# Controlled Growth of Carbon Nanotubes and Graphene

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Recently, nanocarbon materials have attracted a great interest, because of their unique structure and promising properties. In particular, nanoelectronics applications are expected for single-walled carbon nanotubes (SWNTs) and graphene, but difficulties in controlling their structure (chirality, length/width, and edge structures) and assembly on a substrate prevent from the applications. We have studied catalytic growth of nanotubes and graphene on single crystal substrates, such as sapphire ( -$Al_2O_3$) and MgO, to control their structures.

1. Horizontally-aligned SWNTs

We found horizontally-aligned SWNT growth on a- and r-plane sapphire substrates [1]. The SWNT growth was visualized using $^{12}C$-$^{13}C$ isotopes, and we observed a base-growth mode for the aligned nanotubes [2]. This indicates the importance of SWNT-sapphire interaction. We also observed interesting phenomenon, such as unidirectional growth [3], orthogonal growth, and bending at artificial steps created on the sapphire surface [4]. Furthermore, we found interesting crystalline plane dependence of chiral angle of aligned nanotubes; growth of near armchair tubes on r-plane, while near zigzag tubes were mainly observed on a-plane [5]. Our result suggests the possibility of controlling nanotube structure based on epitaxial interaction with the underneath single crystalline substrates.

2. Square and triangular graphene

The CVD growth of graphene films has been reported very recently, but most of the works utilized polycrystalline metal films as catalyst. The polycrystalline nature of the catalyst deteriorates the quality of graphene films, because it leads to small domain size with many domain boundaries. We have studied the growth of graphene on epitaxial metal catalyst deposited on single crystal MgO substrates. By using a unique polymer-decomposition method, we obtained micro-scale square and triangular graphene films preferentially formed inside pits of the metal catalyst [6]. Field-effect transistors using the transferred square graphene were demonstrated. Finally, our recent development of large area graphene synthesis will be also demonstrated.

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# Super-Growth Carbon Nanotubes: Synthesis, Mass Production, and Applications

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While the remarkable physical and mechanical properties of single-walled carbon nanotubes (SWNT) have inspired numerous potential applications from high-performance computer chips, reinforced materials, sensors, to drug delivery devices the development of carbon nanotube (CNT) technology (and consequently a CNT-based industry) is reliant upon the availability of CNTs. To realize this, not only is an efficient and pure process necessary, scalability is essential. Water-assisted chemical vapor deposition (Super-growth CVD) method [1] has become popular in efficiently synthesizing tall, vertically aligned forests with exceptional properties, such as high purity, high surface area, long length, and alignment.

This presentation will provide an overview of our recent progress in the synthesis and application of millimeter-scale, vertically-aligned single-walled carbon nanotubes using Super-growth CVD. First, after providing a brief introduction to the Super-Growth concept, I will discuss some results of our fundamental studies of the mechanism and generality of Super-growth [2-4]. Second, I will present our efforts for industrial-scale SWNT mass production, and third, I will present some applications we currently investigating.

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# Large Scale and Controllable Production of Carbon Nanotubes by Fluidized Bed-Chemical Vapor Deposition

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Chemical vapor deposition(CVD) has been developed as one of the most effective methods to produce carbon nanotubes to this date. Fluidized bed-CVD has the advantage of large reactor volume to offer sufficient space with uniform mass and heat transfer condition, which is crucial to the growth of carbon nanotubes in large quantities. Here, I will summarize the key point of fluidized bed CVD.

One, any suspended particles can be disposed continuously in fluidized bed, which allows the fluidized bed suitable for the production of many kinds of carbon nanotubes, whether grown on the micron-sized agglomerate catalyst particles, or on the surface of millimeter-sized ceramic spheres, as well as on the layered metal oxides. Thus fluidized bed- CVD is suitable for the mass production of agglomerate carbon nanotubes and the millimeter long vertically aligned carbon nanotube array.

Second, the temperature shift two-stage fluidized bed offers an unique operation of catalyst in different temperature zones in different positions, and is effective to tailor the catalyst activity for a high yield production of carbon nanotubes in high temperature.

Third, the coupled down reactor and turbulent fluidized bed reactor is effective to control the balance of catalyst reduction and carbon deposition, and to utilize the maximal activity of the catalyst in the production of high quality of single or double walled carbon nanotubes.

Keywords：Carbon Nanotubes; Fluidized Bed; Chemical Vapor Deposition.

Dr. Weizhong Qian was born in Shanxi, P. R. China, in 1971. He received his B. S. degree in Chemical Engineering from Beijing Institute of Technology in 1992, and M S. degree in Chemical Engineering from Beijing Institute of Clothing Technology in 1999, respectively, and his Ph. D. degree in Chemical Engineering from Tsinghua University, P. R. China, in 2002. He has four year experience worked in a Fine Chemical Factory from 1992 to 1996. And now he is an Associate Professor of Chemical Engineering of Tsinghua University P. R. China. And he worked, as a visiting associate professor, in Department of Materials Science & Engineering, Cornell University, USA from Feb, 2008 to August, 2008. Dr. Qian has published over 80 peer reviewed journal articles. His research focuses on the controlled and bulk synthesis of carbon nano-materials, including: catalyst design for multiwalled carbon nanotube with 500 t/a capacity and carbon nanotube array with 3 kg/h capcaity; process intensification to prepare carbon nanotube in high yield, high purity and high selectivity; the cross-scale growth mechanism of carbon nanotube array; Controlled synthesis of 10-20 cm long single-, double- and triple-walled carbon nanotubes with the growth rate up to 80-90 micron/s; Controlled synthesis of long tube with 35 mm uniformity in their chiral angle and (n,m) index. Dr. Qian has received the 2nd grade of the National Science and technology Progress Award in 2008 and the “Excellent Young Scientist” award of Chinese Particuology Society in 2008.

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# Controlled and Scalable CVD Growth of Drawable Carbon Nanotube Arrays and Its Applications

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Drawable carbon nanotube arrays show great promise in preparing flexible and transparent thin films and new-generation of strong and lightweight carbon-based fibers by ways of “bottom-up” assembly approaches. It also helps open up more opportunities for the facile fabrication of carbon nanotube based electronic and optoelectronic devices. In the report, I will show our recent progress in the controlled growth of spinnable carbon nanotube arrays by both acetylene CVD and ethylene CVD. The effects of catalyst composition, agglomeration upon annealing and carbon sources on the spinnability and carbon nanotube structure properties of the arrays were symmetrically investigated. The growth mechanism of drawable arrays was proposed. By understanding the growth process, we have successfully achieved the scalable growth of spinnbale arrays on 4 inch wafers using the two kinds of hydrocarbons under atmosphere. Moreover, in our group, the drawable arrays have been continuously spun into strong and functional carbon nanotube fibers. And also it has been pulled to prepare flexible, transparent and conducting thin films. The mechanical and electrical properties of the fibers and films from the two kinds of hydrocarbons were comparatively studied.

**Dr. Qingwen Li got her B.S. in chemistry in1987 from Xinjiang University(china), M.S. and PhD in physical chemistry in 1990 and 2000 from Shandong University and Tsinghua University , respectively. She has been doing carbon nanotube research since 2000, whose interests include carbon nanotube controllable preparation, surface modification, property characterization and application development. She once worked with prof. Alan Windle in University of Cambridge from May 2003 to Jan 2005 on carbon nanotube dispersion and organization, and Dr. Y. T. Zhu at Los Alamos national laboratory from March 2005 to Dec. 2007 on controllably growing ultralong carbon nanotube arrays and spinning strong carbon nanotube fibers. She has rich experience in the synthesis and organization of carbon nanotubes. Dr. Li joined Suzhou institute of Nanotech and Nanobionics at the end of 2007, as a professor of "hundred talent project" supported by Chinese Academy of Science. Her current research focuses on controlled synthesis of low-dimensional carbon nanomaterials and their applications. She has published over 50 peer reviewed journal articles and applied 5 American and 6 Chinese patents. Dr. Li has won the Nano 50$^{TM}$ and Micro 25 awards in 2007 (US) and also award of excellence by Los Alamos National lab.**

# Simple Separation of Metallic and Semiconducting Carbon Nanotubes Using Agarose Gel

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Single wall carbon nanotubes (SWCNTs) have attracted a great deal of attention towards versatile applications, especially in the field of electronics, such as flexible transistor and transparent conducting film. However, electrical heterogeneity of as-produced SWCNTs (metal/semiconductor) is one of the most crucial problems preventing useful application of SWCNTs. Here, we show novel separation methods of metallic and semiconducting SWCNTs (MS separation) using agarose gel[1-3]. When SWCNTs/SDS (sodium dodecyl sulfate) dispersion and agarose were mixed and gelled, semiconducting SWCNTs were selectively trapped in the gel. While metallic SWCNTs could be recovered by electrophoresis[1] or freeze, thaw and squeeze method[2], (Fig. A and B). We also succeed in developing simpler MS separation method using a column[3] (Fig. C). This column separation produced gel free semiconducting SWCNT solution, and the column could be used for repeated separation. Because this continuous and repeatable separation method can be applied to a low-cost and large-scale process, it is expected that industrial production of metallic and semiconducting SWCNTs can be realized.

This study was partly supported by the industrial technology research grant program of the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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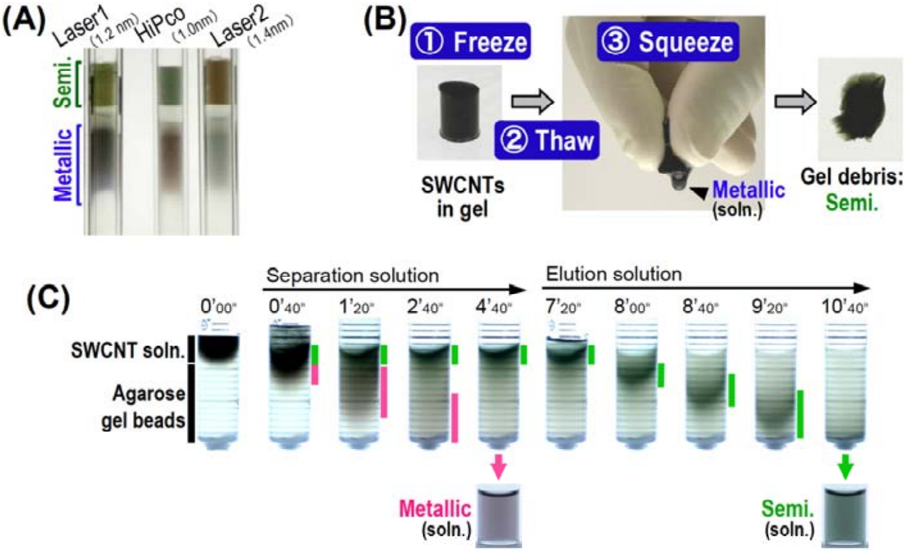

Figure: MS separation using agarose gel. (A) Electrophoresis. (B) Freeze, thaw and squeeze method. (C) Column chromatographic method.

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# Separation of Single-walled Carbon Nanotubes

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Many potential applications of single-walled carbon nanotubes (SWNTs) have been strongly expected because of their excellent mechanical and electrical properties. The SWNTs are typically grown as bundles of metallic and semiconducting tubes. This is a great hindrance to their widespread applications. We have developed convenient separation methods in a simple way.

A typical procedure for the separation of metallic SWNTs (m-SWNTs) is as follows: SWNTs was added to a tetrahydrofuran solution containing an amine. The mixture was sonicated and then centrifugated. When SWNTs in THF were treated with 1-octylamine, a black-colored transparent supernatant solution was obtained. Interestingly, selective extraction of m-SWNTs was achieved under the extraction conditions. The efficiency of the selective extraction depends on the structure and concentration of an amine used.[1] Selective destruction of m-SWNTs was achieved when a randomly networked SWNT film consisted of m-SWNTs and semiconducting SWNTs (s-SWNTs) was irradiated with a microwave. This seems capable of destroying m-SWNTs, however, because of the strong aggregation of SWNT bundles comprising both m-SWNTs and s-SWNTs, the incomplete removal of m-SWNTs, and damage to s-SWNTs neighboring heated m-SWNTs during irradiation are unavoidable. A facile technique combining microwave irradiation with mixed-acid-assisted dispersion has proven to be an efficient method for enrichment of s-SWNTs. Using this technique, electronic type- and diameter-dependent separation of SWNTs were simultaneously achieved. Under mild and controlled experimental conditions, m-SWNTs and smaller s-SWNTs were preferentially removed, yielding purely diameter distribution-narrowed s-SWNTs.[2]

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Dr. Yutaka Maeda was born in Tokyo, Japan, in 1974. He received his M S. degrees and Ph. D. degree in Chemistry from Niigata University, Japan, in 1999 and 2001, respectively. He then spent half year as a postdoctoral fellow in Prof. Takeshi Akasaka's lab at University of Tsukuba, Japan. And now he is an Associate Professor of Chemistry of Tokyo Gakugei University, Japan. Dr. Maeda has published over 100 peer reviewed journal articles. His research focuses on the functionalization and characterization of carbon nano-materials, including: the functionalization of fullerene and endohedral fullerene, separation of single-walled carbon nanotubes, and functionalization of single-walled carbon nanotubes.

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# Growth of Graphene on Surface

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Graphene is a one-atom-thick planar sheet of $sp^2$-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Due to its unique quantum effect and excellent electrical performance, graphene has important potential applications in nano-electronic devices and integrated circuits, flexible electronics, et al. Here we report our recent work about controlled growth of graphene on surface, and its application as transparent conductive film.

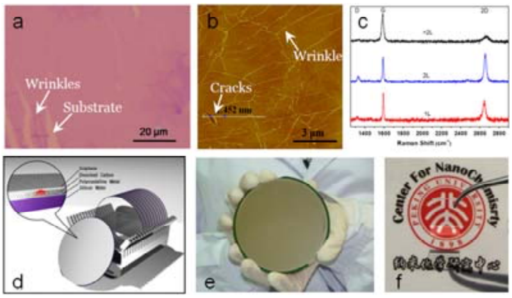

**Fig.1** a, Optical microscope image of graphene transferred on $SiO_2$/Si. b, AFM height image shows wrinkles and crack in single layer or bilayer regions. c, Raman spectra of graphene layers. d, Batch of wafers of segregated graphene. e, A 4-inch graphene wafer segregated on Ni. f, Photo image of graphene films transferred to quartz substrate.

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# Graphene Spintronics

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After the first success of fabricating multi-layer graphene and its field effect transistors (FETs) in 2004 a tremendous number of studies has been implemented in order to clarify attractive physical features of single-layer and multi-layer graphene (SLG and MLG), which induces much interest for graphene electronics. In 2007, introduction of a spin degree freedom to graphene electronics (graphene spintronics) was successfully achieved by several groups, including our group, individually [1-5], where spins were injected, a pure spin current was generated and the spins were manipulated in SLG and MLG up to RT. The reason why people are attracted by spin injection into graphene is based on facts that the low atomic mass of carbon can induce the weak spin-orbit interaction and that 99% of the carbon isotopes has no nuclear spin and therefore hyperfine interaction between nuclei and electronic spins should be weak.

In this talk, I start from how to generate a pure spin current and how to detect it, and our first success in detecting spin current in MLG is introduced [1]. Next, I talk about “robustness” of spin polarization in graphene under a high bias voltage application [4], which could be an important breakthrough for expanding device designing for realization of spin MOS FETs. This means suppression of spin scattering in Co/graphene and graphene itself, which has not been realized in other spin valve systems using metals and inorganic semiconductors. I also discuss degradation of graphene spin valves, which induces disappearance of the robustness [6], and furthermore, gate-induced modulation of a spin current in SLG and a role of an interface between Co and SLG for efficient spin injection [7] will be discussed.

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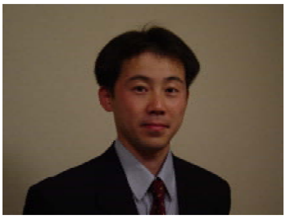

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# Electronic Properties of Nanographene

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The investigation of nano-sized graphene (nanographene) is one of the most important aspects among the current topics for graphene. For nanographene having the large contribution of the edge site, the electronic properties strongly depend on the edge-shape. [1, 2]. In this study, we present the shape-characterization method for graphene edges by Raman spectroscopy and anomalous magnetransport properties of nanographene.

Figure 1(a) shows an optical image of the exfoliated graphene with the edges crossing each other with the angle of ~30°. The position dependence of the Raman G-band is shown in Fig. 1(b), where the laser spot diameter is about 1μm. The G-band peak position taken near the upper edge (A) is almost similar to that for bulk graphite (1582 $\mathrm{cm}^{-1}$). However, a softening of G-band is clearly seen in the vicinity of the lower edge (B). The observed edge direction dependence of the G-band position can be explained in terms of the edge-shape dependence of the Kohn anomaly effect. In fact, our theoretical results show that the Kohn anomaly occurs only near the armchair edge [3]. The present results suggest that G-band can be used for identification of the edge geometry in graphene.

The magneto-transport properties of a ribbon-shaped nanographene with a width of 200nm and a thickness of 5 layers were studied. The sample was fabricated from exfoliated graphene by using oxygen plasma etching and electron beam lithography. The gate voltage dependence of the conductivity showed a significant effect of the extrinsic doping on the as prepared nanographene, which originates from the adsorbed species strongly bound to the chemically active edge site. Since the sample has the thickness of 5 layers, two series of Shubnikov–de Haas oscillations were observed in magnetoresistance after the cleaning process, which are attributed to the contributions from linear and parabolic bands. The oscillation frequency of the linear band exhibits an anomalous hump around the Dirac point for the ribbon-shaped nanographene sample (Fig.2), but not observed for the bulk graphene sample. This observation suggests the presence of the trapped orbital due to the local doping effect at the edge or the strong edge scattering effect.

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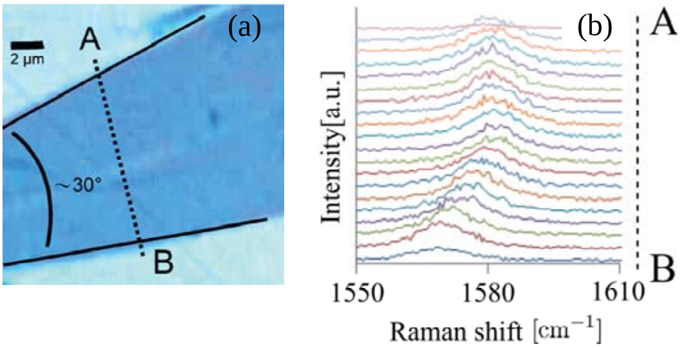

Figure 1. The optical image of graphene sample (a), and the position dependence of Raman G-band (b).

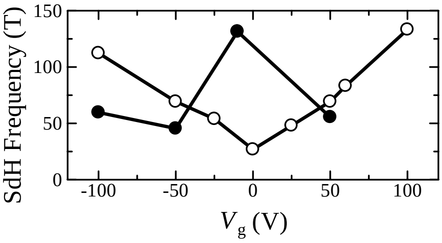

Figure 2. The gate voltage dependence of the SdH oscillation frequency for the ribbon-shaped nanographene (closed circles) and bulk graphene (open circles).

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# Structural Characterization and Controlled Preparation of Graphene

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The properties of graphene are highly sensitive with their atomic structure and surface morphology. In this talk, we will first report on the studies on graphene structure, including layer numbers, stacking, orientation and surface morphology, by transmission electron microscopy (TEM) method. And then we will demonstrate the feasibility of utilizing the staging-phenomena of graphite intercalation compounds (GICs) as a means for achieving the layer number-controlled preparation of graphene sheets. With the use of the readily available, ambient stable $FeCl_3$ intercalated graphite compounds as starting material, a multi-step chemical exfoliation approach was developed that can finally yield a stable colloidal dispersion of the exfoliated graphene sheets in NMP. When varying the stag-number of FeCl3-GICs from 1st and 2nd, we successfully observed the selectively abundance of single and bilayer graphene sheets, respectively, in the product. We will also show the feasibility of utilizing the nanosphere lithography (NSL) in combination with $O_2$ plasma etching as an innovative method for the rational and high-throughput fabrication of patterned ultranarrow graphene nanoribbons. (GNRs).

**Keywords:** Graphene; Structural characterization; Electron diffraction method; Controlled preparation; Graphene nanoribbons

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# Graphene and Nanowire Transistors for Cellular Interfaces and Electrical Recording

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Nanowire field-effect transistors (NW-FETs) have been shown to be powerful building blocks for nanoscale bioelectronic interfaces with cells and tissue due to their excellent sensitivity and their capability to form strongly coupled interfaces with cell membranes. Graphene has also been shown to be an attractive building block for nanoscale electronic devices, although little is known about its interfaces with cells and tissue. Here we report the first studies of graphene field effect transistors (Gra-FETs) as well as combined Gra- and NW-FETs interfaced to electrogenic cells. Gra-FET conductance signals recorded from spontaneously beating embryonic chicken cardiomyocytes yield well-defined extracellular signals with signal-to-noise ratio routinely >4. The conductance signal amplitude was tuned by varying the Gra-FET working region through changes in water gate potential, $V_{wg}$. Signals recorded from cardiomyocytes for different $V_{wg}$ result in constant calibrated extracellular voltage, indicating a robust graphene/cell interface. Significantly, variations in $V_{wg}$ across the Dirac point demonstrate the expected signal polarity flip, thus allowing, for the first time, both n- and p-type recording to be achieved from the same Gra-FET simply by offsetting $V_{wg}$. In addition, comparisons of peak-to-peak recorded signal widths made as a function of Gra-FET device sizes and versus NW-FETs allowed an assessment of relative resolution in extracellular recording. Specifically, peak-to-peak widths increased with the area of Gra-FET devices, indicating an averaged signal from different points across the outer membrane of the beating cells. One-dimensional silicon NW- FETs incorporated side by side with the two-dimensional Gra-FET devices further highlighted limits in both temporal resolution and multiplexed measurements from the same cell for the different types of devices. The distinct and complementary capabilities of Gra- and NW-FETs could open up unique opportunities in the field of bioelectronics in the future.

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# Controllable Synthesis, Efficient Reduction and Application Explorations of Graphene Oxide

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Chemical exfoliation is widely considered to be an efficient method for large scale synthesis of graphene sheets (GSs). However, how to control the structure and realize the efficient reduction of graphene oxide (GO), the direct product of chemical exfoliation, are still a great challenge although both are important for fundamental studies and technological applications of chemically derived GSs. Here we demonstrate the controllable synthesis of GSs with different number of layers, highly conductive GSs, large GSs, and narrow graphene nanoribbons by using chemical exfoliation method. In addition, we will present a simple method for the efficient reduction of GO films. The reduced GO films have high electrical conductivity and maintain the integrity and flexibility of GO films at the same time. Finally, several examples about the applications of chemically derived GSs will be demonstrated, including field emitters, transparent conducting films and electrochemical capacitors.

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# Graphene Based Functional Composites and Their Applications

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Graphene－a flat monolayer of carbon atoms tightly packed into a two dimensional honeycomb lattice was discovered in 2004. Due to its unusual molecular structure, grapheme shows many novel and unique physical and chemical properties, which are generating much attention in composite application. In this paper, the preparation of Thermoplastic polyurethane (TPU) nanocomposites with functionalized graphene using a simple solution processing method is reported. The mechanical properties of the nanocomposites are significantly improved. A 75% increase in tensile strength and a 120% improvement of Young’s modulus are achieved by addition of only 1 wt% graphene. This nanocomposite exhibit repeatable infrared triggered actuation performance.

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# Graphene-Enhanced Raman Scattering (GERS)

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Raman spectroscopy is an important and powerful tool in characterizing the structure of materials. However, due to the low scattering cross-section ($10^{-30}$ $cm^2molecule^{-1}$), the weak intensity of Raman signals result in low sensitivity, which made the application of Raman spectroscopy been neglected for many years. Recently, we found a new material, graphene, which can be used as a substrate for enhancing the Raman signal. Molecules such as phthalocyanine (Pc), rhodamine 6G (R6G), protoporphyin IX (PPP) and crystal violet (CV) was deposited on graphene by some techeniques. First, the fluorescence background of the molecule was observed suppressed by graphene substrate. Furthermore, by comparing the Raman signals of molecule on graphene and on a $SiO_2$/Si substrate, Raman enhancement effect was found existent on the surface of graphene. The Raman enhancement factor of 2-17 was found dependent on the symmetry of vibrations of the molecule. The enhancement efficiency was much remarkable for few-layer graphene. To investigate the mechanism further, chemical mechanism was considered first by theoretical analysis, and the first layer effect was found existent by constructing mono- or multilayers ordered Langmuir-Blodgett films of protoporphyrin IX (PPP). By constructing different molecular configurations contacting with graphene directly, different Raman enhancement factors were found, indicating the strong distance dependence of the enhancement. Besides, electric gate was added between graphene and the substrate to modulate the Fermi level of graphene, and the Raman enhancement factor was found changing and dependent on the electric gate. All the results showed that the Raman enhancement on graphene belongs to the chemical enhancement mechanism. This discovery will expand the application of graphene to microanalysis and is good for studying of the basic properties of both graphene and SERS.

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**Selective Publications**

1. **YG Yao, QW Li, J Zhang*, R Liu, LY Jiao, YT Zhu, ZF Liu*, Temperature-mediated growth of single-walled carbon-nanotube intramolecular junctions, *Nature. Mater. 6(4)(2007)*, 283-286.**
2. **YY Zhang, J Zhang*, HB Son, J Kong*, ZF Liu*, Substrate-induced Raman frequency variation for single-walled carbon nanotubes, *J. Am. Chem. Soc. 127(49)(2005)*, 17156-17157.**
3. **XJ Duan, HB Son, B Gao, J Zhang*, TJ Wu, GG Samsonidze, MS Dresselhaus, ZF Liu*, J Kong*, Resonant Raman spectroscopy of individual strained single-wall carbon nanotubes, *Nano Lett. 7(7)(2007)*, 2116-2121.**
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# Bottom-up Assembly of Carbon nanotubes Electrocatalyst for Polymer Electrolyte Fuel Cell

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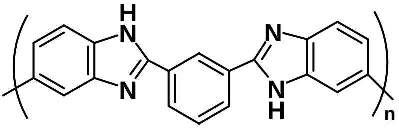

**Fig. 1** Polybenzimidazole (**PBI**).

Polybenzimidazole (**PBI**: Fig. 1) is widely known as a promising candidate for electrolyte membrane of polymer electrolyte fuel cell (PEFC) operating under dry condition. On the other hand, carbon nanotubes (CNTs) have been emerged as a better carbon support material than conventional material such as carbon black. We have reported the **PBI** is adsorbed onto the surface of CNTs and acts as the good solubilizer [1]. By taking advantage of stable wrapping of **PBI** on CNTs, we utilized this composite as a novel carbon supporting materials for loading the metal catalyst such as platinum (Pt). As the result, the **PBI**-wrapped CNTs show better efficiency of Pt loading than that of pristine CNTs due to the coordination between Pt ion and **PBI**. Furthermore, the obtained electrocatalyst (CNT/**PBI**/Pt) shows excellent Pt utilization efficiency mainly due to the formation of ideal interfacial structure constructed by the CNTs, **PBI** and Pt [2]. However, we also noticed the electrochemically active area (ECSA) was gradually decreased during long time operations caused by the aggregation of the Pt.

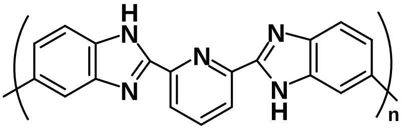

**Fig. 2** Chemical structure of **PyPBI**

In this study, we replaced **PBI** to pyridine-containing PBI (**PyPBI**: Fig. 2), which have a wider operating temperature than **PBI** for the new electrocatalyst (denote as CNT/**PyPBI**/Pt) and found similar electrocatalyst formation (**Fig. 3**)[3]. Detail studies in oxygen reduction, methanol oxidation for CNT/**PyPBI**/Pt and results will be explained in the presentation.

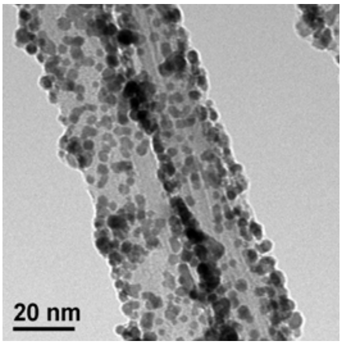

**Fig. 3** TEM image for the CNT/PyPBI/Pt.

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**Dr. Tsuyohiko Fujigaya was born in Saitama, Japan, in 1976. He received his B. S. and M S. degrees in Polymer Chemistry from Tokyo Institute of Technology University, Japan, in 1998 and 2000, respectively, and his Ph. D. degree in chemistry and biotechnology from Tokyo University, Japan, in 2005. He then spent a year as a postdoctoral fellow in Prof. Chad Mirkin's lab at Northwestern University, United States. And now he is an Associate Professor of Applied Chemistry of Kyushu University, Japan. His research focuses on the developments of the functional materials based on carbon nanotube/polymer composites such as the carbon nanotube-based electrocatalyst for polymer electrolyte fuel cell, controlled release of molecules for drug delivery system, photo-active cell cultured dish for positive collection of the cells, chromatographic analysis of the nanotube-molecular interactions using carbon nanotube as a stationary phase. Dr. Fujigaya has received the Research Fellow of the Japan Society for the Promotion of Science in 2004 and Award for Encouragement of Research in Polymer Science; The Society of Polymer Science, Japan in 2009.**

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1. **T. Fujigaya, T. Fukumaru, and N. Nakashima* "Evaluation of dispersion state and thermal conductivity measurement of carbon nanotubes/UV-curable resin nanocomposites" *Synth. Met.* 159, 827-830 (2009).**
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# The Confinement Effect of Carbon Nanotubes in Catalysis

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We report here the unique confinement effect which the one-dimensional channels of CNTs provide for nano-catalysts and catalytic reactions. A method for uniform dispersion of metal particles inside CNT channels was developed. The confinement effect was studied with in situ TEM, Raman, XRD and chemisorption techniques, by using synthesis gas conversion to liquid fuels, C2 oxygenates and ammonia synthesis as probe reactions.[1-3] The confinement effect is also observed in other catalytic reactions.[4]

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**Xiulian Pan received her PhD from Dalian Institute of Chemical Physics of the Chinese Academy of Sciences in 2001 after carrying out a thesis on development of palladium hollow fiber membranes for hydrogen separation and membrane catalysis under the guidance of Prof. Guoxing Xiong. She then spent two years as a postdoctoral fellow at the Fraunhofer Institute of Interfacial Engineering and Biotechnology in Stuttgart, Germany. She joined Prof. Xinhe Bao's group at Dalian Institute of Chemical Physics at the end of 2003 as an associate professor and now she is a professor. Dr. Pan's research interest is fundamental studies on nano-structured carbon for catalysis including carbon nanotubes, nanofibers, graphene and other synthetic mesoporous carbon materials. Her recent focus is on the confinement effects of carbon nanotubes which exhibit well defined nanochannels formed by graphene layers and could modify catalytic reactions through interaction with the confined metal and metal oxide nanocatalysts. The targeted reactions include hydrogenation of CO selectively to liquid fuels and oxygenates, ammonia synthesis, selective oxidation and electrocatalysis.**

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1. **D. Deng, X. Pan*, H. Zhang, Q. Fu, D. Tan, X. Bao*, Freestanding Graphene by Thermal Splitting of Silicon Carbide Granules, *Adv. Mater.* (2010) doi: adma.200903519C.**
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# Fabrication and Characterization of Novel Nanotube-based Hybrid Materials

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Substantial research efforts have been devoted to fabricate metallic or semiconducting low-dimensional materials, such as nanotubes and nanowires, because of their fundamental interest on optical, electrical and magnetic properties, which are qualitatively different from those at larger dimensions, as well as of versatile and promising applications towards nanoelectronic and nanospintronic devices[1]. Recently, we have successfully fabricate various metal and metal complex nanowires with high yield using one-dimensional space of carbon nanotubes[2,3]. These hybrid materials shows specific structure and properties that are distinctly different from that of bulk crystals. For example, HRTEM image of Eu-nanowire@CNTs is shown in figure 1. As clearly illustrated in the figure, Eu atoms align in a one-dimensional fashion with Eu-Eu distances of 4.6 Å, which is much larger than that of bulk crystal of Eu (4.0 Å). By changing diameter of CNTs used, we can produce various kinds of nanowires systematically.

To understand fundamental properties of these materials, correlation of atomic structure and properties is essential. Therefore, we are developing new characterization method using bridge structure. In this presentation, in addition to synthesis and detailed characterization of hybrid materials including CNTs and nanowires@CNTs, characterization using bridged structure will be discussed.

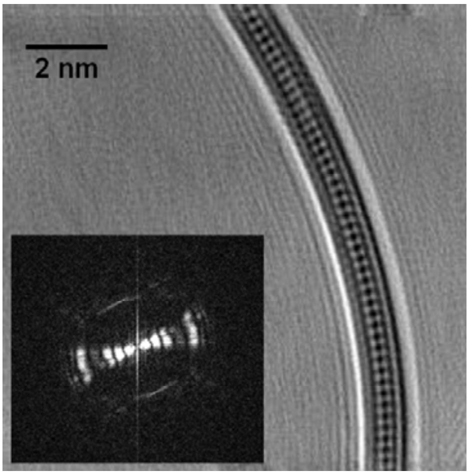

Figure 1. HRTEM image of Eu@DWCNTs (inset shows FFT image)

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**Dr. Ryo Kitaura was born in Nara prefecture, Japan, in 1974. He received his B. S. in Chemical Engineering from Osaka Prefecture University and M. S. degree in Chemical Engineering from Kyoto University in 1998 and 2000, respectively. Then, he joined Prof. S. Kitagawa's group in Kyoto University and obtained his Ph. D. degree in 2003. After two years research work in Toyota Central R&D laboratory, he joined Prof. H. Shinohara's group in Nagoya University as an Assistant Professor. And now he is an Associate Professor of Chemistry of Nagoya University, Japan. His research interests focus on the fabrication and functions of novel nano-materials including nanotubes, nanoclusters, nanowires and hybrid nanotubes; controlled synthesis of carbon nanotubes using CVD method; fabrication of novel nanomaterials using carbon nanotube nanoreactors; structural characterization using High resolution transmission electron microscopy; measurements of transport and magnetic properties; characterization using synchrotron radiation.**

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1. **Kitaura, R. et al. High-Yield Synthesis of Ultrathin Metal Nanowires in Carbon Nanotubes. Angew. Chem. Int. Ed. 48, 8298-8302 (2009).**
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# Synthesis of Endohedral Fullerenes Encapsulating a Small Molecule

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Endohedral fullerenes are so far produced by arc-discharge method using metal-doped graphite, high-pressure/high-temperature treatment with noble gases, and ion implantation with nitrogen, phosphorus, and lithium. These methods are generally conducted under high-energy conditions,[1] so it is difficult to apply for encapsulation of a small molecule such as $H_2$ and $H_2O$ owing to high reactivity toward fullerenes under these conditions.

The molecular surgical approach, involving creation of an orifice on the empty fullerene cage, insertion of a small guest through the orifice, and closure of the orifice with retention of the guest, is a promising method to synthesize yet-unknown endohedral fullerenes and their derivatives. Several open-cage fullerene derivatives have been reported so far, which can encapsulate He, $H_2$, $H_2O$, $CH_4$, $NH_3$ and CO.[2] However, examples of closure of the orifice are still limited to the synthesis of $H_2@C_{60}$, $H_2@C_{70}$, and $(H_2)_2@C_{70}$ from the open-cage fullerenes having a 13-membered ring orifice.[3,4] In order to realize endohedral fullerenes encapsulating a small molecule which is larger than $H_2$, creation as well as restoration of a larger orifice are needed. Herein we report our approach to synthesize endohedral $C_{60}$ encapsulating a small molecule by means of organic synthesis under mild conditions.

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Yasujiro Murata was born in Kanazawa in 1970 and received his B. Eng (1993) and Ph. D. degrees (1998) from Kyoto University under the supervision of Professor Koichi Komatsu. During that time he joined Professor Fred Wudl's group as a summer student (1995). After working as a postdoctoral fellow at Kyoto University in Professor Komatsu's group, he joined Institute for Chemical Research, Kyoto University, as an Assistant Professor (1999) and then as an Associate Professor (2006). He was promoted to a Full Professor in 2009 at the same institute. He received The Chemical Society of Japan Award for Young Chemists (2004), The Osawa Award from the Fullerenes and Nanotube Research Society, Japan (2006), and The Young Scientists' Prize from The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology (2006). During 2005-2009, he joined the PRESTO program "Structure Control and Function" from the Japan Society Technology Agency. His research interests include organo-chemical transformation of fullerenes, specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of ionic fullerene species and their application for the synthesis of functional material, and synthesis of new $\pi$-systems with curved structure by the use of transition metal complex.

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1. The Spin Chemistry and Magnetic Resonance of $H_2@C_{60}$. From the Pauli Principle to Trapping a Long Lived Nuclear Excited Spin State Inside a Buckyball
   Turro, N.; Chen, J. Y.-C.; Satori, E.; Ruzzi, M.; Marti, A.; Lawler, R.; Jockusch, S.; Lopez-Gejo, J.; Komatsu, K.; Murata, Y.
   *Acc. Chem. Res.* 2010, *43*, 335-345.
2. Synthesis and Reaction of Fullerene $C_{70}$ Encapsulating Two Molecules of $H_2$
   Murata, M.; Maeda, S.; Morinaka, Y.; Murata, Y.; Komatsu, K.
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   Murata, Y.; Maeda, S.; Murata, M.; Komatsu, K.
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# Functionalized Fullerene Derivatives: Photoelectric Conversion Applications

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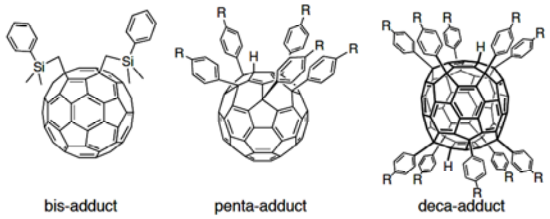
## New Methodology for Functionalization of Fullerenes

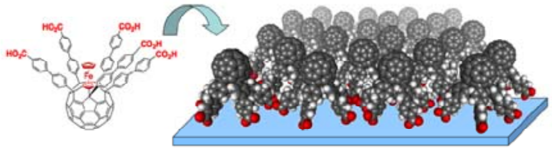
Multifunctionalization of fullerenes has become an important chemical tool for drawing out the maximum capacity of their unique properties in applications in chemistry and material and biological sciences. We have developed various methods for the efficient synthesis of organic functionalized fullerene derivatives.[1] For instance, DMF-modified monoaddition reaction of silylmethyl Grignard reagents to [60]fullerene produced monoalkyl[60]fullerene, $C_{60}RH$, which was able to be regioselectively derivatized into 1,4-bis-adducts, $C_{60}R_2$ via subsequent substitution reactions.[2] The 1,4-bis-adducts are promising organic n-type semiconducting materials.

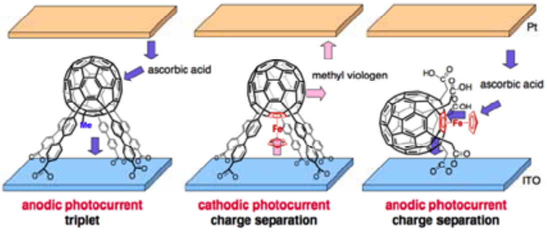


bis-adduct penta-adduct deca-adduct

## Photocurrent Generating Metal-Fullerene Complexes

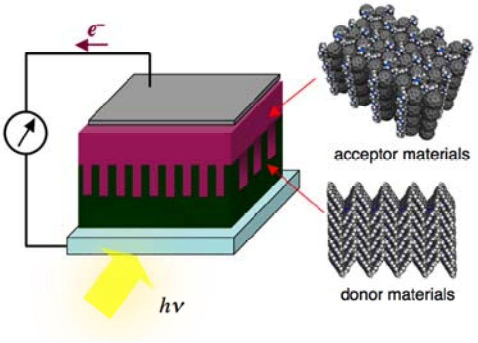
Photocurrent generating molecules possessing photo-induced charge separation properties are functional molecules that are expected to be utilized in photo-current conversion devices as well as light-mediated information transfer devices. With employing fullerenes as acceptors with metal complexes as donors, we have constructed photocurrent generating organometallic molecular devices.[3] For instance, we have synthesized rigid pentapod metal fullerene complexes that have the shape of a lunar lander, and succeeded in switching of photocurrent direction by changing components (organic molecules or metal complexes) and molecular orientations (standing upright or lying down).





## Organic Thin-Film Photovoltaic Devices

We have developed organic photovoltaic devices by means of a chemical approach starting from the design of functional molecules. We newly designed 1,4-di(organo)[60]fullerene derivatives possessing suitable electron affinity for high open-circuit voltage, thermal morphological changes from amorphous to crystalline states, and honeycomb-like packing structure in the crystal. The organic photovoltaic cells using these electron-acceptors have exhibited among the highest class of power conversion efficiencies (5.2%).[4]



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4. Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka, E. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 16048.

**Dr. Yutaka Matsuo was born in Osaka, Japan, in 1974. He received B.S. (1996) and Ph.D. degree (2001) from Osaka University under the guidance of Profs. Kazuhide Tani and Kazushi Mashima. Then, he joined Department of Chemistry, The University of Tokyo (Prof. Eiichi Nakamura's group) as an Assistant Professor. In 2004, he moved to Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency as a Leader. In 2009, he was promoted to Professor in Department of Chemistry, The University of Tokyo. His research interests lie in organic materials science (organic photovoltaics, liquid crystals, luminescent materials, and molecular devices) and carbon cluster chemistry. He was awarded The Chemical Society of Japan Award for Young Chemists for 2005, The Osawa Award of the Fullerenes and Nanotubes Research Society (2007), and The Young Scientists Award of the Japan Society of Coordination Chemistry (2009).**

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**Selective Publications**

**1. Y. Matsuo, K. Tahara, M. Sawamura, E. Nakamura, Creation of Hoop- and Bowl-Shaped Benzenoid Systems by Selective Detraction of [60]Fullerene Conjugation. [10]Cyclophenacene and Fused Corannulene Derivatives, *J. Am. Chem. Soc.* 2004, *126*, 8725.**

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# Latest Development in Raman Spectroscopy for the Characterization of Carbon Nanotubes and Graphene

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Over the past few years, carbon nanotubes (CNTs) and graphene have attracted much attention due to their unique structure, remarkable electrical and optical properties. In this research filed, Raman spectroscopy is recognized as a powerful, nondestructive and standard tool for their characterization. From Raman spectra, electronic, vibrational, and structural properties can be derived. Information on diameter, (n, m) index, transition energy of CNTs, amount of defects in the sample, and many other parameters can also be extracted from Raman spectra.

Benefiting from the latest developments of modern Raman technology, a number of significative works can be carried out conveniently. Single walled carbon nanotubes (SWCNTs) and graphene, can be analyzed in an easy way.

In this talk, we will present the latest development in Raman spectroscopy, and their application to the characterization methods of CNTs and graphene.

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Horiba 广告

# Metal-free Growth of SWNTs

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Selective growth of SWNT with specific helicity is the one of the main challenges towards controlled growth of SWNTs for various applications  Metal nanoparticles (NPs) are indispensable for the growth of SWNTs by chemical vapor deposition (CVD) and Fe family of elements were regarded as the most effective catalysts in the past. However, in recent years many other metal NPs such as Au, Ag, Cu, Pd, Rh,, Mg, Mn, Cr, Sn and Al, semiconductors NPs such as Si, Ge, Te, carbides such as SiC, $Fe_3C$ etc have been reported to be active for nanotube growth although these materials were regarded as inactive catalysts for CNTs. One problem raising from the metal catalysts is that the chemical, redox, magnetic properties of the metal NPs involved in the nanotube materials will interfere the corresponding nanotube properties and performances. In this talk, recent progress in the growth of SWNTs from metal-free catalysts will be summarized and the possible grow mechanism is discussed. The strategy for realizing the controlled growth of SWNTs, particularly for helicity, is proposed.

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**Selective Publications**

1 **SM Huang, QR Cai, JY Chen, Q Yong, LJ Zhang, Catalyst-free growth of SWNTs on substrate** ***J. Am. Chem. Soc. 131(2009)*****, 2094-2095.**

2 **SM Huang, Q Yong，JY Chen, S Wan, L Wang, WB Hu, Identification of the structures of superlong oriented SWNT arrays by electrodeposition of metal and Raman spectroscopy** ***J. Am. Chem. Soc. 130(2008)*****, 11860-11861**

3 **SM Huang, M Woodson, J Liu and R Smalley, Growth mechanism of oriented long single-walled carbon nanotubes using "fast heating" chemical vapor deposition process"** ***Nano Lett. 4 (2004)*****, 1025-1028.**

4 **SM Huang, B Maynor, J Liu, Ultralong ,well-aligned single-walled carbon nanotube architectures on surfaces** ***Adv. Mater. 15(2003)*****, 1651-1654.**

5 **SM Huang, X Cai, J Liu, Growth of millimeter-long and horizontally aligned SWNT on flat substrates"** ***J. Am. Chem. Soc. 125(2003)*****, 5636-5637.**