelectric Generator with Carbon Nanotube Thin Film

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Energy harvesting, which is the process of capturing electricity from energy existing in the surrounding environment, is attracting much attention as a power source for driving IoT sensors. One of the typical energy sources is mechanical motion caused by a machine, human body, and so on. For converting the mechanical energy into electricity, several principles such as electromagnetic induction and piezoelectric effect are well known. Recently, triboelectric generator (TG) is also attracting much interest for new type of the energy harvesters. The TG generates electricity by a combination of contact electrification and electrostatic induction. In addition to the high output voltage, the TG has many advantages such as low cost and simple structure due to its simple mechanism [1,2]. In this work, we report the transparent and stretchable TG composed of a carbon nanotube (CNT) thin film and polydimethylsiloxane (PDMS) toward the realization of wearable energy harvesters.

The CNT TG consists of a CNT thin film sandwiched by PDMS layers as shown in Fig. 1. The CNT thin film was formed by the floating-catalytic chemical vapor deposition and transfer process. To enhance the performance, the top surface of the CNT TG was treated with CF_4 plasma for increasing surface charges. The size of the CNT TG is 5 cm × 5cm. The fabricated CNT TG showed high transparency as a transmittance of 91 % at 550 nm. The CNT TG was tapped with fingers wearing a nitrile grove. The generated voltage across the external load resistance (R = 10 kΩ ~ 1GΩ) was measured.

Figure 2 shows peak power density (P) as a function of load resistance. Maximum P over 8 W/m^2 was achieved at 70 MΩ. We also obtained current density as high as 48 mA/m^2 at 10 kΩ. These values are the highest value for stretchable TG to our knowledge [3]. This high output power is enough to drive 100 blue LEDs as can be seen in the inset of Fig. 2.

Acknowledgment: This work was supported by JST/CREST (JPMJCR16Q2).

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Fig. 1 Photograph of fabricated CNT TG. The inset is a schematic structure of the TG.

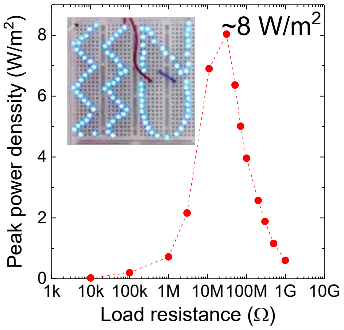

Fig. 2 Peak power density versus load resistance. The inset is a photograph of blue 100 LEDs driven by the CNT TG.

Nitrogen-Doped, Oxygen-Functionalized, Edge and Defect-Rich Vertical Graphene for Oxygen Reduction Reaction

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Due to their excellent physiochemical properties, nanocarbons, e.g. carbon nanotubes and graphene, have been extensively studied in the catalyst fields as catalyst supports for loading metal or metal oxide nanoparticles, or as catalysts with heteroatom doping such as nitrogen, boron, phosphorus, and sulfur, demonstrating promising performances in oxygen reduction reaction (ORR) [1]. Recently, defective nanocarbons without any doping have been employed as ORR catalysts with fantastic electrocatalytic activity, which is attributed to positive effects of edges and defects in nanocarbons, e.g. changing the local density of the π–electrons to increase the chemical reactivity [2, 3]. However, edges and defects as well as dopants have different influences on the deformations of electronic structures, and thereby distinct electrocatalytic activities. Thus, it is possible to design advanced ORR catalysts using nanocarbons as matrix to collect the diverse positive effects of edges, defects and dopants.

Vertical graphene (VG), which is one of three-dimensional graphitic nanocarbons and stands perpendicularly on the substrate, consists of few-layer graphene sheets and has a large amount of open edges and various defects [4]. VG is regarded as an ideal candidate for ORR catalyst. In fact, defect-induced electrocatalysis in VG has been recently investigated and exhibited excellent ORR performances in our group. In this work, we will utilize nitrogen plasma to treat the VG film, which can be obtained from the decomposition of argon and methanol by plasma technique, and explore the synergistic effects of edges, defects and nitrogen-doping in VG on the ORR activities. The ORR performances including onset potential, current density, electron transfer number, selectivity, and stability will be investigated. The detailed results and discussion will be presented in the coming conference.

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Carbon nanotubes and manganese oxide hybrid nanostructures as high performance fiber supercapacitors

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Fiber-shaped supercapacitors (FSCs) constitute a class of one-dimensional key electrical devices for energy storage[1-3]. Their wearable nature, light weight, and high flexibility, make FSCs suitable for powering portable microelectromechanical devices, or other wearable electronic systems. Similar to conventional planar- and cylindrical-shaped supercapacitors, FSCs store energies via either the electrical double layer (EDL) principle or the pseudo-capacitance mechanism[1]. For the EDL-based FSCs, energy density is governed by the overall capability of absorbing electrolytes (cations and anions), by active materials present within electrodes. For the pseudo-capacitive FSCs, on the other hand, the overall amount of the redox-active materials of the electrodes is key for determining the energy density. Above all, the key point is that presently realized power and energy densities of fibers is far from satisfying the ever advancing applications needs, more urgently and significantly, new approaches are needed to bridge this technology gap.

Manganese oxide (MnO_2) has long been investigated as a pseudo-capacitive material for fabricating fiber-shaped supercapacitors but its poor electrical conductivity and its brittleness are clear drawbacks for its use in commercial products. Here we electrochemically insert nanostructured MnO_2 domains into continuously interconnected carbon nanotube (CNT) networks, thus imparting both electrical conductivity and mechanical durability to MnO_2. In particular, we synthesize a fiber-shaped coaxial electrode with a nickel fiber as the current collector (Ni/CNT/MnO_2); the thickness of the CNT/MnO_2 hybrid nanostructures is *ca.* 150 μm and the electrode displays specific capacitances of 231 mF cm^{-1}. When assembling symmetric devices featuring Ni/CNT/MnO_2 coaxial electrodes as cathode and anode together with a 1.0 M Na_2SO_4 aqueous solution as electrolyte, we find energy densities of 10.97 μWh cm^{-1}. These values indicate that our hybrid systems have clear potential for portable energy storage and harvesting devices.

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Fabrication of CNT Thin Films towards Electric Power Generation by Electrolyte Solution Flow

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In the near future of Internet of Things (IoT) era, trillions of small sensors and devices will be around us. Each sensor or device needs power source, and the new technology collecting small energies from the environment are required. Now we are developing new power generation device, where electrolyte solution flow on atomically thin film generates electric power [1]. Single wall carbon nanotubes (SWCNTs) were chosen for the material of the thin film, because of the high mobility and nano-size of SWCNT. In this study, we report the preparation of high-density SWCNT thin film for the power generation device.

Firstly, e-DIPS SWCNTs (EC1.5, Meijo nanocarbon) were separated into semiconducting and metallic SWCNTs by gel column chromatography. To obtain high-density SWCNT thin film, we used vacuum filtration method which used to make aligned-SWCNTs film [2]. Important point to obtain well-aligned SWCNT film is that the speed of filtration should be slow. The atomic force micrograph (AFM) image of thin film made from metallic SWCNTs on polycarbonate filter is shown in Fig. 1. Although overall alignment is not good, densely aligned SWCNT films were obtained. We also prepare aligned SWCNT filter made from single chirality semiconducting SWCNTs separated from HiPco-SWCNTs [3]. Details will be discussed in the presentation.

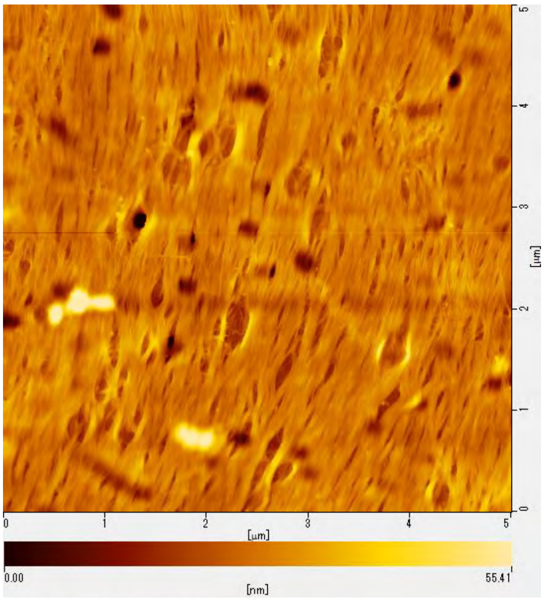

Fig. 1 Typical AFM image of metallic SWCNT thin film.

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Investigation the Effect of CNT wall-number on loaded ORR catalysis performance

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Development of energy storage device and energy conversion device such as fuel cells and metal-air batteries are considered to be the vital step for solving energy and environment problems around the world [1]. Oxygen reduction reaction（ORR）on the cathode of fuel cells and metal-air batteries is the key reaction of these devices. ORR is a reaction of sluggish kinetics, easily generates high overpotential on the electrode. So ORR plays a decisive role for the efficiency of fuel cells and metal-air batteries [2]. Developing high-efficiency catalyst for ORR is the key step to realize commercial applications of fuel cells and metal-air batteries. Now, Pt-based catalysts are the best catalysts for ORR. However, the high cost, poor stability and low abundance of platinum limit the wide-range use of Pt-based catalysts. Therefore, it is highly desired to develop low-cost, high-efficiency, stable ORR catalysts.

Recently, noble-metal-free catalysts such as Fe-N-C catalysts shows high efficiency and good stability [3]. Carbon nanotubes（CNTs）have quasi-one-dimensional structure, large specific surface area, special hollow-core structure. Furthermore, CNTs have functionalizable outer carbon layer for active site loading and highly crystalline inner wall for efficient electron transport. Therefore, CNTs are regarded as ideal support materials for loading Fe-N-C active sites. In our previous work, we developed an atomic-isolation method to load high concentration Fe-N_x doped porous carbon on multi-wall CNTs [4]. In this work, we use the atomic-isolation method to load Fe-N_x doped porous carbon on single-wall, double-wall, and multi-wall CNTs (Fig.1), respectively. The purpose of this work is to obtain high concentration single Fe-N_x cluster active sites and investigate the effect of CNT wall-number on ORR catalysis performance.

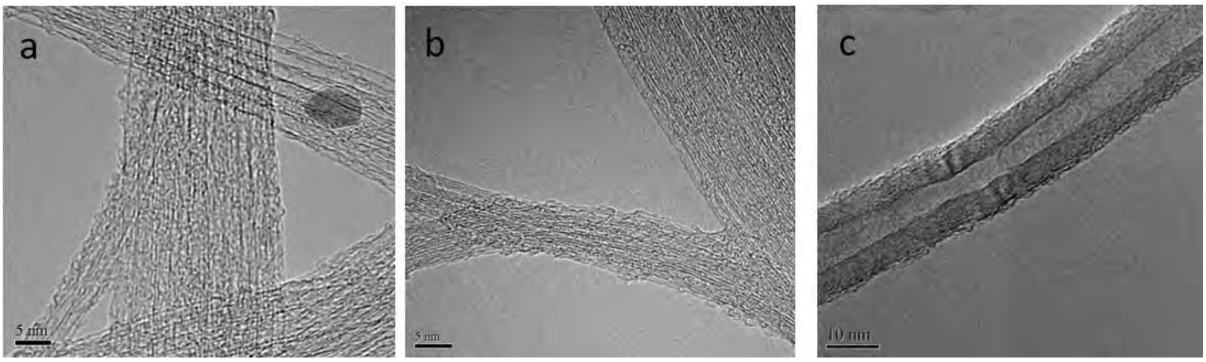

Fig. 1 Typical TEM images of SWCNTs (a), DWCNTs (b), and MWCNTs (c).

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Carbon nanotube based catalysts for selective oxidation of biomass-derived polyols

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Selective oxidation of biomass-derived polyols is one of the important pathways for the high-value utilization of biomass energy.[1] In particular, rational design of heterogeneous catalysts plays key roles in the exploration of green and efficient catalysis technology. Due to their unique structure and abundant surface chemistry properties, carbon nanotubes (CNTs) have been explored as a good support for metal catalysts.[2] We focus on the challenge that the Pt catalysts are in low conversion and poor selectivity for the glycerol oxidation reaction in base-free medium.[3] First, the oxdiation extent of CNTs has been varied to optimize the catalytic activity of supported Pt nanoparticles, as well as tune the product selectivity. Second, CNTs have been decorated with nanocrystals of metal oxides (e.g. CeO_2, TiO_2, Fe_3O_4) or layered double hydroxides to form the composite support for Pt catalysts.[4] These ternary catalysts have been designed with varied size and morphology of the oxides or hydroxides. They show superior catalytic activity and specific selectivity toward glycerol oxidation reaction. Third, graphene oxides have been used as “surfactants” for improving the dispersion of Pt/CNTs catalysts in the reaction medium, thus promote the catalytic activity of the catalysts.

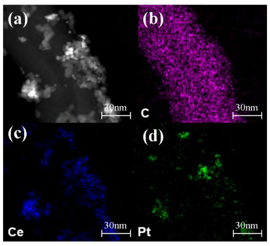

Fig.1 STEM image (a) of the Pt-CeO_2/OCNTs catalyst and elemental mapping images of C (b), Ce (c) and Pt (d)

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Carbon nanotube-polypyrrole surface-modified polyethersulfon conductive membranes and their fouling mitigation

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Electrically conducting membranes have received much attention because their great application potential in fouling prevention [1-3]. However, the widespread application of the membranes is limited, mainly due to the low conductivity, low flux, poor separation performance and inadequate strength of existing conductive membranes [4, 5]. In this study, the carbon nanotubes-polypyrrole/polyethersulfone composite membranes (CNT-PPy/PES) were successfully fabricated though a process of chemical polymerization of pyrrole on a CNT/PES substrate. The resistivity, pure water flux as well as the fouling prevention performance of the CNT-PPy/PES was systematically studied. The surface resistivity of CNT-PPy/PES was greatly reduced and its pure water flux of CNT-PPy/PES was about 136.2 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$. The flux recovery rate of CNT-PPy/PES was increased from 68.18% to 76.38% compared with pure PES membrane. The flux recovery rate of CNT-PPy/PES as a cathode was increased to 81.78% when 1 V/cm electric field was applied, as shown in Fig. 1. Therefore, the membrane cathode could effectively prevent the pore clogging, meaning that the prepared CNT-PPy/PES have significant potential for practical applications in fouling prevention.

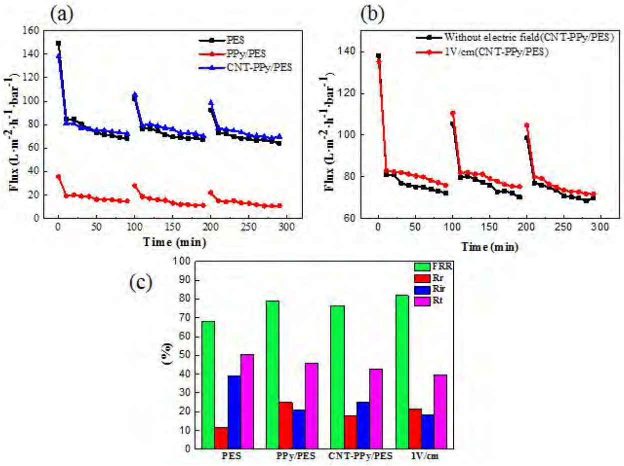

Fig.1 Time-dependent flux of three recycles of antifouling tests of (a) without electric field and (b) under 1V/cm electric field comparing with no electric field, (c) flux recovery ration and fouling resistance of prepared membranes

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SnOx@MWCNTs with different functional groups as highly efficient catalyst for eletrocatalytic reduction of CO_2 to formate

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The development of electrochemical process for the conversion of CO_2 in the atmosphere into value-added products is an effectively innovative method for carbon capture & utilization (CCU), which can alleviate the globle warming and at the same time shift our dependence on fossil fuels. Electrochemical CO_2 reduction reaction (CO2RR) can be driven by renewable energy and easily scale-up to suit the application. In this work, we present a simple and green hydrothermal method to synthesis a ultrathin porous SnOx nanosheet anchored on the surface of the commercial MWCNTs (multi-walled carbon nanotubes) functionalized by –COOH, –OH, or without any groups in order to investigate the influence of different functional groups in the MWCNTs on the properties of SnOx@MWCNTs catalysts. The SnOx@MWCNT-COOH catalysts exhibited a superior catalytic activity for CO_2 conversion to formate. A maximum FE_{HCOO-} was up to 77% at -1.25 V vs. SHE on SnOx@MWCNT-COOH with the low overpotential of 316 mV. The enhanced catalytic activity obtained with the SnOx@MWCNT-COOH is attributed to its high conductivity and ultrathin porous structure (promotes CO_2 adsorption and lowers overpotential) and crystallinity that provides sufficient active sites for CO2RR as well as its distinctive structural configurations which reduces impedance to facilitate faster CO2RR reaction kinetics.

Heteroatom (N, P, B) Doped Hierarchical Porous Carbons from Coal Tar Pitch with High Specific Surface Area for Oxygen Reduction Reaction

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In the past few decades, fuel cells, as a kind of clean, efficient energy sources, which is considered to be the most promising solution to the increasingly serious energy crisis of energy conversion equipment, has attracted significant attention. Oxygen reduction reaction (ORR) in fuel cells play a decisive role in determination of performance, and electrocatalysts with high-performance ORR are essential for practical applications. Up to now, the platinum or its alloyed nano particles have been used to catalyze the sluggish ORR, however, their high cost as well as the limited natural abundance hinder the development and commercialization of these technologies [1]. Recent years witnessed the dramatic interest in using nitrogen-doped porous carbon as one of the promising ORR catalysts. Besides N, other heteroatoms have also been introduced into carbon materials and they also show enhanced catalytic activity for ORR [2]. In this work, we choose N, P and B as doped heteroatoms to fabricate the hierarchical porous carbons derived from coal tar pitch. The catalytic ORR activities of the heteroatom (N, P, B) doped hierarchical porous carbons from coal tar pitch are studied by linear sweep voltammetry (LSV), employing rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques to quantitatively obtain the ORR kinetic constants and the catalysts' possible reaction mechanisms. Catalytic ORR activity were thoroughly examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), low-temperature N_2 adsorption, X-ray photoelectron spectroscopy (XPS). The results show that heteroatom (N, P, B) doped with hierarchical porous carbon from coal tar pitch has high specific surface area and high catalytic activity for ORR.

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High-Performance Paper-based Flexible Micro-Supercapacitors Constructed from Screen-Printable All-Functional Nanocomponents based Hybrid Ink

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Fully-printed in-plane micro-supercapacitors (MSCs) have been considered as the promising on-chip energy storage systems for future wearable miniaturization electronics but still suffer from limited electrochemical performance. Herein, we report the successful combination of screen-printing technology and all-functional nanocomponents-based hybrid ink to facilely produce paper-based flexible MSCs with state-of-the-art performance. The screen-printable hybrid ink is formulated by incorporating hydrous ruthenium(IV) oxide (RuO_2) nanoparticles into a silver nanowires (AgNWs)-graphene oxide (GO) gel system, whereby AgNWs offer high conductivity, GO facilitates gelation process, reduced GO provides rate capability and high cyclability, and RuO_2 nanoparticles contribute high pseudocapacitive. The resultant screen-printed MSCs, achieving outstanding electrode resolution (minimum features down to 50 μm) and conductivity (>5,000 S cm^{-1}), display remarkable electrochemical performance (volumetric capacitance of ~338 F cm^{-3} at 1 mV s^{-1}, energy density of 18.8 mWh cm^{-3}, and power density of 40.9 W cm^{-3}), and exhibit high rate capacity (up to 2,000 mV s^{-1}), excellent cycle stability (80.3% retention after 10,000 cycles), and good flexibility (88.6% retention after 2,000 bending cycles), which all advance the state-of-art of fully-printed MSCs in gel electrolyte without additional metal current collectors. Moreover, the simple printing approach enables the scalable fabrication of MSCs with various geometries and efficient production of MSC arrays in series or in parallel connection.

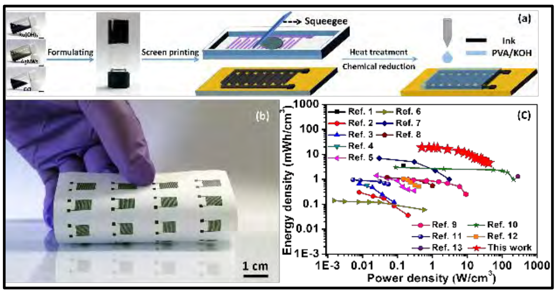

Fig.1 (a) Schematic illustration of the fabrication processes of one-step screen-printed all-functional nanocomponents-based flexible MSCs. (b) Photograph of flexible MSCs printed on filter paper substrate. (c) Ragone plot in comparison to the other state-of-the-art printing-based MSCs.

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Atomic-scale platinum immobilized on single-walled carbon nanotubes: synthesis and high electrocatalytic activity toward hydrogen production

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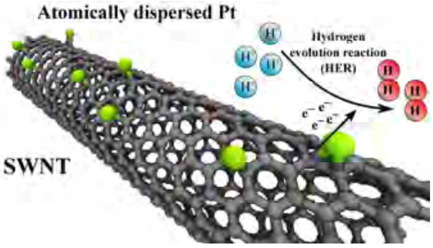
Platinum (Pt) has been widely used as an active catalyst in a wide range of applications but the increasing demand for Pt has been limited by its high price and scarcity. Decreasing the size of Pt catalysts is a valuable approach to significantly reduce the usage and cost of Pt catalysts without compromising catalytic activity. However, the smaller particles are less stable because of the higher surface free energy which enhances the rate of aggregation in small clusters. In this condition, a suitable support that strongly interacts with ultra-small structures of the metal catalyst should be employed to immobilize the metal atoms sufficiently and prevent the aggregation of small clusters or individual atoms (pseudo-atomic-scale catalysts). Finding such a catalyst support for immobilization of ultra-small structures of Pt has been challenging.

In recent years, we have shown the great performance of carbon nanotubes as catalyst support for electrocatalysis [1-4]. In addition, we have found recently that single-walled carbon nanotubes (SWNTs) are promising supports to stabilize individual atoms or subnano clusters of Pt in order to produce much cheaper Pt electrocatalysts with almost a similar activity to that of bulk Pt for hydrogen production from electrochemical water splitting [5]. We developed a simple electroplating method to decorate pseudo-atomic scale Pt on the SWNTs without any pre-treatment on the tubes. We showed Pt atoms can be strongly immobilized on pristine small diameter SWNTs, suggesting SWNTs as promising candidates for the synthesis of single-atom catalysts. We observed that the activation rate of the graphite (GR) electrode with Pt is significantly slower than that of the SWNT. This can be attributed to the faster diffusion rate of Pt on GR than SWNT, which results in a higher agglomeration rate of Pt on GR.

These results were in agreement with our density functional theory calculations which revealed individual Pt atoms can be strongly immobilized on the axial C-C sites of the SWNTs, for the fabrication of a highly active catalyst toward electrochemical H_2 production [5]. Furthermore, the diffusion rate of Pt atoms was calculated to be an order of magnitude slower on SWNT than graphene, attributing to the curved graphitic structure and chirality of SWNTs so that smaller diameter tubes stabilize the Pt atoms more efficiently.



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Carbon Nanotube Fibres for Water Desalination

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Water flows through the inside of carbon nanotubes (CNTs) in an almost frictionless manner; this effect has attracted much attention because it could be exploited to create highly-efficient membranes for filtration and reverse osmosis (RO) [1]. A considerable number of groups are currently working in the design and fabrication of CNT membranes for this purpose; most of the works being computational. In experimental works, most membranes are made of vertically aligned CNTs (VACNTs) in the form of "carpets" or "forests". The CNT material synthesised in Cambridge consists of aligned nanotubes in the form of fibres or films. Cambridge-made fibres have a mechanical edge over VACNT forests and consist, generally, of higher quality (narrower, longer, and more crystalline) CNTs [2], [3]. For this work we have constructed a specialized rig for testing membranes of different morphologies made from Cambridge-produced fibres. Further from describing such equipment, explore the desalination and filtration capabilities of the material and compare it against conventional and other emerging technologies.

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Voltage generation of sub-1 V from raindrops with transparent, flexible semiconducting carbon nanotube sheet

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The voltage generation caused by the movement of the electrolyte on graphene or carbon nanotube (CNT) thin film [1-3] has a possibility of energy harvesting from a small flow of fluids in the environment. Previously, we studied the mechanism and equivalent circuit model for the voltage generation with CNT thin films [4]. The equivalent circuit model suggests that output voltage can be enhanced by increasing shunt resistance of the generator. In this work, we demonstrate the voltage generation of sub-1 V from raindrops by using a large-area semiconducting CNT thin film formed by spray coating method on a flexible plastic film.

Semiconducting CNTs separated by gelchromatography [5] were dispersed in the surfactant solution, and sprayed on an 11 cm x 11 cm polyethylenenaphthalate film. Electrodes were formed with Ag paste at both ends of the CNT thin film. The sheet resistance of the CNT thin film was 334 kΩ/sq.

The generator sheet is transparent as can be seen in Fig. 1. Raindrops were dropped on the CNT thin film. Figure 2 shows the waveform of open-circuit voltage. The voltage of ~500 mV was generated from raindrops, demonstrating a possibility of energy harvesting from commonplace renewable energy.

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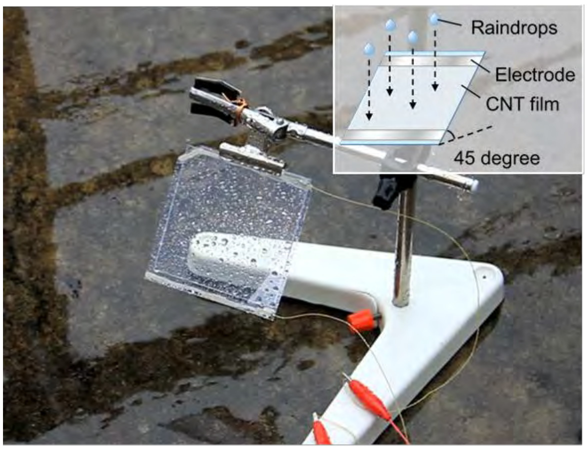

Fig. 1 Experimental configuration

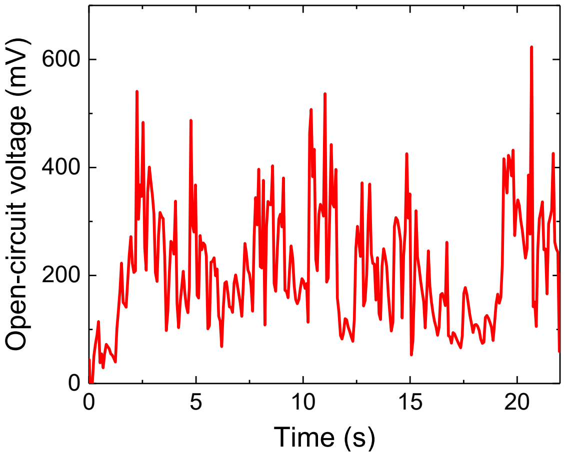

Fig. 2 Waveform of generated voltage

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Synthesis and treatment of CNTs by FCCVD method and its application to conductor-yarn

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“Sustainable Development Goals (SDGs)” became important in the earth, there has been a demand for shifts to new system to achieve a sustainable society. Sustainable energy was emphasized in "The 2030 Agenda for Sustainable Development (2030 Agenda)" adopted at the United Nations Summit (September 2015, United Nations Headquarters in New York). This research is to use carbon nanotubes (CNTs) as vehicle wire harnesses or motor windings. Further it is to produce the lightweight cable of CNTs that will replace copper or aluminum wires used widely. Reducing the weight of conductors leads to not only a reduction in oil consumption but also new energy revolution. The electrical conductivity of CNTs is theoretically estimated to be superior to that of copper. The intrinsic properties of CNTs are not yet fully expressed in experiment. This reason is considered as the following two. It is difficult to control mass production of target CNTs. The conductivity mechanism of CNTs yarn is not so clear. We have found that high conductive CNTs yarn could be prepared by the floating catalytic chemical vapor deposition (FCCVD). We have achieved a CNTs yarn’s resistivity of 6.3×10^{-6} Ω×cm, close to that of copper (1.6×10^{-6} Ω×cm), by optimizing the fabrication of the CNTs, controlling structures of CNTs, and a surface treatment with acid (Fig.1). The fabricated CNTs yarn will be applied as lightweight cable in the future.

This work was supported by JSPS KAKENHI (Grant Number JP16K06258), and Furukawa Electric Co., Ltd.

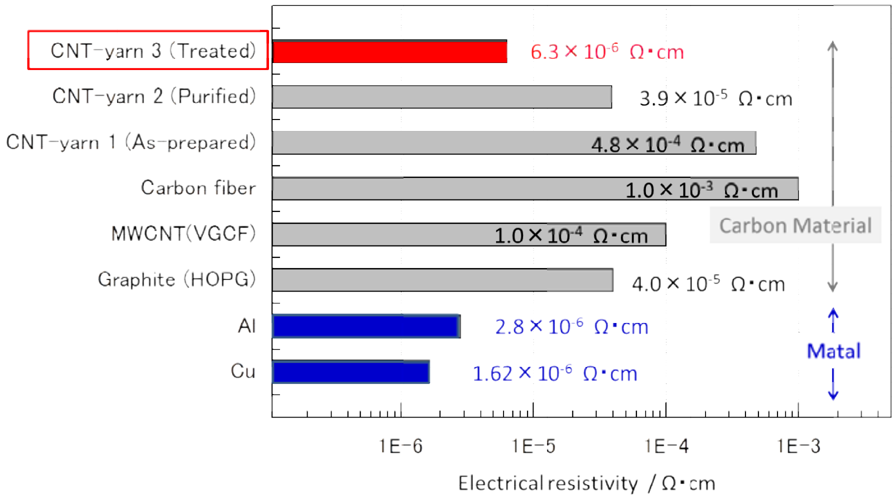

Fig.1 Comparison of electrical resistivity for various materials included CNTs yarn.

Carbon based current collectors for lithium-metal batteries

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The Li-based batteries are a hot research topic because they are the most popular energy storage system for high-energy-density devices. As an important component of the battery, current collectors in both cathode and anode are used to support the active materials, deliver electrons between active materials and the external circuit, and expand internal thermal heat generate in the electrode film. In order to achieve this function, the current collectors have to be (1) free-standing or self-supporting with macro-scale size, (2) mechanically robust, (3) electronically and thermally conductive, (4) electrochemically inert, (5) light in weight, and (6) low cost.

Carbon as the most versatile element manifests itself in a wide variety of allotropic forms that exhibits a diverse range of properties, is one of the most important materials in energy storage applications. sp^2-hybridized carbon materials exhibit excellent electric/thermal conductivity, structural stability, and chemical inertness due to the highly delocalized π electrons. In addition, carbon allotropes have a lower mass density (~2.3 g cm^{-3} for graphite) than metal used for current collectors. Combination of these carbon materials used in complementary ways makes it the promising building constituents for current collectors.

We introduce our recent progress in constructing of 3D scaffolds made of sp^2-hybridized carbon constituents as current collectors for lithium based batteries.[1 – 5] The requirements and the challenges of the 3D carbon based current collector's design are discussed, which provide inspiration for further exploitation of the current collectors for Li-ion batteries and sheds light on batteries based on other electrochemistry.

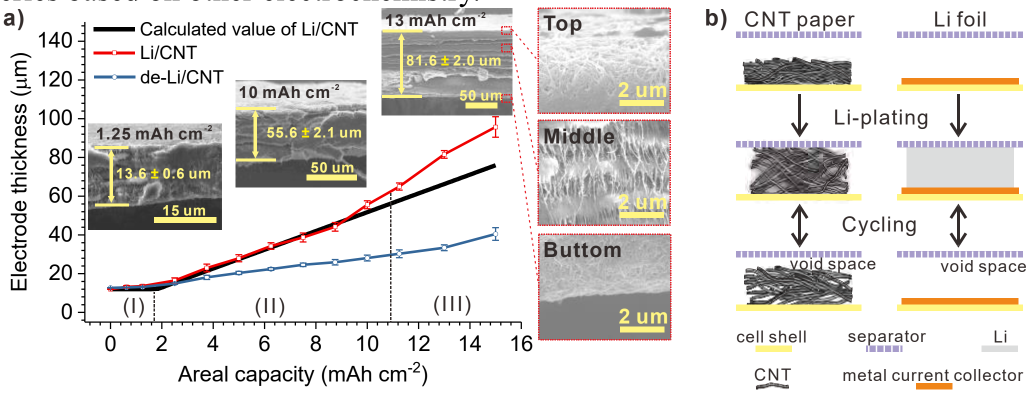

Fig.1 a) Thicknesses of Li/CNT and de-Li/CNT at different Li loadings. Insets show SEM images obtained from cross sections of Li/CNT with Li loadings of 1.25, 10, and 13 mA h cm^{-2}. b) Schematic of volume expansion Li/CNT and Li-metal foil as electrode during Li-stripping/plating.

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Emerging Nanocarbon Materials for Lithium-Sulfur Batteries

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Among various promising candidates with high energy densities, lithium-sulfur (Li-S) batteries with a high theoretical capacity and energy density are highly attractive;[1-2] while the commercial application of Li-S batteries still faces some persistent obstacles, such as the low electrical conductivity of sulfur and lithium sulfide and the dissolution of polysulfides. The introduction of nanocarbon into the field of Li-S batteries sheds a light on the efficient utilization of sulfur by improving the conductivity of the composites and restraining the shuttle of polysulfides. In this presentation, the concept for the rational design of nanocarbon for energy storage is explained. The advances in the use of advanced energy materials in the cathode, separator, and anode is explained.[3-14] New insights on the relationship between the nanostructure and the electrochemical performance are presented.

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Robust, low-fouling and chlorine resistant carbon nanotube reinforced aromatic polyamide membranes: next generation materials for desalination.

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There is a limited supply of clean water and climate changes threatens to reduce fresh-water in the next years. For these reasons, there has been a great interest in desalination technologies. Reverse osmosis desalination is currently the most employed method in large scale desalination projects. The technology has matured and became highly efficient from the energy consumption point of view, however, desalination membranes have a relatively short life due to their degradation, mainly due to inorganic and organic fowling, as well as chlorine attack.

In our group, we have developed thin film composite membranes, whose selective layer is made of a multiwalled carbon nanotube/aromatic polyamide thin film.[1] Carbon nanotubes induces a preferential orientation of the *meta*-phenylendiamine monomers on their surface (Fig. 1). Our calculations indicate that nanotubes restrict the polymer mobility and result in a smaller pore size upon hydration.[2] Reduced pore size might result in higher salt rejection rates whereas the reduced mobility might enable the use of these membranes at higher temperatures. We also studied the diffusion mechanism of the nanocomposite membranes using a multiscale simulation approach.[3] Atomic scale water diffusion was studied by molecular dynamics whereas the diffusion across the membrane was studied using a kinetic Monte Carlo simulation method. These studies confirm that nanotubes induce a percolating path that favors the water diffusion. We believe this type of membrane has high potential to become the next generation of desalination membranes.

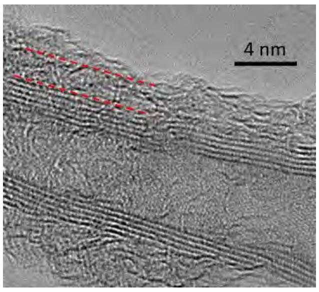

Fig.1 High-resolution transmission electron microscopy image of a multiwalled carbon nanotube embedded in aromatic polyamide. Notice the oriented structure in the regions near the nanotube surface.

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Pencil-drawing skin-mountable micro-supercapacitor

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As a new type of energy storage, supercapacitor has drew increasing interests due to its long life span, fast charging response, high power output, and green safety. [1-3] With the rapid development of miniaturized and portable electronic devices, flexible and wearable energy storage has become an emerging field in recent years. [4,5]

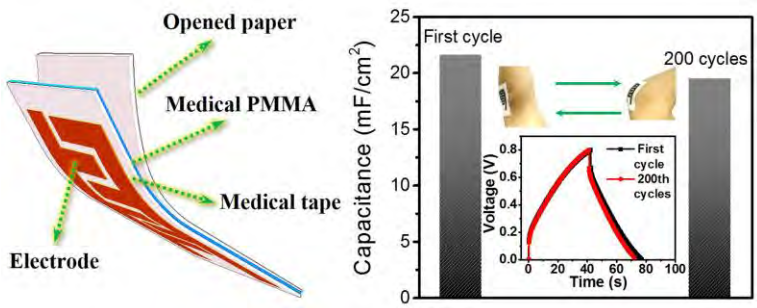

Fig 1. Schematic diagram of the skin-mountable SCs and the capacitive properties.

In current study, integrated plaster-like micro-supercapacitors based on highly flexible and stretchable medical adhesive tape were fabricated by a simple drawing process combined with a mild *in situ* redox method. The solid micro-supercapacitors not only exhibit excellent stretchability, flexibility, and biocompatibility, but also possess outstanding electrochemical performances, such as exceptional rate capability and cycling stability, which may act as skin-mountable and high efficient thin-film energy storages to power miniaturized and wearable electronic devices.

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One Dimensional Nanomaterials for Emerging Energy Storage

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One-dimensional nanomaterials can offer large surface area, facile strain relaxation upon cycling and efficient electron transport pathway to achieve high electrochemical performance. Hence, nanowires have attracted increasing interest in energy related fields. We designed the single nanowire electrochemical device for in situ probing the direct relationship between electrical transport, structure, and electrochemical properties of the single nanowire electrode to understand intrinsic reason of capacity fading. The results show that during the electrochemical reaction, conductivity of the nanowire electrode decreased, which limits the cycle life of the devices. We have developed a facile and high-yield strategy for the oriented formation of CNTs from metal−organic frameworks (MOFs). The appropriate graphitic N doping and the confined metal nanoparticles in CNTs both increase the densities of states near the Fermi level and reduce the work function, hence efficiently enhancing its oxygen reduction activity. Then, we fabricated a field-tuned hydrogen evolution reaction (HER) device with an individual MoS_2 nanosheet to explore the impact of field effect on catalysis. In addition, we demonstrated the critical role of structural H_2O on Zn^{2+} intercalation into bilayer $V_2O_5 \cdot nH_2O$. The results suggest that the H_2O-solvated Zn^{2+} possesses largely reduced effective charge and thus reduced electrostatic interactions with the V_2O_5 framework, effectively promoting its diffusion. We also identified the exciting electrochemical properties (including high electric conductivity, small volume change and self-preserving effect) and superior sodium storage performance of alkaline earth metal vanadates through preparing CaV_4O_9 nanowires. Our work presented here can inspire new thought in constructing novel one-dimensional structures and accelerate the development of energy storage applications.

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Perovskite solar cell using CNT forest for hole transport layer

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Recent researches on perovskite solar cells (PSC) have been exploring potential performance of its high conversion efficiency exceeding 20 % [1,2]. To improve the efficiency and performance stability further, investigations on component materials, including an active layer of perovskite crystals, electron transport layer (ETL) and hole transport layer (HTL), have been carried on. In this work, we introduced a CNT forest as a HTL, instead of using an organic material of Spiro-OMeTAD which has been widely used.

High density multi-walled CNT forests were grown on quartz substrate by chlorine mediated chemical vapor deposition [3]. Since CNTs are strongly bundled on the substrate, a free standing CNT forest mat is easily peeled off and transferred to a solar cell structure. The PSC structure was fabricated on a FTO glass substrate. First, compact and porous TiO_2 layers were deposited as an ETL. Then methylammonium lead tri-iodide ($MAPBI_3$) was deposited by mixing CH_3NH_3I and PbI_2. The free standing MWCNT forest was then just placed on the $MAPBI_3$ layer. Finally, a Pt plate was placed on the CNT forest as a carrier collector. Current density - voltage (J-V) characteristics were measured under light exposure through FTO glass. For the comparison purpose, CNT powder was used as a HTL. Figure 1 compares J-V curves of PSCs. For both CNT forest and powder HTL-PSCs, clear photovoltaic effect is observed though no carrier doping was done on the CNT materials. That is indicative of that MWCNT acts as a hole transport material in PSC. The power conversion efficiency (PCE) of a CNT forest HTL-PSC was obtained as 10.8 % from Fig.1. Solar cell performance parameters for both PSCs are summarized in table 1. Comparing the parameters, we found that higher PCE was obtained for CNT forest HTL one and it was brought by higher short circuit current density (Jsc). By using vertically aligned CNT forest, electrical contacts between a rough surface of $MaPbI_3$ crystal and CNTs were improved comparing with the case of randomly oriented CNT powder HTL.

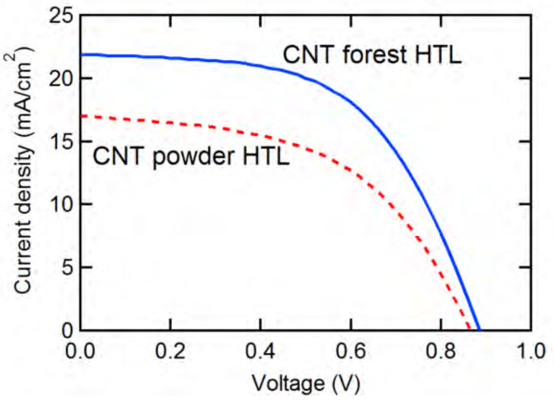

Fig.1 J-V curves of PSC using CNT materials.

Table 1 Solar cell performance parameters

CNT	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)
Forest	21.9	0.89	0.56	10.8
Powder	17.0	0.87	0.52	7.62

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Achieving 19.7% Efficiency Perovskite Solar Cells with High Stability by using Semiconducting Single-walled Carbon Nanotube Grain Bridges

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Since liquid-junction perovskite solar cells (PSCs), the development of organo-lead halide perovskite photovoltaics research has gained momentum with the achievement of the solid-state PSCs in 2012. High absorption coefficient, long-range diffusion length and high defect tolerance of PSCs enable remarkable certified power conversion efficiencies (PCEs) over 20%. Although PSCs are proven to be promising next-generation solar devices, further breakthroughs in terms of efficiency and stability are necessary to supersede conventional silicon solar cells. With regard to the performance and stability of PSCs, perovskite grain boundaries play a significant role. Structural disorders at these boundaries induce shallow trap states and non-radiative recombination of localised charge carriers which serve as limitations to PSC performance. At the same time, these areas are also responsible for the perovskite degradation, as the reaction with moisture in air has been found to initiate from the grain boundaries. Therefore, technologies aiming at passivating the perovskite grains are highly desired.

Over the last two decades, carbon nanotubes (CNTs) with an exceptional charge carrier property with outstanding chemical and mechanical stability have generated a lot of excitement among researchers for their device applicability. Especially, single-walled carbon nanotubes (SWNTs) with a certain chirality possess a wide range of direct bandgap of up to 2 eV, qualifying for a light-harvesting medium with strong absorption and high carrier mobility. Semiconducting SWNTs (s-SWNTs) are highly conductive along the tube axis and therefore can function effectively as a charge-transporter between perovskite grains. While there have been a few reports on phenyl-C61-butyric acid methyl ester (PCBM) as a charge-transporter at the grain boundaries of perovskite films, fullerenes have inherently low carrier mobility and low stability compared to SWNTs. It has also been demonstrated that hydrophobic and air-stable SWNTs can protect the perovskite layer successfully from the oxygen and moisture.

Here, we fabricated PSCs in a configuration of glass/ITO/SnO_2/$CH_3NH_3PbI_3$/spiro-MeOTAD/Au in which the perovskite grains are passivated and connected by s-SWNTs. s-SWNTs here are functioning as a charge-transporter, light-harvester, and protector from the moisture in air. By incorporating a small amount of s-SWNTs in deionised water, 18.0% efficiency of the reference PSCs increased to 19% with reduced hysteresis. due to the increased perovskite grain size arising from favourable vapour pressure of the solvent. Upon addition of s-SWNTs, the PCE further increased beyond 19% with improved hysteresis and air/light stability. Ultimately, s-SWNTs added PSCs showed superior stability over the reference devices.

Synthesis of Large-Area 2-Dimensional Molybdenum Disulfide Nanomaterials for Application in Solar Cells

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2-dimensional transition metal dichalcogenide (TMD) nanomaterials have been focused on in recent years because of their intriguing properties which are different from bulk materials [1]. Unlike graphene, there is an intrinsic band gap in TMD nanomaterials, which further turns into direct gap in their monolayer forms. As a representative of TMD nanomaterials, monolayer molybdenum disulfide (MoS_2) has a direct band gap of ~1.9 eV, and thus opens its exciting prospects for a variety of optoelectronic applications, especially for solar cells [2,3].

In this research, monolayer/multilayer MoS_2 films have been synthesized by low-pressure chemical vapor deposition. The as-synthesized large-area MoS_2 films (cm level) show high quality through the characterizations of Raman and photoluminescence spectroscopy. The MoS_2 films have been further applied to heterojunction solar cells by fabricating MoS_2-carbon nanotube (CNT) hybrids. Furthermore, it has been found that an electron transport layer can facilitate the charge transport in MoS_2-CNT hybrid solar cells (Fig.1). The properties and mechanisms of MoS_2-CNT hybrid solar cells will also be discussed.

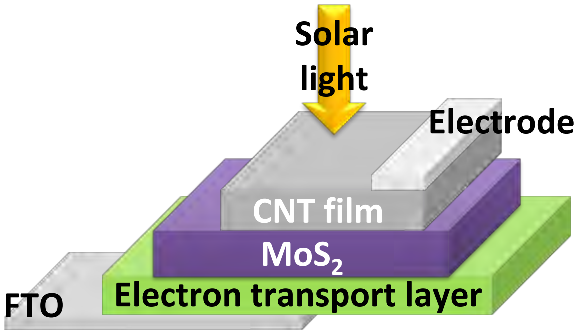

Fig.1 Schematic of the MoS_2-CNT hybrid solar cells.

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Cobalt sulfide-carbon nanotube core-shell nanowires as anode materials for lithium ion batteries

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Carbon nanotube (CNT)-encapsulated metal sulfides are promising candidates for application as anode materials in lithium ion battery (LIB). However, the electrochemical behavior and mechanism of this type of nanomaterials still remain unclear. An understanding of the lithiation mechanism at nanoscale of this type of composites will benefit the design and development of high-performance LIB materials. Here, we use cobalt sulfide nanowire-filled single CNT as a model material to investigate the lithium storage mechanism by in situ transmission electron microscopy. The structure of cobalt sulfide-filled CNT and its electrochemical lithiation-delithiation when serving as the anode for a lithium ion battery has been studied. The results show that the encapsulation of cobalt sulfide by carbon nanotube has significantly improved the stability of the hybrid anode materials during the lithiation-delithiation cycles.

This work was supported by the American Chemical Society Petroleum Research Fund (51766-ND10) and the U.S. National Science Foundation (DMR-0548061 and DMR-1506640).

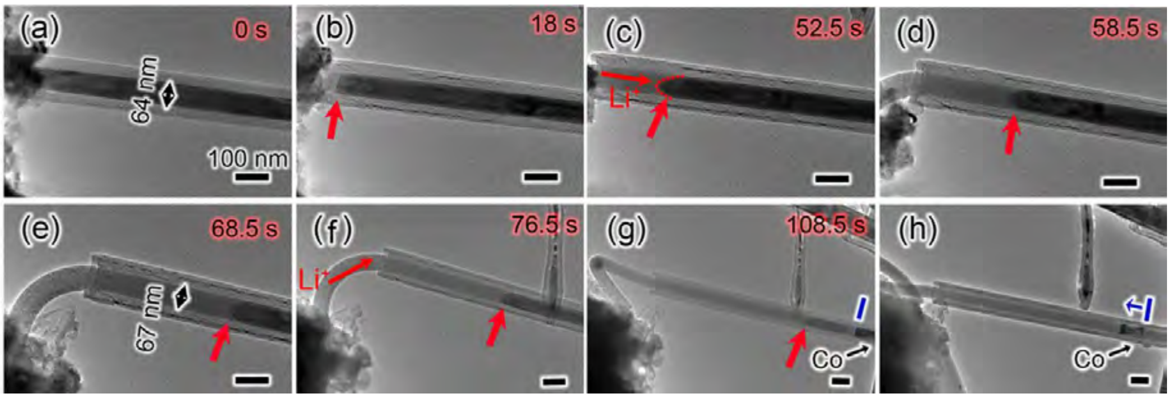

Fig.1 Time sequence of the lithiation process of a cobalt sulfide-filled carbon nanotube with an open end. The cobalt sulfide core has a diameter of 64 nm while the CNT has an out diameter of 128 nm. With the time increase, the lithiated core was extruded out of the open end of CNT in the lithiation process. The red dashed curve and arrows demonstrate the reaction front.

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Flexible Energy Storage Devices Based On Graphene Composite Fibers

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Nowadays, flexible electronics is a hotspot worldwide. As an indispensable component, flexible energy storage devices (FESDs) serving as the power system have witnessed a tremendous advance over the decade. Among a variety of formats, FESDs in fiber or textile shape characterized with high flexibility and wearability are deemed as a promising family.

As for the materials, graphene has been actively studied in FESDs since its advent in 2004. And after 2011, when the graphene fiber was worked out for the first time, much effort has been devoted to the application of the graphene fibers in FESDs. However, because the graphene nanosheets are prone to stacking, the electrochemical properties of the primary graphene fibers are poor or mediocre. To this end, various structures have been engineered together with diverse fillers.

Here, some typical graphene composite fibers proposed by our lab are introduced. Firstly, graphene composite fibers with high-energy active fillers, e.g., MnO_2 and activated carbon, were presented. Secondly, graphene composite fibers with non-active fillers, e.g., PVA polymer and Ag nanowire, were illustrated. Their electrochemical performance was enhanced by improving the properties of wettability and conductivity. Thirdly, graphene composite fibers with designed structures were addressed, e.g., alignment and porosity.

Oriented SnS nanoflakes bound on S-doped N-rich carbon nanosheets with a rapid pseudocapacitive response as high-rate anodes for sodium-ion batteries

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By virtue of abundant sodium resources and low cost, sodium-ion batteries have been considered as a promising candidate compared with the prevailing lithium-ion batteries. However, substantial volume changes and sluggish sodiation kinetics limit their practical application. Incorporating active materials with carbonaceous materials, especially heteroatom doped graphene, has proved to be an efficient way to buffer the volume changes, inhibit the pulverization and stabilize the electrode/electrolyte interface due to their large specific surface area and excellent mechanical properties. Therefore, economical carbonaceous materials that are easy to dope with heteroatoms and accordingly enhance the loading of active materials are highly desired.[1-3]

Here, we prepared a hybrid architecture of oriented tin(II) sulfide nanoflakes bound on S-doped N-rich carbon nanosheets (SnS/CNS) via a facile sol-gel and hydrothermal route. As anode for Na half-cell, this electrode delivers a high reversible capacity of 654 mAh g^{-1} and excellent rate capability of 250.7 mAh g^{-1} at the current densities of 20 A g^{-1}, which outperformed almost all the former tin sulfide anodes for SIBs. The introduction of N and S to carbon nanosheets can not only enhance the electronic conductivity of composite but also induce a large number of topological defects in the surface of the material, which furnish additional active site to adsorb Na$^+$. Further kinetic analyses reveal that the pseudocapacitive contribution accounts for fast Na$^+$ storage at high rates. This work offers a new approach to develop high-rate anode for sodium-ion batteries.

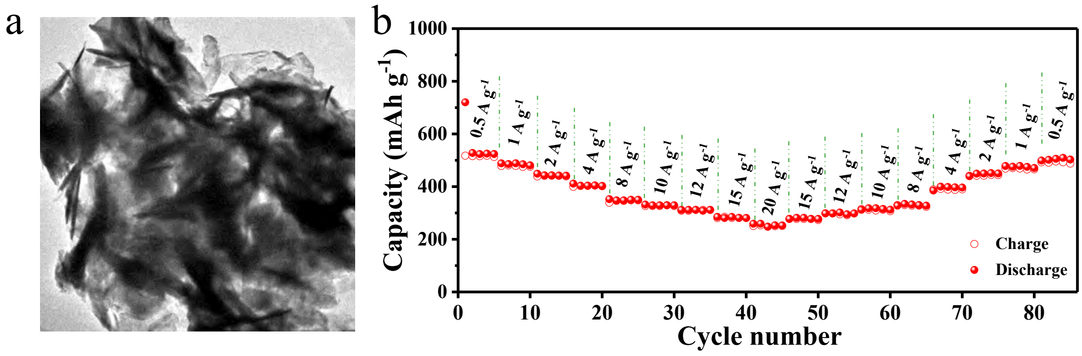

Figure 1. (a) TEM image of SNS/CNS. (b) Rate performance of the SnS/CNS electrodes at a current density between 0.5 A g^{-1} and 20 A g^{-1}.

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Multiscale Principles to Boost Reactivity in Gas-Involving Energy Electrocatalysis on Carbon Electrocatalyst

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Various gas-involving energy electrocatalysis, including oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), have witnessed increasing concerns recently for the sake of clean, renewable, and efficient energy technologies. However, these heterogeneous reactions exhibit sluggish kinetics due to multi-step electron transfer and only occur at triple-phase boundary regions. Up to now, tremendous attention has been attracted to develop cost-effective and high-performance electrocatalysts to boost the electrocatalytic activities as promising alternatives to noble metal counterparts. In addition to the prolific achievements in materials science, the advances in interface chemistry are also very critical in consideration of the complex phenomena proceeded at triple-phase boundary regions, such as mass diffusion, electron transfer, and surface reaction. Therefore, insightful principles and effective strategies for a comprehensive optimization, ranging from active sites to electrochemical interface, are necessary to fully enhance the electrocatalytic performance aiming at practical device applications.

In this talk, we overview our recent attempts toward efficient gas-involving electrocatalysis with multiscale principles from the respect of electronic structure, hierarchical morphology, and electrode interface on 2D electrocatalysts step by step. It is widely accepted that the intrinsic activity of individual active sites is directly influenced by their electronic structure. Heteroatom doping and topological defects are demonstrated to be the most effective strategies for metal-free nanocarbon materials, while the cationic (e.g., Ni, Fe, Co, Sn) and anionic (e.g., O, S, OH) regulation is revealed to be a promising method for transition metal compounds, to alter the electronic structure and generate high activity. Additionally, the apparent activity of the whole electrocatalyst is significantly impacted by its hierarchical morphology. The active sites of nanocarbon materials are expected to be enriched on the surface for a full exposure and utilization; the hybridization of other active components with nanocarbon materials should achieve a uniform dispersion in nanoscale and a strongly coupled interface, thereby ensuring the electron transfer and boosting the activity. Furthermore, steady and favorable electrochemical interfaces are strongly anticipated in working electrodes for optimal reaction conditions. The powdery electrocatalysts are suggested to be constructed into self-supported electrodes for more efficient and stable catalysis integrally, while the local microenvironment can be versatilely modified by ionic liquids with more beneficial gas solubility and hydrophobicity.

Collectively, with the all-round regulation of the electronic structure, hierarchical morphology, and electrode interface, the electrocatalytic performances are demonstrated to be comprehensively facilitated. Such multiscale principles stemmed from the in-depth insights on the structure-activity relationship and heterogeneous reaction characteristics will no doubt pave the way for the future development of gas-involving energy electrocatalysis, and also afford constructive inspirations in a broad range of research including CO_2 reduction reaction, hydrogen peroxide production, nitrogen reduction reaction, and other important electrocatalytic activation of small molecules.

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Li Metal Anode Protection with Carbon Host in Safe Rechargeable Batteries

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Li metal is considered as the "Holy Grail" of energy storage systems. The bright prospects give rise to worldwide interests in the metallic Li for the next generation energy storage systems, including highly considered rechargeable metallic Li batteries such as Li-O_2 and Li-sulfur (Li–S) batteries. However, the formation of Li dendrites induced by inhomogeneous distribution of current density on the Li metal anode and the concentration gradient of Li ions at the electrolyte/electrode interface is a crucial issue that hinders the practical demonstration of high-energy-density metallic Li batteries.

In this talk, we review the lithium metal anode protection in a polysulfide-rich environment. Firstly, the importance and dilemma of Li metal anode issues in lithium–sulfur batteries are underscored, aiming to arouse the attentions to Li metal anode protection. Specific attentions are paid to the surface chemistry of Li metal anode in a polysulfide-rich lithium–sulfur battery. Next, the proposed strategies to stabilize solid electrolyte interface and protect Li metal anode are included. Finally, a general conclusion and a perspective on the current limitations, as well as recommended future research directions of Li metal anode in rechargeable batteries are presented.

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Carbon-Based Membrane toward High-Stable Lithium Sulfur Battery

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Lithium sulfur batteries attract great attention due to their high energy density, while the real applications are still hindered by the rapid capacity degradation. Despite great effort devoted to solving the polysulfide shuttle between the cathode and anode electrodes, it remains as a serious challenge to build high-stable lithium sulfur battery, which related to the diffusion and reaction between polysulfides and the metal lithium anode.

We proposed a strategy of introducing an ion selective membrane to improve the stability and coulombic efficiency of lithium sulfur battery. Generally, porous polymer membrane serves as membranes in batteries to avoid the short circuit between anode and cathode electrodes, which cannot stop the shuttle effect. By the introduction of permselective functional layer, the polysulfide anions can be confined in the cathode side, which would favor the cyclic stability and lower self-discharge performance.

We replace the routine membrane with an ion selective membrane, in which the sulfonate-ended perfluoroalkyl ether groups on the ionic separators are connected by pores or channels that are around several nanometers in sizes. These -SO3-- groups coated channels allow ion hopping of positive charge species (Li+) but reject hopping of negative ions, such as polysulfide anions (Sn2-) in this specific case due to the coulombic interactions. Consequently, this cation permselective membrane acts as an electrostatic shield for polysulfide anions, and confines the polysulfides in the cathode side. An ultra-low decay rate of 0.08% per cycle is achieved within the initial 500 cycles for membrane developed in this work, which is less than half that of the routine membranes.

We also proposed a unique lithium-sulfur battery configuration with ultrathin graphene oxide (GO) membrane for high stability. The oxygen electronegative atoms modified GO into a polar plane and the carboxyl groups acted as ion hopping sites of positively charged species (Li+) while rejected the transportation of negatively charged species (Sn2-) due to the electrostatic interactions. Such electrostatic repulsion and physical inhibition largely decreased the transference of polysulfides across the GO membrane in lithium-sulfur system. By the incorporation of permselective GO membrane, cyclic capacity decay rate is also reduced from 0.49 to 0.23 %/cycle.

Such ion selective membrane is versatile for various electrodes and working conditions, which is promising for the construction of high performance batteries.

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Oxygen Clusters Distributed in Graphene with “Paddy Land” Structure: Ultra-High Capacitance and Rate Performance for Supercapacitors

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The introduction of surface functional groups onto graphene can provide additional pseudocapacitance for supercapacitors, however, the compensation for the loss of electrical conductivity arising from the disruption of the conjugated system remains a big challenge. Here, we report a novel strategy for the design of oxygen clusters distributed in graphene with “paddy land” structure *via* low-temperature annealing process. Moreover, the distribution, content and variety of oxygen groups, and the conductivity of reduced graphene oxide (RGO) can be easily adjusted by annealing temperature and time. First-principle calculations demonstrate that “paddy land” structure exhibits conjugated carbon network, ultra-low HOMO-LUMO gap, and long span of atomic charge value range, which are beneficial for the enhanced pseudocapacitance and rate performance. As a result, the functionalized graphene exhibits high specific capacitance of 436 F g^{-1} at 0.5 A g^{-1}, exceeding the values of previously reported RGO materials, excellent rate performance (261 F g^{-1} at 50 A g^{-1}) and cycling stability (94% of capacitance retention after 10000 cycles). Our findings may open a door for finely controlling the location and density of functionalities on graphene for applications in energy storage and conversion fields *via* a green and energy-efficient process.

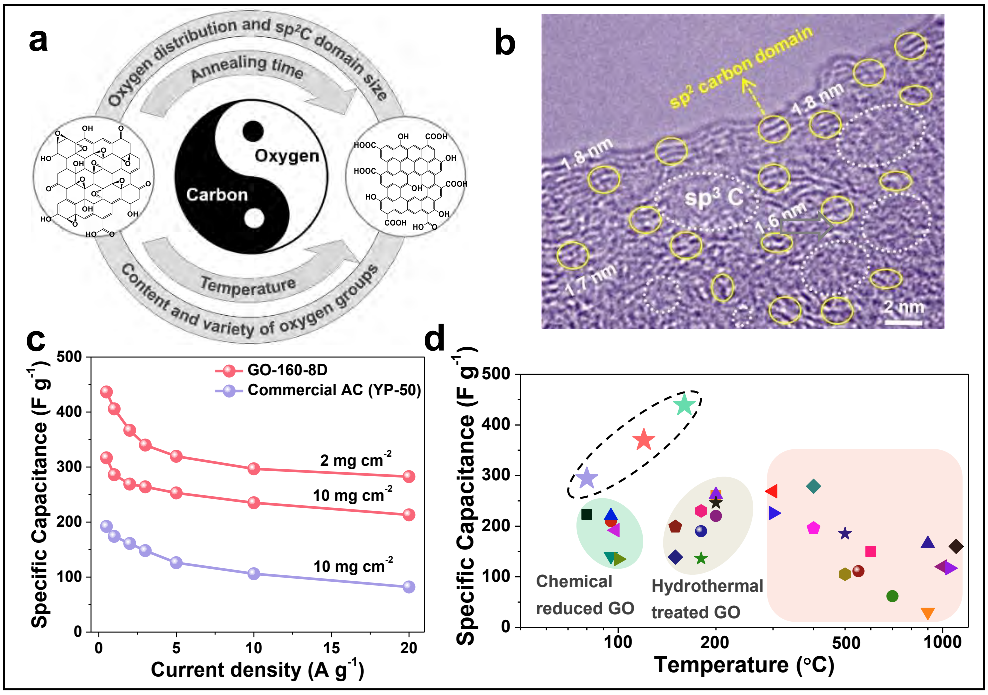

Fig.1 (a) Schematic illustration of the low-temperature balance of the oxygen content and conductivity of RGO with “paddy land” structure. (b) TEM image of RGO obtained at 160 °C for 8 days (GO-160-8D). (c) Specific capacitances of GO-160-8D under mass loading of 2 and 10 mg cm^{-2}, and that of commercial activated carbon (YP-50) under a mass loading of 10 mg cm^{-2}. (d) Comparison of the specific capacitance for GO-160-8D and other RGO reduced at various temperatures.

Hollow Metal Oxide Nanoparticles Encapsulated into B/N Co-Doped Graphitic Nanotubes as High-Performance Lithium-Ion Battery Anodes

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Abstract:

Yolk–shell nanostructures have received great attention for boosting the performance of lithium-ion batteries because of their obvious advantages in solving the problems associated with large volume change, low conductivity, and short diffusion path for Li^+ ion transport. A high concentration of B–N bonds in a carbon framework whereas the one with a lower molecular weight leads to B, N co-doped graphene nanotubes (BCN nanotubes) with segregated B–C and N–C bonds.

Therefore, a universal strategy for making hollow transition metal oxide (TMO) nanoparticles (NPs) encapsulated into B, N co-doped graphitic nanotubes (TMO@BNG (TMO = CoO, Ni_2O_3, Mn_3O_4) through combining pyrolysis with an oxidation method is adopted. herein. The as-made TMO@BNG exhibits the TMO-dependent lithium-ion storage ability, in which CoO@BNG nanotubes exhibit highest lithium-ion storage capacity of 1554 mA h g^{-1} at the current density of 96 mA g^{-1}, good rate ability (410 mA h g^{-1} at 1.75 A g^{-1}), and high stability (almost 96% storage capacity retention after 480 cycles). The present work highlights the importance of introducing hollow TMO NPs with thin wall into BNG with large surface area for boosting LIBs in the terms of storage capacity, rate capability, and cycling stability.

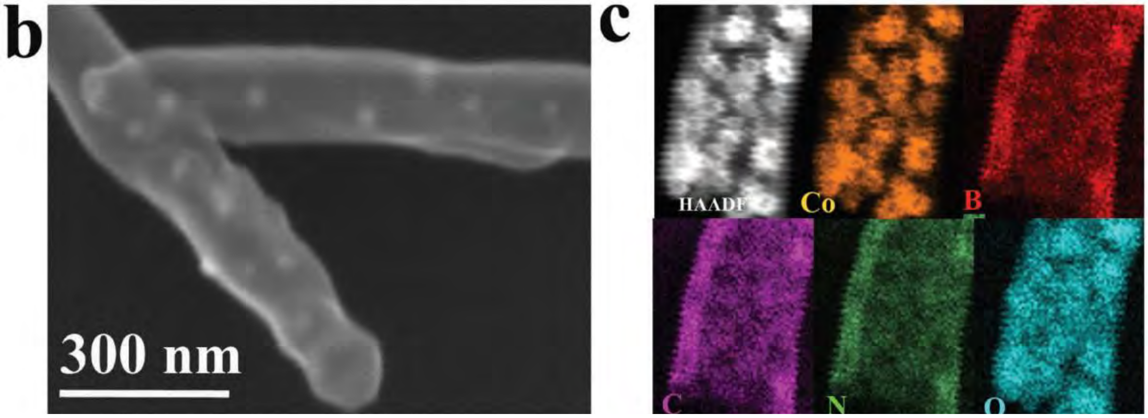

Figure. (b) FESEM images, c) STEM elemental mapping of CoO@BNG Nanotubes.

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Ultrathin graphene-based membrane with precise molecular sieving and ultrafast solvent permeation

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Graphene oxide (GO) membranes continue to attract intense interest due to their unique molecular sieving properties combined with fast permeation[1-9]. However, their use is limited to aqueous solutions because GO membranes appear impermeable to organic solvents[1], a phenomenon not yet fully understood. Here, we report efficient and fast filtration of organic solutions through GO laminates containing smooth two-dimensional (2D) capillaries made from large (10–20 μm) flakes. Without modification of sieving characteristics, these membranes can be made exceptionally thin, down to ~10 nm, which translates into fast water and organic solvent permeation. We attribute organic solvent permeation and sieving properties to randomly distributed pinholes interconnected by short graphene channels with a width of 1 nm. With increasing membrane thickness, organic solvent permeation rates decay exponentially but water continues to permeate quickly, in agreement with previous reports[1-4]. The potential of ultrathin GO laminates for organic solvent nanofiltration is demonstrated by showing >99.9% rejection of small molecular weight organic dyes dissolved in methanol. Our work significantly expands possibilities for the use of GO membranes in purification and filtration technologies.

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Ultra-lightweight Amphiphobic
Carbon Nanotube Foam with High Buoyancy

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Keywords：carbon nanotube foam, amphiphobic, buoyancy, aquatic devices

Aquatic devices which can work on water and oil are considered as of obviously scientific and practical significance in many fields， such as water environmental protection, oil spill cleanup and so on. Generally, special light-weight materials are used to make the devices have excellent repellence to water and oil as artificial supporting legs by mimicking the water strider. However, besides the complicated fabrication process, there still exist challenges in the aspects such as material density, device loading capacity for these kinds of devices. It is of great necessary to develop materials and devices that have lower density, higher buoyancy via simple and low cost approaches.

Carbon nanotube (CNT) foam has very low density and has potentials to provide large buoyancy. However, CNT foam is oleophilicity which limits the application in aquatic devices because oil can be easily adsorbed on and finally destroy the CNT foam. Here we demonstrated the low cost fabrication and properties of amphiphobic buoyancy materials with ultralow density (3 mg·cm^{-3}) based on CNT forms. The CNT foam is obtained after a second growth, and then 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (FDTS) is vapor deposited on the foam to achieve a conformal amphiphobic coating. This method changes the wettability of the CNT foam when the 3D skeleton remains unchanged. Following test shows that the CNT foam has high contact angle in water, dodecane and soybean oil, and can carry 300 times more weight than itself.

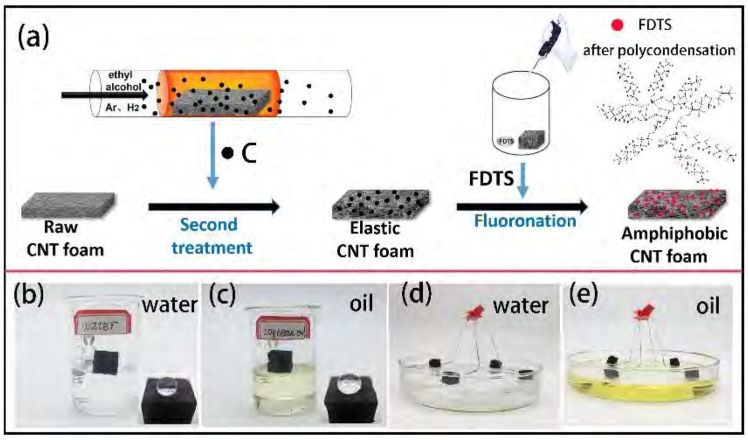

Fig.1 (a) fabrication process of amphiphobic CNT foam; amphiphobic CNT foam on (b)water and (c) oil surface; aquatic buoyancy devices on (d)water and (e) oil surface

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Carbon caging noncarbons for superior volumetric lithium storage

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The replacement of graphitic anodes by noncarbon anodes (e.g. tin and silicon-based materials) holds promise to improve the energy density of a lithium ion battery. However, the real application of these anode materials is currently limited by their huge volume expansion during cycling. Carbons have been used to buffer the volume changes and improve the conductivity of such noncarbon anodes. However, the introduced porosity in current electrode designs to buffer the volume changes of active materials does not afford high volumetric performance. Here, we demonstrate a well-designed method to introduce an accurate amount of void space in three-dimensional graphene networks using sulfur as a sacrificial agent. In a typical synthesis using the capillary shrinkage of networked graphene hydrogels, flowable and deformable sulfur is used with the hard tin oxide nanoparticles inside the shrinking hydrogels, and the void space around the tin oxide particles was precisely controlled by tuning the content of the surrounding and removable sulfur. Our materials design fulfills the most stringent requirements for balancing the complete expansion of tin oxide and the high density of the graphene-caged tin oxide hybrids. An ultrahigh high volumetric capacity for the active material including tin oxide and graphene with good cyclic stability was achieved. This strategy has demonstrated its versatility to silicon anodes for lithium ion batteries to buffer large volume expansions during electrochemical reactions and is an ideal remedy for low volumetric energy density in current energy storage devices.

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Synthesis of perovskites-like $PbBiO_2X$/GO (X = Cl, Br, I) composites enhanced visible-light-driven photocatalytic activity

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Abstract: A novel $PbBiO_2X$/Graphene oxide (GO) heterostructure photocatalyst was synthesized successfully by hydrothermal technique using $PbBiO_2X$ as the starting material for the first time. The composition and morphologies of the composites were controlled by adjusting the experimental conditions: the reaction pH value, temperature, and molar ratio. The samples were characterized using XRD, FE-SEM-EDS, HR-TEM, XPS, DR-UV-vis, BET, PL, EPR, and UPS. These as-prepared samples were subjected to the photocatalytic degradation of Crystal Violet (CV) under visible light irradiation. Under the optimal synthesized conditions, $PbBiO_2I$/GO composites showed greatly enhanced photocatalytic performance in $PbBiO_2I$ composites. Additionally, the rate constant values of $PbBiO_2I$/GO composites are obtained as the maximum degradation rates of 0.1807 h^{-1} by using the first-order linear fit of the data, which are much higher than the $PbBiO_2I$. The enhanced photocatalytic activity can be attributed to the effective separation of photo-generated carriers driven by the photoinduced potential difference generated at these heterostructures interface, transferof photo-generated electrons through the GO skeleton and favorable well-aligned straddling band-structure from the $PbBiO_2X$/GO. The possible photodegradation mechanisms was proposed and discussed in this study. Overall, this work may provide a facile way to synthesize the highly efficient $PbBiO_2X$/GO composites photocatalysts with promising applications in environmental pollution and control.

Keywords: Perovskites-like, $PbBiO_2X$, $PbBiO_2I$, Graphene oxide, Crystal violet, Visible-light-driven.

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Natural Photosynthesis Inspired All-Solid-State Z-Scheme System Mediated by Carbon Nanotubes for Photocatalytic H_2 Evolution

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Photocatalytic water splitting, one of the many endeavors in harvesting solar energy, is anticipated to grow as potential contributor to the future energy mix. Inspired by natural photosynthesis in green plants, Z-scheme photocatalytic water splitting system can be witnessed through the ingenious arrangement of a hydrogen (H_2) evolution photocatalyst (HEP), an oxygen evolution photocatalyst (OEP) and an electron mediator in nano-platform. For years, Z-scheme photocatalytic water splitting studies have been widely conducted by employing ionic electron mediator, for instance IO_3^-/I^- and Fe^{3+}/Fe^{2+} redox couples [1, 2]. However, there is a huge interest towards designing all-solid-state Z-scheme system, ascribed to the backward reaction and shielding effect from redox pairs-aided Z-scheme. Herein, we report a fine-tuned CNT-mediated Z-scheme system which comprises of $Zn_{0.5}Cd_{0.5}S$ as HEP and TiO_2 as OEP. The ternary nanocomposites ($Zn_{0.5}Cd_{0.5}S$-CNT-TiO_2) fabricated by a facile two-step coating and hydrothermal route exemplified a synergistic effect that leads to an enhanced photocatalytic H_2 evolution as compared to the single- and two-component systems. This reveals that CNTs can shuttle electron efficiently from OEP to HEP to accomplish the vectorial electron transfer. Consequently, the ternary system displayed a photocatalytic H_2 production of 21.9 μmol h^{-1} under simulated solar light, which is ca. 4.5- and 2.8-fold enhancement over pristine $Zn_{0.5}Cd_{0.5}S$ and CNT-$Zn_{0.5}Cd_{0.5}S$, respectively [3]. In all, these findings could extend the electron mediator candidates to a larger horizon and pave a future way in the field of Z-scheme photocatalytic water splitting.

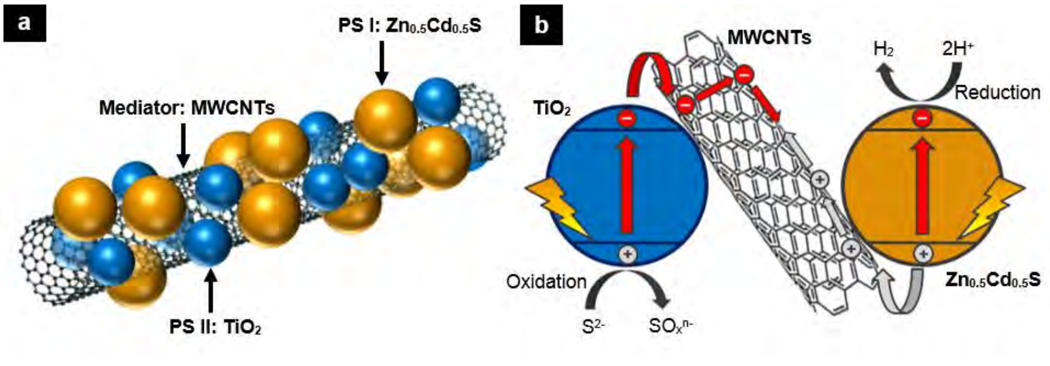

Fig.1 (a) Schematic of $Zn_{0.5}Cd_{0.5}S$-CNT-TiO_2 nanocomposites. (b) Proposed electron-hole transfer mechanism for CNT-mediated Z-scheme system [3].

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Carbon nanotubes as stabilizing phase in metal matrix composites: A study of the structural defects evolution during severe plastic deformation

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Nano-crystalline and ultrafine-grained materials obtained by severe plastic deformation (SPD) processes present an unstable nature as a consequence of the large amount of crystallographical defects and high stored energy present in their extensive grain boundary area. Recently, carbon nanotubes (CNT) have been proposed as enhancers of the microstructural stability (against recovery and grain growth) in these materials subjected to thermal inputs. However, it has been observed that CNT suffer significant structural damage during SPD, mainly due to the highly energetic character of the process, which might compromise their mechanical performance and their stabilization capability during thermal loads.

In this study, we tracked and studied the evolution of the structural defects with increasing accumulated strain on the nanotubes in CNT-reinforced metal matrix composites with different reinforcement weight fractions, namely: 0.5 wt.% (2.4 vol.%), 1 wt.% (4.8 vol.%) and 2 wt.% (9.5 vol.%). Visible Raman spectroscopy was used as the main characterization tool and the typical sp^2 carbon bands (D, G and G' modes as well as their descriptive parameters and intensity ratios) were thoroughly analyzed. Furthermore, an analysis of the shift of the G band was found to be of utmost importance so as to determine the amorphization trajectory undergone by the CNT. Results indicate that the deformation suffered by the CNT is related to the accumulated strain and varies with the partial CNT fractions of these composites. This is associated to their capacity to withstand the plastic strain occurring during deformation. In addition, we observed that the CNT defect situation reaches a maximum value before achieving the saturation in the microstructural refinement, which limits the applicability of this microstructural tailoring approach. These results will help to efficiently optimize the processing of this type of engineering composites.

Towards the development of multifunctional wood coatings based on carbon nanotubes

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Carbon nanotubes (CNTs) have been widely studied in such applications as superhydrophobic coatings [1], fire retardant agents [2], mechanical reinforcement fillers [3] and many others, and all of them can be of use in wood technology. Although, wood has been replaced by concrete and steel over the years, it is still one of the most common construction materials. Moreover, it is biodegradable and environmentally friendly. Diminishing the drawbacks of wood, such as wettability and flammability may renew the interest in wood as constructing material. The aim of the presented research was to assess the wettability and flammability of wood covered with CNTs. For this purpose, we coated wood with industrial grade multiwall CNTs by drop casting and dip coating methods. The scanning electron microscopy and fluorescence microscopy showed that CNTs may form a uniform layer on wood surface. The water contact angle of balsa wood coated with 0.05 g/m^2 CNTs increased from 75±3° (for pure wood) to 143±3° (Fig. 1A). Thus, the surface was almost superhydrophobic. However, CNT coated wood placed in high humidity environment did not show significant decrease in water uptake. In order to investigate the influence of CNTs on the flammability of wood a series of tests, such as vertical burning (VB), limiting oxygen index (LOI) and burning in fire tube (FT) were performed. Although CNT coating did not significantly influence LOI or VB, but some fire retardant effect was observed during FT test for CNT covered wood chips. For example, the presence of CNTs extended the time of decomposition by 25% (Fig. 1B).

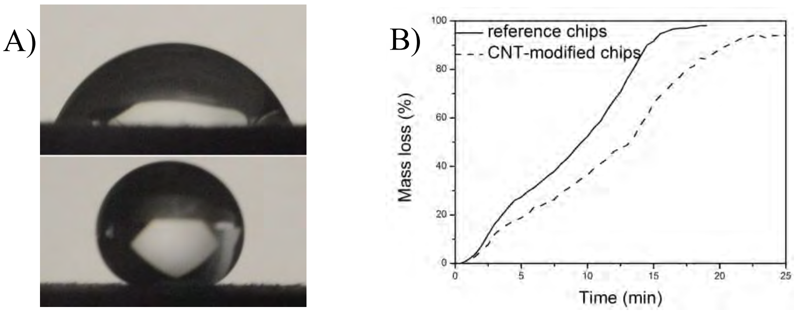

Fig.1 A) Water contact angle of balsa wood (top), balsa wood covered with CNTs (bottom); B) Mass loss dynamics during fire tube test of wood chips and wood chips coated with CNTs.

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Emerging trends in 2D nanotechnology that are redefining our understanding of polymer nanocomposites

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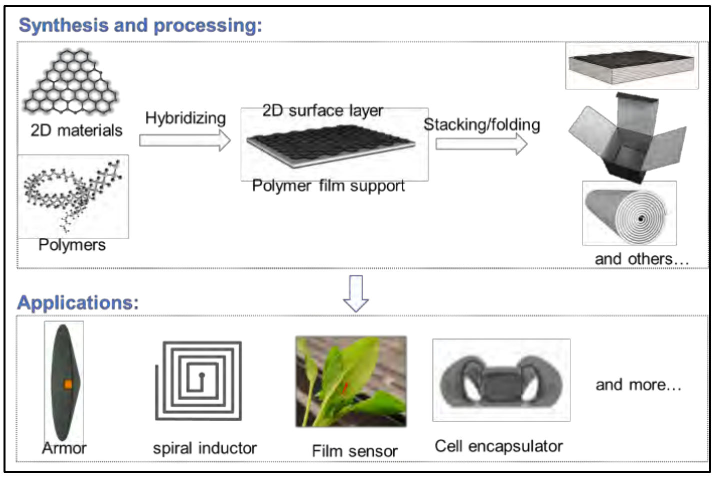
Graphene and other two-dimensional (2D) materials possess desirable mechanical, electrical, and optical properties for incorporation into polymer materials, potentially granting them unique structural and functional reinforcements. In particular, the emergence of large-area, high-quality 2D materials provides a means of positioning nanomaterials onto/into the polymer matrices with a precise structural control at an atomic level, which would give access to new nanocomposites with versatile properties at a minuscule addition of nanoinclusions for new applications. In this talk, I will present our recent work of the layered and scrolled nanocomposites with aligned semi-infinite 2D inclusions. We have recently developed a successive stacking/folding method to generate aligned graphene/polymer composites, and an analogous transverse shear scrolling method to generate Archimedean spiral fibers. The two composites show a significant increase of the effective elastic modulus and strength at exceptionally low volume fractions of graphene (0.085%). The fiber also demonstrates intriguing sticking-slip behavior and exotic telescoping elongation at break (30 times that of Kevlar). Both composites retain anisotropic electrical conduction along the graphene planar axis and transparency across the axis, and the exotically optical properties inherited from the 2D inclusions. We have further demonstrated the "ambient armor" application of these layered composites as well as the strain/temperature sensing and thermal spreader applications of the scrolled fibers. We envision a bright future of the nanocomposites with continuous 2D materials and its potential to produce advanced nanocomposites with previously unobserved combinations of mechanical, electrical, thermal, barrier, optical, and other properties at scale.



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Reinforcement of Functionalized Graphene Oxide/Inorganic Nanoparticle composites for Anticorrosion

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Metal corrosion, a ubiquitous phenomenon in nature, is seriously detrimental to modern industry and causes significant economic costs [1]. To alleviate that, surface coating with organic polymer such as polyvinylbutyral (PVB) is often used due to its higher efficiency and lower costs compared with other methods. Here, we report a further improvement in anticorrosion performance by compositing PVB with functionalized graphene oxide (GO) [2-3] and inorganic nanoparticles (IN, such as SiO_2 and TiO_2). We find that GO modified with p-phenylenediamine (P-GO) possesses remarkable dispersion stability in acidic conditions and compatibility with the polymer. A systematic research has been conducted to explore the optimal content of P-GO/IN in the PVB coating. The results show that P-GO is highly exfoliated and uniformly embedded in the PVB matrix. Potentiodynamic polarization tests revealed the highest anticorrosion efficiency and the lowest corrosion rate of coating films reinforced with P-GO/IN PVB composites, which is more than two hundred times better than that with individual IN or GO/IN PVB composites. This has been further substantiated by electrochemical impedance spectroscopy measurements on the coating films, revealing that an optimized 0.8 wt% of P-GO could be well dispersed in PVB and effectively prevent permeation of corrodents from the environment. The mechanism of effectively synergistic reinforcement of P-GO/IN in PVB on anticorrosion was also proposed and give a guide to the application of GO for heavy anticorrosion.

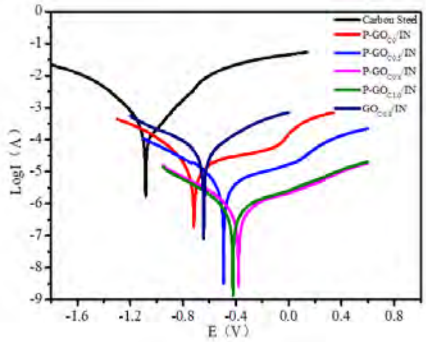

Fig.1 Tafel plots for the composite coatings with the content of 0, 0.5, 0.8, 1.0% of P-GO and 0.8% of GO in PVB comparing with carbon steel in 3.5% NaCl solution for 4 h

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[3] Z.-J. Luo, H.-Z. Geng, X. Zhang, *et al*, Nanotechnology **27**, 055601 (2016).

Development of space qualified super black coating using single walled carbon nanotubes

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Super black coating is a surface treatment on substrates which can be used to absorb maximum amount of light with very minimal reflection. These coatings play an important role in space applications such as baffles for optical sensors. Surrey Nanosystems' Vantablack vertically aligned multi walled nanotubes array grown by various chemical vapor deposition (CVD) ~500 ˚C absorbs light in all wavelength (0.2- 200 µm). But these films are not fully space qualified due to the ease with which they peel off [1].

Also, deposition of Carbon Nanotube films by CVD on different substrates is challenging and has issues related to adhesion of the films. Spray coating is an alternate choice to deposit the carbon nanotubes [2, 3]. In the present work, we are reporting spray coating process of single walled carbon nanotubes on the variety of substrates. The process of spray coating involves a] preparation of a homogeneous mixture of SWCNT, binder and a solvent, b] spraying the solution on the substrate which is heated to 60˚C- 80˚C and c] post deposition annealing to burn out the organic components. The thermos-optical properties measurements carried on various samples indicates promising application in the area of high absorbers. The samples have shown the absorbance of around 0.97 and the average total integrated reflectance of around 3% in the wavelength region of 300 to 2500 nm and absorbance of 1 for normal incidence. The scanning electron microscope (SEM) microstructural images shows the coral line structures. Further, experiments are being conducted to obtain the improved thermos-optical properties of the coatings.

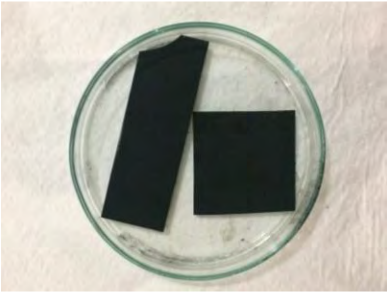

Fig.1 NoPo Super Black coating.

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Facile Synthesis of TiO_2-CNTs Composites for Water Purification

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Reusability and low photocatalytic ability are two important barriers that limit the usage of nanoscale TiO_2 in water pollution control [1, 2]. In this work, the TiO_2 nanorods were synthesized on carbon nanotubes (CNTs) by a facile hydrothermal method. The TiO_2 and CNTs composites (TiO_2-CNTs) were used as photocatalysts to photodegrade methylene blue in water solutions, and show a significantly improved photodegradation ability under both ultraviolet and visible light. The enhancement of the photodegradation ability is caused by the synergic effects [3] of TiO_2-CNTs system. Additionally, the novel photocatalyst shows a limited decreasing of the photocatalytic efficiency even after the several cycled degradations, this indicate the recyclability of the photocatalyst. The well designed TiO_2-CNTs structure presents an effective avenue for developing efficient photocatalysts, which provides a reference for further research on synthesis of reusable photocatalysts with higher efficiency.

This study was supported by the National Natural Science Foundation of China (No. 51661145025, 11274055).

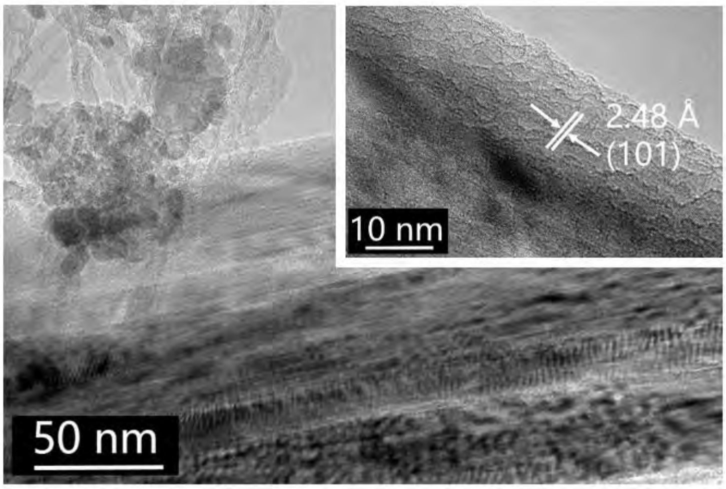

Fig.1 TEM image of TiO_2-CNTs composites

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Salt rejection behavior of MWCNT-polyamide nanocomposite reverse osmosis membranes in several salt solutions

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Because of worldwide industrialization and increase of population, we are facing a problem concerning water. Therefore, desalination of saline water (brackish water, sea water, wastewater, etc.) by reverse osmosis (RO) membrane is very important technology for producing a large amount of clean water. Although remarkable progress has been made in the fabrications of membranes, there is still a challenge to produce reliable membranes with anti-fouling properties, high mechanical strength, high tolerance on chlorine attack and minimal thickness of the membrane barrier layer to provide a high flux. We have developed a high-performance RO nanocomposite membrane[1] using multi-walled carbon nanotubes (MWCNT) and fully aromatic polyamide (PA), hereafter abbreviated as MWCNT-PA. The membrane was successfully prepared by interfacial polymerization in a simple process. We have found that a suitable amount of MWCNT in PA is 15.5 wt.%, which improved not only the membrane performance in terms of permeate flow and antifouling[2,3], but also the chlorine resistance[4].

The present paper reports the desalination performance of RO membranes of MWCNT-PA complex and commercial PA membranes in NaCl, $MgCl_2$, $MgSO_4$ and Na_2SO_4 aqueous solutions. The permeate flux, salt rejection, and salt flux were determined in a cross-flow experiment. The salt rejection increased with increasing running pressure and decreasing salt concentration. The zeta potential measurement of CNT-PA demonstrated that it is negatively charged due to the presence of CNT. Accordingly, it showed salt rejection performances against the four salt solutions ($Na_2SO4 > MgSO_4 > NaCl > MgCl_2$) that differed from that of the usual PA membranes ($Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$). These data are explained based on the Donnan model (MWCNT-PA) and steric hindrance pore model (PA), except for the case of chlorides under low-flux or high ionic strength conditions, where the diffusion and molecular size exclusion of the salts dominate over their mas-transport.

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Polyimide (PI) is a high-performance polymer with ultrahigh heat stability while carbon nanotube (CNT) possesses high mechanical strength, excellent electrical and thermal conductivity. Here we report a facile and low-cost method free from CNT pre-dispersion for fabricating super-aligned carbon nanotube (SACNT) / PI composite film which combines the advantages of both SACNT and PI. Flexible and scratch-resistant composite film with high CNT content, uniform dispersion of CNTs, and controlled patterned CNT structures can be fabricated easily via in situ imidization. Compared with pristine PI, SACNT/PI composite film exhibits dramatic improvement in mechanical strength, Young's modulus, thermal stability, electrical conductivity, etc. Thanks to these superb properties, a flexible, stable, addressable, electromagnetic wave permeable, and high-temperature fast-response multifunctional heater as well as a thermo-mechanical actuator based on SACNT/PI composite film have been demonstrated in this paper. And it also shows great potential in a variety of applications such as flexible/wearable electronics, RFID, other thermo-related devices and so on.

Post growth high density vertical alignment of HiPCO single walled carbon nanotubes inside a polymer matrix

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Aligned Carbon Nanotubes play an important role in realizing potential of Carbon Nanotubes in bulk applications. Vertical alignment of Carbon Nanotubes has been achieved by growing Carbon Nanotubes on a substrate [1]. These structures exhibit a high density and are referred to as a forest. Despite their excellent properties; they are difficult to produce on a large scale. [2]

Here we report a three-step process to obtain high density vertical alignment of SWCNT with the support of polymer matrix after the purification of HiPCO SWCNT. 1) aligning SWCNT on substrate in a horizontal direction using shear forces [3]. 2) stacking them to form working block with polymer 3) microtome them to obtain a vertical aligned polymer film. The process can be easily scalable due to their simplicity in the process. The vertically aligned structure can be used for various applications such as electron source, water filtration membrane, ion thruster, etc,

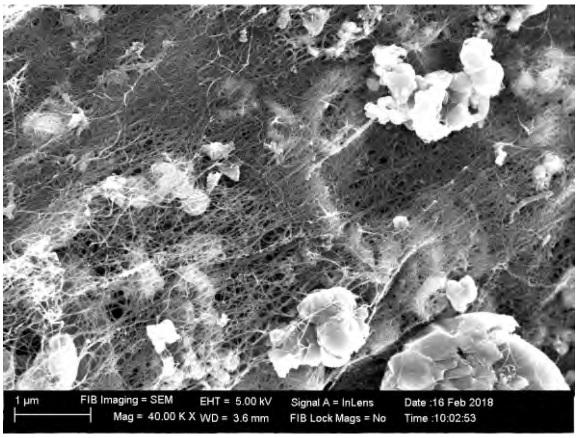

Fig.1 SEM image of aligned single walled carbon nanotubes

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Direct Observation of Single Walled Carbon Nanotubes inside Silk

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Many researchers have showcased that incorporation of nanomaterial into the silk protein increases the toughness of natural fibers such as silk [1]. Increased mechanical strength of the nanomaterial enhanced fibers would lead to innovative application in various industries [2]. Many researchers have tried coating the nanomaterial over the silk to improve its conducting and mechanical property.

Qi Wang *et al.* showcased the first study in embedding Nanotubes into silk [1]. In our study we have expanded the control group and number of worms by 10 times. For the first time we have made a direct observation of Carbon Nanotubes inside silk fibers and correlated the same with strength.

We incorporated single walled carbon nanotubes into the silk worm silk inner protein by feeding the silk worm with nanotubes. The feed was prepared just by coating the nanotubes on the mulberry leaves. We found that the small diameter nanotubes are easily attached to the inner protein of silk. The silk worms were fed with very high concentration of SWCNT (1%). We have also found that the mortality rate of silk worm reduced as we increase the concentration of nanotubes.

Fig.1 Silk worms fed with SWCNT coated on mulberry leaves

[1] Qi Wang *et al.,* Nano Lett., ***16****, 10 (2016)*
[2] Emiliano Lepore *et al* 2D Mater. ***4,*** *031013 (2017)*

Novel preparation of water-dispersible multiwalled carbon nanotubes via noncovalently anchored acidified multiwalled carbon nanotubes

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Multiwalled carbon nanotube (MWCNT) has attracted tremendous interest as reinforcing fillers due to its unique structure and excellent physical properties. However, efficient reinforcement has been largely limited because MWCNT tends to agglomerate within a polymer matrix. In this study, using the nitric acidified MWCNT directly as a dispersant to uniformly disperse pristine MWCNT in water is of significance to form a stable mixed MWCNT aqueous dispersion while without suffering the decrease of conductivity and mechanical property. Polyvinylbutyral (PVB) composites containing the mixed MWCNT were then prepared by a simple solution casting method. The SEM image results indicate that the mixed MWCNT are well dispersed throughout the PVB matrix. Due to the synergistic interaction of the two kinds of MWCNTs, the tensile strength is significantly improved by 135.12% at a relatively low content of 0.5wt%. Besides, the thermal stability and the conductivity increased by 8.4 ℃ and 4 orders of magnitude. Therefore our work therefore provides a new way to prepare nanomaterial water dispersion with the help of its own functional one as dispersant to preserve its pristine properties and make use of the potential properties of the synergistic effect.

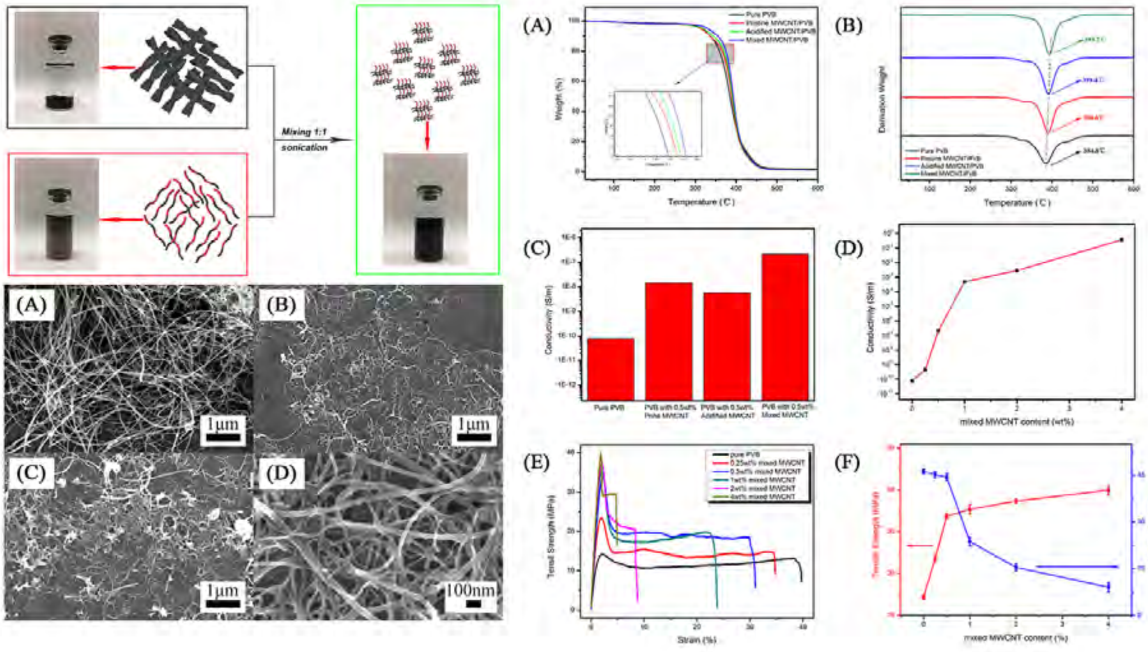

Fig.1 Schematic mechanism and SEM image for formation of the mixed MWCNT hybrid structure (left) and the thermal stability, conductivity and mechanical properties of the MWCNT/PVB nanocomposites (right).

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Designing solvent-resistant hollow fiber membranes consisting of P84 polyimide and amine-functionalized carbon nanotubes with potential applications in food, pharmaceutical, and petrochemical industries

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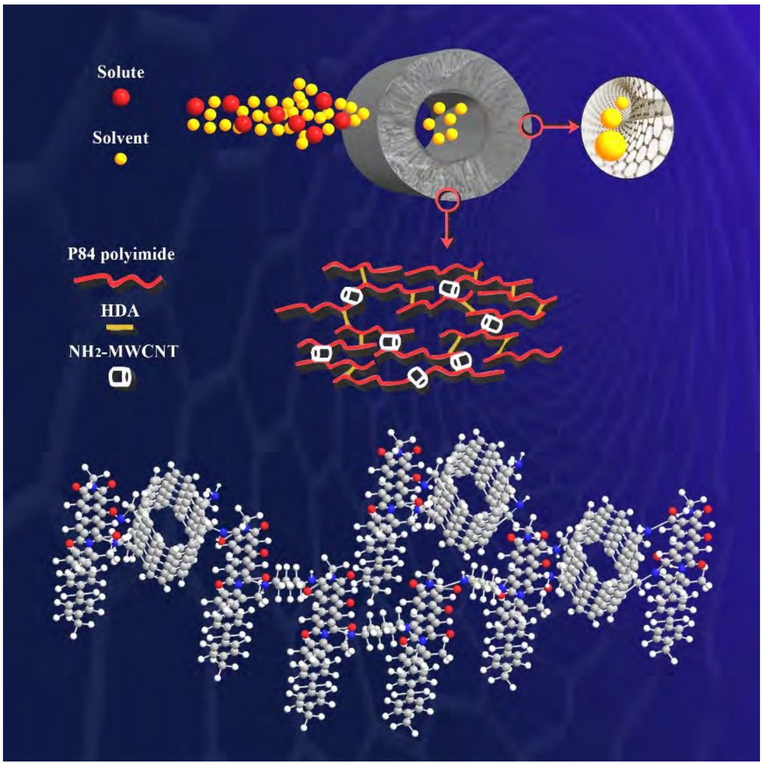
Robust P84 and NH_2-MWCNT/P84 hollow fiber membranes have been designed by adjusting spinning parameters and then crosslinking them by 1,6-hexanediamine to achieve desirable separation performance for organic solvent nanofiltration (OSN). A weak bore fluid, an adequately high dope flow rate and a small air gap length were required to produce the desired hollow fiber membranes. Compared the neat P84 hollow fiber, the addition of NH_2-MWCNTs into P84 resulted in an amidation reaction between the imide groups of P84 and the amine groups of NH_2-MWCNTs, leading to greater mechanical properties and thermal stability as well as higher dope viscosity. Moreover, NH_2-MWCNT/P84 hollow fibers exhibited great permeances of 4.31, 2.26, 1.45, and 1.17 LMH/bar for acetone, methanol, ethyl acetate, and ethanol, respectively, while having smaller pore sizes with notable rejections. The crosslinked P84 and NH_2-MWCNT/P84 membranes showed extraordinary rejections of 97.2, and 99.8% to methylene blue (320 g/mol), respectively. Also, the newly developed hollow fibers demonstrated great potential for separating tetracycline/IPA, L-α-lecithin/hexane, and BINAP-Ru(II)/methanol solutions, representing their applicability in the pharmaceutical, food, and petrochemical industries.



Hierarchical bi-dimensional alumina/palladium nanowire nano-architectures for hydrogen detection, storage and controlled release

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2. Faculty of Science

We report on the fabrication of bi-dimensional alumina/palladium nanowire nano-architectures for hydrogen detection, storage and controlled release. This nanostructured material was fabricated by growing the palladium nanowires directly in the nanosized channels of nanoporous alumina membrane followed by atmospheric-plasma jet treatment to fabricate the interconnected surface structure mostly suitable for hydrogen-related applications such as controlled release and sensing. Several interesting properties are demonstrated, including high sensitivity levels (up to 0.1 % of H_2 in air) and short response times. Large resistance response reaching 100 % for 0.5 % of H_2 in air makes it possible to use the fabricated sensors without complex and expensive amplifying circuits.

Near-Infrared Photoluminescent Carbon Nanotubes for Imaging of Brown Adipose Tissue

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Near-infrared photoluminescent single-walled carbon nanotubes (CNTs) are effective bio-imaging agents, providing clear vascular imaging for mice, as their fluorescence wavelengths are above 1000 nm, where the low biological auto fluorescence, high light transmittance, and low light scattering enable the clear *in vivo* observation. We previously showed that CNTs can image brown fat depots, such as brown adipose tissue (BAT), in mice when the CNTs are coated with an amphiphilic and biocompatible polymer, poly(2-methacryloyloxyethyl phosphorylcholine-co-n-butyl methacrylate; PMB) as presented in Figure 1[1]. Since BAT has an exceedingly high heat-productive capacity, it has been considered as a new therapeutic target for obesity-associated metabolic disorders. Its characteristic brown color is due to the densely packed capillaries and abundant mitochondria that contain iron compounds. Although PET-CT is commonly used for BAT imaging in a clinical setting, it cannot widely be applied to preclinical animal tests due to economic reasons. In this context, the fluorescent imaging with CNTs will be a unique and useful method for the BAT study.

By using phospholipid polyethylene glycol (PLPEG) instead of PMB, interesting phenomena were observed in BAT through CNT-fluorescent imaging. BAT of a normal mouse was not imaged by PLPEG-CNT, however, depending on the body condition, BAT became clearly visible. In the case of PMB-CNTs, they absorb apolipoproteins in the plasma and selectively accumulate on capillary endothelial cells of BAT that express apolipoprotein receptors [1]. This mechanism is not applicable for the PLPEG-CNT accumulation in BAT as will be explained in the presentation.

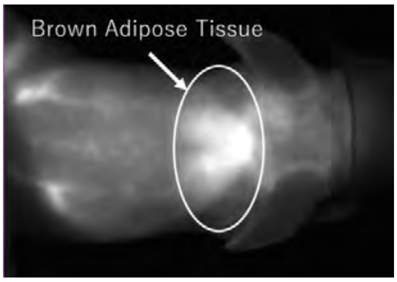

Figure 1. NIR-fluorescence image of BAT in mouse by using PMB-CNT as a probe.

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ZnO Nanowire FEAs Based Flat Panel X-ray Source for Biomedical Imaging

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X-rays have a variety of applications in science and engineering, and their most widely recognized application is in transmission contrast imaging [1]. The cold cathode flat-panel X-ray source is a new type of X-ray source with the great potential of small footprint and low-dose imaging [2,3]. In this study, a transmission-type flat panel X-ray source in diode structure has been fabricated using ZnO nanowire field emitter arrays(FEAs). The parameters of ZnO nanowire FEAs and the transmission anode were optimized. The imaging performance was evaluated. Figure 1(a) shows a schematic of the device structure and set-up for the measurement. Kilovoltage X-rays were generated by the flat panel X-ray source in diode structure operated in a vacuum chamber with a pressure about 1×10^{-5} Pa. The transmission tungsten target and beryllium window were separated by 10 cm. A flat-panel CMOS X-ray detector was used to record the image. Clear X-ray absorption image was taken by the radiation from flat panel X-ray source. A 2D planar image of biomedical subject was demonstrated as shown in Figure 1(b). The image shows a crucian carp with size about 21 cm×6 cm. The image was obtained at an emission current of 1 mA and a total exposure time of 70 ms at 40 kV, and the flat panel detector was 60 cm away from the beryllium window. The high-contrast X-ray absorption image shows the source can be utilized to capture the X-ray images of biological materials. Our results show the promising application of flat panel X-ray source for mammography and digital breast tomosynthesis.

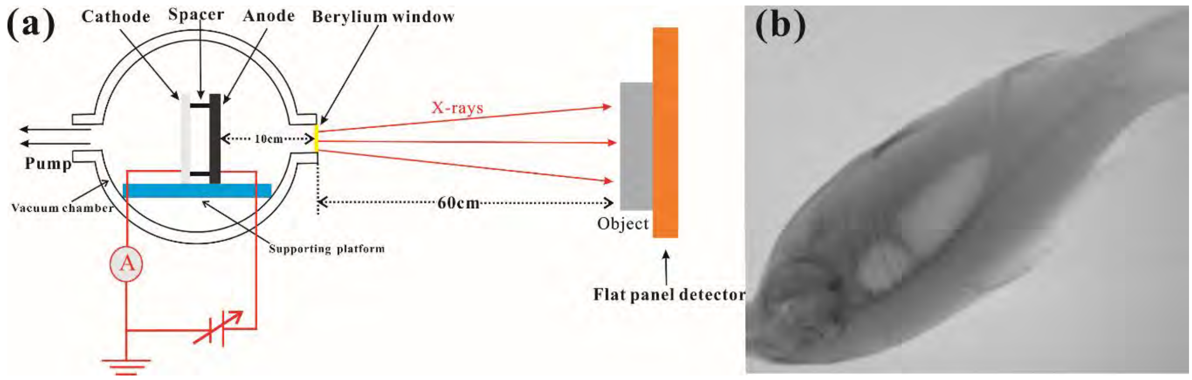

Fig. 1. (a) Illustration of the set-up for measurement; (b) The absorption X-ray image of a crucian carp.

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Nanocarbon materials for soft and multimodal neural electrical interfacing

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Implantable electrical probes have led to advances in neuroscience, brain-machine interfaces, and treatment of neurological diseases, yet they remain limited in several key aspects, including the challenges in achieving chronically-stable and large-scale brain interfaces. In this presentation, I will overview our recent progress in developing nanocarbon based materials and technologies for soft and multimodal neural electrodes. Soft implantable neural electrodes made of carbon nanotube (CNT) fibers elicit much reduced inflammatory responses and can reliably isolate and track single units neural activity for months. The conformal interface formed between the soft graphene contact lens electrodes and cornea results in high electroretinogram (ERG) signal amplitude and stability, preserved ocular acuity, and minimized corneal irritation from ERG recording. For multimodal neural interfacing, we have developed CNT and graphene fiber based highly MRI compatible neural electrodes which induce negligible artifact under high field MRI scans. Transparent CNT based surface electrode array was used to map the brain activities under simultaneous optogenetic stimulation and calcium imaging, providing complementary cellular information in addition to the high temporal resolution electrical recording. These results demonstrate the unique capabilities of nanocarbon based materials for neural electrical interfacing, and providing effective platforms for both fundamental brain studies and clinical applications.

Self-assembled Nanodiamond Supraparticles for Anticancer Chemotherapy

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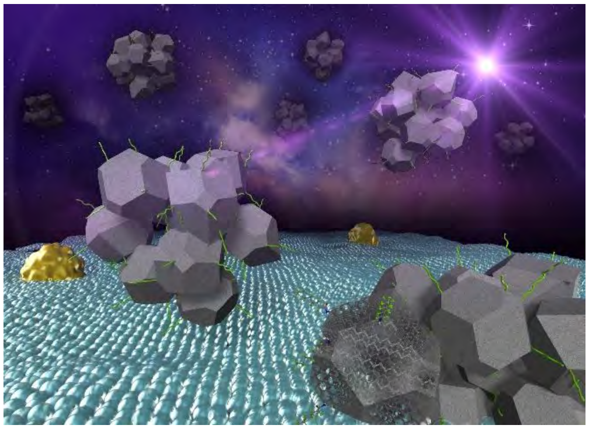
Nanodiamond (ND) is a promising material for drug delivery applications owing to its relatively low cost, amenability to large-scale synthesis, unique structure, and low toxicity. However, synthesizing drug-loaded ND conjugates with uniform and tunable sizes, high loading capacity, efficacy in drug delivery, and versatility in terms of surface functionalization has been challenging. Here we show that perfluorooctanoic acid-functionalized NDs spontaneously transform into well-dispersed and biocompatible supraparticle (SP) nanoclusters. We demonstrate that the synthesized ND-based SPs (ND–SP) exhibit high penetration through the cell membrane and is therefore superior as a drug carrier to conventional nanomedicines such as polyethylene glycol and phospholipid-based nanocapsules and simple drug-loaded ND conjugates. We confirm the efficacy of ND–SPs in the eradication of cancer cells *in vitro* and *in vivo*. Our results demonstrate that the synthesized ND–SPs are useful for targeted drug delivery in a variety of biological applications.



Cell membrane penetration of Nanodiamond Superaparticles to achieve effective cancer therapy

Immobilized ferrous ion and glucose oxidase on graphdiyne and its application on one-step glucose detection

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Graphdiyne (GDY) is a novel two-dimensional (2D) carbon allotrope with sp-hybridized carbon atom and hexagonal ring. Due to its unique structure and electronic property, GDY was reported as a promising candidate applied in energy storage, catalysis, biosensing and so on. However, using GDY as a platform to immobilize metal ion or enzyme was still not reported. Here, we presented a GDY based composite with dual-enzyme activity by immobilizing ferrous ion and glucose oxidase onto GDY sheet. GDY showed great adsorption capacity and maintained the high catalytic activity of ferrous ion. The ferrous ion preferred to adsorb in between the neighboring two C-C triple bonds of GDY with lower adsorption energy (-5.64 eV) if compared to graphene (-1.69 eV). Meanwhile, GDY exhibited the ability of adsorbing glucose oxidase while did not obviously influence the structure and catalytic activity of the enzyme. The as-prepared composite was successfully used in one-step blood glucose detection. This work provides a new insight on ion and enzyme immobilization by 2D material.

Fig.1 GDY based composite with dual-enzyme activity for one-step glucose detection

Dynamical Evaluation of CNTs Toxicity during Degradation by Macrophages

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With the increase of CNT-based products appearing into commerce, the public concern regarding possible toxicities has attracted many attentions. When CNTs entered into living body, they would be mainly entrapped and partially biodegradated by macrophages. Therefore, investigation of the intercellular quantity change of CNTs and the resulted cytotoxicity changes after uptake by macrophage would be helpful to fully understand their toxicity. In this study, we have measured the macrophage uptake of CNTs as well as their quantity changes in 1-7 days by using an optical absorption method [1] and Raman spectra of CNTs in the cell lysates. Our results indicated that the quantity of CNTs inside of macrophage decreased about 20-50 % of CNTs in macrophage cells of RAW 264.7 as well as the primary cells within 3 days, and almost no decrease by the longer period incubation. In addition, we have also investigated the dynamic toxicity changes during CNT degradation in macrophages. Data showed the cell viability, cell total protein amount and caspase 3/7 amount basically not changed during the degradation. However, the amount of reactive oxygen species (ROS) generated by macrophage after CNT-uptake. We have found that the amount of ROS dynamically decreased with time after CNTs uptake and only a few ROS detected after 3 days. The tendency of CNT-decrease inside of macrophages was consisted with that of ROS amount reduction. These results not only suggested that CNTs were degraded by ROS generated in macrophages but also indicated that the residues of un-degraded CNTs persisted in macrophages without toxicity.

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Deep-Tissue Optical Thermometry Using Carbon Nanotubes

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Because of near-infrared photoluminescence (PL) of single-walled carbon nanotubes (SWNTs) [1] in the wavelength range known as the second optical window of biological tissues [2], SWNTs have been considered as promising luminescent probes for deep tissue bioimaging. Moreover, efficient phonon-assisted up-conversion photoluminescence (UCPL) in SWNTs, for which the excitation light wavelength can be longer than the emission one, has recently been discovered [3]. With regard to the UCPL, the UCPL intensity increases with increasing temperature, while Stokes PL (hereafter, just referred to as PL) intensity decreases [3]. Thus, the temperature dependent variation of the ratio of the UCPL and PL intensities may potentially be useful for optical thermometric imaging applicable to determining the temperature of deep inside of biological tissues. Development of such a new method will facilitate, for instance, the hyperthermia treatment that has been considered to be effective for the treatment of tumors [4]. The hyperthermia treatment requires strict control of the tumor temperature. However, the exact temperature control still remains a challenge because of the difficulty in measuring the temperature of the tumor in deep tissue. Thus, development of an effective method for the deep tissue optical thermometry has been strongly desired.

In this study, we observed UCPL and PL of SWNTs that were chemically functionalized in order to enhance both the UCPL from the free excitons and the longer wavelength PL from the localized excitons [5,6], and used the ratio of these intensities to determine the local temperature of deep inside of the biological tissues. The SWNTs were dispersed in water, and it was sealed in a thin circular cell, and their UCPL and PL intensities were measured using an InGaAs near-infrared camera. The temperature of the dispersion was directly controlled using a rubber-heater and a thermostat, and the luminescence images of the UCPL (1000 nm) and the PL (1150 nm) were obtained under epi-illumination using a 1064 nm laser. The PL and UCPL images were obtained under the same temperature, and the UCPL/PL intensity ratio at each spatial position were obtained to construct a ratiometric image. As the temperature of SWNTs increased, the luminance intensity of UCPL (I_{UCPL}) increased but the PL (I_{PL}) counterpart decreased. Consequently, the value of the ratio ($I_{\mathrm{UCPL}}/ I_{\mathrm{PL}}$) increased as shown in Figure 1. Clear increase of the intensity ratio indicates high sensitivity of this method to a small temperature variation.

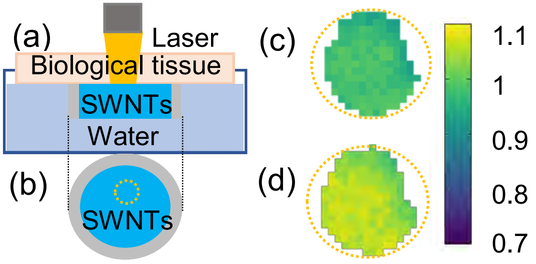

Fig. 1 (a, b) Schematic of a thin circular cell filled with an aqueous dispersion of SWNTs covered by biological tissue (a) side, (b) top view. (c) $I_{\mathrm{UCPL}}/ I_{\mathrm{PL}}$ images at 37 ° C and (d) at 40 ° C. The dotted circles indicate the excited region.

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Modulating the immunological effects of nanomaterials for cancer immunotherapy

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The interactions between nanomaterials and the immune system has become a hot topic in nanobiology. During our investigations of the immunological effects of various nanomaterials and the underlying mechanisms, we find that the interactions of these nanomaterials with immune factors/immune cells could be modulated through regulating their surface chemistry. Our recent work have shown that upconversion nanoparticles (UCNPs) with certain surface modifications can serve as an effective nano-adjuvant for dendritic cell (DC) based cancer vaccine and induce strong cellular immune responses, suggesting promising applications in cancer immunotherapy as well as DC tracking[1]. We further load UCNPs with chlorin e6 (Ce6), a photosensitizer, and imiquimod (R837), a Toll-like-receptor-7 agonist. The obtained multitasking UCNP-Ce6-R837 nanoparticles under near-infrared (NIR) irradiation with enhanced tissue penetration depth would enable effective photodynamic destruction of tumors to generate a pool of tumor-associated antigens, which in the presence of those R837-containing UCNPs as the adjuvant are able to promote strong antitumor immune responses. More significantly, photodynamic therapy (PDT) with UCNP-Ce6-R837 in combination with the checkpoint blockade not only shows excellent efficacy in eliminating tumors exposed to the NIR laser but also results in strong antitumor immunities to inhibit the growth of distant tumors left behind after PDT treatment. Furthermore, such a cancer immunotherapy strategy has a long-term immune memory function to protect treated mice from tumor cell rechallenge[2]. Our work presents an immune-stimulating UCNP-based PDT strategy in combination with CTLA-4 checkpoint blockade to effectively destroy primary tumors under light exposure, inhibit distant tumors that can hardly be reached by light, and prevent tumor reoccurrence via the immune memory effect. Our results also highlight the critical roles of surface chemistry for the rational design of nanomaterials for immunotherapy.

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Industrial production of ultra-stable sulfonated graphene quantum dots for Golgi apparatus imaging

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The wide use of functionalized graphene quantum dots (GQDs) in stable dispersions is currently hampered by the lack of industrially scalable, low-cost, and eco-friendly methods. We have developed the first realization of the industrial-scale (20 L) production of high-quality fluorescent GQDs via a molecular fusion route from a low-cost, active derivative of pyrene. By a wholly "green", conventional sulfonation reaction at low hydrothermal temperature, the molecular precursor is wholly converted into highly water-soluble, sulfonated GQDs without byproducts such as insoluble carbon. The GQDs are applied as biological fluorescent probes for visualizing and targeting Golgi apparatus in Hela and MCF7 live cells.

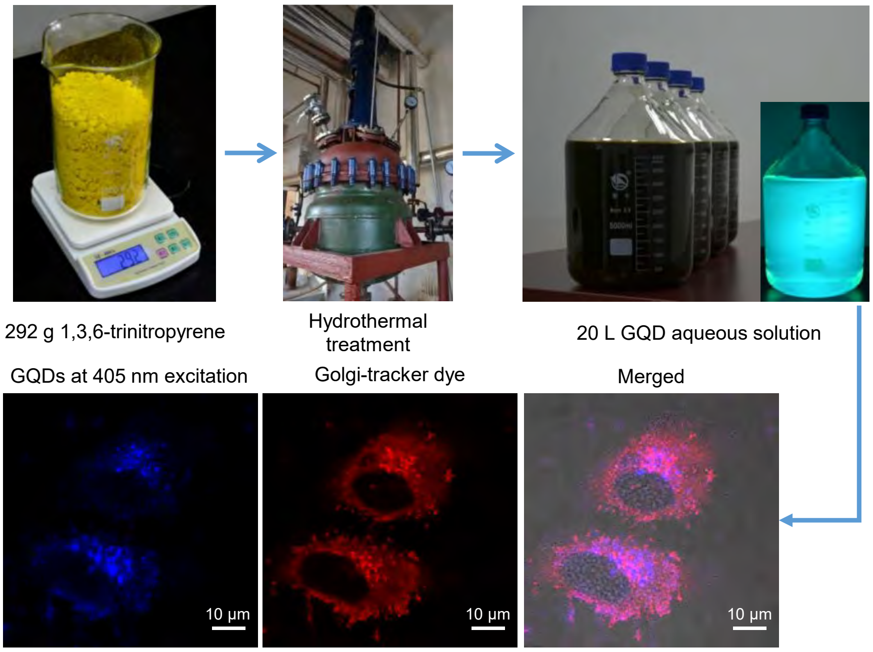

Fig.1 Schematic illustration of the synthesis of ultra-stable sulfonated graphene quantum dots for Golgi apparatus imaging.

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Three-minutes Super-rapid Synthesis of Graphene Quantum Dots via Microwave and their Multiple Applications

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Graphene quantum dots (GQDs), as one of the recently studied fluorescent nanomaterials, have attracted increasing attention and play a vital role in many fields. Here we introduce a simple, superfast, and scalable strategy that obtains GQDs within 3 min under microwave irradiation (MA-GQDs). The MA-GQDs exhibit excellent fluorescence quantum yields up to 35% in the optimum reaction condition. The MA-GQDs with single-crystalline and few-layer structure can reach the visible region with the longest absorption wavelength at 700 nm. Moreover, these ultrabright-fluorescence and stable MAGQDs as a phosphor and fluorescence probe could be efficiently applied in white light-emitting diodes and cellimaging fields.

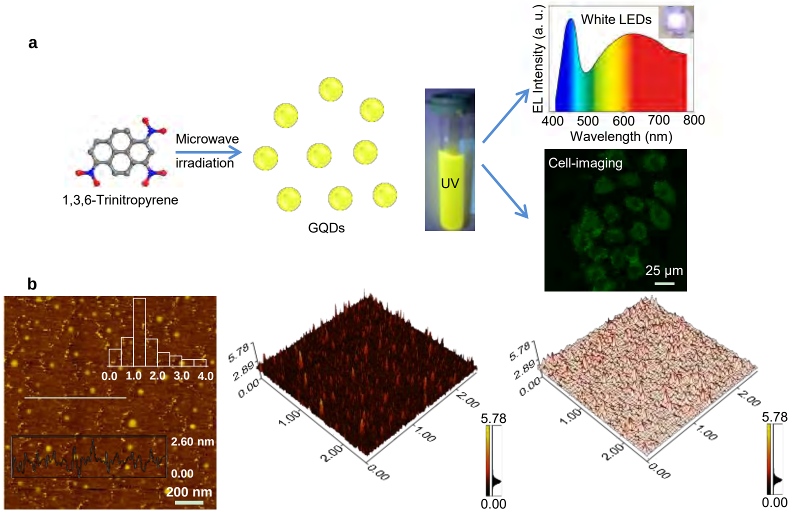

Fig. 1 (a) Schematic illustration of the preparation route for MA-GQDs in 3 min, (b) AFM images of MA-GQDs.

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Graphitic Nanocapsules Based Raman Imaging And Bioanalysis

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Raman spectroscopy offers certain fingerprints to identify chemical compounds. Graphitic nanocapsules are emerging nanomaterials which are gaining popularity along with the development of carbon nanomaterials. Graphitic nanocapsule has demonstrated extraordinary performance as both SERS substrate for Raman bioimaging and bioanalysis. We fabricated corrosion-resistant, water-soluble, and graphene-protected AgCu nanoparticles (ACG). Such stable ACG have been utilized for cell labelling, rapid Raman imaging and SERS detection. We also developed a graphene-isolated-Au-nanocrystal (GIAN) nanostructures. Multimodal cell imaging and NIR photothermal-enhanced chemotherapy have been realized with such GIAN platform. Cancer cell-specific aptamers were further functionalized on the graphitic surface through simple modification to realize imaging selectivity through differential cancer cell recognition. All these results indicate graphitic nanocapsule is an optimum choice for SERS analysis in complex systems.

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Comparison of carbon-based materials for neural interfaces

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Cortical neural prostheses require chronically implanted small-area microelectrodes that simultaneously record and stimulate neural activity. Magnetic resonance imaging (MRI) compatible neural electrodes are important for deep brain stimulating (DBS) electrodes. Various kinds of carbon-based materials are used as novel implantable neural electrodes. This study is therefore to evaluate and compare typically 4 types of carbon-based materials (aCNT, GF, fCNT, CF) with Pt wire microelectrodes in details. Given that all of the aspects had been discussed here (electrochemical characterization, stability test, mechanical property comparison, in vivo neural recording, chronic immunohistochemistry and MRI-compatibility), aCNT and GF fiber show much better performance as long-term implantable neural interfaces than the others. This work may be beneficial to the selection of a certain carbon-based material related to neurophysiological studies, continuous electrophysiological recording/ stimulation and anatomical/ functional MRI studies.

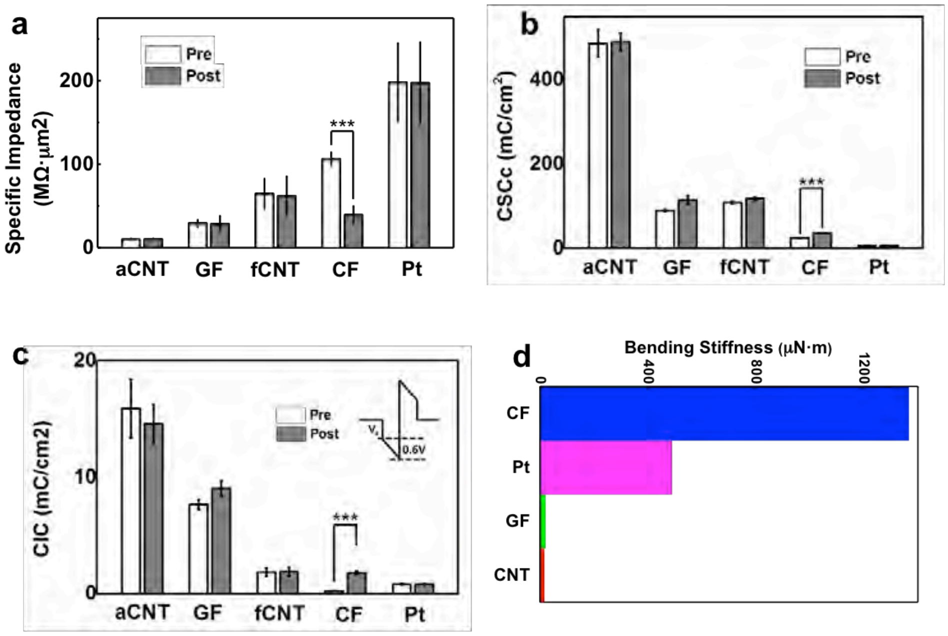

Fig. 1 6-hour current pulsing and mechanical properties. (a-c) Specific impedance, cathodic charge storage capacity (CSCc) and charge injection capacity (CIC) of 4 types carbon-based fiber microelectrodes and Pt wire microelectrodes before (white column) and after (gray column) 6h current pulsing. Error bars show s.e.m. (n=8). (d) Bending stiffness of CNT (aCNT = fCNT), GF, CF and Pt microelectrodes. All above metrics show that aCNT, GF and fCNT microelectrodes are not significantly degraded by 6 hours of current pulsing at 0.016mC/cm2 (clinical parameter) and these materials also have ultraflexibility.

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The fibroblast growth factor modified nitrogen-containing graphene for regeneration of photo-damaged retinal pigment epithelial cells

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Age-related macular degeneration (AMD) is one of the most common ocular diseases which may cause irreversible blindness, particularly among people who are aged more than 65 years. AMD is mainly caused by the apoptosis of retinal pigment epithelial (RPE) cells. RPE cells contain lipofuscin and rich long-chain unsaturated fatty acids which are sensitive to reactive oxygen species (ROS). Presence of excessive ROS inside cells always results in the damage or apoptosis of cells. Thus, it is a big challenge for both scientists and clinicians on how to decrease the level of ROS inside damaged RPE cells and realize the regeneration of RPE cells, for the treatment of AMD related diseases.

In this work, we synthesized nanocomposites from the basic fibroblast growth factor (bFGF) and graphene which could efficiently facilitate the reduction of ROS. Our recent study discovered that nitrogen-doped graphene (NG) exhibited superb catalytic activity for reduction of oxygen [1]. It is thus interesting to investigate the capability of NG on the reduction of ROS inside cells. This work presents a facile way to prepare nitrogen containing molecules (such as bFGF) modified graphene (bFGF-NG) via a self-discovered edge-functionalized ball milling method [2, 3]. The capability of the resulting bFGF-NG to eliminate the ROS inside photo-damaged RPE cells will be discussed. Presence of bFGF can further inhibit the oxidative stress of cells by enhancing the activity of signal pathways such as PI3K/AKT and Nrf$_2$. Incorporation of graphene with bFGF is also beneficial for improving the poor stability and half-life period of bFGF inside cells. Our preliminary results support that the ROS level of photo-damaged RPE cells could be significantly reduced by the utilization of the as-synthesized bFGF-NG nanocomposites, suggesting possibility for the regeneration of ROS induced apoptotic cells.

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Red fluorescent graphene quantum dots as self-targeted fluorescence probes for cell imaging

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Graphene quantum dots (GQDs), as one of the recently studied fluorescent nanomaterials, have attracted increasing attention and play a vital role in many fields.[1-4] However, there are few reports of long-wavelength fluorescent GQDs, which have good prospects in the field of red and orange fluorescence. Here we introduce a simple one-pot strategy that obtains full-color GQDs. The GQDs exhibit excellent fluorescence stability and low toxicity. Through morphology characterization, the GQDs with single-crystalline are consist of few-layer structure. Moreover, these ultrabright-fluorescence and stable GQDs as a phosphor and fluorescence probe could be efficiently applied in cellimaging fields.

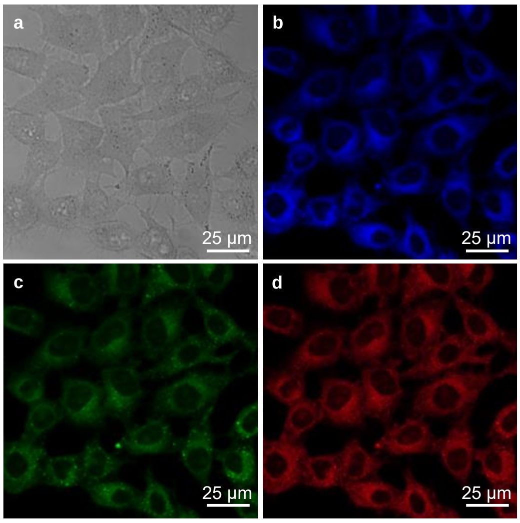

Fig. 1 (a) Schematic illustration of the preparation route for MA-GQDs in 3 min, (b) AFM images of MA-GQDs.

References:

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High-Yield Production of MoS_2 and WS_2 Quantum Sheets from Their Bulk Materials

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Mass production of two-dimensional quantum sheets (2D QSs) is highly desired to fully exploit their properties. Herein, we present a general strategy for the high-yield production of molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) QSs by a sequential combination of salt-assisted ball-milling and sonication-assisted solvent exfoliation of their bulk materials. Such a strategy enables reproducible production of intrinsic and defect-free MoS_2 and WS_2 QSs with exceedingly high yields of 25.5 and 20.1 wt %, respectively. By precipitation-redispersion treatment, the QSs can be redispersed in a wide range of solvents with redispersion concentration up to 20 mg/mL or even higher. Remarkable nonlinear absorption saturation is demonstrated in the QSs-poly(methyl methacrylate) (PMMA) hybrid thin film with loading content of merely 0.1 wt %. Our method provides an avenue toward mass production and full exploration of 2D QSs.

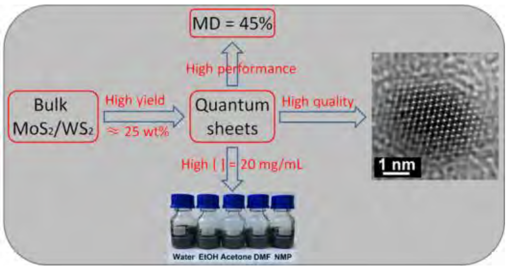

Fig.1 “4H” character of the MoS_2 and WS_2 quantum sheets.

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Clean, fast and scalable transfer of ultrathin/patterned vertically-aligned carbon nanotube arrays

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Abstract

The difficulty of transferring vertically-aligned carbon nanotube (VACNT) arrays onto specific substrates limits their use in many fields, for instance as thermal interface materials or electrical interconnects in microelectronics. Current transfer techniques are either limited by the type and shape of the target substrate, or their inability to transfer patterned and thin VACNT arrays.[1,2] Here, we report a simple and clean press transfer method that does not use transfer media, and involves only pressing and lifting steps.[3] This method enables not only the transfer of patterned and very thin VACNT arrays but also the tight adhesion of the arrays onto various flat or curved target substrates. Flexible and transparent electrodes were fabricated by transferring inter-digitated VACNT patterns onto a PET substrate. VACNT arrays with a thickness of 20 µm were transferred onto target substrates cleanly, showing a very low thermal resistance of ~26 K mm2 W-1. The transferred clean, thin VACNT arrays show good heat dissipation as thermal interface material when integrated into a desktop computer CPU cooling system.

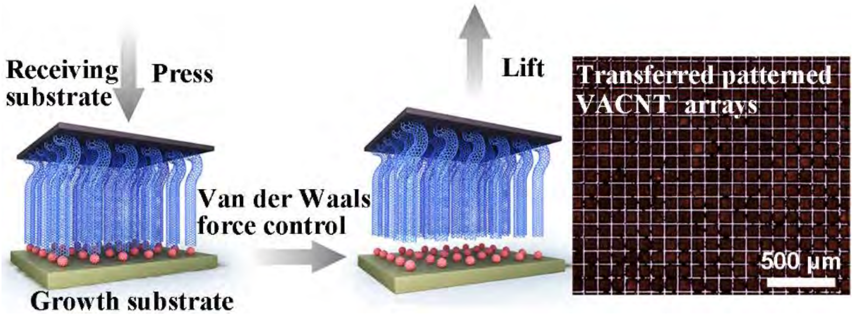

Fig.1 Press transfer mechanism of a high-density VACNT array and transferred patterned VACNT arrays.

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Flexible Semiconductor Manufactured from Industrial Waste Gas

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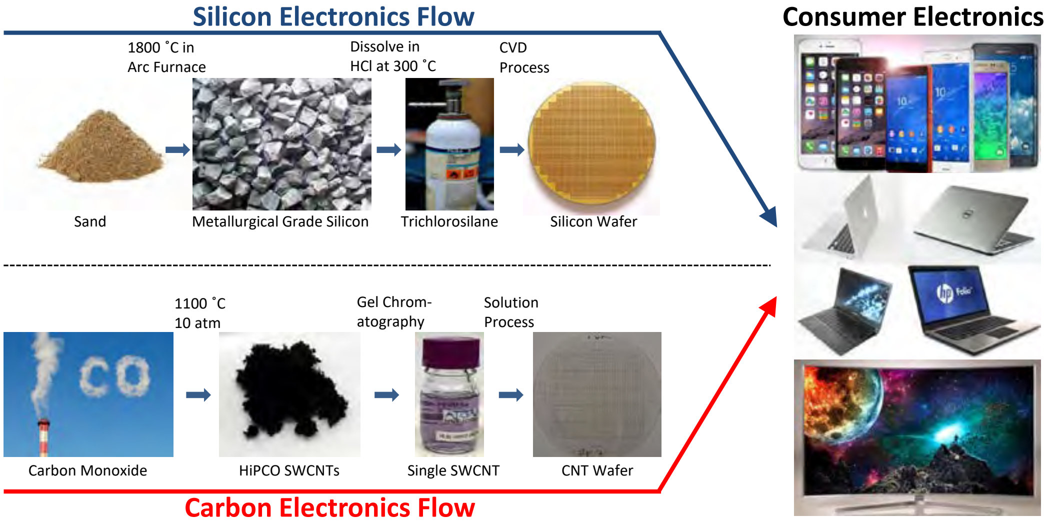
With the size scaling down, the performances of current semiconductor electronics approach their physical limits. IBM and other institutes demonstrated that semiconducting Single-walled carbon nanotubes (SWCNT) could be the right candidate for the replacement. The leakage current densities of compound semiconductors increase with the increasing temperature, leading to the failure at high temperature. Also, the compound semiconductors are brittle, cannot resist the shocking, pressing, bending, and stretching. The inherent flexibility and mechanical strength of single-chirality/diameter SWCNT perfectly circumvent these problems in contemporary semiconductors. Moreover, the produce of compound semiconductors, like silicon, requires extensively high temperature reaction with metal, chemical conversion and physical chemical vapor deposition. These procedures consume the tremendous amount of energies. Contrastly, the produce of single-chirality/diameter SWCNT requires much less energy, purification and deposition using aqueous solution.



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Functional inkjet printing inks of graphene/metal oxide for gas sensors

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Sensors find widespread use in environmental monitoring, industrial processes, agriculture, smart buildings and increasingly, healthcare. For sensor development for toxic gases (e.g. NO, NO_2, NH_3), graphene and metal oxide nanohybrids offer promising performance in terms of sensitivity and selectivity at low temperatures. Among them, graphene/iron oxide (α-Fe_2O_3) is particularly interesting for NO_2 sensor development. Exploiting graphene/α-Fe_2O_3 *via* scalable manufacturing such as inkjet printing opens up the opportunity for economic, scalable device fabrication [1]. Current inks of graphene derivatives and hybrids (and indeed 2d materials in general), however, do not support controlled material patterning for reproducible manufacturing, or require the use of ink binders that can significantly compromise device performance.

Here we present a binder-free ink formulation to deliver controllable, spatially uniform inkjet printing of graphene/α-Fe_2O_3 for large-scale sensor fabrication. The graphene/α-Fe_2O_3 is synthesised through hydrothermal reaction of iron chloride with either graphene oxide or graphene, followed by washing and redispersing in a mixed solvent carrier for ink formulation. The ink composition is balanced with optimal fluidic properties and drying dynamics for precise droplet placement and ideal ink-substrate interaction. We show the selection mechanism of the solvents differing in evaporation rates influences the Marangoni flows to suppress the coffee ring effect. The formulated ink allows excellent controllability over the printed patterns and print-to-print consistency, potentially enabling scalable device fabrication. Using these inks, we demonstrate inkjet-printed sensor arrays with device-to-device consistent sensing performance, offering the promise for economic, scalable sensor manufacturing.

Beyond graphene/α-Fe_2O_3, we show that this universal ink formulation strategy applies to a range of other 2d materials that could be exploited for photonic and optoelectronic devices [2, 3].

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Continuous Fabrication of Meter-Scale Single-Wall Carbon Nanotube Films and Their Use in Flexible and Transparent Integrated Circuits

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Single-wall carbon nanotube (SWCNT) thin films are a promising material for use in flexible, transparent and wearable electronics. However, the area of SWCNT films fabricated in academic laboratories is usually limited to a square centimeter scale. The direct production of large-size high-quality SWCNT thin films by an efficient and scalable process remains a big challenge for their practical application in electronics.[1,2] For the first time, we have developed a continuous growth, deposition and transfer technique for the fabrication of high-quality and large-area SWCNT thin films. To the best of our knowledge, the SWCNT thin films obtained exhibit top-level optoelectrical performance, and more importantly, the geometrical dimension in meter-scale of our films is about two orders of magnitude larger than previous reports. Using these SWCNT thin films, high flexible and transparent all-CNT TFTs and ICs including 101-stage ring oscillators have been constructed and show excellent performance.

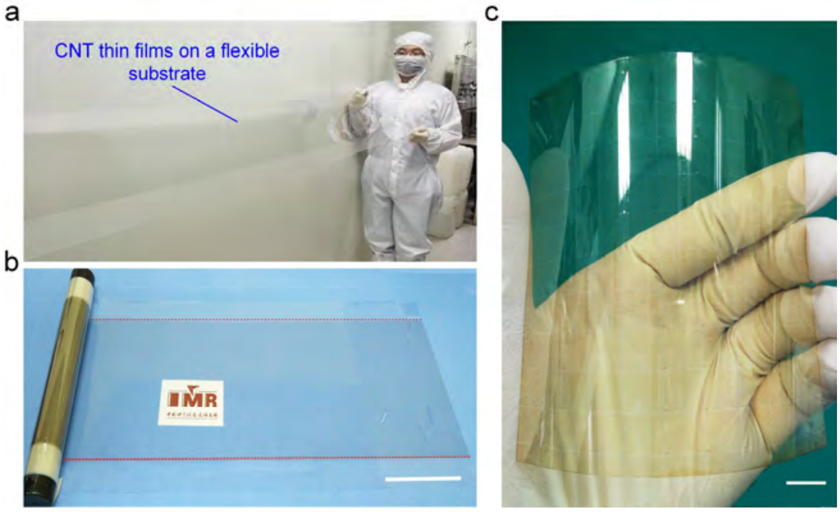

Fig.1 (a) A single-wall carbon nanotube (CNT) thin film on a flexible PET substrate with a length of more than 2 m. (b) A roll of uniform SWCNT thin film on the PET substrate (scale bar, 0.1 m). (c) Photograph of all-CNT thin film transistors and integrated circuits fabricated on a flexible PEN substrate with a size of 100 × 100 mm^2 (scale bar, 10 mm).

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Reduced Graphene Oxide: from Scale-up Preparation to Supercapacitor & Functional Applications

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With natural graphite as precursor, Hummers oxidation-thermal reduction is becoming a primary strategy for scale-up graphene powder materials. Due to the special two dimensional nano-structure, it is a big challenge for the large scale production of graphene material, with controllable quality and bunch stability, by a continuous, safe and green process. Moreover, it is quite urgent to find the “killer” applications of graphene, so as to promote the sustainable development of the industry. In our institution, we are engaged in building up the innovation chain for graphene, which bridge up materials, devices to applications. Firstly, based on our experiences in pilot scale production, we will discuss several key technological issues for the controllable and continuous preparation of graphene. Secondly, we will present our recent research results on the surface chemistry and nano-assembly of graphene towards electrochemical energy storage and functional composites. Finally, we will show the successful fabrication and demonstration of graphene boosted supercapacitor devices. No matter in electrodes or composites, graphene materials are proven to be high efficiency additives, to remarkably improve the performance even with low loading ratio.

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Application of Raman spectroscopy for monitoring the integration process of individual single-walled carbon nanotubes into field-effect transistor based sensors

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Raman spectroscopy is one of most powerful tools for the characterization of carbon nanostructures, including single-walled carbon nanotubes (SWCNTs), and for the detection of the impact of various physical and chemical treatments on their properties [1]. By evaluating nanotube Raman spectra, one can detect reversible and irreversible impacts of various device fabrication steps and help optimizing the processes with the goal to maintain the nanotube properties important for final device functionality.

In this work, Raman spectroscopy utilizing predominately a 532 nm laser with a power of 0.4 mW, focused with a 100x magnification objective (NA 0.8), was used to monitor the fabrication impact on nanotubes for devices with field-effect transistor (FET) architecture. The CNFET devices were built on individual single-walled carbon nanotubes (SWCNTs) serving simultaneously as the transistor channels and sensing elements. SWCNTs were synthesized on SiO_2/Si chips or oxidized SOI MEMS structures for devices using substrate-bound or suspended nanotubes. In both cases ferritin-based, Fe catalyst nanoparticles with pre-selected diameter distribution were used as nucleation centers for CVD synthesis of nanotubes in CH_4/H_2 at 850°C [2]. Raman spectroscopy was used to determine the localization and orientation of as grown nanotubes and for estimation of their diameter distribution and structural quality. Devices based on preselected SWCNTs were fabricated either by standard photo- or electron-beam lithography combined with metal lift-off fabrication of Cr/Au or Cr/Pd electrodes (substrate bounded CNTs) [3], or by ultra-clean mechanical transfer from dedicated growth MEMS substrates onto the final device structures with suspended nanotube [4]. In the latter case the top-clamping of nanotubes on prefabricated Cr/Pd electrodes [5] was performed by selective atomic layer deposition (ALD) of Pt 10-20 nm layers at 300°C. Passivation of the device electrodes (for gas sensors) was performed by selective Al_2O_3 ALD process at 300°C leaving the CNT channel unpassivated – which means active for gas sensing.

In the case of substrate-bound nanotubes, an application of the Raman monitoring of the CNFET fabrication lead to an optimized process flow producing devices with 8 times reduction of the variation of their electrical resistance and prolonging of the device life time, exceeding 90 days even for non-passivated contacts [6].

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Production of High-Purity Semiconducting Carbon Nanotubes by acid-assisted gel chromatography

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Single-wall carbon nanotubes (SWCNTs) possess one-dimensional structure with remarkable electrical and optical properties, and have great potential applications in the next-generation of electronic and optoelectronic devices [1]. For these applications, highly purified semiconducting SWCNTs (S-SWCNTs) are required. Industrial production of S-SWCNTs with gel chromatography have been successfully reported [2, 3], but the semiconductor purity is not enough for their application in the high-performance electronic devices. Here we report a new technique for the purification of high-purity S-SWCNTs with gel chromatography method, in which the H^+ ions are used to selectively oxidize metallic SWCNTs and thus enhance the difference in the interaction of metallic and semiconducting SWCNTs with gel. The results show that the H^+ ions can finely tune the interaction of carbon nanotubes with gel and effectively improve the semiconductor purity of the sorted S-SWCNTs. The present technique is effective for the industrial production of high-purity S-SWCNTs, which would accelerate the applications of carbon nanotubes in the electronics and optoelectronics.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51472264, 11634014, and 51361022) and the Key Research Program of Frontier Sciences, CAS, Grant No. QYZDB-SSW-SYS028.

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Mass production of multiple single-chirality species (*n, m*) by temperature tuning the interaction of compound surfactants with carbon nanotubes

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Industrial separation of single-chirality species (*n, m*) with identical properties is critical for their application in the fields of electronics, optoelectronic, and bio-imaging etc. In the past several years, gel chromatography method was developed to achieve the high-resolution structure separation of small-diameter (0.8-1.2 nm) [1-3] and large-diameter (1.2-1.6nm) SWCNTs [4]. Most recently, triple surfactants were employed to improve the separation efficiency of single-chirality species. With this technique, industrial-scale separation of several single-chirality species was achieved [5-7].However, for the application in optics and optoelectronics, more types of single-chirality S-SWCNTs are needed because of their different band-gaps. In this presentation, we systemically investigated the influence of temperature on the adsorbability of SWCNTs into gel in the compound surfactant system. The results show that temperature can finely tune the interaction of the co-surfactants of sodium dodecyl sulphate (SDS) and sodium cholate (SC) with carbon nanotubes, and multiple single-chirality species (*n, m*) were produced in industrial scale. Our present work could accelerate the application of carbon nanotubes in high-performance electronic and optoelectronic circuits.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51472264, 11634014) and the Key Research Program of Frontier Sciences, CAS, Grant No. QYZDB-SSW-SYS028.

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Batch production of 6-inch uniform monolayer MoS2 catalyzed by sodium in glass

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Monolayer transition metal dichalcogenides (TMDs) have become essential two-dimensional materials for their perspectives in engineering next-generation electronics. For related applications, the controlled growth of large-area uniform monolayer TMDs is crucial, while it remains challenging. Herein, we report the direct synthesis of 6-inch uniform monolayer molybdenum disulfide on the solid soda-lime glass, through a designed face-to-face metal precursor supply route in a facile chemical vapor deposition process. We find that the highly uniform monolayer film, with the composite domains possessing an edge length larger than 400 μm, can be achieved within a quite short time of 8 min. This highly efficient growth is proved to be facilitated by Na catalysts that homogenously distributed in glass, according to our experimental facts and density functional theory calculations. This work provides insights into the batch production of highly uniform TMD films on the functional glass substrate with the advantages of low cost, easily transferrable, and compatible with direct applications.

Low-dimensional quantum confined semiconductor for solar fuels production

PRESENTATION TYPE: Oral Presentation Preferred

AUTHORS (FIRST NAME, LAST NAME): Songmei Sun
INSTITUTIONS:
International Institute for Carbon-Neutral Energy Research, Kyushu University, Fukuoka, Japan.

ABSTRACT BODY:

Photocatalytic solar fuels production represents one of the most potential strategy for replacing the dying-up fossil feedstocks and dealing with the environmental problems caused by the combustion of fossil fuels. However, this technology has not been widely applied because of its low solar energy conversion efficiency which is usually limited by the microstructure and the electronic structure of the semiconductor photocatalysts. After more than 10 years studies on this area, we found well designed low-dimensional atomic scale materials have peculiar advantageous as high performance photocatalysts for N_2 or CO_2 reduction under ambient conditions. Here we systematically present a discussion in detail on the relationship between the crystal microstructure, the electronic structure and the photocatalytic performance which apparently influence the light response, charge carrier separation/migration, and reactants activation etc. The material is focused on atomic scale bismuth, tungsten, and molybdenum based semiconductor material. Their facile synthesis process will also be introduced.

Formation of nanocrystalline graphene on Germanium

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Graphitization of a polymer layer provides a convenient route to synthesize nanocrystalline graphene on dielectric surfaces. The transparent and conducting wafer scale material is of interest as membrane, coating, for generation and detection of light, or strain sensing [1,2]. In this work, we study the formation of nanocrystalline graphene on Germanium, a surface which promotes the CVD synthesis of monocrystalline graphene [3]. The surprising result that we obtained through graphitization is the formation of cavities in Germanium, over which nanocrystalline graphene is suspended. Depending on the crystallographic orientation of the Germanium surface, either trenches in (110)-Ge or pits in (111)-Ge are formed, and their dimensions depend on the graphitization temperature. By Raman spatial imaging, we can show that nanocrystalline graphene is formed across the entire wafer in spite of the cavity formation. Interestingly, the Raman intensity is suppressed when the material is supported by Germanium and is enhanced when the material is suspended. Through simulations, we can show that these effects are induced by the high refractive index of Germanium and by interferences of the light field depending on the spacing between graphene and Germanium. Using atomic force and scanning electron microscopy, we determined that ripples in the suspended material are induced by the mismatch of thermal expansion coefficients. Our results provide a new route to lithography-free fabrication of suspended membranes.

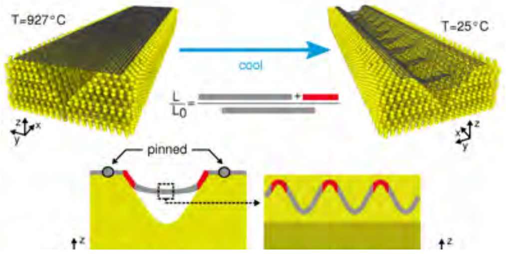

Fig.1 Formation of nanocrystalline graphene (NCG) in Germanium

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Novel rod to tube type spark discharge generator for the FC CVD growth of SWCNTs

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Abstract

Floating catalyst chemical vapor deposition (FCCVD) is one of the most widely used technique for CNT synthesis. The catalysts for CNT synthesis in FCCVD are strongly tied with the CNT yield, morphology, and chirality. However, the catalyst aerosol in conventional FCCVD, is made with the pyrolysis of sublimable organometallic compounds, e.g. Ferrocene. This conventional process of catalyst fabrication in FCCVD, not only limits the composition of the catalyst but also hinders to regulate the concentration and configuration of the catalyst. Here, we introduce a unique gas phase method of FCCVD catalyst fabrication, i.e spark discharge generation. Based on the physical vapor condensation process, this process can produce variety of highly pure metal or alloy nanoparticles with controllable number concentration and particle size distribution [1]. Specifically, the well-designed rod to tube type spark discharge generator (R-T SDG) which can produce highly time stable nanoparticles for long time under the small flow rate of carrier gas. We synthesized monometallic catalyst particles (Fe, Co, Ni, Cu) and bimetallic particles (Co-Fe, Co-Ni) from R-T SDG. The time stability and size distribution of the particles were studied by a scanning mobility particle sizer with an electrometer. Compared to other spark designs, R-T SDG can produce a more time stable number size distribution of the nanoparticles for 24 hours. The Fe, Co, Co-Ni nanoparticles were used as catalysts for SWCNT growth in vertical FCCVD reactor using ethylene as carbon source. These SWCNTs were deposited in gas phase on membrane filter to form CNT films which can be applied in high-performance transparent electrodes. This novel R-T SDG has great potential in academic and industrial fields of CNT synthesis.

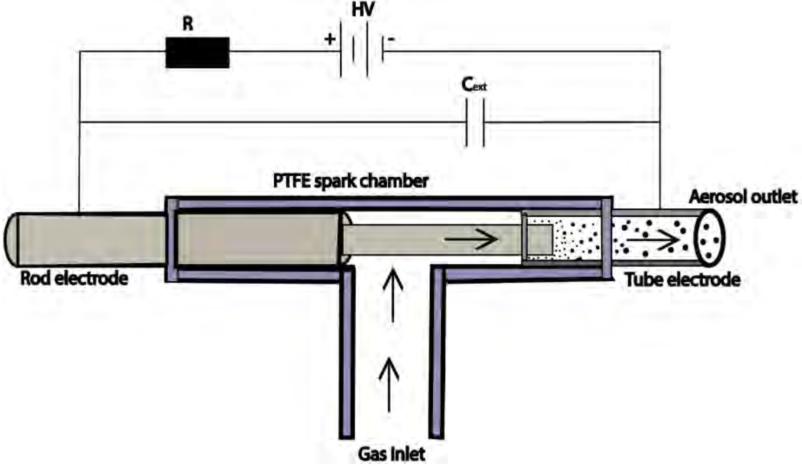

Fig. 1 The schematic of rod to tube type SDG for producing time stable distribution of monometallic and bimetallic nanoparticles for the FCCVD growth of SWCNTs.

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Light-stimulated Neuromorphic Electronic Devices Based on Printed Carbon Nanotube Thin Film Transistors

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Keywords:
Neuromorphic device, Printed electronics, Carbon nanotube,Thin film transistors

Abstract:

Printed thin film transistors (TFTs) are one of the most basic building blocks in printed electronics, which can be used to fabricate backplanes for displays, logic circuits, biologic and chemical sensors, artificial electronic skin and neuromorphic devices. Semiconducting single-walled carbon nanotubes (sc-SWCNTs) have been regarded as one of ideal semiconductor materials to construct high-performance printed TFTs due to high carrier mobility, solubility, and high chemical and physical stability.[1-5] In this work, we have developed a new light-stimulated neuromorphic device based on printed SWCNT TFTs. It can be seen from Figure 1a that the effective mobility and the on/off ratios of printed SWCNT TFTs can reach 68 $cm^2V^{-1}s^{-1}$ and 10^7, respectively. It is very interesting that the output currents of printed SWCNT TFTs are gradually increased under pulse light illumination shown in Figure 1b-d. The on/off current ratio can reach two or three orders with pulse light illumination, at the same time, the currents can keep constant after pulse light stimulation shown in Figure 1d. It indicates that these kinds of devices have the ability of learning and memory. The relative studies are still under way.

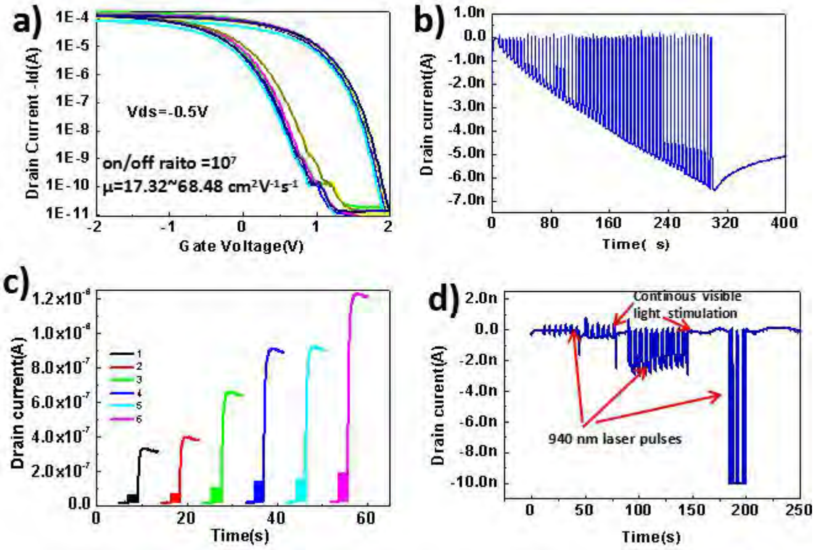

Figure 1 a） transfer curves of CNT TFTs (Vds=-0.5V), b-d) electrical properties of printed TFTs under pulse light illumination. b) visible light with pulse frequency 0.2 Hz, c) visible light with pulse frequency of 50 Hz, and d) 940 nm laser with frequency of 0.2 Hz.

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Microtomed membranes of carbon nanotube ion channels for high-yield activation of the pores and facile exchange of analytes

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An experimental platform was developed for the fabrication and recording of carbon nanotube ion channels with yield of 90%. A centimeter-long and horizontally aligned array of carbon nanotubes with diameter of ~ 4 nm was embedded into an epoxy matrix and microtomed with 10 μm thickness, which yielded hundreds of membranes containing nearly identical carbon nanotube channels. The membrane was glued at the end of a glass capillary, and the ion current through the nanotubes was recorded using a patch-clamp amplifier. Repeated measurements of the IV curves gradually increased the pore conductance, thereby activating the pores in 90% of the membranes. Observed from 28% of the activated membranes were stochastic pore-blocking events caused by translocation of cations through the interior of nanotubes. Via the repeated voltage-ramping protocol, threshold voltages for the ionic transport were determined to be -90 mV for K^+, -30 mV for Na^+, and -10 mV for Li^+. Analyzing the blocking events gave mobility of 7.6×10^{-8} m^2/Vs, 3.6×10^{-8} m^2/Vs, and $5.0 \times 10^{-9} m^2/Vs$ for K^+, Na^+, and Li^+, respectively. In the capillary platform, the fluidic exchange is as simple as dipping the capillary into solution of another analyte. Our approach demonstrated with carbon nanotubes can be potentially applied to testing a broad range of solid-state nanopores, including nanopores of planar nanostructures.

Direct conformation detection of cocaine aptamer based on graphene electrodes

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Since cocaine abuse is regarded as a major global challenge, the detection of traces of cocaine is of great significance in the recognition of addicts, prohibiting smuggling drug into country. Aptamers are oligonucleotides (DNAs or RNAs) that specifically bind to a large range of molecular targets with and high affinity, including small molecules、metal ions、proteins and even the whole cells. The high affinity and specificity, low cost and reliability of the aptamer makes it a great candidate for biomolecular recognition.

The cocaine aptamer was first created by Stojanovic[1] for developing an anti-cocaine aptamer sensor. Since then, many works have focused on developing cocaine aptamer sensors with lower detection limit and higher selectivity based on fluorescent[2], electrochemical[3] and FET[4] signals. However, these methods lack the exploration of intrinsic properties of cocaine aptamer, and the functional moieties and the exact conformational changes are blurry during the process of binding and therefore limit the amelioration of the structure of cocaine aptamer and the improvement of the performance of cocaine aptamer sensors. Uptill now, only a few works have studied the conformational changes of cocaine aptamers by NMR[5], 2D PELDOR[6], CD spectroscopy[7] et al. Whereas, these techniques could not do real-time detection and the results were the ensemble average of a great many of molecules which would conceal the details of a single molecule conformational changes.

Since our group has a great platform for single-molecule dynamic detection, we combined the aptamer conformational changes with ultra-high sensitivity of electrical signals. We designed a partially complementary double stranded DNA with cocaine aptamer sequence in one strand and immobilized it with graphene electrode by amide linkage. The conformational changes of the aptamer would lead to the varieties of currents. By means of the analysis of current data, we could further decide which kind of conformational changes happens before and after cocaine binding, which would provide robust and precise evidence for real time conformational knowledge of cocaine aptamer.

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A reversible single-molecule switch with stochastic and controllable switching modes at room temperature

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For almost all electronic devices, switches are the necessary components and vital functional units. To meet the demand for device miniaturization and performance improvement, the fabrication of reliable molecular switches has been intensively studied for two decades[1-3]. There are mainly two kinds of conductance switching modes in single–molecule switches: stochastic and controllable switching. The stochastic switching, summarized in some classical reviews[4-5] , is often related to temperature, which is usually caused by external bias electric field or intrinsic vibration effect. As for the controllable switching, we mainly focused on the molecular photoswitch with a core photochromic center, as a kind of conformation-induced switches, which can effectively tune the molecular conduction by means of changing the light radiation condition. In the last twenty years, the key challenge researchers [6-8] focused on is to attain suitable interaction couplings since the individual photochromic molecule in the junction is sensitive to the electrode-molecule contact interface. Until 2016, Jia *et al.* overcame this challenge and solved the interaction couplings through molecular engineering, enabling the construction of fully reversible and stable single diarylethene molecular switches[9]. And the stochastic switching was also oberseved in their experiment at 180 K, which encouraged us to further study the phenomena of two kinds of switching modes.

Based on our previous work, we designed the dithienylethene-based metal complex (named as M-DTE), a photochromic diarylethene (DAE) derivatives and fabricated the graphene-M-DTE-graphene junctions using covalent-bond linkage. The conformational changes of the M-DTE induced by different light would lead to the varieties of currents. Interestingly, we realized the reversible controllable and stochastic photoswitching at the same time at room temperature. By means of the analysis of *I-V* and *I-t* characteristics, we obtained there is an obviously difference in molecular conductivity when the molecular junction was exposed to different light radiation. The high conduction state under UV radiation belonged to the M-DTE molecule in closed form and the low one belonged to that in open form. As for the controllable switching, we succeed in constructing the fully reversible single M-DTE molecular switches working at the room temperature, with high ON/OFF ratio up to 600 (the average is ~100) and stability (12 devices over 100 cycles). As for the stochastic switching, we obtained reproducible multiple states of the same device with the closed form of M-DTE in the UV and dark, which is most likely due to the stereoelectronic effect like that the rotation of single Sigma bond induces different conformation and thus different conductance, which we have observed in our group's previous work[9-10].

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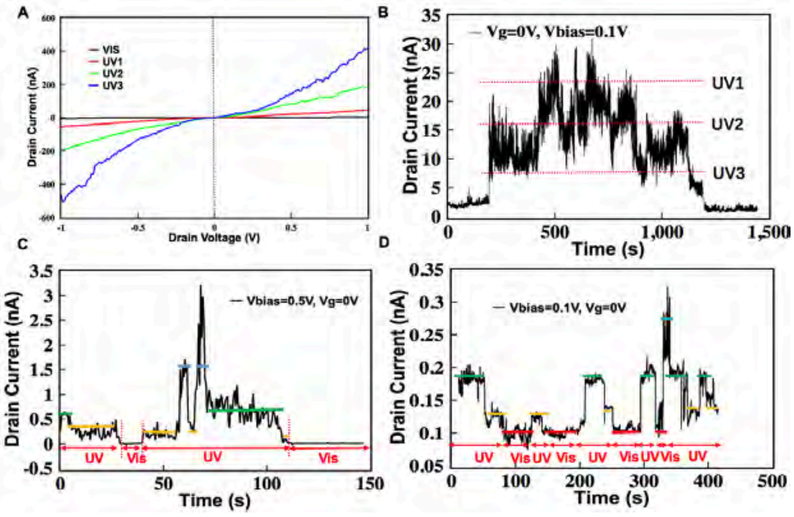

Fig. 1 Reversible photoswitching of graphene-dithienylethene-based ruthenium complex-graphene junctions. **(A)** *I-V* characteristics of individual M-DTE molecule in open (black line) and closed (red, green and bule line) form at gate voltage Vg = 0 V, upon exposure to visible (Vis) and ultraviolet (UV) radiation, respectively. **(B)** Real-time measurement of the current through a M-DTE molecule that stochastically switches between three main molecular states in closed form under ultraviolet (UV) radiation. **(C)** **/(D)** Real-time measurement of the current through a M-DTE molecule that reversibly switches between the closed and open forms under ultraviolet (UV) and visible (Vis) radiation, at drain current V_{bias} = 0.5 V and V_{bias} = 0.1 V, respectively.

Carbon nanotube directed 3D porous Li_2FeSiO_4 composite for lithium batteries

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Lithium iron silicate (Li_2FeSiO_4) is capable of affording a much higher capacity than conventional cathodes, thus holding great promise for high-energy battery applications. However, such a high capacity has often been hampered by poor reaction activity, due to extremely low electronic and ionic conductivity of silicates [1-4]. Here, we report on a rational engineering strategy towards a highly active Li_2FeSiO_4 by designing a carbon nanotube (CNT) directed three-dimensional (3D) porous Li_2FeSiO_4 composite [5]. As the CNT framework enables rapid electron transport and the rich pores allow efficient electrolyte penetration, this unique 3D Li_2FeSiO_4 and CNT composite affords a high capacity of 214 mAh g^{-1} and retains 96% of this value over 40 cycles, outstripping many previously reported Li_2FeSiO_4 materials. Kinetic analysis reveals a high Li^+ diffusivity, due to the coupling of migration of electrons and ions. This research highlights the potential of engineering 3D porous structure to construct highly efficient electrodes for battery applications.

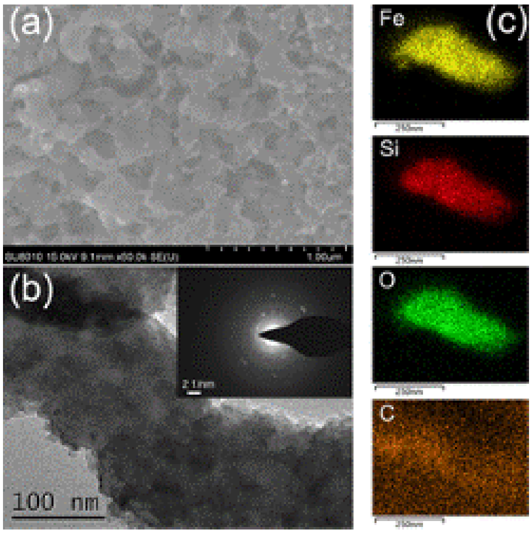

Fig. 1 (a) SEM and (b) TEM images of 3D Li_2FeSiO_4-CNT. Inset in (b) shows corresponding selected-area electron diffraction. (c) Elemental mapping of Fe, Si, O, and C by TEM-EDS.

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Reduced graphene oxide decorated with $Bi_2O_{2.33}$ nanodots for lithium storage

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Bismuth oxides are important anode materials for lithium-ion battery due to their ability to electrochemically react and alloy with Li. However, this high Li-storage capability is hampered by the poor electrochemical cyclability and rate capability [1-3]. Here, we reported a hybrid structure consisting of ultrafine $Bi_2O_{2.33}$ nanodots anchored on Graphene oxide (rGO) nanosheets (denoted as $Bi_2O_{2.33}$/rGO) [4]. Graphene oxide possesses good conductivity and can anchor on active materials owing to rich functional groups [5]. $Bi_2O_{2.33}$/rGO exhibits a high reversible capacity of 680 mAh g^{-1} at 0.2 C and superior cycling durability of 346 mAh g^{-1} over 600 cycles at 10 C, outstripping many Bi-based materials previously reported. The superior stable electrochemical performance indicates that $Bi_2O_{2.33}$/rGO may introduce new possibilities for the development of stable and robust metal-oxide electrodes.

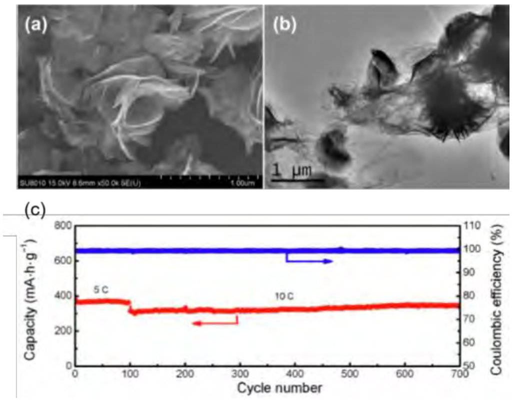

Fig.1 (a) SEM and (b) TEM images and (c) Long-term cyclability of the $Bi_2O_{2.33}$/rGO hybrid.

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Modeling Interlayer Interactions in Layered Materials

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In the past two decades low dimensional layered nano-materials have been at the forefront of scientific research. Owing to a variety of novel outstanding physical properties graphene, hexagonal boron nitride (*h*-BN), and transition metal dichalcogenides (TMDC) hold great promise for becoming key components in the next generation of advanced electronics, strong lightweight materials, and friction reducing technologies. The interlayer interactions in these materials play a central role in shaping their mechanical and electronic properties. In my lecture, I will present a new methodology for modeling these interactions using specially tailored classical force-fields. The computational capabilities of the developed methodology will be demonstrated via several applications addressing the structural, mechanical, and tribological properties of layered materials including the super-structure of the graphene/*h*-BN heterojunction, which has been shown to alter graphene's electronic properties, and the occurrence of circumferential faceting in double-walled nanotubes. Then I will turn to describe interlayer electrical conductance across a twisted graphene interface, where I will show the strong correlation between interlayer structural commensurability and cross-layer electrical transport.

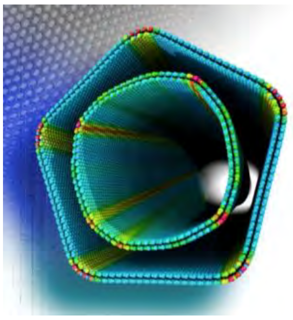

Fig. 1: Facetted double-walled Boron-Nitride nanotubes simulated using the developed ILP

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Machine Learning for Atomistic Simulations of Carbon Nanomaterials

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Today's empirical force fields (FFs) such as Tersoff, Brenner, ReaxFF, etc. which are used for simulating carbon nanomaterials employ fixed mathematical expressions to describe the interatomic potential between atoms. These mathematical expressions are ”user defined” meaning that they are derived from theory or purely empirical. Parameters for the mathematical expressions are then fitted so that the FFs agrees with the results from higher accuracy calculations such as density functional theory (DFT) or experimental data. Having a fixed set of mathematical expressions is clearly a limitation, since there is no certainty that the chosen expressions correctly model the underlying quantum mechanics for a system of interest. Therefore, the next logical step is to get rid of having fixed mathematical expressions and allow for the description of interatomic potentials to be derived automatically. This can be done using machine learning to create neural network force fields (NNFFs) that can describe interatomic potentials with DFT levels of accuracy. Until now, most published NNFFs have been developed for bulk systems such as metals and oxides [1]. Here we investigate the possibility of creating NNFFs for carbon nanomaterials using the Atomistic Machine-learning Package [2] (AMP) with training data generated from DFT calculations. The ultimate goal is to develop NNFFs capable of performing atomistic simulations of carbon nanomaterials with DFT levels of accuracy in energies and forces, but with speeds similar to today's empirical force fields. This would allow researchers to model carbon nanomaterial processes (such as growth) at timescales and accuracies that are currently not possible.

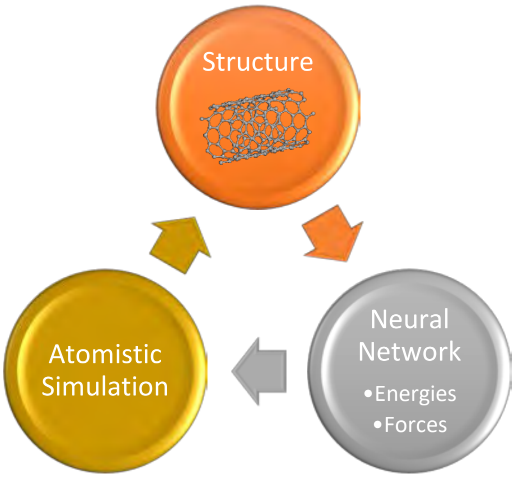

Fig.1 Schematic use of NNFFs. A representation of the structure is feed into a neural network which determines energies and forces, these are then used by an atomistic simulation software to generate a new structure.

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Growth modes and chiral selectivity of Single-Walled Carbon Nanotubes

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Since 25 years, significant progress has been achieved in the controlled synthesis of Single Walled Carbon Nanotubes (SWNTs), but we are still facing difficult issues concerning the yield and selectivity of their synthesis by Chemical Vapor Deposition. In such a complex problem, real understanding only results from coupling different experimental techniques, from chemical engineering approaches to atomic scale investigations by e.g. Transmission Electron Microscopy, with modelling and computer simulations. In this context, we developed an original atomistic metal-carbon interaction model, based on a tight binding approximation, coupled with Monte Carlo simulations in canonical and Grand Canonical ensembles[1]. In close collaboration with experimental groups, we analyzed different aspects of SWNT growth.

We first focus on a simple catalyst (Ni) and investigate tube nucleation[2] and the state of the catalyst in presence of carbon[3]. Sustainable tube synthesis requires a dewetting of the catalyst nanoparticle, along with the growth of the carbon walls, to avoid its encapsulation and deactivation. We show that the properties of the Ni/sp^2 carbon interfaces are driven by the carbon fraction dissolved in the NP[4] that depends on the CVD process parameters, in particular on the choice of the carbon bearing precursor. These different carbon feeding regimes give rise to different growth modes[5], corresponding to different structures of the NP/nanotube contact areas. For carbon saturated nanoparticles[7], the interface is reduced to a line contact, in which case a near armchair selectivity is sometimes reported, while lower dissolved carbon fractions lead to a lateral surface contact between the tube and the catalyst NP[8,9].

We then develop a statistical thermodynamics model, valid in the case of perpendicular growth, that enables to relate the stable (n,m) tube structure, to the tube/catalyst interfacial energies for zigzag (E_{int}^{Z}) and armchair $\left(E_{int}^{A}\right)$ edges and temperature. This model shows that, at low temperature, only zigzag or armchair tubes should be stable. Chiral tubes become stable at higher temperature because of the configurational entropy of the tube edge, that is indeed the key element of the model. This enables to produce chiral stability maps or "chirality phase diagrams". These computer simulation and modelling results will be discussed, in relation with experiments.

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Symmetry breaking at the interface between (6, 6) SWNTs and Pt (111) surface and the fast growth of armchair SWNTs on Pt (111) surface

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The (6, 6) SWNTs have been synthesized on solid Pt (1 1 1) surface in high purity [1], which seems against the theoretical analysis that the fast growth of chiral SWNTs on a flat solid catalyst surface is prohibited due to the large barrier of carbon addition[2]. Here, we present a theoretical study of the SWNT-metal interface, in which the mirror symmetry of interface between (6, 6) SWNT and the Pt (111) surface is found broken. The lowered symmetry allows the relatively faster addition of the carbon atoms into the SWNT wall at the interface. Besides, we predict that, among the solid catalysts, the Pd (111) surface is the best candidate for the fast growth of the (6, 6) SWNT. This study opens a route for the synthesis of conducting SWNTs for many applications, such as the high performance transparent electrodes.

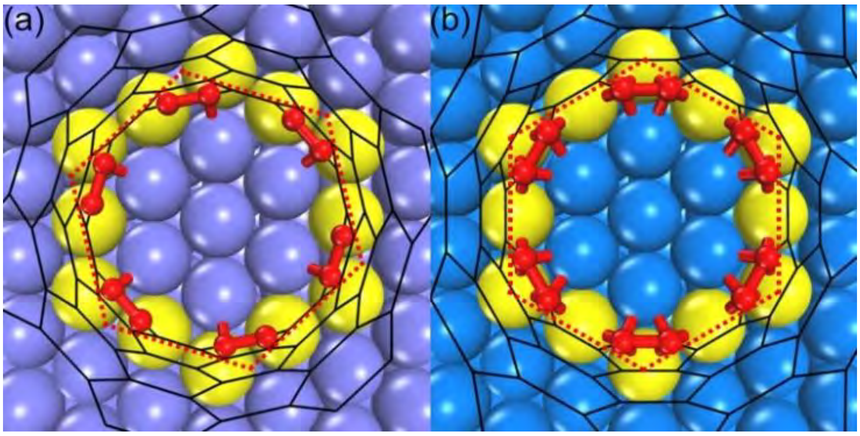

Fig.1 The optimized structures of (6, 6) SWNT on Pt (1 1 1) (a) and Co (1 1 1) surfaces, implying the symmetry breaking of (6, 6) SWNT on Pt (1 1 1) surface.

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CCTN18

Strain and Curvature Engineering of Geometries and Electronic Properties of Nanotubes and Atomic-Layer Materials

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Electronic properties of carbon nanotubes (CNTs) are known to depend not only on the network topology (chirality and formal radius) [1,2] but also on the detailed values of geometrical parameters [3,4]. The latter gives rise to the possibilities of strain engineering of their electronic properties. In this talk we first report the geometry-dependent electronic properties of BN nanotubes [5] and transition-metal-dichalcogenide (TMD) nanotubes [6] as well as those of hexagonal BN (h-BN) sheet and TMD sheets, and discuss the possibilities of strain and curvature engineering of these materials. In the case of h-BN atomic layers, even the ionization energies of substitutional impurities can be modified by strain and the curvature, showing that h-BN atomic-layer materials can be utilized as semiconductor atomic layers for nanoelectronics in the future. Finally, we revisit the strain-induced plastic deformation of CNTs which has been discussed theoretically for the case of axial stress by applying the dislocation theory [7]. We extend the dislocation-theory analysis to the general case with combined axial stress and torsional stress applied to CNTs in order to achieve the comprehensive understanding of the plastic response of CNTs [8]. This analysis shows that CNTs can show a variety of plastic deformations depending on the details of the combined stress, and opens the way to manipulating the CNT geometries and consequently their electronic transport properties via external strain.

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Theoretical Design of Low-dimensional Magnetic Materials

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Abstract: Since the exfoliation of graphene, the magnetic orderings in two-dimensional (2D) materials have been intensively searched for the great potentials in nanostructured spintronics or valleytronics applications. By density functional theory based first-principles calculations, we have predicted that substitutional doping of Co atoms at the edge of the most stable configuration of zigzag WSe_2 nanoribbons can induce long-range ferromagnetic ordering and robust half-metallicity that enables spin-selected transport along the nanoribbon edges.[1] The half-metallicity was also found quite robust against large size, low doing density, and large tensile strain. Further, we have investigated a series of transition metal thiophosphate monolayers and predicted their stable long-range ferromagnetic orderings with room-temperature T_C.[2] Integrated with 2D transition metal dichalcogenides (TMDCs) as heterostructures, they allow spin-valley coupled carrier injection from transition metal thiophosphate into TMDCs.

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Structures and Mechanisms Responsible for the Chemical Toxicities of Nanocarbons by Computations

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Atomistic-level knowledge on the structures and mechanisms responsible for their toxicities are the base for the safe bio-applications and rational design of nanomaterials, which is, however, one of the challenges of the bio-applications of sp^2 carbon nanomaterials. Carbon nanomaterials, which include fullerenes, carbon nanotubes, and graphene, are composed primarily by sp^2 carbon atoms and can also be referred to as sp^2 nanocarbons. Despite their intriguing structural and physical properties, chemical modifications are usually necessary before they can be practically applied to bio-systems. Owing to their unique sp^2-network structures, chemical addition reactions are among the few approaches that are efficient to chemically functionalize sp^2 nanocarbons. However, multiple addition reactions occurring on these carbon materials are hard to control. The resulted derivatives of nanocarbons usually have amorphous structures, which greatly hinder the subsequent characterizations of their bio-active structures and mechanisms of toxicities. Computational studies have demonstrated their power in revealing the functional structures and mechanisms for energy and environmental nanomaterials. In this presentation, we will review the principles obtained by computations that govern the stable product structures of multiple addition reactions of sp^2 nanocarbons [1-3], and further discuss the mechanisms responsible for the chemical toxicity of some of the sp^2 nanocarbons [4,5].

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Application of Up-Conversion Luminescence of Carbon Nanotubes to Deep-Tissue Optical Bioimaging

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Individually dispersed semiconducting single-walled carbon nanotubes (SWNTs) show robust photoluminescence in the near infrared wavelength range more than ~ 1000 nm [1]. Since the near infrared light readily penetrates into highly scattering media such as biological tissues, SWNTs have been considered as promising luminescent probes for deep-tissue bioimaging [2]. However, detection of luminescence at longer wavelengths than ~1100 nm, which is necessary to avoid autofluorescence from the biological tissues, can be hardly achieved using standard Si-based image sensors such as CMOS and CCD. Recently, efficient up-conversion luminescence of SWNTs has been discovered [3]. The up-conversion luminescence enables SWNTs excited at wavelengths longer than ~1050-1200 nm to emit luminescence shorter than 1000 nm in which Si-based detectors have finite sensitivity [3,4]. Thus, the availability of the up-conversion luminescence may enhance the usefulness of SWNTs as luminescent probes in their bioimaging applications. We will report our recent progresses in the autofluorescence-free whole-body imaging of living mice using up-conversion luminescence of SWNTs. Application of the up-conversion luminescence phenomena of SWNTs for near-infrared optical thermometry in deep tissue will also be discussed.

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Distribution of Single-Walled Carbon Nanotubes in Sub-Tissue Levels in Brown Adipose Tissue

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Near-infrared (NIR) photoluminescent single-walled carbon nanotubes (CNTs) are effective bio-imaging agents because their fluorescence wavelengths are above 1000 nm, where the low biological auto fluorescence, high light transmittance, and low light scattering enable the clear *in vivo* observation. It is reportedly shown that CNTs coated with phospholipid polyethylene glycol (PLPEG) provides cleat vascular images for mice [1, 2]. We previously showed that CNTs can image brown adipose tissue (BAT) in mice when the CNTs are coated with an amphiphilic and biocompatible polymer, poly(2-methacryloyloxyethyl phosphoryl choline-co-n-butyl methacrylate; PMB) [3]. In contrast with PLPEG-CNTs, PMB-CNTs quickly accumulated in BAT after the intravenous injection, being not suitable for the vascular observation. To reveal the mechanism of PMB-CNTs accumulation in BAT, NIR fluorescent microscopy was useful. PMB-CNTs were localized in BAT capillary endothelial cells, from which it is estimated that, PMB-CNTs absorb apolipoproteins in the plasma and selectively accumulate on capillary endothelial cells of BAT that express apolipoprotein receptors [3].

BAT of a normal mouse is not imaged by PLPEG-CNTs, however, we have recently found that BAT became clearly visible with PLPEG-CNT depending on the mouse body condition. The accumulation sites of PLPEG-CNTs in BAT has been studied through the histological observation applying the NIR fluorescent microscopy. The results suggested a possible mechanism, which will be discussed in the presentation.

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Polymer Functionalized Nanodiamond Supraparticles Enhance Drug Efficacy for Tumor Cells- *in vitro* and *in vivo* Evidence

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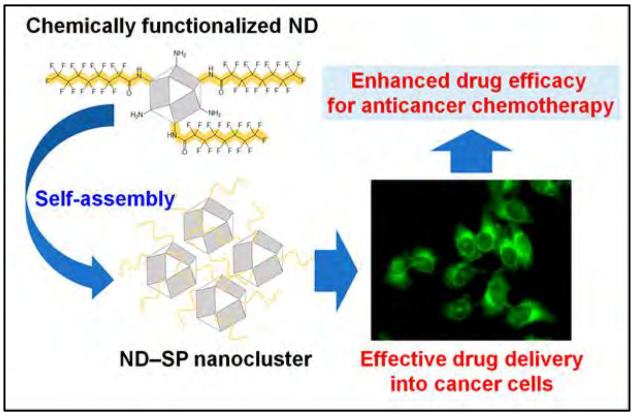
Carbon-based nanomedicines hold great potential for drug delivery to achieve more effective and safer cancer treatment due to their many technological advantages such as facile modification, high carrier capacity, high chemical stability, and feasibility of incorporating both hydrophilic and hydrophobic substances. Herein, we developed a new type of Nanodiamond supraparticles (ND-SPs) as a drug delivery carrier for enhanced cancer therapy. The ND-based SPs spontaneously assembled under physiological conditions by simple surface functionalization with perfluorooctanoic acid. We described chemically functionalized NDs that can be easily transformed into SP structures with low toxicity and high capacity for transmembrane transport that have a suitable size for the EPR effect even after loading with drug molecules. Molecular analyses revealed U2OS cancer cells treated with Camptothecin (CPT)-loaded ND-SPs (CPT@ND-SPs) showed dose-depended growth arrest and apoptosis that was much stronger as compare with free CPT treatment. *In vivo* subcutaneous xenograft assays in nude mice demonstrated CPT@ND-SPs could accumulate in tumor section and inhibit tumor growth effectively. Of note, no inflammatory response and systemic side effects were observed in CPT@ND-SPs injected mice, suggesting these ND−SPs could be a promising drug delivery system for cancer therapy.



Scheme of ND-SP systhesis and application for enhanced cancer treatment

Dynamical Changes in Toxicity and Quantity of CNTs after Uptake by Macrophage

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With the increase of CNT-based products appearing into commerce, the public concern regarding possible toxicities has attracted many attentions. When CNTs entered into living body, they would be mainly entrapped and partially biodegradated by macrophages. Therefore, investigation of the intercellular quantity change of CNTs and the resulted cytotoxicity changes after uptake by macrophage would be helpful to fully understand their toxicity. In this study, we have measured the macrophage uptake of CNTs as well as their quantity changes in 1-7 days by using an optical absorption method [1] and Raman spectra of CNTs in the cell lysates. Our results indicated that the quantity of CNTs inside of macrophage decreased about 20-50 % of CNTs in macrophage cells of RAW 264.7 as well as the primary cells within 3 days, and almost no decrease by the longer period incubation. In addition, we have also investigated the dynamic toxicity changes during CNT degradation in macrophages. Data showed the cell viability, cell total protein amount and caspase 3/7 amount basically not changed during the degradation. However, the amount of reactive oxygen species (ROS) generated by macrophage after CNT-uptake. We have found that the amount of ROS dynamically decreased with time after CNTs uptake and only a few ROS detected after 3 days. The tendency of CNT-decrease inside of macrophages was consisted with that of ROS amount reduction. These results not only suggested that CNTs were degraded by ROS generated in macrophages but also indicated that the residues of un-degraded CNTs persisted in macrophages without toxicity.

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Bio-Functionalized Carbon Nanotube Nanohybrids: from Single-Molecule Investigations to Multiplexed Sensing

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We present a universal approach for the generation of multifunctional nanomaterials that employ molecular building blocks assembled on single-walled carbon nanotubes (SWCNTs) electrodes. We will demonstrate single-molecule control in the formation of both static and dynamic nanohybrids via the in-solution assembly of classes of biological materials to CNTs.

We recently demonstrated the ability to form molecular transport junctions directly in solution linking metallic SWCNTs with different conjugated molecular wires, highlighting the potential of an all-carbon based approach for solution-processable molecular electronics.[1] Building on this, we will report here the controlled assembly of both static and stimuli-responsive single-molecule heterostructures where DNA linkers of differing lengths were used as molecular rulers to control the distance, and hence tune the energy/charge transfer between bio-functionalized single Quantum Dots (QDs) univocally linked at the terminal ends of individual SWCNTs (Figure 1a). One-to-one SWCNT-QD heterostructures were obtained with tunable electronic coupling, as evidenced via photophysical investigations at the single nanohybrid level. Moreover, stimuli-responsive SWCNT-DNA-QD hybrids were assembled using a G-quadruplex DNA linker; the distance between the SWCNT and QD was then dynamically modulated by the introduction and removal of potassium ions (K^+) (Figure 1b);[2] the system was further found to be sensitive to K^+ concentrations from 1pM to 25mM.

Additionally, we will show report the site-specific coupling of single proteins to individual carbon nanotubes in solution and with single-molecule control. Green Fluorescent Protein (GFP) was engineered bound to CNT ends in different configurations: in close proximity or at longer distances from the GFP's functional center. Investigations at the single-protein level confirmed the importance of bioengineering optimal protein attachment sites to achieve direct protein−nanotube communication and bridging, demonstrating the selective electrical addressability of proteins via the use of carbon nanoelectrodes (Figure 1c).[3]

Finally, we will report the fabrication of solution processable nanoscale biosensors with multi-sensing capability, based on single walled carbon nanotubes (SWCNTs). Distinct CNTs were functionalized with different aptamers and then immobilised from solution onto distinct pre-patterned electrodes on the same chip. Multiplexed detection of three different biomarkers was successfully performed, and real-time detection was achieved in serum down to physiologically relevant concentrations.[4]

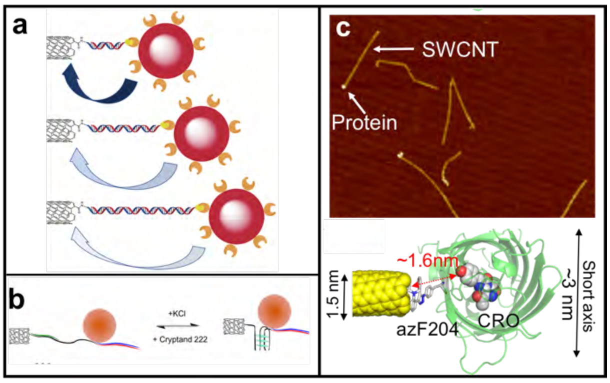

Fig.1 Examples of the different CNT-based nanohybrids

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A One-Pot Fabrication of Chlorin e6-loaded MoS$_2$ Nanosheet and Its Application to Photothermal and Photodynamic Combination Cancer Treatment

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Cancer phototherapy (PT) has attracted extensive interest in recent years due to the advantages over the traditional cancer therapeutic approaches such as surgery, radiotherapy, and chemotherapy, in terms of side-effects and damages to healthy tissues. PT, including photodynamic therapy (PDT) and photothermal therapy (PTT), is a non-invasive and region-specific therapy activated solely by light irradiation, thus offering targeted treatment of cancer with minimized destruction to normal organs.

We have been developing an efficient and scalable method to produce 2D nanosheets from the bulk materials by use of exfoliant through wet bath-sonication or dry ball-milling [1,2]. In this context, we found a very efficient method for fabricating graphene-chlorine e6 (G-Ce6) composite with high Ce6 loading ratio through liquid phase exfoliation [3]. The G-Ce6 composite exhibited much higher (7-75 times higher) phototherapeutic efficacy to kill cancer cells than that of other nanomaterial-Ce6 composites. However, the composite has problem in its stability in cell culture medium, though it was stable in phosphate-buffered saline (PBS).

In this study, we prepare Ce6 loaded-MoS$_2$ (MoS$_2$-Ce6) in a similar process to that of G-Ce6 [3]. After bath-sonication and centrifugation of the mixture of bulk MoS$_2$ and Ce6 in water, the nanocomposite from the supernatant, composed of a few layer MoS$_2$ and Ce6, exhibited good dispersibility and stability in cell culture medium. The loading capacity of Ce6 in MoS$_2$-Ce6 is 121 wt%, which is lower than G-Ce6 (160 wt%) mainly because of the large difference in their atomic weights of C, Mo and S. Then, we carried out cell experiments with or without light irradiation at 660 nm to evaluate cytotoxicity of MoS$_2$-Ce6. The nanocomposite did not show any cytotoxicity up to 0.20 μg mL^{-1} of Ce6 concentration without light irradiation. Under irradiation of light, however, more than 95% of the cancer cells were killed at Ce6 concentration larger than 0.05 μg mL^{-1} (Fig. 1). This efficiency is higher than that of G-Ce6 and other nanocarriers loading photosnesitizer.

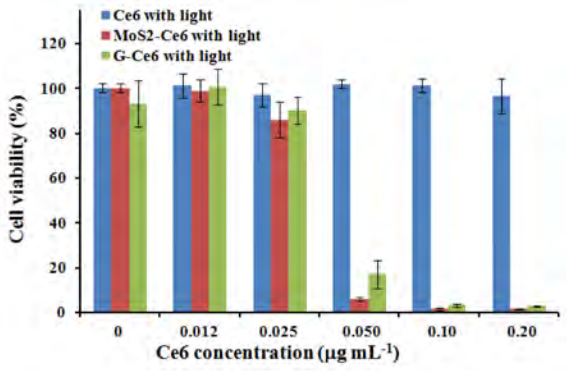

Fig. 1 Cell viability for HeLa cells incubated with Ce6 (left), MoS$_2$-Ce6 (center) and G-Ce6 (right) at different concentrations with irradiation of a 660 nm light.

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Customizing biodegradable CNT-coated therapeutic carriers

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Carbon nanotubes (CNT) are incredible materials for many bionanotechnological and biomedical applications. From the biological point of view (i) their surface reactivity, (ii) their morphology, and (iii) their biopersistence are critical and unique properties to be exploited. CNTs can adsorb ca. 1/3 of their mass of proteins as part of their biocorona[1], and this fact makes CNTs highly customizable for many different applications in biotechnology. On the other hand, their shape and dimensions allow CNT endo-lysosomal escape and, inside the cellular cytoplasm, intermingling with the intracellular cytoskeletal polymers[2,3] and interference with many biomechanical cellular mechanisms such as cell migration[4–6] and cell division[2,7,8]. Unfortunately, as for any nanostructure to be used in clinics as nanomedicines or as part of sophisticated nanodelivery vectors, their biopersistence is a major drawback. This seminar will delve into different aspects of the design of CNT-coated nanostructures that we have recently investigated in our laboratories[9,10]. Among the topics we will discuss: (i) custom-functionalization with proteins designed and produced *ad hoc,* (ii) nanocarrier target-directed cellular interaction, (iii) endocytic engulfment and endolysosomal escape, (iv) target release delivery, and also (v) CNT-coated carrier system biodegradation.

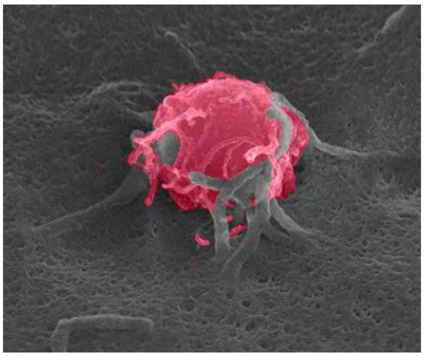

Fig.1 CNT-coated particle (pink) interacting with the HeLa cell surface phyllopodia (grey)[9,10].

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Gd-metallofullerenol as an Efficient Antitumor Agent via Regulating Tumor Microenvironment

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Cancer has become the leading cause of death. Without new treatments, WHO predicted that the number of new cancer patients could increase to twenty-seven million a year by 2030. Researches have shown that metastasis, chemotherapeutic resistance and recurrence are the major hurdles to successful treatment of cancer which may be mediated by a subpopulation of tumor cells, cancer stem cells, displaying stem cell properties and giving rise to metastases. Nanomedicines hold great promise in biomedical applications especially in cancer therapeutics. Currently, nanomaterials have been used as carriers of conventional drugs, oligonucleotides or bioactive molecules where the nanomaterials may improve their bioavailability. In this talk, we will summarize the progress of polyhydroxylated $Gd@C_{82}(OH)_{22}$ on the molecular mechanism for antineoplastic properties.

Since 2004, we found that polyhydroxylated $Gd@C_{82}(OH)_{22}$ possessed exciting antineoplastic properties. One of the most fascinating features is its strikingly low cyto- and systemic-toxicity in the normal mouse despite its remarkable anti-tumor capacity in a variety of solid cancers. With a size of approximately one nanometer, $Gd@C_{82}(OH)_{22}$ nanoparticles can be formed via hydrogen bond interaction in solution with sizes ranging from 20 to 120 nm, depending on the concentrations and microenvironmental pHs. The size variation with pH alterations can be understood by the deprotonation of the hydroxyl groups on the cage surface. The flexible feature of microenvironment-dependent size makes their efficient uptake by hypoxic cells under hypoxic conditions.

$Gd@C_{82}(OH)_{22}$ nanoparticle blocks epithelial mesenchymal transition with resultant efficient elimination of breast cancer stem cells. This leads to a striking abrogation of tumor initiation and metastasis in mouse models. $Gd@C_{82}(OH)_{22}$ mediates these effects by blocking TGF-β signaling under normoxia and as a bi-potent inhibitor of HIF-1α and TGF-β under hypoxia. We also found that $Gd@C_{82}(OH)_{22}$ contribute to cancer immunotherapy by regulating macrophages. The activated macrophages inhibit the growth of several cancer cell types, which is dependent on an NF-κB-mediated release of multiple cytokines. It is noteworthy that we developed a karyon-like hybrid nanoparticle using fullerenol, which significantly reduced the chemodrug side effects by utilizing the radical scavenging ability of fullerenol. This novel combination strategy with chemodrugs together with low toxicity of these nanomaterials in normal tissue holds a promise on their clinical therapeutic potential.

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Single Carbon Nanotube Imaging Reveals the Live Brain Extra Cellular Space at the Nanoscale

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The extracellular space (ECS) of the brain represents up to a fifth of brain volume with an undisclosed complex miniaturized topology. While it has long been seen as a passive brain area, it however constitutes an important signaling region for the development, function and communication of neuronal and glial cells. Here we show that super-localization imaging and single particle tracking of luminescent single wall carbon nanotubes can be used to probe the local ECS architecture in live brain tissue at the nanoscale[1-3]. Moreover, the interplay between the nanotube geometry and the extracellular space local environment, allows extracting information about the ECS local viscosity [1] that no other method can currently access. In this presentation, I will also show our recent results about the specific ECS properties near identified brain structures [4] (e.g synapses) and in neurodegenerative disease animal models [5].

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Design biocompatible graphene materials for imaging and therapy

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Graphene-based materials are showing tremendous potential in the biomedical field. Indeed, they are explored for many biomedical applications, particularly for cancer treatment, due to their unique physicochemical characteristics. In addition, they can be also developed as powerful imaging tools. In this presentation, I will illustrate the biological activity of different types of graphene materials (i.e. few-layer graphene, FLG and graphene oxide, GO). For example, FLG have shown to have a specific impact on monocytes, without cytotoxic effects on the other types of immune cells. FLG was further explored in a therapeutic application towards neoplastic monocytes, obtained from myelomonocytic leukemia patients. FLG have the ability to target and successfully trigger the death of monocytic cancer cells. I will also present our recent results on the development of graphene materials associated with fluorescent molecules to follow their cell uptake, overcoming the problem of fluorescence quenching, always associated to graphene and graphene oxide.

Progress Towards Single-Walled Carbon Nanotube Applications in Biomedicine and the Exoneration of Toxicity

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Single-walled carbon nanotubes exhibit unique photophysical properties that enable the detection of biomarkers [1,2], metabolites [3], and drugs [4] in living cells, tissues, and organisms. The intrinsic near-infrared photoluminescence of nanotubes exhibits unique photostability and sensitivity to the local environment to transduce molecular binding events via changes in the nanotube optical bandgap. We developed carbon nanotube-based optical sensors to detect metabolites and cancer biomarkers in vivo, in order to improve early cancer detection and accelerate drug discovery for cancer and allied diseases. We introduced carbon nanotubes into disease models via implantation within devices, as well as by intravenous injection (Fig 1). In all cases, we found that properly-functionalized single-walled carbon nanotubes exhibit no deleterious effects in live cells or in vivo at concentrations needed for measurement. Single-walled carbon nanotubes enable new tools to allow biologists to ask previously unanswerable questions and provide translational technologies to measure disease states in situ.

Fig.1 Single-walled carbon nanotube sensor implant.

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Large-scale High-purity Semiconducting Single-Walled Carbon Nanotube (sc-SWCNT) and Their application for Printed Devices and Simple Circuits

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Keywords:

Printable, Semiconducting Single-Walled Carbon Nanotube (sc-SWCNTs), Printed Circuits

Abstract:

Printed thin film transistors (TFTs) are the key units to construct driving circuits for OLED, LED and QLED displays, E-paper, printed logic gates and circuits, biologic and chemical sensors, and wearable electronics.[1-6] Semiconducting single-walled carbon nanotubes (sc-SWCNTs) have been become one of promising semiconductors for especially for flexible printed TFTs and circuits (driving circuits, CMOS inverters, ring oscillators and so on), since SWCNTs show excellent electrical properties, solubility, flexibility, high chemical and physical stability, and process temperatures compatible with flexible substrates[1-9]. In this report, we presented a valid approach to produce large-scale, high-purity and high-performance sc-SWCNTs from commercial SWCNTs. Furthermore, printed SWCNT TFTs, CMOS inverters and driving circuits, including hybrid CMOS inverters, diode-transistor logic (DTL) circuits, driving circuits and ring oscillators were constructed on different flexible and rigid substrates.

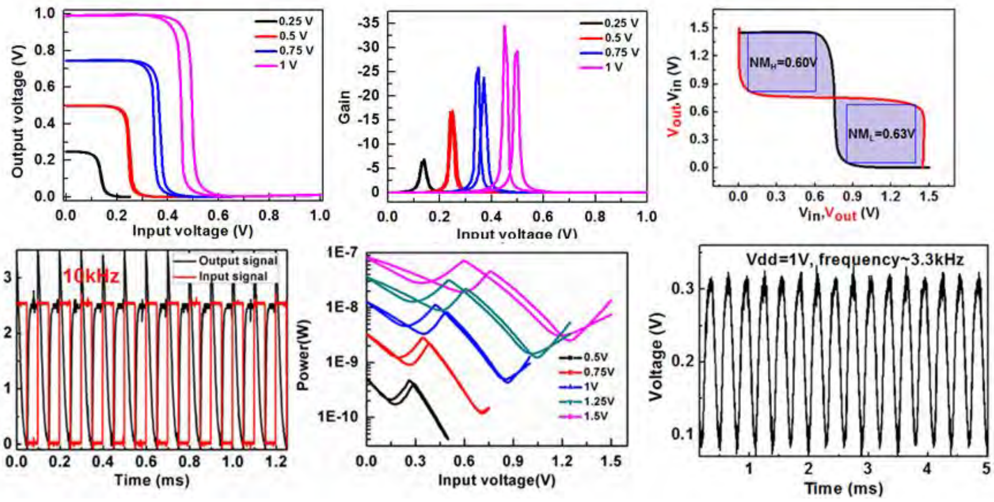

Figure 1 Flexible printed CMOS inverters and ring oscillators.

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Carbon Nanotube-Based Flexible Electronics

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Flexible and stretchable electronics are now widely studied for a next class of electric devices replaced from the silicon-based conventional inflexible devices. To build the flexible electronics platform, many materials including organics and inorganics have been proposed for the use of active components such as transistors and sensors. One of the potential material candidates is carbon nanotubes (CNTs) due to good mechanical flexibility, high electrical performance, and stability. In this talk, our recent progress about the CNT-based flexible transistors[1-4] and sensors[4-5] will be presented. In particular, flexible complimentary metal-oxide-semiconductor (CMOS) circuits and flexible sensors using all CNT network films are discussed for the future material systems. Finally, integrated flexible wearable healthcare patches[4,5] are demonstrated as the first proof-of-concept.

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2D-material-based Soft Bioelectronics

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Although recent efforts in device designs and fabrication strategies have resulted in meaningful progresses to the goal of soft electronics [1,2], significant challenges still remain in fabricating a soft form of the image sensor array. In this presentation, we report our recent achievement in a high-density soft curved image sensor (CurvIS) array (Fig. 1) by using a heterostructure of inherently soft 2D materials (MoS_2 and graphene), by employing an ultrathin device structure, and by applying strain-isolating/-releasing array designs [3]. This high-density soft CurvIS array with the single-lens optics successfully acquires pixelated images without optical aberration and infrared noises (Fig. 1 inset). We also present a human-eye-inspired soft implantable optoelectronic device based on the developed CurvIS array. Theoretical analysis in conjunction with supporting experiments corroborates the validity of the proposed soft materials and device designs.

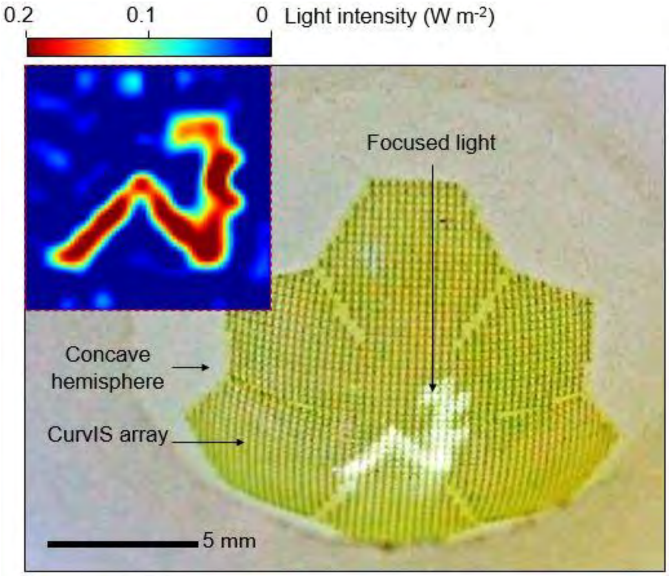

Figure 1. Soft Curved Image Sensor Array

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Carbon Nanotubes: From Logic Technology to Flexible Electronics

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The superior electrical properties of carbon nanotube (CNT) make it a promising replacement for silicon in scaled logic technology. In this invited talk, I will first review the major challenges in developing CNT logic technology, including purification, placement, transistor scaling, as well as integration. In particular, I will talk about the recent progress on contact engineering in CNT NFETs [1], length scaling with end-bonded contacts [2-3], and demonstration of high-speed logic integrated circuits [4]. I will also discuss the remaining roadblocks to deliver a viable CNT logic technology. In the second half of this talk, I will talk about the promising applications of CNT thin-film transistors (TFTs) in flexible electronics and sensors, enabled by their high mobility and mechanical flexibility. Our recent work demonstrates high-speed CNT CMOS integrated circuits, featuring the fastest flexible ring oscillator, can be built on flexible substrates with high yield using a scalable and reliable process [5]. Furthermore, an integrated flexible pressure sensor is demonstrated with high sensitivity, high resolution, and fast response [6]. Future applications of CNT TFTs by integrating flexible sensing, computation and communication will be discussed in the end.

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Transparent conducting films prepared by mixing of CNTs and PEDOT:PSS and application to OLEDs

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Carbon nanotubes (CNTs) and PEDOT:PSS conductive polymers have attracted more and more attentions because of their good electrical conductivity[1-5]. They have been applied in various fields. PEDOT:PSS, as a conductive polymer, its electrical conductivity varies with different treatments. In this study, a thin film formed by mixing of CNTs and PEDOT:PSS was prepared by a simple spin coating process. PEDOT:PSS was introduced to fill the gaps among CNTs, and CNTs helped to maintain the life of devices. PEDOT:PSS increases the contact area between the CNTs and reduces the large resistance caused by the point contact. In addition, the internal morphology of the PEDOT:PSS was changed by the mixed treatment of alcohol and acid, which was beneficial to greatly reduce the sheet resistance of films while maintaining high transparency. The adhesion of the film could be reflected by the change of transmittance before and after tape test. The experimental results showed that the best film performance of the mixture of CNTs and PEDOT:PSS was 92.2 ohm/sq.@ 95.9 T%. High transmittance, low resistance, low surface roughness, and super adhesion are all available at the same time. Basic on this electrodes, the OLEDs owned low opening voltage (3 V) and its luminance reached 2973 cd/m^2 when the voltage was 20 V. In addition, the existence of CNTs contributed to maintain the life of OLEDs.

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Sorting of sc-SWCNT in Polar Solvents with an Amphiphilic Conjugated Polymer Provides General Guidelines for Enrichment

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Conjugated polymer extraction (CPE) has been shown to be a highly effective method to isolate high purity semiconducting single-walled carbon nanotubes (sc-SWCNTs)[1]. High selectivity is typically obtained in non-polar aromatic solvents, yet polar solvents may provide process improvements in terms of yield, purity and efficiency. Using a novel amphiphilic fluorene-*alt*-pyridine conjugated copolymer with hydrophilic side chains we have investigated the enrichment of sc-SWCNTs in polar solvents[2]. Various conditions such as polymer/SWCNT ratio, solvent polarity, solvent dielectric constant, as well as polymer solubility and SWCNT dispersability were explored in order to optimize the purity and yield of the enriched product. Herein, we provide new insights on CPE by demonstrating that a conjugated polymer having a hydrophobic backbone and hydrophilic side chains provides near full recovery (95%) of sc-SWCNTs using a multi-extraction protocol (Figure 1). Taking into consideration the solvent dielectric constant, polarity index as well as polymer solubility and SWCNT dispersability provides new insights and a better understanding of structure-property effects on sc-SWCNT enrichment. The resulting hydrophilic SWCNT dispersions demonstrate long-term colloidal stability, making them suitable for ink formulation and high performance thin film transistors (TFT) fabrication. A fully inkjet-printed TFT is demonstrated with excellent performance (mobility 9.3 $cm^2/(V\ s)$ and on/off ~10^5).

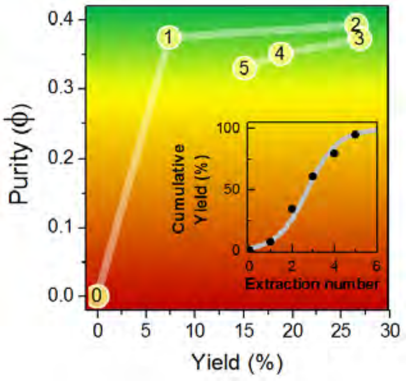

Fig. 1. The enrichment performance as a function of extraction number. The inset shows the cumulative yield is approaching full recovery (95%) of sc-SWCNTs as the extractions number increases.

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Assembly of Aligned Semiconducting Carbon Nanotube Arrays

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This presentation will detail our recent efforts on manipulating and assembling semiconducting carbon nanotubes wrapped by conjugated polymers for carbon nanoelectronics. We have developed a self-assembly approach that enables the wafer-scale deposition of arrays of well-aligned nanotubes called floating evaporative self-assembly (FESA). In FESA, a layer of polymer wrapped nanotubes in organic solvent is cast onto an aqueous sub-phase, and the nanotubes spontaneously segregate at the organic/water interface. The aligned nanotubes deposit onto a substrate as it is withdrawn through the interface.[1] We have realized nearly ballistic nanotube array field effect transistors (FETs) at a density of 70 nanotubes μm^{-1} that exhibit on-state conductance as high as 0.9 G_o per nanotube where G_o is the quantum conductance limit. The small bias on-state conductance reaches as high as 3.8 mS μm^{-1} and the saturated on-state current density reaches 1100 $\mu A\ um^{-1}$ and is similar to or exceeds Si FETs when compared at equivalent gate oxide thickness, off-state current density, and channel length. High frequency RF and thin film transistor FETs have also been demonstrated.[2]

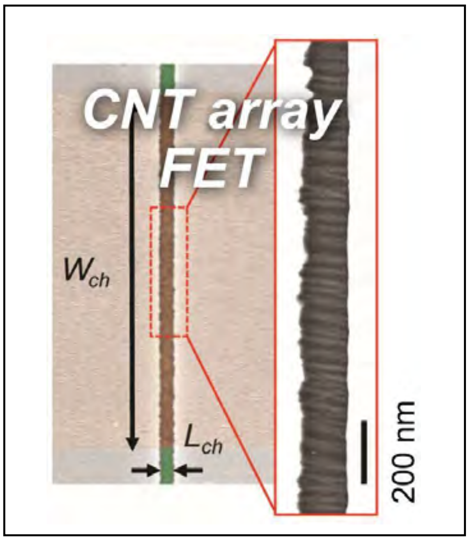

Fig. 1 SEM image of aligned semiconducting carbon nanotube (CNT) array FET.

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Carbon nanotube TFTs and ICs for wearable sensor devices: Device modeling, circuit design tools, and fabrication

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Wearable sensor devices have the potential to revolutionize preventive medical care and health promotion technologies. Carbon nanotube (CNT) thin films are promising electronic materials for transistors and integrated circuits [1-3], biosensors [4,5], and other passive components to build flexible and stretchable devices with excellent wearability and performance. Recently, high-yield and reproducible fabrication of CNT TFTs have become possible by using purified semiconducting CNTs, leading extensive study on circuit applications. An integration of analog circuits with a sensor is essential for wearable sensor devices to amplify the sensing signal as preventing external noise. A differential amplifier is a fundamental analog amplification circuit used for various sensor devices. In this work, we are focusing on the analog circuit application of CNT TFTs. To design CNT-based analog circuits, circuit simulation tools have been developed with a precise device model which has been built on the basis of electrical characterizations of CNT TFTs. We have realized differential amplifiers on a flexible and transparent plastic film.

Device modelling is indispensable for circuit design. We built the RC-ladder device model based on the charge based model for CNT TFTs, where a correction of pinch off condition was taken into account, considering the contact resistances between CNTs. In order to fit the subthreshold current, the charge equation in weak inversion characteristics was modified. The proposed model well expresses the output characteristics. The frequency dependence of capacitance-voltage characteristic was also built by considering the non-quasi-static effect in the Mayer model. CNT-based analog or analog/digital mixed circuits such as differential amplifiers and analog/digital converters were designed by using the circuit simulation with proposed device model.

We also realized the differential amplifiers on a flexible plastic film. Bottom-gate CNT TFTs with purified semiconducting CNTs were used as the active device. A differential output was obtained with respect to a differential input. Maximum voltage gain of 16.3 (24.3 dB) was achieved for a sinusoidal wave input of 100 mV_{pp} at 100 Hz with a power source of -12 V. Figure 2 shows the gain as a function of frequency, exhibiting -20 dB/ decay. The voltage gain cut-off frequency was 210 kHz.

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Development of Wearable Devices based on Pseudo two-dimensional networks of Super-growth CNTs

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Motivated to develop low-dimensional, wearable devices which could tolerate the strains of daily activities, we utilized the intrinsic strengths of Super-Growth single-walled carbon nanotubes (SG-SWCNTs) [1], specifically, the length, purity, and their assembly into homogeneous dispersed network structures [2]. The assembled structures, both aligned and randomly aligned, were found to be highly robust, flexible, and stretchable while maintaining a high electrical conductivities. These features enabled the development of various enabling technologies, such as electrically conducting rubbers, adhesives, and porous thin films to afford the fabrication of several types of stretchable and flexible, pseudo two-dimensional devices spanning from sensors, energy storage, and switches. Each of these technologies was essential to realize devices, which demonstrated key features, such as tolerance to mechanical strain, miniaturization in size, or wide operational range.

In this presentation, I will provide an overview of our work in the development of wearable devices based on pseudo two-dimensional networks of super-growth carbon nanotubes. I will highlight the importance of the starting SWCNT forest material, the various indispensable technologies which we have developed along the way, and several examples of operational devices, such as a strain sensor with 280% dynamic range [3], a mechanically durable and robust, all elastomeric FET [4], and a lithographically integrated and designable micro-supercapacitor [5]. Further, having developed these devices possessing the general functions of sensing, stretchability/flexibility, energy storage, and robustness, we now envision the development of devices possessing a combined set of functions and properties.

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Aligning Solution-Derived Carbon Nanotube Film with Full Surface Coverage for High-Performance Electronics Applications

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The main challenge for application of solution-derived carbon nanotubes (CNTs) in high performance field-effect transistor (FET) locates at how to align CNTs into an array with high density and full surface coverage. We develop a directional shrinking transfer method to realize high-density aligned array based on randomly orientated CNT network film. Through transferring a solution-derived CNTs network film onto a stretched retractable film followed by a shrinking process, alignment degree and density of CNT film will increase with the shrinking multiple. The quadruple shrunk CNT films present well alignment, which is identified by the polarized Raman spectroscopy and electrical transport measurements. Based on the high quality and high density aligned CNT array, the fabricated FETs with channel length of 300 nm present ultra-high performance including on-state current I_{on} of 290 μA/μm (V_{ds}=-1.5V and V_{gs}= -2V) and peak transconductance g_m of 150 μS/μm, which are respectively among the highest corresponding values in the reported CNT array FETs. High quality and high semiconducting purity CNT arrays with high density and full coverage obtained through this method will promote the development of high performance CNT based electronics.

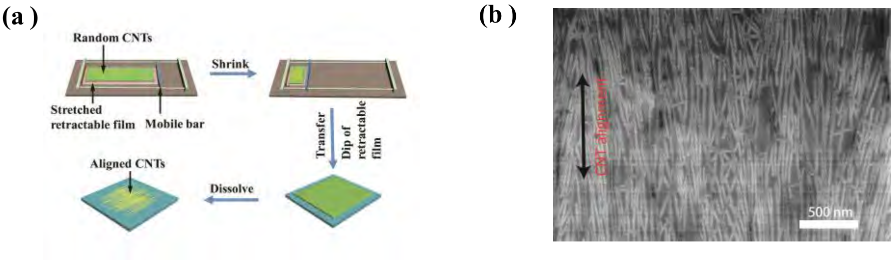

Fig.1 Process and characteriation of CNT film based on the diractional shrinking transfer alignment Method. a) Flow chart showing the major steps of the directional shrinking transfer alignment technique. b) SEM image of the quadruple shrunk CNT film**.**

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Exploring performance uniformity of carbon nanotube thin film transistors on wafer scale

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Excellent performance uniformity is very important for the practical application of transistors especially in large scale integrated circuit. In this work, we have fabricated top-gated field-effect transistors (FETs) based on solution derived random carbon nanotube (CNT) film on 2-inch wafers, and then investigated their performance uniformity systematically. For CNT FETs with large channel area, the subthreshold voltage (V_{TH}) hysteresis of the FETs could reach as small as 32 mV and the subthreshold swing (SS) could reach near 100 mV/dec and the average of SS have reached 118±7 mV/dec of high uniformity. The on-state current, on/off ratio were all with high uniformity. The coefficient of variation(COV) of the main metrics to characteristic the FETs could be still lower than 20% when the gate length of the transistors scales down to 2 μm. The high uniformity of the FETs constructed with wafer-scale has shown that the CNT film based FETs have the potential in large-scale integrated circuits.

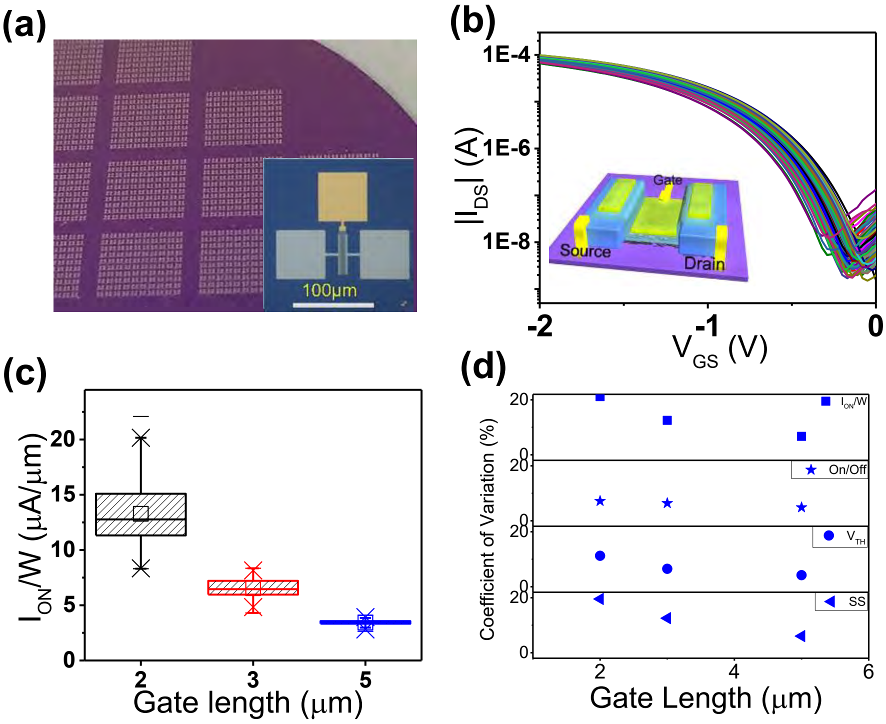

Fig.1 Electronic characteristics of CNT film top-gated field effect transistors with different channel area on wafer scale.

We explore the vertical scaling-down behavior of carbon nanotube (CNT) network film field-effect transistors (FETs) and show that by using a high-efficiency gate insulator, we can substantially improve the subthreshold swing (SS) and its uniformity. By using an HfO_2 layer with a thickness of 7.3 nm as the gate insulator, we fabricated CNT network film FETs with a long channel (>2 μm) that exhibit an SS of approximately 60 mV/dec. The preferred thickness of HfO_2 as the gate insulator in a CNT network FET is between 7 nm and 10 nm, simultaneously yielding an excellent SS (<80 mV/decade) and low gate leakage. However, because of the statistical fluctuations of the network CNT channel, the lateral scaling of CNT network film-based FETs is more difficult than that of conventional FETs. Experiments suggest that excellent SS is difficult to achieve statistically in CNT network film FETs with a small channel length (smaller than the mean length of the CNTs), which eventually limits the further scaling down of this kind of CNT FET to the submicrometer regime.

Low-power and highly-uniform carbon nanotube integrated circuits with integration capability to biological surfaces

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Devices and integrated circuits (ICs) with bio-integration capability can significantly expand functions of electronics, which is of growing interest in clinical and biological applications. Generally, intimate and conformal biotic/abiotic interface is an essential. However, as many efforts have been demonstrated for the bio-integration purpose, ICs, the core unit of electronic systems, are still lacking with certain complexity and low power consumption for in situ biological data computation. The presentation will present carbon nanotube based devices and ICs with both high uniformity and low power consumption that can be transferred onto biological surface, such as plant leaves, person's wrists and biological polymers, and the wafer-scale platform demonstrated operation on a curved plant leaf. The carbon nanotube transistors exhibited ultralow power consumption with off-current as low as 0.1pAμm^{-1}, a subthreshold swing of 62 mVdec^{-1}, and static power consumption of 2.5×10^{-13} W was observed in an inverter. Meanwhile, with 80mV standard deviation in threshold voltages, the transistors demonstrated high-uniformity and could be used for IC construction. The most complex carbon nanotube based ICs

on flexible substrates, such as a full adder with rail-to-rail outputs and a read-only memory were present driven by a small supplied voltage of 2V.

Using Approximate Circuit to Improve Process Induced Failure in CNFET Circuits

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Studies on emerging low dimensional materials (LDMs) including Carbon Nanotube Field Effect Transistor (CNFET) based Technology have demonstrated superior device performance in comparison to silicon, thus LDMs are being thoroughly investigated as channel materials in place of silicon for future advanced nodes; however studies have also shown the current fabrication processes for CNFETs can still not guarantee the perfect circuits and target yield required for high precision mainstream applications in near future. Though these imperfect emerging technologies are not ready for general purpose computing, there are applications like approximate computing, which can tolerate few errors and can be suitable for these technologies even suffering from immature and imperfect process.

Since its introduction in 1991, CNT is extensively studied and is seemingly closest in comparison to other LDMs in terms of high volume manufacturing. The CNFET fabrication process consisting of separation and placement of solution based CNTs has become quite popular, because of the consistent reporting of excellent semiconducting purity (> 99.9% of semiconducting CNTs after separation step). Thus with the current fabrication process, the problem of unwanted shorts caused by presence of metallic CNTs (< 0.01%) seems to be under control. However, after the placement of solution based CNTs onto the substrate, there are missing CNTs (also referred as open CNTs) in trenches connecting source and drain of CNFET. The open CNTs can lead to open circuits (CNFET without single semiconducting CNT) or reduction in driving current. The percentage of open CNTs ($PCNT_{open}$) in recent reports, have been reported to be > 30% for narrow trench widths, and is expected to increase with further scaling of trench widths. A high percentage of open CNTs would cause reduced drive currents, thus inducing failure in (1) meeting the minimum frequency requirement (due to increase in critical path delay), (2) meeting the minimum Static Noise Margin (SNM) requirement. Thus, the presence of open CNTs should be considered for the fair evaluation of the performance of CNFET circuits.

In recent years, there is significant growth of interest in approximate computing targeted towards applications like image, video processing where few errors during computation does not affect the quality of results to great extent. These applications thus relax the requirement to realize exact functionality; thus the circuits can be made much simpler with lesser nodes, reduced stages, and reduced capacitances at few nodes; thus enabling lesser critical path delay and lesser chances of violation of SNM requirement. For the mature technologies like silicon, the approximate circuits are obtained with the objective of reducing the energy consumption and area with minimal logic error; however, for emerging technologies including CNFETs the approximate circuits are obtained with the primary objective of reduced process induced degradation.

In this work, we first present a methodology to evaluate process induced degradation in CNFET based circuits due to imperfect process; followed by methodology to generate approximate circuits in order to reduce the process induced degradation. With an example of 16-bit CNFET adder; we have shown that approximate circuits have great potential in reducing the process-induced degradation with minimal logic error; along with additional benefits of reduced energy-delay product and area. This work shows the applicability of CNFET based circuits (even with current imperfect fabrication process) for error resilient applications.

A simple method for aligning CNTs toward electronics devices

S. Iijima

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One of applications of carbon nanotubes has been sought in electronic devices since their discovery [1]. The potential of the CNT devices has been demonstrated in earlier time on the basis of single tube devices. For industrial applications it is obvious to establish a way of a large scale preparation of horizontally aligned CNTs. A lot of efforts have been made in realizing aligned CNTs but a plausible method for this purpose has not yet been established.

The methods for CNT alignment will be categorized into two techniques, direct growth of CNTs on a substrate in a horizontal fashion and controlling a process of aligning CNTs which have been prepared in conventional ways. The former approach has been reviewed recently by the Tsinghua University group [1] but in terms of the efficiency and cost such a growth process might be limited to a small scale application. The latter case has been also demonstrated recently as “Films of Spontaneously Aligned Single-Walled Carbon Nanotubes” by the Rice University group [2].

In this presentation I would like to propose a simple method for vertically aligned CNTs that were not grown directly on a substrate but prepared by controlling a flow of a CNT suspension through a membrane film. The membrane film has through-holes with diameters ranging from 200~8000nm. The CNTs flow down along the inside hole walls and some of CNTs are suspended on the walls. In this way the CNTs can aligned vertically on the hole walls along the direction from the flow inlet membrane surface to the outlet surface. It is my hope to realize a large scale CNT device on a membrane at the end of this project.

[1] Sumio Iijima, “Helical microtubules of graphitic carbon ”, Nature, **354**, 56 (1991).
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[3] Rufan Zhang, ‡a Yingying Zhang b and Fei Wei, “Horizontally aligned carbon nanotube arrays: growth mechanism, controlled synthesis, characterization, properties and applications”, Chem. Soc. Rev. , **46**, 3661 (2017)

FC-CVD synthesis with dry deposition of SWNT thin films for flexible electronics applications

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Single walled carbon nanotubes (SWNT) have many applications in the emerging flexible electronics. We have developed the dry and continuous thermophoretic deposition of pristine, individual SWNTs grown using a floating-catalyst chemical vapor deposition (FC-CVD) process. Based on aerosol loss measurements, the thermophoretic terminal velocity of SWNTs is much lower i.e. approximately only one third of the usual free molecular regime prediction and shows a weak dependence on the nanotube diameter. Scanning electron microscopy and atomic force microscopy of the deposited samples indicate that pristine, as-synthesized SWNTs with controllable densities, ranging from individual, separated nanotubes to multilayer thin films, can be deposited on practically any flat substrate with high efficiencies close to unity. Depending on the lateral flow inside the precipitator, the angular distribution of the deposited SWNTs can be changed from uniform to non-uniform. As a demonstration of the applicability of our technique, we have used thermophoretic deposition to fabricate both carbon nanotube transparent conductors comparable to standard conductors made from indium-tin-oxide (ITO), and thin film transistors with uniform electrical properties and a high, over 99,5% yield and high field effect electrical mobility exceeding 400 cm^2/Vs while simultaneously having a I_{ON}/I_{OFF} in excess of 10^6.

In addition, we will present current status of industrial manufacturing of SWNT based commercial touch sensor products for the emerging 3D sensor markets. Also, we present recent results on SWNT (n,m) control in the FC-CVD synthesis processes using different carbon sources i.e. CO, C_2H_4, ethanol and toluene.

First-principles calculations on the multiferroic properties of two-dimensional materials

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Multiferroics, which possess two or more properties of ferromagnetism, ferroelectricity and ferroelasticity over a certain range of temperatures, are important electronic materials because of their promising applications in advanced electronic devices. In this work, first-principles calculation is employed to investigate the multiferroic properties of two-dimensional (2D) materials [1-2]. Ferromagnetism, ferroelectricity and ferroelasticity are explored in graphene oxides and phosphorene oxides with a thickness of 1-2 atomic layers. Electronic structures and elastic properties of those 2D oxides are determined in searching for the phase transitions closely related with the multiferroic properties. The existences of multiferroic properties are found to be caused by the coupling between electronic and structural ordering states in those 2D oxides.

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Modulating Interface Interactions in 2-Dimensional Materials and Their Heterostructures

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2-dimensional (2D) van der Waals structures built up from layered materials, such as graphene, MoS_2, and their heterostructures, have received growing attention owing to their simple fabrication by straightforward stacking and various types of band alignments. Interface interactions in 2D materials and their heterostructures are of vital importance to determine the properties of the 2D layers. In this talk, I will introduce some efforts in my group on probing and modulating interface interactions in 2D systems, including mechanically characterizing their interlayer interactions, employing surface enhanced Raman technique to probe local strains, and inducing interlayer connections by defect engineering. Lastly, I will present an example of modulating properties of a 2D semiconductor by interfacing it with an active, phase-change material. Our results not only provide an insight to understand interface interactions in 2D van der Waals structures, but also potentially allow engineering of their properties as desired.

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[10] X. W. Wang, W. Fan, K. Liu*, et al. **Nanoscale** 2018, *10*, 3540.

Evaluation of contact properties for semiconducting 2H phase of MoTe$_2$ via scanning gate microscopy

Kohei Sakanashi[1], Hidemitsu Ouchi[1], Kota Kamiya[1], Tomoki Yamanaka[1],
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The transition metal dichalcogenides (TMDs) has been receiving the large attention because of their rich physical properties such as valley degree of freedom, superconductivity and polymorphism for future electronics devices. In this time, we realize the semiconductor/metal junction in a thin exfoliated 2H-MoTe$_2$ crystal patterned by using laser-irradiation induced structural phase transition from semiconductor to metal. S. Cho and his collaborators indicate laser-patterned metallic phase has better ohmic properties for 2H phase by using as source-drain contacts [1]. However, MoTe$_2$ shows p-type, n-type or ambipolar carrier polarity and it is unclear that the laser-patterned metallic phase can take ohmic contact for all of them. In this study, we fabricated a MoTe$_2$-FET device one of whose contacts has conventional metal (Pd) and another has laser-induced metallic phase as shown in Fig.1 (Left). We studied the transport and scanning gate microscopy (SGM) measurements. SGM has been visualized the electron trajectory and quantum interference effect in low temperature ballistic regime and also barrier formation and existence of defects in FET device, and so on [2]. From the current-voltage measurement, we observed the diode-like rectification property for n-type carrier and then back-gate characteristics showed large current difference in n-type region of ambipolar action. Also, SGM images indicate the barrier formation at the Pd/2H interface as shown in Fig.1(Right) and a large electric potential drop is confirmed via electrostatic force microscopy. Although, we observed the Schottky barrier formation at the Pd/2H interface for any carrier polarities and injection directions, laser-patterned metallic phase/2H contact interface has no barrier.

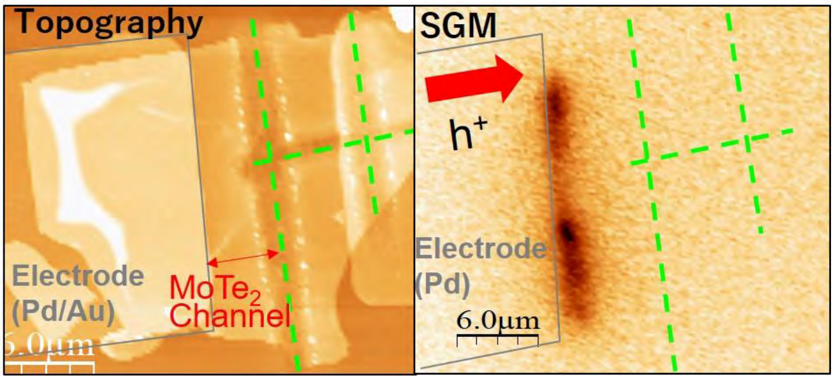

Fig. 1 Topography (left) and SGM image (right). SGM response is only active at Pd/2H interface. Solid line indicates interface of Pd/2H and dotted lines indicate laser-irradiated region. The arrow indicates the direction of the carrier injection.

[1] S. Cho *et al.*, Science **349**, 625 (2015)
[2] M. Matsunaga *et al.*, ACS Nano **10**, 9730 (2016)

Control of FET Property by Laser Irradiation and Device Application of MoTe$_2$ Crystal

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Transition metal dichalcogenides (TMDCs) have attracted a lot of interest due to their interesting electrical and optical properties [1]. We are very interested in MoTe$_2$ since it has relatively small band gap of ~1 eV and is relatively easy to be controlled its crystalline structure from usual 2H to 1T' by a laser irradiation [2], a chemical treatment [3], even stretching the crystal [4] compared to the other TMDC materials. Combining with van der Waals transfer technique, we are trying to fabricate electric devices using MoTe$_2$ crystals.

In order to realize electronic devices using TMDCs, ohmic contact is a very important issue. Recently, we have realized good ohmic contacts with a metallization technique using a focused laser irradiation in a MoTe$_2$-field effect transistor (FET). This effect has been confirmed using scanning gate microscopy. By controlling the laser power density, we found that we could control the carrier density in a MoTe$_2$ crystal over a wide range in both n- and p-type FET and even the carrier polarity. We think the mechanism of the change based on the effect of the Te vacancies by the irradiation. These techniques would be useful to fabricate a monolithic electronics within a TMDC crystal for future flexible devices. We will demonstrate a p-n inverter (Fig. 1) and a tunneling FET fabricated using the laser irradiation technique.

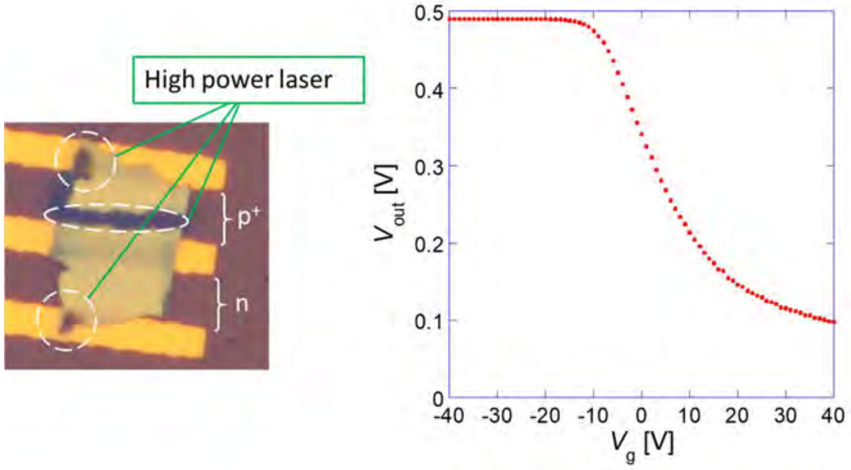

Fig. 1 Picture of p-n inverter device (left) and the inverter action (right).

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[2] S. Cho, et al., Science **349**, 625 (2015).

[3] R. Kapera et al., Nat. Mater. **13**, 1128 (2014).

[4] K.-A. N. Duerloo, et al., Nature Comm. **5**, 4214 (2014).

Dispersion and aggregation of graphene oxide in aqueous media

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Graphene oxide (GO), as a typical two-dimensional material, possesses a range of oxygen-containing groups and shows surfactant and/or polyelectrolyte-like characteristics. Herein, GO sheets with narrow size distribution were prepared by an ultracentrifugation-based process and the aggregation behavior of GO in pure water and an electrolyte aqueous solution were studied using laser light scattering (LLS). When adding common electrolytes, such as NaCl and $MgCl_2$, into the GO dispersions, aggregation occurs and irreversible coagulation eventually occurs too. However, the GO dispersion can still remain stable when adding excess $AlCl_3$. The zeta potential of the GO dispersion changes from negative to positive after the addition of access $AlCl_3$, indicating that electrostatic repulsion is still responsible for the dispersion of GO, which is in good agreement with the LLS results. This finding on the dispersion of GO may be applied in the solution processing of GO. It also expands the scope of the design and preparation of new GO-based hybrid materials with different functions.

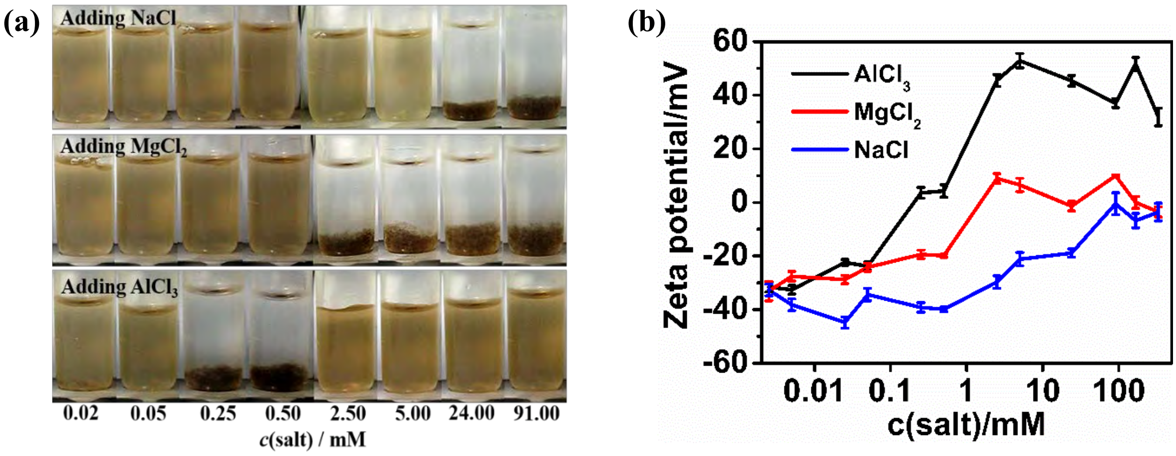

Figure: (a) Evolution of the aggregation state of GO dispersions with different concentrations of NaCl, $MgCl_2$ and $AlCl_3$ in GO dispersion solutions prepared under a centrifugal force of 150 000g; (b) The zeta potential of GO aqueous dispersions dependent on the concentration of NaCl, $MgCl_2$ and $AlCl_3$. GO sheets were prepared at 150 000g and the concentration was ~0.041 mg mL^{-1}.

[1] M. Wang, Y. Niu, Y. Li*, *et al.* Nanoscale **8**, 14587-14592 (2016).

An efficient and scalable production of 2D material dispersions using hexahydroxytriphenylene as a versatile exfoliant and dispersant

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Since thin layer 2D materials have been attracting enormous interest, various processes have been investigated so far to obtain these materials efficiently. In view of their practical applications, the most desirable source is the pristine bulk material with stacked layers such as pristine graphite. On their exfoliation, we have many options in terms of conditions such as wet or dry, with or without additive, and kind of solvent. In this context, we have found versatile exfoliant, 2,3,6,7,10,11-hexahydroxytriphenylane (Fig. 1), which works efficiently for exfoliation of typical 2D materials, graphene, MoS_2, and h-BN, in both wet and dry processes using sonication and ball-milling, respectively, in aqueous and organic solvents.

As for graphene, stable dispersions with relatively high concentration (up to 0.28 mg/mL) in water and tetrahydrofuran were obtained from graphite in presence of hexahydroxytriphenylene by wet process using bath sonication and via dry process using ball-milling. Especially, most of graphite was exfoliated and dispersed as thin layer graphene (Fig. 2) in both aqueous and organic solvents through ball-milling even at large scale (47 - 86% yield). In addition, the exfoliant can be easily removed from the precipitated composite by heat treatment without disturbing the graphene structure. Bulk MoS_2 and h-BN were also exfoliated in both wet and dry processes. As in graphene, MoS_2 and h-BN dispersions of high concentrations in water and DMF were produced in high yields through ball-milling.

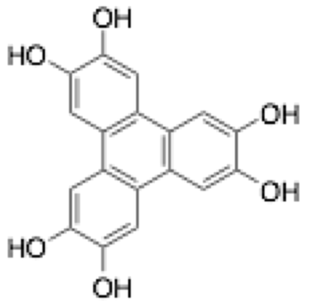

Fig. 1 Chemical structure of hexahydroxytriphenylene.

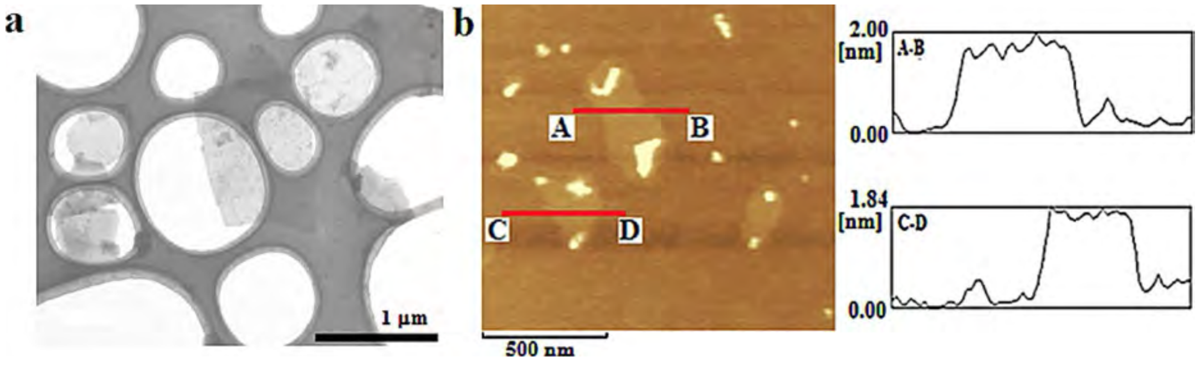

Fig. 2 Typical a) STEM and b) AFM images of the graphene sheets exfoliated with hexahydroxytriphenylene in water.

[1] G. Liu, N. Komatsu* *ChemNanoMat*, 2 (6), 500 - 503 (2016) [highlighted at the front cover].

[2] G. Liu, N. Komatsu* *ChemPhysChem*, 17 (11), 1557–1567 (2016) [highlighted at the front cover].

Readily Available “Stock Solid” of MoS_2 and WS_2 Nanosheets through Solid-Phase Exfoliation by Ball Milling

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In this paper, we report simple, scalable and high-yield production of MoS_2 and WS_2 nanosheets through solid phase exfoliation using ball milling in the presence of sodium cholate (SC) [1]. The exfoliated MoS_2 and WS_2 nanosheets are stored as “stock solid“ and readily dispersed in water simply by shaking with hand prior to use. While solid phase exfoliation using ball milling has been applied to the production of graphene nanosheets, this methodology has not been demonstrated in the exfoliation of TMDs such as MoS_2 and WS_2. Although we have reported scalable method using hexahydroxytriphenylene as an exfoliant through ball milling, bath sonication for half an hour has been required to obtain stable dispersion [2]. As compared with wet-grinding and liquid phase ball milling, the dry process reported here is considered to be more preferable to keep the solid as it is for longer time, because the presence of liquid may facilitate aggregation as mentioned above. In addition, simple dispersion with controlled concentration can be prepared from the dry ball milled solid, while the liquid used for exfoliation under wet conditions may make solvent system complicate, and concentration less precise and less controllable.

First, the effect of surfactant amount in the ball milling process was studied; the amount of MoS_2 was fixed at 0.20 g and the amount of SC was varied from 0.010 to 0.40 g. The powder obtained after ball milling was dispersed in deionized water (100 mL) and the resulting dark-greenish suspension was centrifuged at 3000 rpm (1025*g*) for 60 min. The top 75% of the supernatant (Fig. 1a) was subjected to UV/vis spectroscopic analysis. The yield, the mean number of layers, and lengths of the napnosheets were calculated using the extinction and the reported coefficient at 345 nm, the wavelength of the exciton peak (λ_A), and the ratio of the extinction at 605 and 345 nm (Ext_{605}/Ext_{345}), respectively. As shown in Fig. 1a and 1b, the yield of MoS_2 increased according to the increase of the weight ratio of SC/MoS_2. The yield of 9% obtained at the SC/MoS_2 weight ratio of 2 is much larger than that obtained by liquid phase sonication. The morphology of MoS_2 nanosheets was determined to be two layers and 60 - 80 nm in size, from the λ_A observed at 658 nm and the value of Ext_{605}/Ext_{345}.

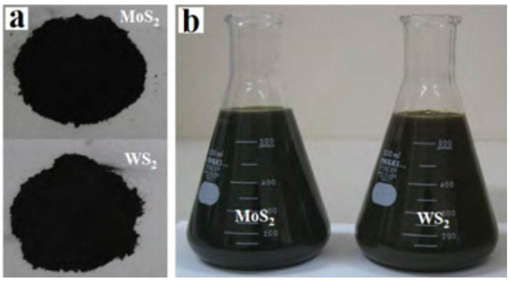

Fig. 1 Photographs of (**a**) ball milled MoS_2 and WS_2 powder and (**b**) aqueous dispersion from the powder shown in (**a**) by shaking with hand followed by centrifugation.

[1] G. Liu, N. Komatsu* *ChemNanoMat*, 2 (6), 500 - 503 (2016) [highlighted at the front cover].
[2] G. Liu, N. Komatsu* *ChemPhysChem*, 17 (11), 1557–1567 (2016) [highlighted at the front cover].

Degradation Chemistry and Stabilization of Exfoliated Few-Layer Black Phosphorus in Water

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Exfoliated black phosphorus (BP), as a monolayer or few-layer material, has attracted tremendous attentions owing to its unique physical properties for applications ranging from optoelectronics to photocatalytic hydrogen production. Approaching intrinsic properties has been, however, challenged by chemical reactions and structure degradation of BP in ambient conditions. Surface passivation by capping agents has been proposed to extend the processing time window, yet contamination or structure damage rise challenges for BP applications. Here, we report experiments combined with first-principle calculations that address the degradation chemistry of BP. Our results show that BP reacts with oxygen in water even without light illumination. The reaction follows a pseudo first order parallel reaction kinetics, produces PO_2^{3-}, PO_3^{3-}, and PO_4^{3-} with reaction rate constants of 0.019, 0.034, and 0.023 per day, respectively, and occurs preferentially from the P atoms locating at BP edges, which yields structural decay from the nanoflake edges in water. In addition, a negligible decay ratio (0.9 ± 0.3 mol%) and preserved photocatalytic activity of BP are observed after storing in deoxygenated water for 15 days without surface passivation under ambient light. Our results reveal the chemistry of BP degradation and provide a practical approach for exfoliation, delivery and application of BP.

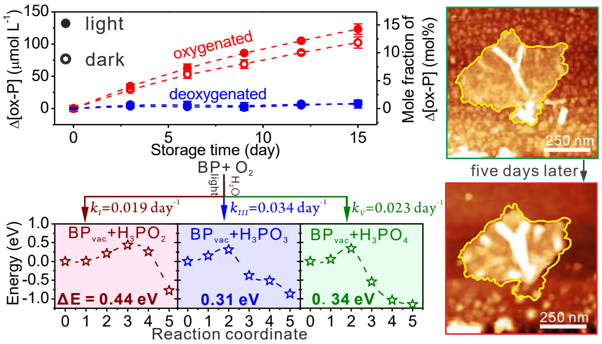

Fig.1 Table of Contents Graphic.

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Modeling electronic excitations in thin films: the issue of the environment

Lorenzo Sponza[1,*], Claudio Attaccalite[2], Hakim Amara[1], François Ducastelle[1]

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The unceasingly growing interest towards 2D materials is mostly due to their exceptional electronic properties when reduced to atomically thin films. Among these, electronic excitations play a role of primary importance in relation to the use of spectroscopic techniques for investigation and characterization or in view of possible technological applications.

Owing to their low dimensionality, the surrounding environment has an impact on their electronic and optical properties through electrostatic, chemical and physical interactions upon and across the exposed surfaces. This sensitivity leads to a high tunability of their properties, that is what makes thin films so versatile and attractive, but can also be a drawback, for instance when investigating intrinsic properties. In this respect, theoretical models and first-principle calculations have an irreplaceable role in producing reference data for free-standing systems as well as in permitting the discrimination between concurrent effects.

In this talk I will present some examples of how models and first principle calculations can contribute to the understanding of thin films and how the presence of the environment (be it vacuum, stacking sequence, substrate or liquid solvent) can be taken into account (see Fig.1). I will show our recent results on excitonic properties of hexagonal boron nitride [1,2,3] and black phosphorus thin layers [4]. They have been obtained by coupling first-principle calculations carried out at the Bethe-Salpeter level with simpler analytical or numerical schemes. Comparisons with existing experimental data [4,5,6] will be done as for validation of our predictions or support to phenomenological models. Throughout the talk I will strive to stress advantages and limitations of the theoretical approaches presented.

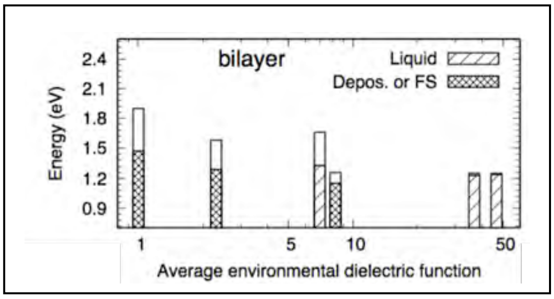

Fig.1 Electronic and optical gap of bilayer black phosphorus in different environments.

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[2] L. Sponza, H. Amara, F. Ducastelle, and A. Loiseau, Phuy. Rev. B **97**, 075121 (2018)

[3] L. Sponza, H. Amara, C. Attaccalite, *et al.*, to be published

[4] E. Gaufrès, F. Fossard, V. Gosselin, L. Sponza, *et al.*, to be published

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[6] L. Schué, L. Sponza, *et al.*, arXiv:1803.03766 (2018)

Tunable graphene-based membranes

K.-G. Zhou[1,2], K. S. Vasu[1,2], C. T. Cherian[1,2], M. Neek-Amal[3], J. C. Zhang[4], H. Ghorbanfekr-Kalashami[3], K. Huang[1,2], O. P. Marshall[5], V. G. Kravets[5], J. Abraham[1,2], Y. Su[1,2], A. N. Grigorenko[5], A. Pratt[4], A. K. Geim[5], F. M. Peeters[3], K. S. Novoselov[5], R. R. Nair[1,2,*]

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Permeation through nanometre-pore materials has been attracting unwavering interest due to fundamental differences in governing mechanisms at macroscopic and molecular scales, the importance of water permeation in living systems, and relevance for filtration and separation techniques. Latest advances in the fabrication of artificial channels and membranes using two-dimensional (2D) materials have enabled the prospect of understanding the nanoscale and sub-nm scale permeation behaviour of water and ions extensively.[1] In particular, graphene oxide (GO) membrane containing 2D graphene capillaries showing unique permeation properties such as ultrafast permeation of water and molecular sieving have been developed by our group. Our recent works have revealed various intriguing phenomenon such as control of mass transport via external stimuli.[2] By purposefully changing the external conditions, we can reversibly tune the mass transport through GO membranes. In my talk, I will discuss our recent results on tuning the mass transport through GO membranes and its prospect for several applications.

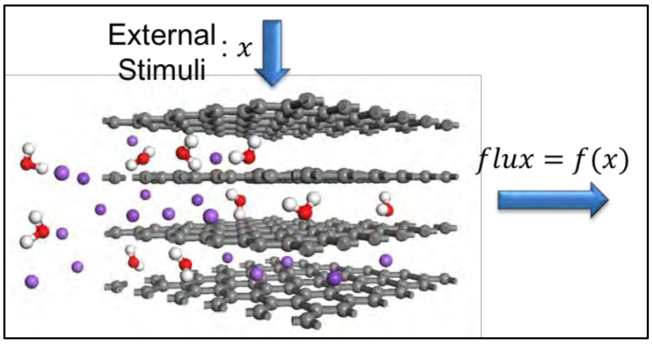

Fig.1 Schematic showing the design of smart membrane based on 2D materials: when the flux of mass transport is a function of external stimuli x, we can purposefully tune the flux by varying the factor x.

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CVD Synthesis, Characterization and Applications of Three Dimensional (3D) Graphene for Advanced Applications

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Two-dimensional (2D) graphene has been extensively studied. Less attention has been paid on fabrication and characterization of 3D graphene structures. Here, we report synthesis of a novel 3D graphene body called graphene pellet and making use of it by fabricating graphene paper [1]. Graphene pellet was synthesized by CVD using Ni particles with defined grain size. This porous metal body served as a catalyst and produced 3D graphene when exposed to a gas mixture of methane, hydrogen and argon at 1000˚C. The obtained graphene pellet was treated with acid for removing the remaining Ni catalyst, which yielded almost 100% pure 3D graphene structure-**Fig**. **1a.** The latter was characterized by SEM, ICP, Raman and 4 probe electrical measurements. The 3D graphene was then converted into a thin graphene paper by pressing, which exhibits a breaking stress of 22 ± 1.4 MPa and electrical conductivity of up to 1136 ± 32 S cm^{-1}. The graphene paper preserves the initial 3D structure. Paper with thickness of 50 μm revealed 60 dB electromagnetic interference shielding effectiveness, which makes it a promising shielding material [1]. Fabrication of electrodes for supercapacitors using 3D graphene will be presented along with performance data of such energy storage devise [2]. Flexible Micro Super Capacitor will be reported-**Fig. 1b and 1c**, which revealed power density of 14.4 mW cm^{-2} and energy density of 0.38 μWh cm^{-2} [3].

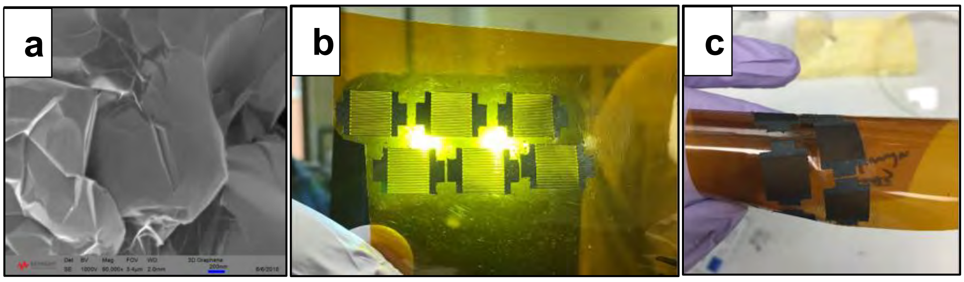

Fig. 1 SEM of 3D graphene-(a); Pictures of multiple Micro Super Capacitors, which are flexible and can be produced on any substrate of interest-(b) and (c).

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3D Graphene for Energy Conversion and Storage

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3D graphene is assembled by the 2D graphene and inherits its properties. With the novel structure, 3D graphene shows special properties of its own. We reported a kind of 3D graphene with super compressive elasticity and near-zero Poisson's ratio [1]. Such 3D graphene could be directly pushed by light and the mechanism was studied [2]. For energy storage, a rechargeable aluminum ion battery with high-rate capability was made using an aluminum metal anode and a three-dimensional graphitic-foam cathode [3]. Based on the aluminum ion battery, a novel 3D graphitic foam was derived through chloroaluminate anion intercalation, with vertically aligned graphene sheets. Such 3D structure afforded a suitable cathode for rechargeable Al-ion battery and lead to a high performance [4].

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[2] Tengfei Zhang†, Huicong Chang†, Yingpeng Wu† (co-first author), Peishuang Xiao, Ningbo Yi, Yanhong Lu, Yanfeng Ma, Yi Huang, Kai Zhao, Xiao-Qing Yan, Zhi-Bo Liu, Jian-Guo Tian & Yongsheng Chen*. Nature Photonics **9**, 471 (2015)

[3] Meng-Chang Lin†, Ming Gong†, Bingan Lu†, Yingpeng Wu† (co-first author), Di-Yan Wang, Mingyun Guan, Michael Angell, Changxin Chen, Jiang Yang, Bing-Joe Hwang and Hongjie Dai*. Nature **520**, 324 (2015)

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On-Chip Heat Management by Boron Nitride Nanosheets

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Faster and smaller electronic devices have led to a universal issue: high heat density on the device chips due to inevitably leakage current. Heat sinks, blowing fans, and cooling fluids are presently use for heat management of high-performance electronic devices and electrical components. Unfortunately, these heat management systems are bulky, and could not be applied directly on the electronic chips due to the risk of an electrical short circuit. Therefore, electrically insulating but highly heat conducting materials that can be applied directly on devices are important for next generation on-chip heat management. Here we report for a novel class of boron nitride nanosheets (BNNSs) that can promote heat dissipation up to 250%.

Boron nitride nanosheets (BNNSs) and boron nitride nanotubes (BNNTs) have generated interest in nanotechnology for being chemically inert, mechanically robust, electrically insulating, and thermally conducting [1, 2]. Flat BNNSs are known for their exceptional in-plane thermal conductivity. Unfortunately, these 2D BNNSs can conduct heat only along the hot surfaces, therefore, not applicable to promote heat away from electronic devices. Here, heat dissipation properties of vertically-aligned BNNSs (VA-BNNSs) are presented. VA-BNNSs are synthesized on silicon substrates by chemical vapor deposition (CCVD) using our growth vapor trapping method [3, 4]. All samples are heated up to 140 ºC and allow to cool to room temperature in static air under *in-situ* monitoring of the chip temperatures. Real-time temperature measurement suggests that Si chips coated with VA-BNNSs has a cooling rate ~250% higher than a bare Si chip. For comparison purpose, VA-BNNTs coated on Si chips are also prepared for comparison. We found that Si chips coated with VA-BNNTs also has ~75% cooling rate faster than that of a bare Si chip, but inferior than the performance of VA-BNNSs. This means, VA-BNNSs can out performed VA-BNNTs by more than ~330% for on-chip heat management. A series of experiments further indicate that performance of VA-BNNSs are higher when the VA feature sizes are increase. Transmission electron microscopy (TEM) suggest that these VA-BNNSs are unique in the edge structures, making them hydrophilic, noticeable different from what have been reported in literatures. Furthermore, these VA-BNNSs can also be peeled and transferred to arbitrary substrates for heat management applications. Details of all these results and the cooling mechanism will be discussed in the meeting.

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Stable reconstructed edge structure in bilayer WSe_2

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The edge structures of two-dimensional materials is of critical importance to influence their electrical[1], magnetic[2], catalytic[3] and photoluminescence[4] properties. Compare to graphene and monolayer transition metal dichalcogenids (TMDs), bilayer TMDs present a diversity of edge structures and the associated electronic structures, and hence it may provide us an extra opportunity to build a new structure with unique material properties. Herein, we report a microscopic study on the edge structures of bilayer tungsten diselenide (WSe_2) via *in situ* atomic-resolution angular dark-field scanning transmission electron microscopy (ADF-STEM). Upon heating at 850 °C, two different types of edge reconstructed from the pristine bilayer WSe_2 edge. The reconstructed edges remain stable in atmospheric environment and at series of temperature below 850 °C including room temperature.

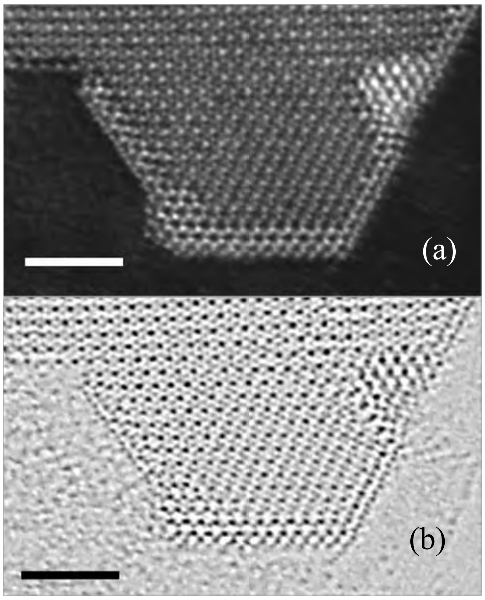

Fig.1 (a) ADF-STEM image and (b) bright field image of a representative reconstructed edge structure in bilayer WSe_2. Scale bar=2 nm.

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Anisotropic strain relaxation of graphene by corrugation on copper crystal faces

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Corrugation is a ubiquitous phenomenon for graphene grown on metal substrates by chemical vapor deposition (CVD), which greatly affects the electrical, mechanical, and chemical properties. Recent years have witnessed great progress in controlled growth of large graphene single crystals; however, the issue of surface roughness is far from being addressed. Here, the corrugation at the interface of copper (Cu) and graphene, including Cu step bunches (CuSB) and graphene wrinkles, were investigated and ascribed to the anisotropic strain relaxation. We found that the corrugation strongly relied on Cu crystallographic orientations, specifically, the packed density and anisotropic atomic configuration. Dense Cu step bunches were prone to form on loose packed faces due to the instability of surface dynamics. On an anisotropic Cu crystal surface, Cu step bunches and graphene wrinkles formed in two perpendicular directions to release the anisotropic interfacial stress, as revealed by morphology imaging and vibrational analysis. Cu(111) is the suitable crystal face for growth of ultraflat graphene with roughness as low as 0.20 nm. We believe the findings would contribute to clarifying the interplay between graphene and Cu crystal faces, and reducing surface roughness of graphene by engineering the crystallographic orientation of Cu substrates.

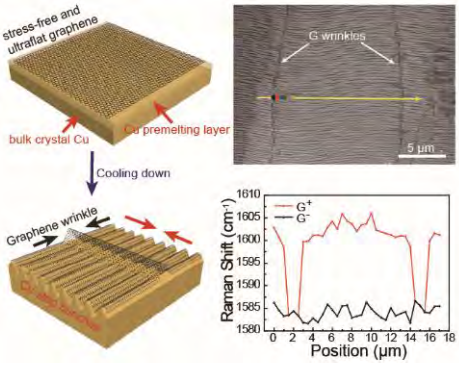

Fig.1 Strain relaxation and corrugation of graphene on Cu substraets.

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Precise control of graphene etching by remote hydrogen plasma

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Graphene with atomically smooth and configuration-specific edges is a vital element in graphene-based electronic devices, the electrical properties of which are significantly affected by the edge states [1]. Remote hydrogen plasma etching of graphene has been proven to be an effective way to create smooth edges with specific zigzag configuration [2]. With the help of our home-built plasma enhanced chemical vapor deposition (PECVD) system, the detailed etching process of graphene in remote hydrogen plasma is revealed. Moreover, a geometrical model is built to illustrate the configuration evolution of graphene edges during etching, which explains the experimental results well and predicts as well the probability of creating armchair edges of graphene justified by subsequent experiments (Fig. 1). We hope that this understanding of the etching process would facilitate the fabrication of graphene-based electronic devices with controlled edges and the exploration of more fantastic properties.

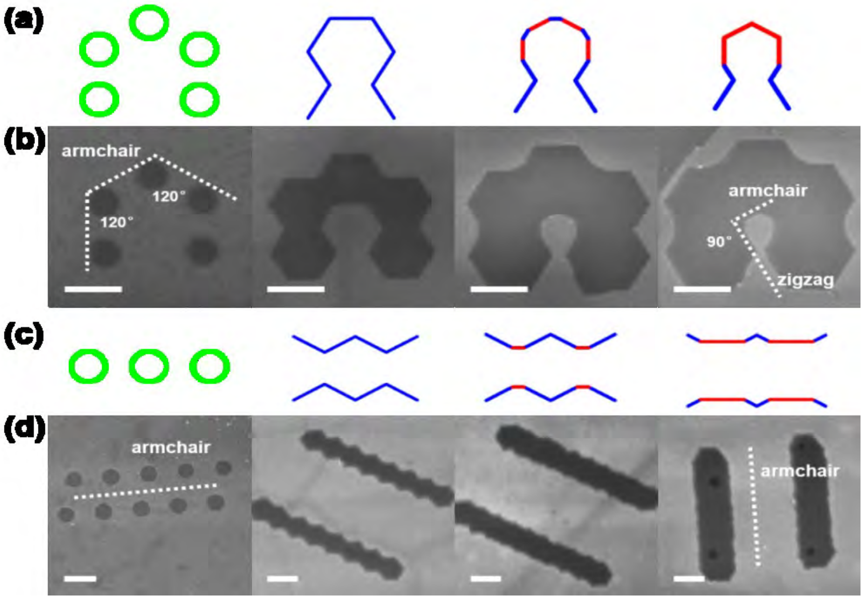

Fig. 1 ((a) and (c)) Illustration of the creation of armchair edges from zigzag edges of graphene in a kinetics-controlled way. ((b) and (d)) SEM images of trilayer graphene to demonstrate the illustration in Figs. 1(a) and 1(c). The orientation of armchair edges is shown by the dashed lines. All the scale bars are 300 nm.

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Single Crystal Graphene on Cu(111) foil: Strain Relaxation, Chemical Functionalization, and Control of Adlayers

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CVD of graphene on single crystal Cu(111) foil can yield epitaxial growth of single crystal graphene suggesting it as, currently, the most promising method for the preparation of large area single crystal graphene [1-2]. I will mainly talk about:

Single crystal graphene islands grown on Cu(111) foils are found to be free of wrinkles and to have compressive strain. The compressive strain in the epitaxial regions (0.25-0.40%) is higher than regions where the graphene is not epitaxial with the underlying surface (0.20-0.25%), with the formation of wrinkles in the non-epitaxial regions. (A very small fraction of the islands have 2 regions—one is epitaxial, the other non-epitaxial—roughly 1 in every 100,000 islands.) DFT calculations suggest a large frictional force between the epitaxial graphene and the Cu(111) substrate that provides an energy barrier to the formation of wrinkles in the graphene. Enhanced chemical reactivity is found in epitaxial graphene on Cu(111) foils as compared to non-epitaxial graphene on polycrystalline Cu foils for certain chemical reactions [3].

An adlayer-free single layer graphene film is always obtained on Cu(111) foil for a relatively wide synthesis window of H_2/CH_4 ratios and CVD pressures. In contrast, graphene film with adlayers is always obtained on as-received polycrystalline Cu foils under the same growth conditions. LEED shows that the adlayer-free single layer graphene film grown on Cu(111) foil is single crystal, as is also found by micro-LEED and UHV-STM. Carbon present inside the polycrystalline Cu foil leads to the presence of adlayers, and this C was identified by ToF-SIMS depth profiling, and combustion analysis, of the Cu foils. After removing any dissolved carbon in the polycrystalline Cu foil by annealing in hydrogen, an adlayer-free polycrystalline single layer graphene film is obtained.

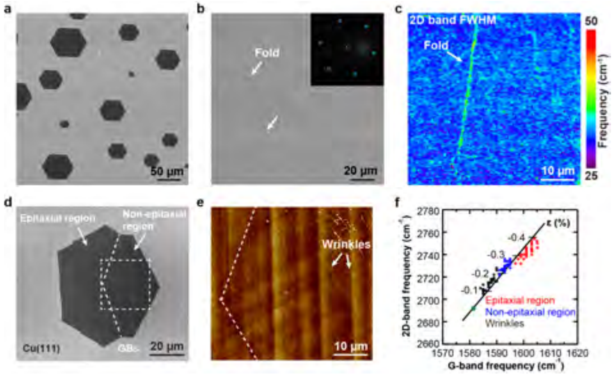

Fig. 1 (a-b) SEM images of (a) graphene islands and (b) adlayer-free graphene film grown on Cu(111) foils. Inset in (b) shows a LEED pattern of graphene film. (c) Raman map of 2D band width of adlayer-free graphene film on 300 nm SiO_2/Si wafer. (d) SEM image of a multicrystalline graphene island grown on Cu(111) foil. (e) AFM image of a graphene region within the dashed box in (d). (f) Correlation between the frequencies of the G and 2D bands acquired from wrinkles, epitaxial, and non-epitaxial graphene regions.

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Characterization of Industrial CNT materials (powders, fibers, etc)

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More than 25 years has pasted since the discovery of carbon nanotubes (CNT), and now many real applications are well recognized in the market such as Li ion batteries electrodes, CNT touch panel used in smartphones, etc, and much more are going to show up soon. AIST has established the CNT Application Research Center whose primary mission is to support the CNT industry.

In general, the CNT users who are developing applications do not care what CNT (e.g., whether it is MWNT or SWNT) they are going to use, but would choose the best CNT suited for their purpose. Frequently, people who have started using CNT`s has asked me

"There are many different CNTs in the market, and which one should I use?"

The same question could be done for many types of CNT materials such as fibers, master batches, dispersions.

The CNT Application Research Center has developed many new CNT characterization techniques specialized to evaluate industrial CNT materials. Examples of the new characterization techniques are using plasmon resonance to measure the length of CNTs and using CPS disc centrifuge to characterize the size of the CNT aggregate dispersions.

In this talk, I would overview our efforts to characterize and classify many CNT materials with the help of these tools from which we have and found many intrinsic and fundamental trends.

Raman Spectroscopy of Individual Single-Walled Carbon Nanotubes

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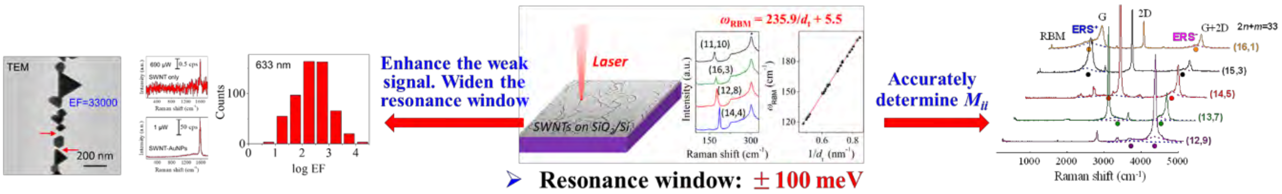
Single-walled carbon nanotubes (SWNTs) have been one of the most intensively studied materials since the discovery in 1993 [1]. Among all the characterization methods of SWNTs, Raman spectroscopy is a versatile tool that can achieve the most information with the maximum simplicity [2]. To explicitly explore the intrinsic structures and properties of SWNTs, we study Raman spectra of individual SWNTs at the single-tube level to minimize the ambiguities caused by the assortment of different tube species. In this work, we study individual SWNTs by Raman spectroscopy, including resonant Raman spectroscopy [3,4], electronic Raman spectroscopy (ERS) [5,6], and surface-enhanced Raman spectroscopy (SERS) [7]. In addition, a bilayer plot that can be used to accurately determine the chirality of SWNTs under complex environments is also reported [8]. A program for accurate determination of the chirality of SWNTs under six common environments based on the bilayer plots is launched on our group Web site (www.chem.pku.edu.cn/cnt_assign).



- **Maximum SERS enhancement:** 33000
- **Resonance window:** ±100 meV
- ω_{RBM} **range:** ±2.5 cm^{-1}
- **ERS-based Raman:** ±1 meV

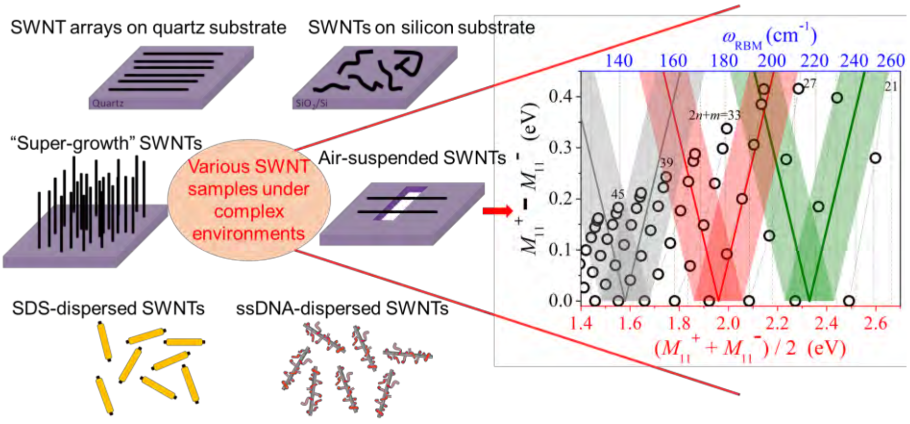


Fig.1 Raman spectroscopy of individual single-walled carbon nanotubes and the bilayer plots for accurately determining the chirality of SWNTs under six different environments

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Detection of Off-Resonance Single-Walled Carbon Nanotubes by Enormous Surface-Enhanced Raman Scattering

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The resonant Raman spectroscopy can only detect on-resonance single-walled carbon nanotubes (SWNTs) within the laser resonance window [1,2]. In principle, surface-enhanced Raman scattering (SERS) spectroscopy can expand the resonance window [3]. However, detection of off-resonance SWNTs by SERS remains challenging due to the difficulties in locating the SWNTs exactly at the hot spots with enormous SERS enhancements [4,5]. Here, we report a facile design of a ultrasonic spray pyrolysis method to in-situ form closely spaced polyhedral gold nanocrystals (AuNCs) on one-dimensional SWNTs [6]. The fact that the edges of the AuNCs attach to the SWNTs ensures the location of SWNTs at the hot spots. Consequently, we achieve enormous enhancements of the Raman signal of the SWNTs that are two orders of magnitude higher than any previous values. The enormous enhancements not only enable the detection of many off-resonance SWNTs but also allow the detection of several Raman bands of the SWNTs that have not been reported previously.

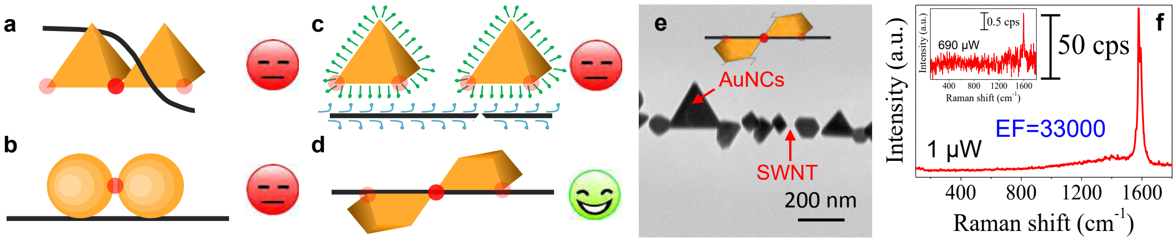

Fig.1 Schematics of SERS enhancements of SWNTs in various cases, the maximum EF and the corresponding morphology of AuNCs-SWNT.

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Low Defect SWCNTs by Repetitive Sonication–Ultracentrifugation

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Single-wall carbon nanotubes (SWCNTs) are promising for building block of future electronic devices due to their high carrier mobility. Well known problem of this material is that the as-synthesized SWCNT is always a mixture of metallic (M-) and semiconducting (S-) ones and post-purification is necessary. Within this decade anionic surfactant based M/S separation techniques have been highly improved and are very useful as post-purification of SWCNTs. For the M/S separation, however, bundled SWCNTs need to be dispersed into individual forms using ultrasonic dispersion. It is also well known that this process unavoidably generates structural defects on the SWCNTs that degrade device performance. To minimize the defect introduction keeping high dispersion yield, the sonication process has to be optimized. Shirae et al. [1] reported that a repetitive sonication–centrifugation process can produce less-defective and longer SWCNT dispersion suitable for conductive film. For the M/S separation, however, we need individually dispersed SWCNTs, which require stronger sonication and ultracentrifugation process. In this study, therefore, we aimed to obtain highly-dispersed and less-defective SWCNTs using repetitive sonication-ultracentrifugation process.

Pristine SWCNTs were sonicated in sodium cholate (SC) aqueous solution for relatively short time and then ultracentrifuged. Supernatant was collected as individually dispersed SWCNT solution. A sediment was dissolved in SC solution again and was used for the second cycle of the sonication and ultracentrifugation. The repetitive sonication–ultracentrifugation process was repeated until the total sonication time reaches 150 min. Fig. 1 shows G/D Raman intensity ratio of each supernatant and the sum of the collected SWCNT as supernatant for 20 and 30 min sonication case. Result for 150 min one-time sonication is also indicated. Clearly, 20 min sample shows higher G/D and higher yield than for 30 min and 150 min ones for any intermediate sonication time. This result strongly suggests that shorter sonication time is better for getting better quality SWCNTs with higher yield. Only one but serious problem is time and effort. We have to further optimize a cost-effective process towards high-performance device applications. Detailed discussion will be given in the presentation.

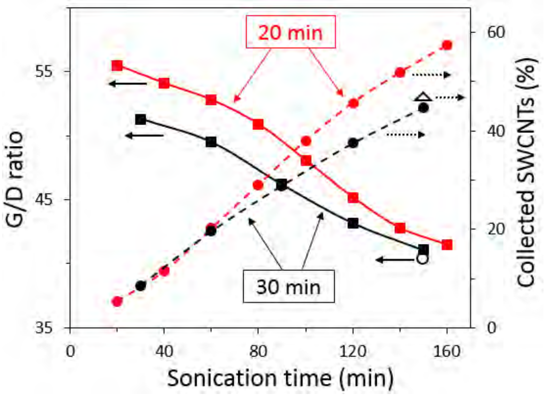

Fig. 1. The G/D ratio of dispersed SWCNTs as a function of sonication time. And, the amount of collected SWCNTs with the increasing of sonication time. The open cycle and triangle indicate the G/D ratio and the amount of SWCNTs dispersed by one cycle of sonication for 150 min, respectively.

This work was supported by JST CREST Grant Number JPMJCR16Q2, Japan.

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Double-resonance Raman scattering in carbon nanotubes and transition metals dichalcogenides

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Double-resonant Raman scattering is a sensitive probe to study electron-phonon interaction in both carbon nanomaterials and 2D transition metals dichalcogenides. For carbon nanotubes, double resonance process involves different cutting lines in the 1D Brillouin zone. The selection of different quantized wavevectors is highlighted by a step-like dispersive behavior in the two-phonon 2D band. The step-like dispersive behavior is observed when the laser excitation light is tuned and the measurements are performed in single or few-chiralities SWNT samples [1]. For semiconducting two-dimensional transition-metal dichalcogenides, the double-resonance Raman process involves different valleys and phonons in the Brillouin zone. Here we present a multiple energy excitation Raman study that unveil the double-resonance Raman scattering process in monolayer and bulk MoS2. Results show that the frequency of some Raman features shifts when changing the excitation energy and such bands arise from distinct acoustic phonons connecting different valley states. The double-resonance Raman process is affected by the indirect-to-direct bandgap transition, and a comparison of results in monolayer and bulk allows the assignment of each Raman feature near the M or K points of the Brillouin zone [2]. Moreover, we show the temperature dependence on the double resonance Raman process where the changing of the exciton energy when the sample temperature is changed is responsible for a dispersion of the double resonant peaks associated with acoustic phonons.

Acknowledgements

This work was supported by the Brazilian agencies CNPq, CAPES and FAPEMIG.

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Systematic aqueous two-phase separations of carbon nanotubes to investigate the separation mechanism

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Aqueous two-phase (ATP) separation has been demonstrated as a fast, highly-scalable separation technique to sort single-wall carbon nanotubes (SWCNTs) by diameter, chirality, metallicity, etc.[1-2] In ATP, two water-soluble, yet immiscible polymers are mixed together at sufficiently high concentration after which they spontaneously form two phases with different hydrophilicity. In a typical separation protocol, SWCNTs are added to this two-polymer mixture with a combination of different surfactants, resulting in separation of different chiral species among both phases. While very promising separations have been achieved, the separation mechanism is not well understood.

In this paper, we present a series of ATP separations, in which surfactant combinations and concentrations are systematically varied. Absorption spectroscopy, multi-wavelength resonant Raman scattering and wavelength-dependent photoluminescence-excitation spectroscopy, combined with detailed two-dimensional spectral analysis, is applied to characterize the full composition of the resulting separated fractions and as such study the underlying separation mechanism. These systematic studies reveal that chirality-dependent surfactant interactions determine the separation order.

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Resonance Raman spectroscopy on Linear Carbon Chains

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Recently we demonstrated synthesis of confined one-dimensional linear carbon chains (LCCs) inside double-walled carbon nanotubes with the shortest chains consisting of around 30 carbon atoms (polyyne) and the longest chains with a record length of more than 6000 carbon atoms (carbyne) [1]. In this presentation, I will show our results on the resonant Raman spectroscopy of these chains with different lengths. For example, the optical energy gaps of the confined chains have been determined in the range of 1.8-2.3 eV [2]. A linear relation between the energy gap and the Raman frequency has been proposed, which allows one to easily estimate the energy gap of the unknown LCCs via Raman spectroscopy [2]. In addition, the excited states of the confined chains will be discussed and the displacement between the ground state and the excited state can be obtained from the Albrecht equation [3].

This work was supported by the Austrian Science Funds (FWF, P27769-N20) and the European Union’s Horizon 2020 research and innovation programme under grant agreement No 664878.

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Standardization of the defectiveness for multi-walled carbon nanotubes via Raman spectra

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The quality of multi-walled carbon nanotubes (MWCNTs) is a complex parameter consisting of different properties of individual tubes and their structure: defect concentration within graphene blocks forming nanotube walls, nature and relative amount of functional groups on the nanotube surface, accessibility and content of catalyst remains, *etc.* The development of MWCNT synthesis in the reactors with fluidized beds has shifted the attention from the price to the properties of the nanotubes. Taking into account that any potential application requires nanotubes with specific characteristics, influence of catalyst nature and growth conditions on MWCNT quality becomes a key factor to be solved. However, MWCNTs are class of materials with wide range of properties. This restrains the development of fine theoretical models for MWCNT structure. E.g. Raman spectroscopy theory - one of the most common and suitable express methods to study nanotube structure – mostly deals with more convenient nanocarbons: graphene and single-walled carbon nanotubes. Thus, only phenomenological experimental approach can be applied nowadays to examine MWCNTs. Most of the corresponding models consider the ratio of intensities of G and D bands of MWCNT Raman spectra as a metric for defective structure. However, as it was already shown for graphene and single-walled carbon nanotubes, the of G/D ratio as a function of defect concentration has extremum, providing certain ambiguity without additional studies. Moreover, the G band is strongly affected by "saturation" of carbon defects with hydrogen.

Here we present the systematic study of the ratio of 2D and D bands of MWCNT Raman spectra. The influence of the catalyst particle size and chemical nature (Fe, Co, Mo, Mn, and their combinations), reaction temperature, posttreatment (defect annealing, ball milling) have been studied from the 2D/D point of view. The model of nanotube structure and Raman metrics for MWCNTs has been proposed.

This work is supported by the Russian Science Foundation (grant 17-73-20293) and Russian Foundation for Basic Research (grant 18-02-01103_A to S.N. Bokova-Sirosh to conduct Raman spectroscopic studies).

The Observation of Electronic Raman Scattering in Suspended Semiconducting Carbon Nanotubes

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Recently, the Electronic Raman Scattering (ERS) is reported to be a particular Raman feature arising from the inelastic scattering of the photoexcited electrons by a continuum of low-lying electron-hole (*e-h*) pairs across the linear electronic subbands near the Fermi level of the metallic single-walled carbon nanotubes (M-SWNTs) [1-4]. However, such process has not been predicted and observed in semiconducting (S-) SWNTs previously due to the absence of those low-lying *e-h* pairs. In this work, we report that the ERS spectra are not only applicable to M-SWNTs, but also can be observed in S-SWNTs. Although S-SWNTs do not possess the low-energy *e-h* pairs across the linear electronic subbands near the Fermi level like the M-SWNTs do, S-SWNTs have high-energy *e-h* pairs that can also contribute to the ERS processes (Fig. 1). Similar to the case for M-SWNTs, the ERS process reveals a wealth of information about the electronic structures for S-SWNTs, which are of great importance to nanotube-related science and technology.

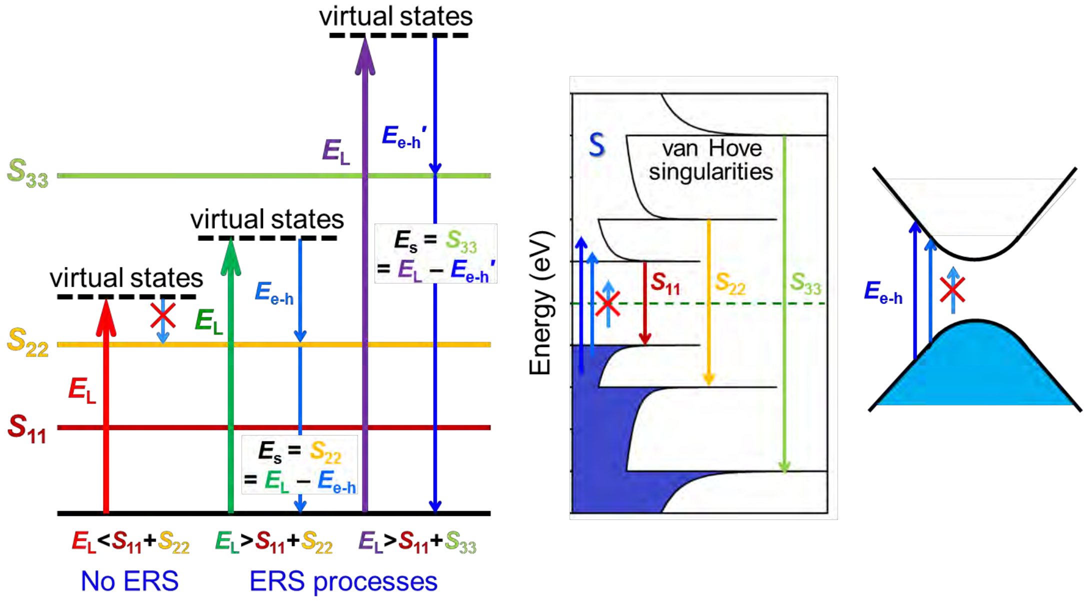

Fig.1 The ERS processes in S-SWNTs.

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The helical conformation of poly(3,5-disubstituted phenylacetylene)s tuned by nanomaterials

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The novel poly(phenylacetylene)s (PPAs) substituted at the *meta* position(s) by chiral alkylamide group, R-I and S-I, were used. The dependence of the screw sense of helical polyene backbone on the structure influenced by different kinds of nanomaterials, i.e., HiPCO SWNTs, graphene, C_{60}, Au NPs, SiO_2 NPs, was systematically investigated in organic solution. The chain structures and helical transitions were mainly characterized by UV-vis absorption and circular dichroism (CD). The CD spectra shows that R-I and S-I's CD signal changes after the above-mentioned nanomaterials were added. We propose that the helical transitions of the polyene backbone is related to the spatial configuration of pyrene group, which is dependent on the nanomaterials.

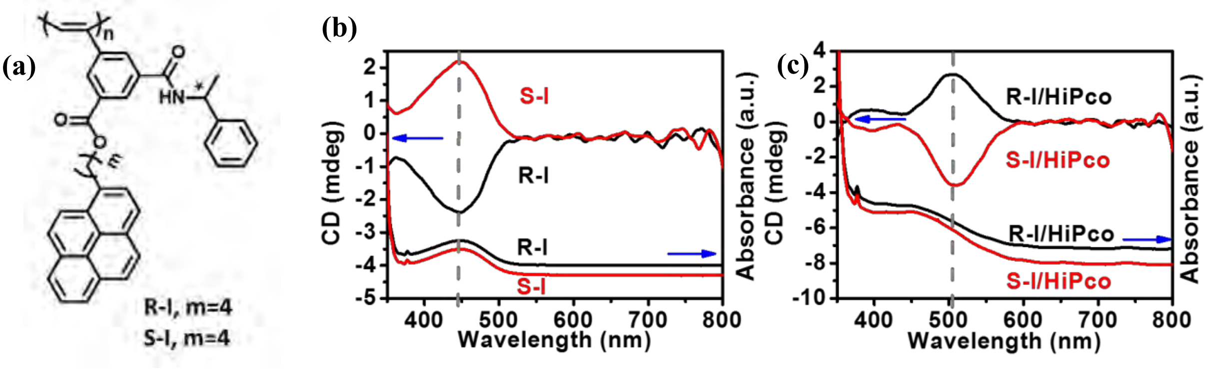

Figure: (a) Suctures of **R-I** and **S-I**; (b,c) CD spectra of 0.01mg/mL R-I/S-I in NMP (b) and 0.05mg/mL **R-I/S-I** HiPCO in NMP (c)

Carbon/Li Metal Composite Anode in Safe High-Energy-Density Rechargeable Batteries

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Li metal is considered as the "Holy Grail" of energy storage systems. The bright prospects give rise to worldwide interests in the metallic Li for the next generation energy storage systems, including highly considered rechargeable metallic Li batteries such as Li-O_2 and Li-sulfur (Li–S) batteries. However, the formation of Li dendrites induced by inhomogeneous distribution of current density on the Li metal anode and the concentration gradient of Li ions at the electrolyte/electrode interface is a crucial issue that hinders the practical demonstration of high-energy-density metallic Li batteries.

In this talk, we review the lithium metal anode protection in a polysulfide-rich environment. Firstly, the importance and dilemma of Li metal anode issues in lithium–sulfur batteries are underscored, aiming to arouse the attentions to Li metal anode protection. Specific attentions are paid to the surface chemistry of Li metal anode in a polysulfide-rich lithium–sulfur battery. Next, the proposed strategies to stabilize solid electrolyte interface and protect Li metal anode are included. Finally, a general conclusion and a perspective on the current limitations, as well as recommended future research directions of Li metal anode in rechargeable batteries are presented.

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Porous carbon for Li-ion storage

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Porous carbon is one of the most promising anode materials for rechargeable lithium-ion batteries, because of their possess high surface area, pore volume, and electrical conductivity. The mesoporous carbon materials were synthesis by chemical vapor deposition method because of decomposition of ethylene or toluene on iron doped calcium tartrate catalytic system. These materials are different in morphology, quantity of defects and surface area. The porous carbon produced from ethanol consists of corrugated thin graphitic layers, while toluene-produced carbon comprises multi-layered shells. Here, we study the behavior of Li accumulation in mesoporous carbon materials using in situ X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS). The samples of mesoporous carbon were exposed to Li vapor for 5 min at a current ~ 8 A under ultra-high vacuum and at room temperature. XPS and NEXAFS spectra of the samples were measured right after Li deposition without their exposure to air. The Li-induced changes in the composition and electronic structure of the samples were revealed. The concentration of lithium was estimated to be higher in the porous carbon, which was produced from ethanol, than that from toluene. The Li atoms penetrate more dipper into the carbon material produced from ethanol, than that produced from toluene. The electrochemical measurements and electrochemical impedance spectroscopy were performed on the half-cells with carbon cathode and lithium anode. The porous carbon material produced from toluene (ethanol) possesses average capacities 280 and 170 $mA \cdot h \cdot g^{-1}$ (340 and 170 $mA \cdot h \cdot g^{-1}$) at 0.1 and 1 $A \cdot g^{-1}$. The capacities of the sample produced from ethanol reduced to 290 and 140 $mA \cdot h \cdot g^{-1}$ at 0.1 and 1 $A \cdot g^{-1}$ after annealing of the sample at 400 °C. According to XPS data, the concentration of the lithium adsorbed on the sample produced from ethanol strongly decrease in the result of its previously annealing at 400 °C. We suggest that the thermal treatment led to the rearrangement of atomic structure, which closed some channels for lithium penetration. This finding provides new insight into the centers of Li storage into the porous carbon and provides recommendations for designing carbon-base anode materials for high-performance Li-ion batteries.

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Effect of the component coupling on electrochemical properties of MoS_2/holey graphene hybrids in lithium-ion batteries

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One of the open questions in a research of MoS_2/carbon support(C) systems for Li-ion batteries is the influence of component interaction on the hybrid capacity. Hybrid structures based on layers of MoS_2 and graphite have properties different from those of individual components. At present, many synthetic procedures have been proposed for the synthesis of MoS_2/C and these materials are different in morphology, anisotropy, size, and component coupling. All these factors may influence stability and electrochemical capacity of the MoS_2/C composites. As regarding the coupling, usually, the layers of MoS_2 and graphene interact weakly via van der Waals forces. However, a strong bonding in heterostructure is also possible, as shown for MoS_2 grown on the surface of reduced graphene oxide [1]. Revealing of such interactions requests a set of experimental techniques including Raman spectroscopy and near-edge X-ray absorption fine structure (NEXAFS). A way for direct component bonding in the MoS_2/C hybrids is the use of a support with defects, for example, holes, with active carbon atoms on the edges [2].

In the present work, we develop a new method for the synthesis of MoS_2 layers on the surface of graphene. Thin MoS_2 layers were grown as the result of decomposition of amorphous MoS_3 under high mechanical pressure and high temperature (Fig.1). The pressure was expected to provide crystallization of MoS_2 layers and their coupling with graphene. To increase this interaction, MoS_3 was deposited on holey graphene (HG) layers, obtained by heating of graphite oxide (GO) in concentrated sulfuric acid (H_2SO_4). The structural characteristics, composition, and interaction of MoS_2/HG hybrids, evaluated by a wide range of the methods Raman scattering, X-ray photoelectron spectroscopy (XPS), and NEXAFS spectroscopy. The MoS_2/HG hybrids synthesized under pressure showed better rate capability in lithium-ion batteries as compared to non-pressed samples.

The work was supported by the Russian Science Foundation (Grant 16-13-00016).

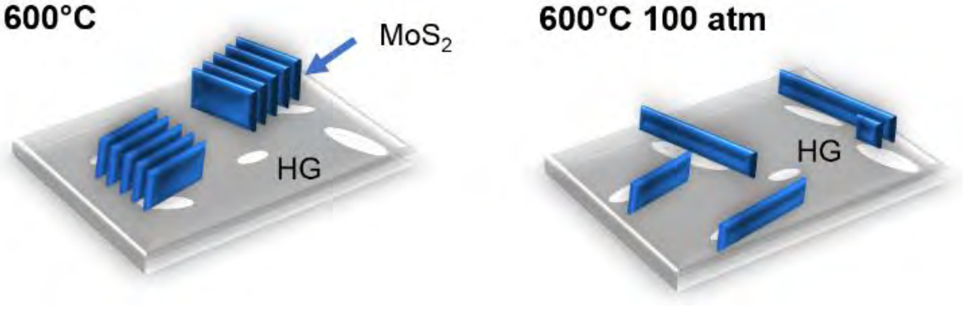

Fig. 1. Schematic representation of MoS_2/HG hybrids synthesized without (left) and with (right) pressure.

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Bioinspired Multi-Scale Pores and Channels

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There are varieties of multi-scale pores/channels existing in nature, ranging from nano-scale, micro-scale to macro-scale. After millions of years' evolution, those pores/channels' mechanisms existing in nature serve as sources of inspirations for us to develop new smart materials and systems. On the micro-scale, the big issues exist are energy saving, anti-fouling, controllability, and good stability. Here we show a versatile bio-inspired strategy for creating liquid gating mechanism with tunable multiphase selectivity and antifouling behaviour. On the nano-scale, we have prepared various geometries of nanopores and nanochannels, and through modification and functionalization, they have shown great potential applications in substance transport and energy utilization. In particular, the carbon nanochannel membranes we have fabricated exhibit outstanding corrosion resistance, high separation efficiency, and excellent ion selectivity in seawater desalination.

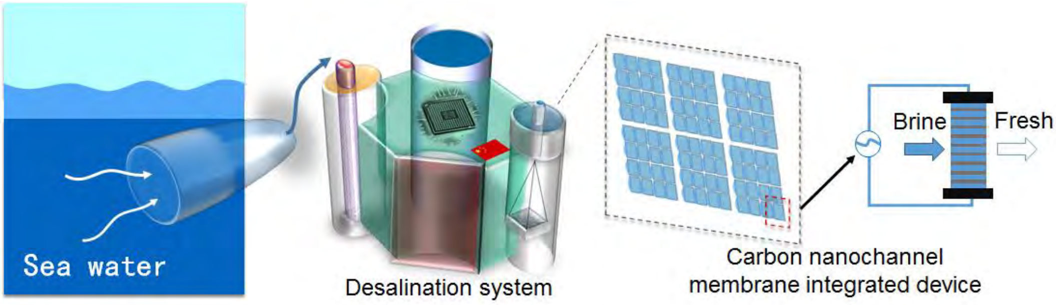

Fig.1 Schematic of carbon nanochannel membrane for seawater desalination system.

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Production and functionalization of carbon nanotubes for energy devices

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To efficiently use renewable energy at larger scale and support society, energy devices should be produced at lower cost using abundant chemical elements. Carbon nanotubes (CNTs), which are composed of carbon, are attractive due to their properties including high specific surface area, high electric conductivity, lightness, flexibility, thermal/chemical stability, and good compatibility with solution processing. We focus on their use as passive electrode materials in combination with various active materials in energy devices.

Battery/capacitor electrodes are an attractive target in which carbon black and carbon nanofibers have been used as conductive fillers. Small-diameter CNTs show the unique self-supporting nature, and we are trying to replace heavy 2D metal foils with light-weight 3D CNT sponges for current collectors. We use >99 wt%-pure, submillimeter-long few-wall CNTs by fluidized bed [1]. 1 wt% CNTs realized self-supporting $LiCoO_2$ cathodes and graphite anodes via simple co-dispersion and co-filtration, which minimized the use of metal foils in lithium ion batteries (Fig. 1) [2]. Si is an emerging material having a huge theoretical capacity. We have realized a-few-s synthesis of Si nanoparticles by gas-evaporation and realized high-capacity, self-supporting Si-CNT electrodes [3]. CNT sponge-based S cathodes will also be presented.

Transparent conductive films (TCFs) are another attractive target, which uses only 5−10 mg CNTs per 1 m^2 and thus is cost effective. But such small amount of CNTs need to carry sufficient current. We have proposed the repetitive dispersion-centrifugation process to overcome the quality-quantity trade-off and realized >90% conversion of CNTs into TCFs of 80% transmittance and 50 Ω/sq resistance with HNO_3 doping [4]. We used such solution-processed CNT-TCFs to fabricate CNT-Si heterojunction solar cells and realized ~10% power conversion efficiency with flat n-Si wafer with HNO_3 doping and with textured n-Si wafer without doping (Fig. 2) [5]. This technology will be combined with our large-grain Si films fabricated in 1 min by rapid vapor deposition [6] toward low-cost, stable, and flexible CNT-Si solar cells.

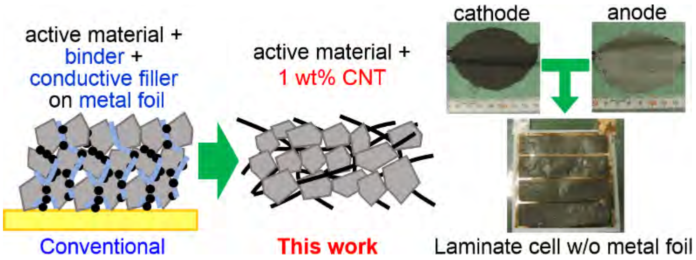

Fig. 1. LIBs based on 3D CNT current collectors [2].

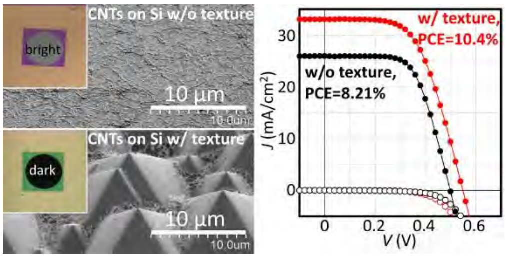

Fig. 2. Si-CNT solar cell [5].

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Highly-Ordered Low-Dimensional Telluride/Selenide Anchored on a Carbon Nanotube Scaffold for Flexible Thermoelectrics

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Flexible thermoelectrics (TEs) are attracting great interest as potential component of renewable energy technologies to convert heat into electrical energy for micro/nano electronics, such as wearable devices and smart sensor networks. There remains a struggling against the trade-off between flexibility and TE performance. However, synthesis of flexible and high-efficiency TE materials is still a challenge, which might restrain their application in new generation flexible electronic component. Herein, we present a novel approach to fabricate flexible thermoelectric nanocomposites through depositing M_2C_3-based (M=Bi, Sb; C=Te, Se) alloys on single-walled carbon nanotubes (SWCNTs) scaffold. [1] The nanocomposite reveals highly-ordered and nanoporous microstructures, which consists of (000*l*) textured M_2C_3 nanograins grown on SWCNTs with good adhesion. The freestanding M_2C_3 nanocomposite exhibits remarkable mechanically reliable flexibility over hundreds bending circles, of which the bending deformation radius could be as high as a few millimeters. Large power factors of ~1550 to 1100 $\mu W/m\cdot K^2$ are obtained for the Bi_2Te_3/SWCNTs nanocomposite from room temperature (RT) to 473 K. Owing to the high density of defects, such as Bi_2Te_3/SWCNTs interfaces, stacking faults and nanopores, the in-plane thermal conductivity is as low as ~0.6 W/m·K. Such high power factor and low thermal conductivity give rise to a TE figure of merit (ZT) of ~ 0.9 at RT. Our approach opens up a new way to fabricate flexible TE materials with high performance, which could have promising applications in flexible electronics.

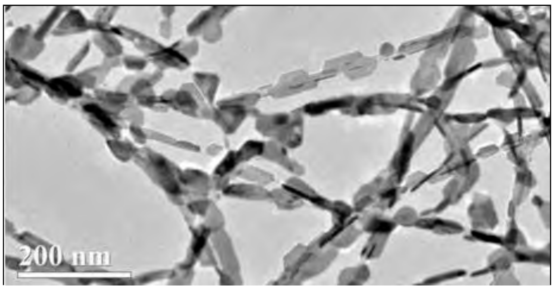

Fig.1 Bright-field transmission electron microscope (TEM) images of the Bi_2Te_3-SWCNT hybrid

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Laser-assisted recovering of fluorinated graphene for preparation of flexible energy storage devices.

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Graphene, among large number of carbon-based materials, have used one of the basic components in the fabrication of flexible electrodes for supercapacitors [1, 2]. It has unique 2D structure of sp^2-hybridized carbon atoms with maximal specific area of 2450 cm^2/g, inertness and possibility of chemical modification exhibit usage as a component in the electrochemical supercapacitors [3]. Moreover, superior mechanical strength proposed to make stretching, bending or twisting electrodes. For now, scalable and cheap patterning, efficient converting to graphene and development of graphene-based composites are still of great interest for fabrication of high-performance in-plane micro-supercapacitors (MSCs).

We used irradiation of ultraviolet low-power laser to fabricate conductive graphene electrodes on the surface of fluorinated graphene films. Laser treatment leads to simultaneous exfoliation and conversion of material into few-layered graphene, while dielectric graphene fluoride serves as a separator/electrolyte storage. Under ultraviolet laser irradiation fluorine atoms could be detached separately recovering sp^2-conjugated structure or with carbon atoms forming huge number of nm-sized holes. The structure and composition of resulted material depends on the power density of laser, which influence on the electrochemical performance of device. This technique enables to fabricate monolithic in-plane MSCs without use of binders, conductive additives, masking or lithography. The obtained laser reduced graphene fluoride electrodes are used as an electroactive material due to good conductivity, developed structure and holes, which are useful for high-performance electrodes with accessible for ion diffusion. Such material has appropriate areal capacity of 0.3 mF/cm^{-2} at 1 V/s, fast response and could operate at ultrahigh scan rates in the aqueous electrolyte.

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Transition metal selenide nanoparticles embedded in carbon matrix for extraordinary cycling and rate performance of sodium ion batteries

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Development of electrode materials with high capacity, superior rate performance, long cycle life and low cost is critical to commercialize sodium ion batteries (SIBs). Transition metal chalcogenides (TMCs) are capable of delivering appropriately high energy capacities as anode of sodium ion batteries (SIBs). But, TMCs suffer from poor cycle life and rate capabilities, mainly due to the large volume expansions causing electrode deteriorations and poor conductivities. To address the conductivity and volume expansion issues, we put forward a compelling combination of nano-sized (3-10nm) cobalt selenide ($Co_{0.85}Se$) particles embedded in carbon spheres (CoSe@CSs). Carbon matrix of these spheres acts as support materials to $Co_{0.85}Se$ particles, provides necessary space for volume changes and most importantly, offers a conductive path for electron transfer during intercalation/de-intercalation of ions. Due to these features, the CoSe@CSs present excellent electrochemical properties when used as an anode of SIBs. With a stable life of more than 10,000 cycles, CoSe@CSs composite delivered a discharge capacity of 260 mA h g^{-1} at 4000 mA g^{-1} scan rate. It also exhibits a high discharge capacity (554 mA h g^{-1} at 100 mA g^{-1} after 50 cycles) and superior rate capability (900 mA h g^{-1} at 100 mA g^{-1} and 286 mA h g^{-1} at 8000 mA g^{-1}). Furthermore, binary TMCs with a spinel structure of AB_2X_4 (where A, B are transition metals and X is chalcogenide) benefit from enhanced intrinsic conductivity and larger crystal structure compared to their mono-metal counterparts (AX_2). Therefore, a mesoporous structure of such binary metal selenides with carbon modification is expected to be a promising anode for SIBs and rectify above issues. Considering these facts, we designed and synthesized hierarchically porous spheres of nanoparticles of iron cobalt selenide (Fe_2CoSe_4) assembled in a carbon matrix (termed as FCSe) in our second study. Due to superior intrinsic conductivity, larger crystal size of binary metal selenide (compared to mono-metal selenide), presence of hierarchical pores, and the existence of intimate contact between nanoparticles of FCSe and carbon matrix, FCSe anode presented outstanding electrochemical properties. The specific capacity of FCSe was as high as 614.5 mA h g^{-1} at 0.1 A g^{-1} after 100 cycles and when observed at the current rate of 4 A g^{-1} the specific capacity still remained 350 mA h g^{-1} even after 5000 cycles. Additional to this, the material showed excellent rate capability, i.e. 816.3 mA h g^{-1} at 0.5 A g^{-1} and 400.2 mA h g^{-1} at an extremely high current rate of 32 A g^{-1}. Following the outstanding performance of FCSe in half-cell configurations, it was further combined with home-made $Na_3V_2(PO_4)_3/C$ cathode in Na-ion full cells to evaluate its commercial significance. A reasonably high and stable specific capacity of 360.2 mA h g^{-1} was achieved for Na-ion full cells with a retention of 247.6 mA h g^{-1} after 100 cycles (at 0.2 A g^{-1}) in the voltage range 0.5-3.0 V. Post cycling morphological analysis prove that the FCSe was able to maintain the spherical shapes after 100 charge/discharge cycles. Overall, these strategies will open up a new way to produce transition-metal based binary-metal selenides for high-rate capability and long-term cyclability for next generation SIBs.

Pt lean and fee CNT electrocaltayst for hydrogen evolution

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Based on the recent IEA energy outlook [1], both solar and wind based energy supply will increase by more than one decade by the year 2040. Such drastic increase requires development of energy storage technologies, as their availability already now is considered forming the bottleneck for further adoption of renewables. Electrochemical water splitting in electrolysis cells is one of the most promising technologies for converting excess electrical energy into chemical bond energy, namely hydrogen. Hydrogen can serve as an energy carrier and connect energy sector to chemical industry and transportation sectors. In electrolysis cells, the water splitting proceeds via two half reactions: the hydrogen evolution reaction at the cathode (HER: $2H^+ + 2e^- \rightarrow H_2$) and the oxygen evolution reaction met in the anode (OER: $H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$). In acidic membrane cells, scarce platinum group metals (PGMs) are utilized at both the electrodes for electrocatalyzing the above-mentioned reactions.

The anode reaction is one of the major sources for energy losses in electrolyzers but the cathode processes contribute to degradation and consequently, affect the durability of the device. Moreover, it is well recognized that the known PGM reserves cannot cover the foreseen increasing need. Hence, developing earth-abundant element based durable electrocatalyst for HER is essential.

Carbon nanotubes (CNTs) have several beneficial properties needed for electrocatalyzing: In addition to high conductivity and good stability, they have appropriate properties for fabricating 3D electrodes. CNTs can function as support for ultra-low-Pt electrocatalysts [2], or function as a scaffold for synthetizing hybrid electrocatalyst materials comprising only of earth-abundant elements. The latter include doped CNTs [3] as well as transition metal nanoparticles encapsulated in few carbon layers on CNT supports [4]. These materials have inherently different activities towards the HER, but their activity can be also affected by selected synthesis method and starting materials resulting in end product with different morphology, surface properties or conductivity, for example. The most active hybrid materials show similar activity to the commercial Pt/C catalyst and excellent durability under the HER conditions. In this presentation, CNT based electrocatalysts promoting the HER are introduced and their properties are discussed.

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Graphite and polymer modified black phosphorus anode with stable solid electrolyte interface for high energy density Li ion batteries

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Increasing demands for higher energy density lithium ion batteries stimulate the research of electrode materials with high capacity and long lifespan. However, seeking an anode material with stable-high capacity is still a challenge, and the research about the SEI of anode is still lacking up to date. Here we report the design of a black phosphorus (BP) nanocomposite consisting of polyaniline coated BP-graphite hybrid (BP-G/PANI) for high rate Li-storage. Our composite delivers a high initial capacity of 2170 mAh $g^{-1}_{compo.}$ at current density of 0.26 A g^{-1}, and a reversible capacity of 790 mAh $g^{-1}_{compo.}$ with capacity retention 93% when cycled at 5.2 A g^{-1} for 2000 cycles. Especially, after charge-discharge at 13 A g^{-1} for 2000 cycles, the BP-G/PANI retains a reversible capacity of 440 mAh $g^{-1}_{compo.}$ *In-situ* X-ray absorption spectroscopy(XAS) result reveals that P-C bond between BP and graphite maintain the edge atoms of BP flakes, which is critical for exploiting the Li^+ storage capability. And PANI coating mitigates the detrimental effects of volume changes in the BP-based electrode result in ultra-long cyclic performance. Importantly, swelled PANI in electrolyte benefits the efficient access of electrolyte to BP-G, which promotes the formation of stable solid electrolyte interface between the anode and the electrolyte according to the *ex-situ* time-of-flight secondary ion mass spectrometry (ToF-SIMS) results. As a summary, under the synergy of graphite and PANI, our composite with high reversible capacity and stable cyclic performance shows great potential for high energy density Li ion batteries.

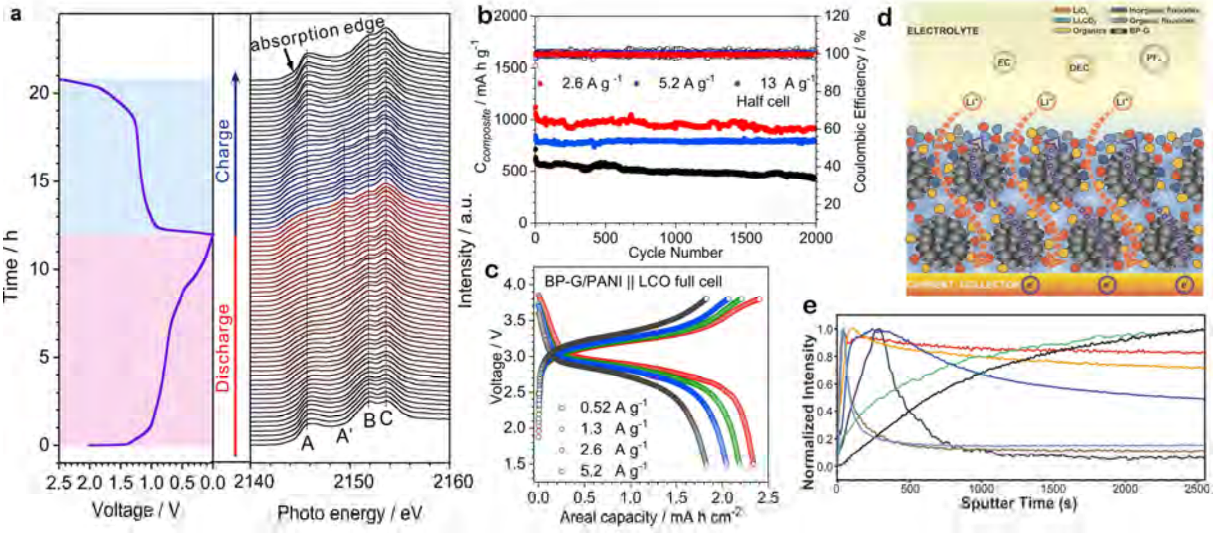

Fig.1 a) In-situ XAS measurement of BP-G electrode. **b)** Half cell and **c)** full cell performance of BP-G/PANI. **d)** Schematic of the PANI maintaining stable SEI. **e)** ToF-SIMS results of BP-G/PANI after 100 cycles.

Enhanced cycling stability of lithium metal batteries by Lithium metal partial alloying

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The lithium metal has many advantages as anode, which includes light weight (0.534 g cm^{-3}), high theoretical specific capacity (3860 mAh g^{-1}) and lowest electrochemical potential (-3.04 V versus standard hydrogen electrode), and is considered as a "Holy Grail" for anode materials of next generation high energy density battery[1]. However, the commercial application of Li metal batteries has faced several key issues: 1) high reactivity, 2) huge volume change, 3) dendritic deposition, which cause a series of problems, such as low Coulomb efficiency, high resistance and even safety risk [2-3].

In order to overcome these problems and improve the performance of lithium metal batteries, we designed Li/C and Li/C/Sn composites metal anode by mixing CMK-3 and CMK-3/Sn in Li and then melting the mixture to partially alloy Li metal at 270 ºC in argon glove box. A symmetrical LiX|LiX cells with two identical electrodes were assembled and tested to evaluate the cycling stability. As comparison, a symmetric bare Li|Li cell was also tested and exhibited a sudden drop in voltage after only 310 h at 1 mA cm^{-2}(Fig.1a). However, symmetrical Li/C/Sn|Li/C/Sn cells can stably cycle for more than 2200 h without any voltage fluctuation. Similar performance improvements can also be observed at 2 mA cm^{-2}(Fig.1b). As shown in Fig.1c, SEM images exhibit that Li uniformly plated and stripped on the surface of Li/C and Li/C/Sn composites metal anode during cycle process and no any lithium dendrite was observed.

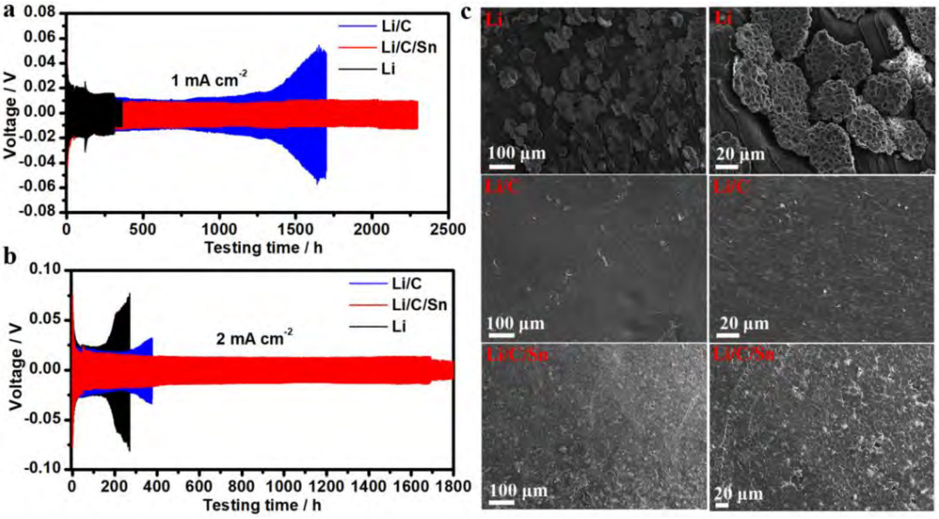

Fig.1 Voltage-time curves of Li plating/stripping at 1 (a) and 2 mA cm^{-2} (b), and SEM images of Li metal, Li/C, Li/C/Sn electrodes after 50 cycles at a current density of 2 mA cm^{-2}.

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Applications of Nanocarbons for Energy Devices

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Nanocarbons are the carbon materials with tailored structure in nanoscale in order to obtain the designed performances and functions for the specific applications. Nanocarbons have attracted lots of attention because of their excellent properties for energy devices such as lithium ion batteries[1-3], supercapacitors[4] and fuel cells[5], which are important components in the green era for environment and sustainability. In this context, the contribution of nanocarbon-based energy devices should be one of the key in the present century of smart grid using renewable energy. In the present paper, the current use of nanocarbons in the energy devices, as one of the important component of lithium ion secondary batteries, supercapacitors and also fuel cells with a special emphasis on the nanostructured carbons will be discussed. We envisage that the use of nanocarbons in the commercialized energy devices will dramatically increase considering the trend towards clean energy-oriented society. Moreover, further development of nanostructurally well-controlled carbons should be the essential factor for innovation.

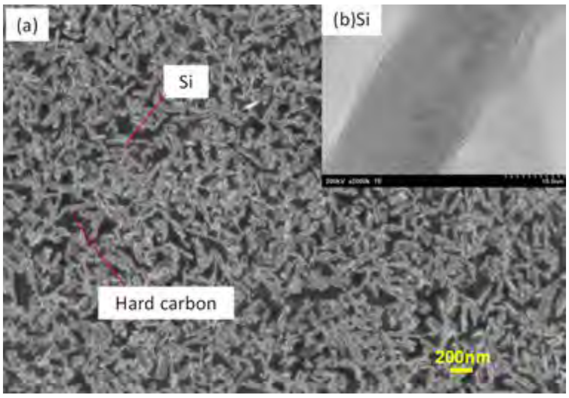

Fig.1 Thin carbon film coated Si nanoparticles are formed the nanocomposite with soft carbon matrix by carbonization of molecular weight controlled PVC at 600°C, which shows outstanding high capacity and long cyclability as anode of LIB[3].

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Ultrafast Hydrothermal Assembly of Nanocarbon Microfibers in Near-critical Water for Micro-supercapacitors

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Translating the advantages of carbon nanomaterials into macroscopic energy storage devices is challenging because the desirable nanoscale properties often disappear during assembly processes. We first describe a new nonequilibrium subcritical hydrothermal method capable of independently manipulating the temperature and pressure to create unique assembly conditions crossing the commonly used liquid-vapor boundary.[1] Highly conductive and dense-packed yet ion-accessible nanocarbon microfibers can be obtained from graphene oxide (GO) sheets, single-walled carbon nanotubes, and a nitrogen-doping crosslinker under 20 min of hydrothermal assembly, 80% energy saving compared to standard hydrothermal methods, and one of the shortest time in the field of hydrothermal processing of carbon nanomaterials. Using those microfibers, we built micro-supercapacitors that reach a high volumetric capacitance of 52 F cm^{-3}, an energy density of 7.1 mWh cm^{-3}, and a power density of 1645.7 $mWcm^{-3}$, respectively. We further demonstrate the 3D integration of multiple fiber micro-supercapacitors that reduces the device footprint by 75% while expanding the operational voltage and current window.

The next task is to significantly increase the energy storage capacity of microscale fiber electrodes while retaining their high power density. We incorporate ultrahigh mass loading of ruthenium oxide (RuO_2) nanoparticles (up to 42.5 wt.%) uniformly on nanocarbon-based microfibers composed of holey reduced GO (HrGO). Our approach involves: (1) space-confined hydrothermal assembly of highly porous but 3D interconnected carbon structure, (2) impregnating wet carbon structures with aqueous Ru^{3+} ions, and (3) anchoring RuO_2 nanoparticles on HrGO surfaces. Solid-state micro-supercapacitors assembled using those fibers demonstrated a specific volumetric capacitance of 199 F cm^{-3} and an ultrahigh energy density of 27.3 mWh cm^{-3}. Furthermore, integrating twenty pieces of micro-supercapacitors with two commercial flexible solar cells as a self-powering energy system, we can light up an LED panel stably. Overall, our work highlights the excellent potential of carbon nanomaterial-based composite fibers for constructing micro-supercapacitors for wearable electronic devices.

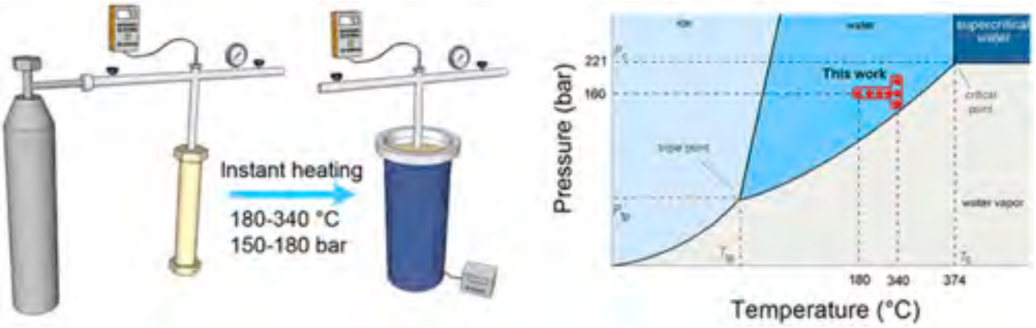

Fig. 1 A new hydrothermal system for ultrafast assembly of carbon nanomaterials into carbon architectures

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Chemical Design and Synthesis of Nanostructured Hybrid Materials for the Cathode of Lithium-Sulfur Batteries

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Lithium-sulfur (LS) batteries, have been considered as promising power source for future electric vehicles (EVs) due to their high energy and power densities. Thus, many efforts have been made on new electrode materials that can bring the realization of these devices. However, structural disintegration, limited access to redox sites and loss of electrical contact have long been identified as primary reasons for capacity loss and poor cyclic life of these materials. Thus, rational design can inhibit the side reaction by surface protection, make all redox sites accessible by increasing the intrinsic conductivity of the active materials, maintain a continues network for ionic and electronic flow and keep the structural integrity, resulting improved performance and excellent capacity retention with long cyclic life to meet the requirements set by United States Advanced Battery Consortium (USABC) for electrode materials in EVs. Here, upon combining active materials with conductive matrix, we have developed different hybrid nanostructures of metal oxides, hydroxides and metal alloys with N-doped graphene or carbon to control above mentioned problems and to achieve the goals set by USABC. The resulted nanostructured hybrid materials possess extraordinary performances as the electrodes of Lithium Ion Batteries or LS Batteries with long cyclic stability and excellent rate capability. The high performance of the hybrid materials was resulted from the defined nannostructures and the synergistic effect of several components. These strategies to combine the different properties enhancing factors in one composite with engineered structures will bring the realization of these devices in broad markets.

Two-dimensional Phosphorus Carbide: Competition between sp^2 and sp^3 Bonding

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We propose previously unknown allotropes of phosphorus carbide (PC) in the stable shape of an atomically thin layer, as shown in Fig. 1. Different stable geometries, which result from the competition between sp^2 bonding found in graphitic C and sp^3 bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. Depending on the category, we identify 2D-PC structures that can be metallic, semi-metallic with an anisotropic Dirac cone, or direct-gap semiconductors with their gap tunable by in-layer strain.

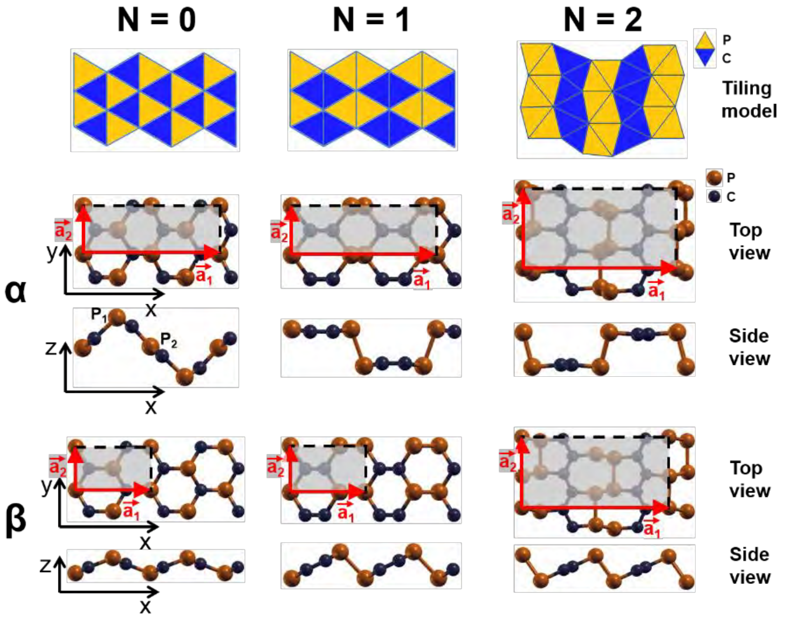

Fig.1 Tiling pattern and ball-and-stick model of atomically thin PC monolayers

Power generation from moving water droplet on nitrogen doped graphene

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Liquid-flow-induced generation of electricity using nanocarbons, particularly graphene-water interface, has received attention for energy harvesting. Here, we have obtained voltage generation from a single water droplet motion on graphene. We have investigated the effect of surface condition of graphene on flow-induced voltage generation, which is controlled by heteroatom doping.

Nitrogen-doped graphene is shown to generate 3 times higher voltage and 1.5 times higher power compared with pristine graphene due to surface charges and increase in effective interfacial area. Thus, doping-induced surface tuning of graphene enhances output performance. The flow-induced power generation using doped-graphene allows relaxing the material selection constraints in the triboelectric series.

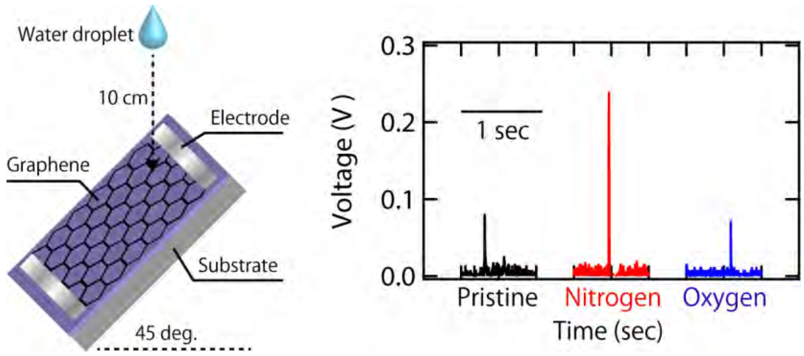

Fig.1 Left: Schematic image of flow-induced power generation from graphene-water interface. Right: Typical signal of generated voltage from single water droplet on graphene.

[1] Okada *et al.*, Applied Physics Letters **112** 023902 (2017)

Mesostructured porous carbons for multi-functioned energy and environmental applications.

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Porous carbons have a critical role in addressing the demands on energy- and environment-related issues due to their superior physicochemical properties, wide availability, and mass production. Considerable efforts have been made in carbon technology during the last decade to develop multi-functioned nanostructured carbon materials, both through continuous ameliorant of pre-existing synthetic methods and through introduction of new technologies. In this presentation, however, I will introduce our new synthetic approaches for producing novel mesostructured carbons based on meso-crystals and metal-organic coordination. Mesostructured crystal based synthesis have provided advantageous hierarchical pore architecture with miscellaneous functionality in energy storage and pollutant removal systems. We will show an exemplified porous carbon synthesis based on carbon nitride mesostructure and energy storage application thereof. In addition, we will introduce a facile synthesis of highly-ordered mesostructured carbons based on metal-organic coordination. We presumed that these proposed synthetic approaches will provide a straightforward strategy to design the novel functioned porous carbons.

Carbon nanotube and graphene oxide hybrid polyvinylidene fluoride membranes for flux sensing

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Separation membrane have attracted more and more attention for their widely used in membrane separation [1]. However, membrane fouling will inevitably occur during membrane separation [2-3]. Therefore, we need to modify the membrane or look for an effective way of monitoring membrane fouling in order to improve the anti-pollution performance of the membrane itself and realize the prediction of membrane fouling. In this study, we prepared polyvinylidene fluoride (PVDF) membranes incorporated with functionalized carbon nanomaterial by a simple and efficient phase inversion method. Compared with pure PVDF membrane, the performance of the hybrid membrane was enhanced by the synergistic effect of oxidized multi-walled carbon nanotubes (OMWCNT) and graphene oxide (GO). The hybrid membranes showed better surface pore structure, hydrophilicity, higher surface roughness, high water flux and rejection rate. The results demonstrated that the optimized PVDF/OMWCNT/GO hybrid membrane showed the low contact angle and the high water flux. The bovine serum albumin rejection of PVDF/ OMWCNT/GO blend membranes was enhanced about 26 %. In addition, what's more important, the PVDF/ OMWCNT/GO hybrid membrane also has good electrical conductivity compared with those of the pure PVDF membranes, which can be used for sensing and monitoring the water flux and pollution by the conductivity change of hybrid membrane.

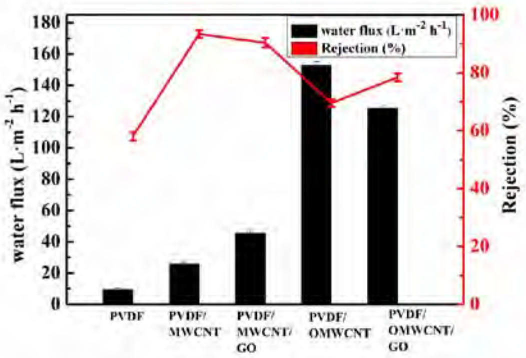

Fig.1 Tap water flux and BSA rejection of pure PVDF, PVDF/MWCNT, PVDF/MWCNT/GO, PVDF/OMWCNT, and PVDF/OMWCNT/GO membrane

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Synthesis and Supercapacitor Performance of Nitrogen-doped Porous Carbon–Carbon Nanotube Hybrids

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Carbon structures are widely used as a material for electrodes due to their unique properties, such as high electrical conductivity, high surface area, corrosion resistance, relatively high temperature stability. In comparison with oxidation-reduction electrodes from transition metal oxides and conductive polymers, electrodes based on carbon materials have an advantage such as stability of cycling and low production costs. The electrode material should have a high and accessible specific surface area with good electrical conductivity. Such requirements are just fully satisfied by a hybrid material consisting of a porous carbon characterized a high surface area on one side and carbon nanotubes showing high values of electrical conductivity on the other one. The obtained electrode material will combine the best physicochemical characteristics of each of individual carbon material. A combination of porous carbon and carbon nanotubes (CNTs) is a promising strategy to the creation of electrode materials for various electrochemical applications. The replacement of part of carbon atoms by nitrogen ones provides the material wettability by electrolyte.

The work will pay attention both of the study of the effect of synergism on the properties of two materials and the introduction of a heteroatom into the structure of hybrid materials on their electrochemical properties. Synthesis of such hybrid carbon structures will contribute to the creation and development of new energy storage devices based on carbon materials.

In this investigation, we show that such hybrid materials can be synthesized by thermal decomposition of nitrogen-containing carbon molecules over MgO-supporting transition metal clusters. The metals catalyze the growth of multi-walled CNTs, while MgO nanoparticles template the porous carbon. Using three kinds of supporting polyoxomolybdates, we find the influence of the used catalyst (Fe/Mo, Ni/Mo, or Co/Mo) on the structure and nitrogen content in the material and relate these parameters with electrochemical performance of the electrodes.

The work was supported by the Russian Foundation for Basic Research (grant № 18-33-01053).

Confining polysulfide shuttle through metal sulfide nanoparticles encapsulated in graphene nanoshells

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Lithium-sulfur batteries (LSBs) offer fascinating features, such as low cost of sulfur, the safer operating voltage and in particular non-toxic nature. Despite of such appealing advantages over conventional lithium-ion batteries (LIBs), LSBs are facing numerous challenges, which hinders it from being a serious competitor to LIBs on commercial scale.[1, 2] Among the mainstream challenges, the polysulfide (PS) shuttle effect, insulating nature of sulfur, volume expansion of sulfur, and self-discharge are very crucial factors, which need to be resolved urgently to improve the electrochemical performance of LSBs.[3] We proposed a novel strategy by engineering a coreshell nanostructure as a host for sulfur. A novel low-temperature graphene growth on metal nanoparticles is carried using vegetable oil as a liquid precursor in the absence of compressed gasses. Nitrogen-doped graphene nanoshells were synthesized by introducing low flowrate of N_2 gas, during the annealing process. In the second step, metal NPs were etched partially, and sulfidized or nitridized. These coreshell nanostructures with metal sulfide/nitride NPs covered with graphene were employed as a host material for sulfur loading (Fig. 1). The cathode materials showed extraordinary electrochemical performance by confining PS species, thus prolonging the cyclic life of the battery. In addition to the excellent electrical conductivity of the graphene nanoshell, it serves as a physical trapping material for PS intermediate species, whereas metal sulfide/nitride NPs restrain PS through chemical confinement and catalyze chemical conversion reaction of PS intermediates. Our study laydown foundation as a step forward towards commercialization of LSBs.

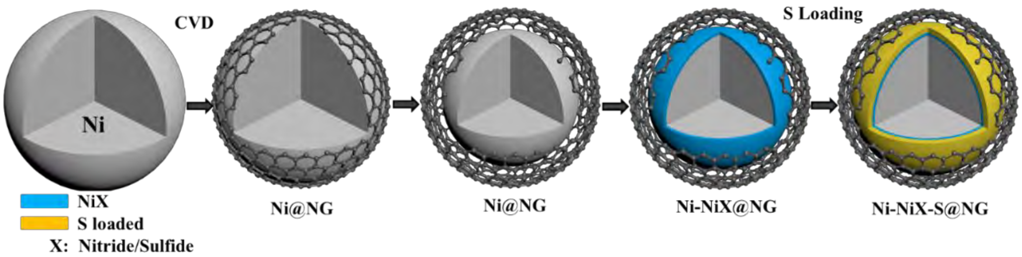

Fig.1 Schematic illustration of synthesis S-loaded on NiX nanoparticles inside N-doped graphene nanoshells. X could be either nitride, sulfide or oxide.

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High-Performance 3D Graphene Electrodes for Energy Storage and Conversion

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3D graphenes are most desired to deliver the unique “nano” properties of graphenes to the macroscale, yet their practical production and applications remain insufficient: the discontinuous connection between isolated graphene flakes and unavoidable agglomeration/re-stacking caused by *van der* Waals forces-induced adhesion severely suppresses the intrinsically high conductivity, strength and accessible surface area. In the past several years, we established several synthetic methods for making 3D graphenes, especially the chemical blowing approach for producing 3D graphenes (as well as 3D boron nitride nanosheets). The chemical blowing is featured by substrate-free graphitization and it is productive. The 3D graphenes provide a freeway for electron/phonon transports, a huge accessible surface area and robust mechanical properties. 3D graphenes open up a wide horizon for many applications. We have studied the 3D-graphene-based ultra-high-power electrochemical capacitors, achieving the maximum-power-density of 10^6 W/kg in an aqueous system [1]. We have also realized the high energy density of 50 Wh/kg at the high maximum-power-density of 340 kW/kg at the electrochemical capacitors in organic systems and we studied the related potassium ion batteries [2,3]. The electrocatalysts, *e.g.* transition metal nitrides for oxygen and hydrogen evolutions, are loaded on such 3D electrodes to reach high-performance water splitting.

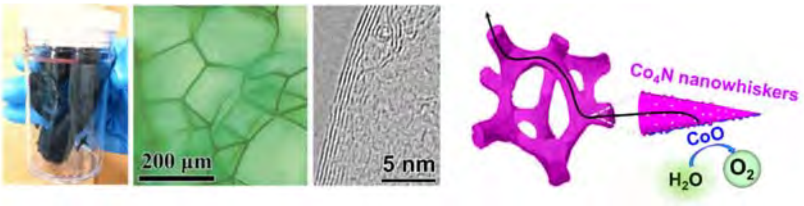

Fig. 1 A synthesized 3D graphene: photo, optical image, transmission electron microscopy image, and its hybrid 3D electrode loading cobalt nitride with surface oxide coating for oxygen evolution in water splitting.

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Graphene Based Micro-Supercapacitors

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Micro-supercapacitors (MSCs) are one novel class of on-chip micro-power sources that could be directly coupled with miniaturized integrated electronics. Using 2D atomically thin graphene, new designs for planar MSCs with outstanding performance have become possible, taking full advantage of the atomic layer thicknesses and flat morphology of graphene[1]. In this talk, I will present our recent advances on the reasonable construction of high-performance MSCs based on graphene based materials. First, we demonstrate graphene-based flexible and high-power MSCs through micropatterning of methane-plasma or photochemically reduced graphene films[2,3], allowing for operations at ultrahigh rate up to 2000 V s^{-1}. Second, we describe large-area, highly uniform, ultrathin, heteroatom (N, B, S)-doped graphene films for MSCs[4,5], providing enhanced volumetric capacitance of 400~600 F cm^{-3}. Third, we show the universal construction of graphene compact films (polyaniline/polypyrrole nanosheets[6,7], activated graphene[8], thiophene nanosheets[9], phosphorene[10]) for high-energy pseudocapacitive MSCs of 46 mWh cm^{-3}, and lithium ion MSCs of >50 mWh cm^{-3}. Finally, new-concept MSCs, e.g., symmetric and asymmetric sandwich-like planar MSCs[11,12], stretchable MSCs[13], hybrid MSCs[14], and high-voltage integrated MSCs[15] will be presented.

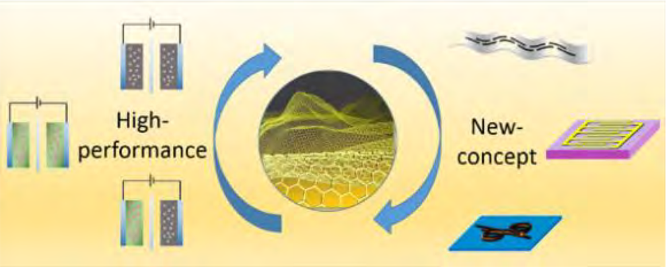

Fig.1 Graphene based materials for planar MSCs

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High Temperature and High Frequency Superapacitors Using Graphene and 2D Nanomaterials

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With increasing demand for high performance energy storage systems, the feasibility of reliable and functional energy storage devices that well operates under extreme conditions is of prime importance for expanding applicative fields as well as for understanding materials' intrinsic and extrinsic properties and device physics. However, achieving both performances and functionalities remains a critical challenge due to the property trade-offs of materials. In this talk, I will introduce two kinds of functional ultracapacitive energy storage devices such as high temperature flexible supercapacitor and ultrahigh volumetric capacitive flexible AC filter. (1) Firstly, I will address high temperature operating, flexible supercapacitors based on graphene electrodes and DN gel electrolytes that can efficiently deliver electrical energy under electrochemical, mechanical and thermal stresses. In particular, our new gel electrolytes could overcome the property trade-off as existing electrolytes between ionic conductivity and mechanical (thermal or electrochemical) stability, as well as the dilemma of common gels between mechanical strength and toughness. (2) Secondly, I will introduce ultrafast frequency response of flexible AC filtering supercapacitors integrating MXene hybrid electrodes and polymeric gel electrolyte. Ultrahigh volumetric capacitance of this device at high frequency can resolve the critical challenge of conventional capacitor-based AC filter for applications into pulse energy harvesting, self powered system, and current ripple filtering.

Carbon Nanomaterials for Cathodes in Lithium Sulfur Batteries

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Lithium sulfur batteries attract great attention due to their advantages in high theoretical energy density. However, the practical applications of Li-S batteries are still hindered by the insulating nature of sulfur, the volumetric fluctuation during cycles, and also the dissolution/shuttle of polysulfides. In this presentation, the rational design of cathode and separator materials based on graphene materials for Li-S batteries will be discussed.

To tackle the problems in the sulfur cathode towards the full utilization of active sulfur materials, a series of hierarchical nanocarbon hosts were developed to accommodate sulfur materials. Further introduction of heteroatom doping and other additives like TiC, etc. realized the chemisorption of polysulfide, and the propelling of kinetics in polysulfide redox reactions. The further demonstration of a "lithiophilic" and "sulfiphilic" surface, we constructed by the incorporation of nitrogen-doped graphene and Ni-based layered double hydroxide interface. In the interface, nitrogen-containing functional groups interacted with lithium atoms in polysulfides, while the sulfur atoms interacted with Ni sites to ensure a strong affinity of polysulfides towards the conducting interface. Therefore, the redox kinetics can be greatly improved towards the high rate performance of lithium sulfur batteries.

These concepts also enabled the fabrication of highly efficient sulfur cathode with high areal loading towards practical applications.

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Graphene-based Membrane toward High-Stable Lithium Sulfur Battery

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Lithium sulfur batteries attract great attention due to their high energy density, while the real applications are still hindered by the rapid capacity degradation. Despite great effort devoted to solving the polysulfide shuttle between the cathode and anode electrodes, it remains as a serious challenge to build high-stable lithium sulfur battery, which related to the diffusion and reaction between polysulfides and the metal lithium anode.

We proposed a strategy of introducing an ion selective membrane to improve the stability and coulombic efficiency of lithium sulfur battery. Generally, porous polymer membrane serves as membranes in batteries to avoid the short circuit between anode and cathode electrodes, which cannot stop the shuttle effect. By the introduction of permselective functional layer, the polysulfide anions can be confined in the cathode side, which would favor the cyclic stability and lower self-discharge performance.

We replace the routine membrane with an ion selective membrane, in which the sulfonate-ended perfluoroalkyl ether groups on the ionic separators are connected by pores or channels that are around several nanometers in sizes. These -SO3-- groups coated channels allow ion hopping of positive charge species (Li+) but reject hopping of negative ions, such as polysulfide anions (Sn2-) in this specific case due to the coulombic interactions. Consequently, this cation permselective membrane acts as an electrostatic shield for polysulfide anions, and confines the polysulfides in the cathode side. An ultra-low decay rate of 0.08% per cycle is achieved within the initial 500 cycles for membrane developed in this work, which is less than half that of the routine membranes.

We also proposed a unique lithium-sulfur battery configuration with ultrathin graphene oxide (GO) membrane for high stability. The oxygen electronegative atoms modified GO into a polar plane and the carboxyl groups acted as ion hopping sites of positively charged species (Li+) while rejected the transportation of negatively charged species (Sn2-) due to the electrostatic interactions. Such electrostatic repulsion and physical inhibition largely decreased the transference of polysulfides across the GO membrane in lithium-sulfur system. By the incorporation of permselective GO membrane, cyclic capacity decay rate is also reduced from 0.49 to 0.23 %/cycle.

Such ion selective membrane is versatile for various electrodes and working conditions, which is promising for the construction of high performance batteries.

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Synthesis of bilayer graphene with ordered mesopores for high power energy storage

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Design and synthesis of effective electrode materials with a precise structure is essential but challenge for current energy storage applications. Herein we report the design and synthesis of oxygen and nitrogen cohybridized bilayer mesoporous graphene materials for high-power energy storage. They were prepared through a chemical vapor deposition (CVD) of methane (CH_4) on nanostructured magnesium oxide (MgO) catalyst, followed by removal of the catalyst. Such graphene materials have many critical features that are required for energy storage, including hierarchically porous channels, high conductivity, *in-situ* doping of nitrogen and oxygen atoms, and excellent structure durability, which enable the materials to efficiently host Li^+ or Na^+ more based on the surface reaction and adsorption rather than ion-intercalation reaction at high charging/discharging rates. Thereby, it leads to high power performance and impressive cycling stability when the graphene materials used as electrode materials. Considering the structure properties, such graphene materials may have important applications for energy storage.

An Adaptive and Stable Bio-Electrolyte for Rechargeable Zn-Ion Batteries

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Sulfate solutions with high safety, low cost and wide electrochemical windows are widely used as electrolytes for aqueous batteries. However, the practical application of such batteries, especially for wearable devices is still limited by the lack of a stable polymer electrolyte, due to the strong ability of the favorably-selected sulfate electrolytes to precipitate polymers. Herein, we report a very stable sulfate-tolerant gum bio-electrolyte prepared by readily mixing xanthan bio-polymer with aqueous sulfate solutions. The gum electrolyte is highly conductive (1.46×10^{-2} S cm^{-1}), hydrating, adhesive, and adaptive. Zn-ion batteries assembled using such gum electrolyte show competitive performance to aqueous batteries, which include high capacities (about 260 mAh g^{-1} for MnO_2 at 1C), high rate capability, good cyclability (about 90% capacity retention and about 100% Coulombic efficiency over 330 cycles at 1C, and about 127 mAh g^{-1} capacity over 1000 cycles at 5C), and high durability to bending and twisting. Moreover, the use of the gum electrolyte could prohibit the growth of zinc dendrite. Considering the wide suitability of aqueous sulfate electrolytes for rechargeable aqueous metal-ion batteries, our gum electrolyte would also be applicable for boosting the practical application of such batteries.

Carbon-based metal-free electrocatalysis for efficient energy conversion and storage

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Green and renewable energy technologies, such as fuel cells, batteries, and water-splitting systems, hold great promise to solve current energy and environmental challenges. However, noble metal catalysts (*e.g.*, Pt, Pd, RuO_2, IrO_2) are generally needed to promote the *hydrogen evolution reaction* (HER) for hydrogen fuel generation from photo-electrochemical water-splitting, *oxygen reduction reaction* (ORR) in fuel cells for energy conversion, and *oxygen evolution reaction* (OER) in metal-air batteries for energy storage. The high cost of precious metal-based catalysts and their limited reserve have precluded these renewable energy technologies from large-scale applications.

Along with the recent intensive research efforts in non-noble metal based ORR catalysts, we have previously demonstrated that vertically-aligned nitrogen-doped carbon nanotubes could actively catalyze ORR *via* a four-electron process free from the CO poisoning effects with a 3-time higher electrocatalytic activity and better long-term durability than that of commercial Pt/C catalysts. The improved catalytic performance was attributed to the doping-induced charge transfer from carbon atoms adjacent to the nitrogen atoms to change the chemisorption mode of O_2 and to readily attract electrons from the anode for facilitating the ORR.

Subsequently, it was demonstrated that various graphitic carbon materials, doped with heteroatoms of different electronegativities from that of carbon atom, physically adsorbed with certain polyelectrolytes, and even without any apparent dopant or physically adsorbed polyelectrolyte, could also exhibit good ORR performance. More recent studies have further demonstrated that certain heteroatom-doped carbon nanomaterials could act as metal-free bifunctional catalysts for ORR/OER in metal-air batteries for energy storage, and even ORR/OER/HER trifunctional catalysts for self-powered water-splitting to generate hydrogen fuel and oxygen gas from water.

In this talk, I will summarize some of our work on the metal-free catalysts based on carbon nanomaterials for various energy-related reactions, along with an overview on the recent advances and perspectives in this exciting field.

Densifying graphene hydrogels: remedy for compact energy storage

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Being smaller is one of the most important targets of advanced energy storage devices, which means storing more energy in a limited space and the present nanotechnology rarely do well. Graphene goes the same way as other nanomaterials and has been widely investigated as the electrode for supercapacitors to make the devices "lighter" and "faster". Nevertheless, graphene is still hardly converted into a real commercial application considering its cost-effectiveness vs. traditional activated carbon-based supercapacitors. In recent years, our group restarted our study on graphene supercapacitors highlighting its role as an ideal remedy for low volumetric performance of the traditional carbon-based capacitors (due to the low density of carbons). We have been devoting to making carbon-based supercapacitors "smaller" through dense assembly of graphene units. We have proposed a general strategy, namely nano-densification of networked graphene by interfacial capillary shrinkage, for producing dense carbon- or carbon caged-electrodes towards high volumetric performance energy storage. In this talk, we will present strategies, methods, materials, electrodes and devices for producing high volumetric performance energy storage devices and give typical examples including electrode and device constructions in supercapacitors, lithium ion batteries and post-lithium ion batteries.

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