# PKU-UTokyo Joint Research Center of Excellence for Nanocarbons

# 2017 PKU-UTokyo Nanocarbon Summer Camp

Place: Hongo Campus, The University of Tokyo Time: July 27<sup>th</sup> - August 2<sup>nd</sup>, 2017



# 2017 PKU-UTokyo Nanocarbon Summer

# **General information**

This year's Summer Camp will bring together 35 participants, including 15 (3 faculty members and 12 graduate students) from PKU, and 20 (8 faculty members + 12 students) from UTokyo. For a week time, participants will intensively discuss recent progress in Nano-carbon research, and propose potential collaborations between PKU and UTokyo.

On 28<sup>th</sup>, we will hold a one focused workshop where representatives from both sides will give lectures on their recent results related to nano-carbon research. After All participants are suggested to attend.

From 29<sup>th</sup>, student participants will be divided into 6 teams for independent work and discussion. Each team will propose a potential collaborative research direction between PKU and UTokyo. To help everybody know each other, a selfintroduction session will be held in the morning of 29<sup>th</sup>, and all students give a 5 min presentation including brief introduction of themselves and their research.

After intensive work and discussion, students give their final report and presentation on 31<sup>st</sup>.

The official language of summer camp is English.

#### Notes:

Participants from PKU *must* give your boarding pass to our staff at the registration. Please send a scanned copy of the boarding pass for your return flight.

The dress code for the Camp is casual; you do not need any formal clothing.

Summers in Tokyo are fairly hot and humid, expecting temperature is 25-35°C, and it may rain.

#### Contacts:

Email: <u>maruyama@photon.t.u-tokyo.ac.jp</u> (Prof. Shigeo Maruyama) <u>xiangrong@photon.t.u-tokyo.ac.jp</u> (Assistant Prof. Rong Xiang)

TEL: <Mon.-Fri. worktime> Maruyama office: +81-3-5841- 6421 <Afterwork time> Rong Xiang: +81-90-8486-1982

#### Facilitators:

Hua An (安华): <u>anhua@photon.t.u-tokyo.ac.jp</u> Keigo Otsuka (大塚 慶吾): <u>otsuka@photon.t.u-tokyo.ac.jp</u> Hiroya Minowa (箕輪 紘弥): <u>minowa@photon.t.u-tokyo.ac.jp</u>

Agenda for 2017 PKU-UTokyo Nanocarbon Summer Camp							[	Student	Pro	fessor	Both			
	8 am	9	10	11	12	1 pm	2	3	4	5	6	7	8	9
July 27 (Thur.)								Arrival at Narita, JL860 (An, Minowa, Ogamoto) Hotel check in <sup>2</sup> access to Super Hotel Ueno-okachimachi		Registration and reception <sup>3 access to UTokyo</sup> @ 2-73C2				
July 28 (Fri.)		<u> </u>	orkshop o UTokyo <sup>1</sup> @ 2-31	orogram	<b>Groug</b> photo o Luncł	ξ. τ	rkshop of PKU- JTokyo 2-31A	stud	our for ents <sup>7</sup> ang)	Break		Banquet @ Restaurant ABREUVOIR <sup>4</sup> place information		
July 29 (Sat.)		(Ots Prof	t presenta suka) @ 2 <sup>.</sup> cessor mee (if needed	31A eting	Lunch a discussi		8	p working Internet info ofessor m (if need	neeting	<u> </u>	Break	Group working @ 2-31A (If needed)		
July 30 (Sun.)		Tour to Ueno Park, (An, Liu) Professor meeting (if needed)		Lunch a discussi		Group working @ 2-3 (F. Yang) Professor meeting (if needed)		g) neeting	L	Break Group working @ 2-31A (If needed)				
July 31 (Mon.)		Group working @ 2-31A Professor meeting (if needed)		Lunch and discussion Group working @ 2-73C2			Final esentation 9 @ 2-31B Discussion, din refreshment Committee mee @63D4		nent neeting	Summary and Awards @ 2-31B				
Aug. 1 (Tues.)			Free discus TEM Discussion (Maruyama, Li, F. Yang)			scussion	sion @2-31A			_				
Aug. 2 (Wed.)									Departur	re to Beiji (An Hua)	-	9		

\*All activities except Banquet are held in engineering building 2; Room 2-31A, 2-31B are on 3<sup>rd</sup> floor, and 2-73C2 is on 7<sup>th</sup> floor.



# 2017 PKU-UTokyo NanoCarbon Workshop

Time: July 28 (Fri.), 2017, 9:00-14:45

Place: Room **31A** (3<sup>rd</sup> floor), Eng. Bld. 2, Hongo Campus, The University of Tokyo Co-organizer: Shigeo Maruyama and Yan Li

9:00 - 9:20	Registration					
9:20 - 9:30	Shigeo Maruyama					
	Opening					
9:30 -10:00	Kosuke Nagashio (UTokyo)					
	Interface engineering for 2D layered semiconductors					
10:00 -10:30	Suguru Noda (Waseda Univ.)					
	Production and functionalization of carbon nanotubes for energy devices					
10:30 -11:00	Ryo Shimano (UTokyo)					
	Ultrafast THz nonlinear optics in a Landau-quantized graphene					
11:00 -11:30	Hideaki Shiroyama (UTokyo)					
	Science and Technology Governance and the Role of Technology Assessment					
11:30 -12:00	Juan Yang (PKU)					
	Raman spectroscopy of individual SWNTs					
12:00 -13:00	Group Photo & Lunch					
13:00 -13:30	Yuichiro Kato (Riken)					
	<i>Exciton-exciton annihilation and exciton-carrier interactions in carbon nanotubes</i>					
13:30 -13:55	Keigo Otsuka (UTokyo)					
	Water-assisted Self-sustained Burning of Metallic Single-walled Carbon Nanotubes toward Scalable Transistor Fabrication					
13:55 -14:20	Feng Yang (PKU)					
	<i>Characterization of the Chiral Structure of Aligned SWNTs and TEM study on W6Co7 Catalysts</i>					
14:20 -14:45	Hua An (UTokyo)					
	Chirality specific and spatially uniform synthesis of single-walled carbon nanotubes from sputtered Co-W bimetallic catalyst					
15:00 -17:00	Lab tour					
18:00 -	Banquet					

# 2. Hotel for students

Hotel information:

http://www.superhotel.co.jp/s hotels/okachimachi/

Hotel name:	スーパーホテル上野・御徒町			
	SUPER HOTEL UENO-OKACHIMACHI			
Address:	〒110-0005 東京都台東区上野 5 丁目 23-12			
Contact:	TEL : 03-5818-9000 / FAX : 03-5818-9010			
Check-in date:	2017-7-27 (Thur.)			
Check-out date:	2017-8-2 (Wed.)			

#### About check in:

You will need to pay the hotel fee when you check in, so please first leave your luggage at front desk (already confirmed with hotel) and come to University of Tokyo for registration (and cash!!!). After dismiss, go back to hotel, check in and pay.

List of guest: 刘启东 (Liu Qidong) 郭 佳 (Guo Jia) 朱 胜 (Zhu Sheng) 周子硕 (Zhou Zishuo) 俄 娜 (Zhang Na) 单婧媛 (Shan Jingyuan) 单婧媛 (Shan Jingyuan) 慈海娜 (Ci Haina) 邹明初 (Zou Mingchu) 赵晨怡 (Zhao Chenyi) 刘力俊 (Liu Lijun) 姚凤蕊 (Yao Fengrui) 王 孟 (Wang Meng)

# 3. Access to UTokyo, Engineering Building #2

It is about 20 min walk from hotel to UTokyo. It is a good experience to go across or along Ueno-Park.



Maruyama Chiashi Lab. in Engineering Building 2, Office room number 63C2 Registration at 3<sup>rd</sup> floor, room number 2-31A



# 4. Banquet information

Everybody (both faculties and students) from Japan and China side is invited to banquet.

Banquet: July 28, 18:00-21:00 Restaurant ABREUVOIR The University of Tokyo, Yayoi Campus, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-0032 Japan TEL 03-5805-2505 FAX 03-5805-2565 http://www.u-tokyo.ac.jp/campusmap/cam01\_00\_30\_j.html

#### !!Important!!

Due to fund regulation in Japan, unfortunately, all participants must share the cost for the drinks (Food is covered).

We will collect money at registration or entrance of the Banquet

Professors: 2000 yen

Students: 1000 yen



# 5. Students presentation

All the student participants from both China and Japan side will be asked to give a 5 min presentation including your self-introduction and research direction (morning of 29<sup>th</sup>). You are advised to come a bit earlier to test the functioning of your ppt file.

# 6. Grouping

You are suggested to form 6 team x 4 people. Please make teams freely, but each team is suggested to have 2 PKU students and 2 UTokyo students. A team with all Chinese is not allowed. Furthermore, each team should have at least one female student.

# 7. Lab tours

15:00-15:30	Takagi-Kinefuchi Lab. @ Mechanical Engineering
	http://www.fel.t.u-tokyo.ac.jp/index_en.html
15:30-15:50	Maruyama-Chiashi Lab. @ Mechanical Engineering
	http://www.photon.t.u-tokyo.ac.jp/
15:50-16:00	Walk to Asano Campus
16:00-16:30	Crystal Interface (Ikuhara) Lab. @ Institute of Engineering Innovation
	http://interface.t.u-tokyo.ac.jp/japanese/index.html

#### 8. Internet

All participants from PKU side will be provided by a guest account at registration for wifi access in UTokyo. However, since the password change automatically every week, we will reannounce the new one on Monday. You are also encouraged to bring your wifi, or make eduroam account.

Participants from UT side please use your own wifi access (UTokyo-wifi, istmember, etc.) and please do NOT share your UTokyo account with our visitors (due to the recent network attack to UTokyo known in newspapers, UTokyo is now very sensitive to the security issue). However, you may help your teammates to download the journal papers.

#### 9. Final presentation

- ✓ Each team proposes a potential collaborative project between PKU and UTokyo
- $\checkmark$  Topic should be related but not limited to Nano-carbon research
- ✓ Each team gives a 15 min presentation on their proposal. (10 min talk + 5 min Q&A)
- ✓ All members of a team need to present, and the contributions of each member need to be clarified at beginning of the presentation.
- ✓ Each team needs to submit one page summary (format not limited), as well as their presentation PowerPoint for final score.

# 10. Participant list

Name	Kanji	Affiliation	Supervisor	e-mail
Yan Li 李彦		Peking University		<u>yanli@pku.edu.cn</u>
Juan Yang	杨 娟	Peking University		<u>yang juan@pku.edu.cn</u>
Feng Yang	杨 烽	Peking University		fengyang@pku.edu.cn
Suguru Noda	野田 優	Waseda University		noda@waseda.jp
Shigeo Maruyama	丸山 茂夫	The University of Tokyo		<u>maruyama@photon.t.u-okyo.ac.jp</u>
Tatsuya Okubo	大久保 達也	The University of Tokyo		okubo@chemsys.t.u-tokyo.ac.jp
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Hiroya Minowa	箕輪 紘弥	The University of Tokyo		<u>minowa@photon.t.u-tokyo.ac.jp</u>
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Xueqiang Zhang	张学强	Tsinghua University	Qiang Zhang	zhangxq16@mails.tsinghua.edu.cn

# Abstract

#### Selective etching of metallic single-walled carbon nanotube by H<sub>2</sub>O/H<sub>2</sub>

#### Qidong Liu<sup>1</sup>

<sup>1</sup> Beijing National Laboratory for Molecular Science, Key Laboratory for the Physics and Chemistry of Nanodevices, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China liuqidong@pku.edu.cn

Semiconducting single-walled carbon nanotube (s-SWNT) is a promising material for electronic devices. Apart from selective growth of s-SWNTs on substrate, etching metallic single-walled carbon nanotube (m-SWNT) is another method to get pure s-SWNTs since m-SWNT is more active. Although after growth of SWNT arrays by CVD, we can obtain high-purity s-SWNT arrays using etching agent such as H<sub>2</sub>O, NO<sub>2</sub>, etc., their density are much smaller compared to original ones, which is unfavorable to their application. Thus, we produced carbon nanotube thin film with high density on Si/SiO<sub>2</sub> modified with APTES and we used H<sub>2</sub>O/H<sub>2</sub> as etching agent instead of H<sub>2</sub>O only, and we think H<sub>2</sub> can widen difference between s-SWNTs and m-SWNTs thermodynamically during etching.

#### Self-introduction



My name is Qidong Liu, and I was born in Henan province in 1994. I received a B.S. in chemistry from Nanjing University in 2016 and since then I work at Peking University as a graduate student. My professor is Yan Li and my research focus on the growth of carbon nanotubes and I am also interested in the synthesis and application of nanomaterials.

# Iron Ultrathin Film Catalyzed Methanol Enhanced Chemical Vapor Deposition of Vertically Aligned Carbon Nanotube Forests

Jia Guo, Yan Li\*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China guojia nmns@pku.edu.cn

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

However, efficient and facile method to grow ultralong vertically aligned carbon nanotube (VACNT) forests still needs further development. Here we add methanol to suppress the sharply thermal decomposition of acetylene and may maintain catalyst actively with longer lifetime. With the addition of methanol, the ultrathin iron film catalyst forms large-scale, centimeter-long, high-density, uniform VACNT forests, which may have great potential in a wide range of fields. Reference :

- 1. Jiang K, Fan S. Nature 2002, 419, 801.
- 2. S. Maruyama. Chem. Phys. Lett.. 2002, 360, 229.
- 3. Ding L. Li Y. Nano Res. 2009, 2, 903.
- 4. Zhang R, Wei F. Acc. Chem. Res. 2017, 50, 179.

#### Self-introduction



Jia Guo was born in Luoyang which situated on the central plain of China, and is one of the cradles of Chinese civilization and the Four Great Ancient Capitals of China. She received her BS in Materials Science and Engineering, Zhengzhou university. She is now studying for the doctorate in Peking University and is committed to research the growth and the application of vertically aligned CNT forests. In her spare time, ball games, bridge (one traditional game) and literature are her favorite things. Great pleasure to make friends

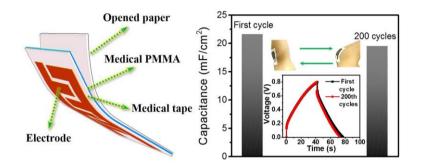
with you, and explore interesting and meaningful science and technology together.

#### Pencil-drawing skin-mountable micro-supercapacitor

#### Zhu Sheng

# College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China shengzhu@pku.edu.cn

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. With the rapid development of miniaturized and portable electronic devices, flexible and wearable energy storage has become an emerging field in recent years.



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.

#### Self-introduction



As a Ph.D student in Peking University, I am 25 years old. My hometown is Anhui province located in the east of China, which is a very beautiful place and have many places of interests, such as Mount Huang, tianzhu mountain and jiuhuashan mountain. My research focus on the solid energy storages based on nanomaterials. I also have a wide range of interests including singing, playing chess, playing balls, watching movies, making friends and so on.

#### Synthesis of Open-cage Fullerenes as ligands of metal complexes

Zishuo Zhou, Liangbing Gan\*

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

Selective cleavage of multiple carbon-carbon bonds around a local area on the surface of fullerene cages can produce many different open-cage fullerenes.<sup>[1]</sup> The Lewis-base functionality of the orifices arising from the introduction of different heteroatoms make it possible for open-cage fullerenes to coordinate to metal ions.<sup>[2]</sup> In the present work, we report the preparation of open-cage fullerenes with both amino and hydroxyl groups on the rim of the orifice, which are suited for coordination to metal ions. Single crystal structure of a nickel complex was obtained as shown below (**Figure 1**).

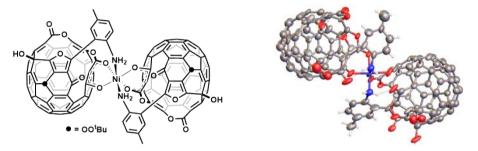


Figure 1 Structure of a nickel complex with open-cage fullerenes as the ligand.

#### **Reference:**

- For Reviews on open-cage fullerenes: (a) M. Murata, Y. Murata, K. Komatsu, *Chem. Commun.* 2008, 6083; (b) G. C. Vougioukalakis, M. M. Roubelakis, M. Orfanopoulos, *Chem. Soc. Rev.* 2010, *39*, 817; (c) L. J. Shi, L. B. Gan, *J. Phys. Org. Chem.* 2013, 26, 766.2.
- (a) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. J. Am. Chem. Soc. 1996, 118, 3775. (b) Aghabali, A.; Jun, S.; Olmstead, M. M.; Balch, A. L. J. Am. Chem. Soc. 2016, 138, 16459.

#### Self-introduction



Name: Zishuo Zhou(周子硕) Age: 25 Hometown: Beijing, China Education: 2010.9-2014.7 B.S., Peking University, 2014.9-present Ph.D., Peking University. (with Professor Liangbing Gan) Interest: Playing table tennis

# Raman Enhancement on Anisotropic Two-dimensional Layered Materials

Na Zhang, Jingjing Lin, Lianming Tong\*, Jin Zhang\*

Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, P. R. China

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Surface-enhanced Raman scattering (SERS) on anisotropic 2D materials, including orthorhombic black phosphorus (BP) and triclinic rhenium disulfide (ReS<sub>2</sub>), provides a unique platform to study the chemical mechanism (CM) of the enhancement due to their unique anisotropic electrical and optical properties owing to their in-plane anisotropic structural nature.

Herein, we reported strong anisotropy of Raman enhancement on few-layered BP and ReS<sub>2</sub> using copper phthalocyane (CuPc) molecules as Raman probe. For the random distributed CuPc molecules in contact with BP and ReS<sub>2</sub>, the anisotropic enhancement was identified by Angle-Resolved Polarized Raman Spectroscopy (ARPRS), while it is totally absent in SERS on graphene and h-BN. Raman tensor analysis and density functional theory (DFT) calculations were performed to understand the underlying mechanism, and found out that a linear charge redistribution and the intrinsic anisotropic carrier mobility of the 2D materials should contribute to the anisotropic Raman enhancement. To further confirm the mechanism, flat metal film is added to modulate the electronic structure of anisotropic 2D materials. This experimental observation not only provides new insights into the chemical mechanism (CM) process in SERS, but also opens up new avenues for the possible exploration of the electronic properties of anisotropic 2D layered materials.

#### Self-introduction



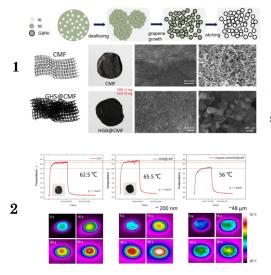
I come from Dezhou, a city famous for its specialty of braised chicken, and that may be the reason why I'm so fond of looking for new delicious food. I love watching Japanese TV drama, and Operation Love and Legal High are my favorites. I have watched a lots of movies, and feature film is my preference. My favorite music style is folk music. My hobbies also include softball, squash, yoga. Now I start to go in for photography.

### Graphene hollow spheres combined with carbon nanotube macrofilm for efficient solar-thermal conversion

Jingyuan Shan<sup>1,2</sup>, Huaying Ren<sup>1,2</sup>, Zhongfan Liu<sup>1\*</sup>

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Developing affordable, eco-friendly methods for effective utilization of solar energy is one of the most important strategies to meet ever growing demand of clean energy. Energy conversion by solar illumination is the most effective and clean strategy to utilize the solar energy. Here we demonstrate a GHS@CMF film with hierarchical structure consisting of graphene hollow spheres combined with carbon nanotube macrofilm for efficient solar-thermal conversion.



Graphene is an ideal material for solar-thermal conversion for its outstanding broadband absorption, at the same time, the hollow structure enhances the light absorption. We develop a facile way to get graphene hollow spheres by chemical vapor deposition on a dealloyed nickel-aluminum alloy substrate. Figure 1 shows the schematic of graphene growth on the dealloyed substrate and how it combined with carbon nanotube macrofilm. Figure 2 illustrates the extraordinary solar-thermal conversion performance of the GHS@CMF film.

#### Self-introduction



My name is Shan Jingyuan, 22 years old, born in Shanxi province in China. My major is physical chemistry and I have been a PhD candidate of Center for Nanochemistry in Peking University for almost one year. Now I focus on the growth of graphene and its application in energy storage and conversion. I usually play board games or watch movies in spare time.

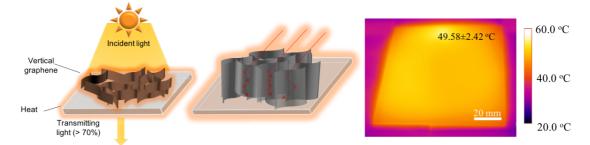
# Vertically-oriented Graphene Growth on Soda-lime Glass for Photothermal Applications

Haina Ci<sup>1, 3</sup>, Yanfeng Zhang<sup>2, \*</sup>, Zhongfan Liu<sup>3, \*</sup>

<sup>1</sup> Academy for Advanced Interdisciplinary Studies, <sup>2</sup> Department of Materials Science and Engineering, College of Engineering, <sup>3</sup> Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

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Vertically-oriented graphene (VG) possesses advantageous characteristics over flat lying graphene, including large surface area, exposed sharp edge, non-stacking three-dimensional geometry, etc. Here, we report the direct synthesis of vertically-oriented graphene on traditional soda-lime glass, considering its low-cost, good transparency and compatibility with daily life applications. This synthesis is achieved by a direct-current plasma enhanced chemical vapor deposition (dc-PECVD) route at 580 °C, which is right below the softening point of glass, and featured with a scale-up size ~6 inch. Particularly, the achieved VG nanosheets-glass hybrid materials at a transmittance range of 97-34% have exhibited excellent solarthermal performances, reflected with 70%-130% increase of surface temperature under simulated sunlight irradiation.



### Self-introduction



I'm Haina Ci, twenty-six years old. I'm from Shandong Province, China. Playing table tennis and badminton are my interests, however, sometimes they are hard for me. For my education, I graduated with my Bachelor's degree from Lanzhou University in Physics. And now I'm as a Ph.D student doing research at Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University.

# Flexible and porous 3D carbon nanotube electrodes: controllable preparation and stable electrochemical properties

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In recent years, flexible electronic devices has been required urgently, with the rapid increase in demand of portable and wearable electronics. However, as the power source, conventional lithium-ion batteries (LIBs) and supercapacitors (SCs) are typical rigid and heavy, due to the addition of redundant additives and the metal current collector. Here, we develop a three dimensional (3D) porous carbon nanotube (CNT) sponge with excellent conductivity, high porousity and stable mechanism properties, which is an ideal framework for flexible LIBs and SCs electrode. As a conductive framework, CNT sponges are deposited with a uniform layer of  $TiO_2$  to be used as anodes for LIBs. In particular, these composite sponges maintain the electrochemical performances even if be compressed more than ten times, which can significantly enhance the areal specific capacity. In addition, we combine the CNT sponge with single CF and fabricate macroscopic-thickness highly porous monolithic CNTs@CF fibers. These CNTs@CF fibers can act as a template for introducing active materials, and a solid-state fiber-shaped supercapacitor with volume-specific capacitance is demonstrated. Our CNT sponges-based porous 3D materials may serve as stable and flexible electrodes for portable energy storage systems such as Li-S, LIBs and SCs.

#### Self-introduction



My name is Mingchu Zou. I am 26 years old, born in Liaoning province, China. I obtained my bachelor degree from Northeast Normal University in 2014. I am a PhD student at the Collage of Engineering, Peking University and my current research interests are synthesis of 3D carbon materials and their applications in energy storage, flexible devices such as lithium-ion or sodium-ion batteries and supercapacitors. In my spare time, I like playing football and badminton.

#### High performance field effect transistor based on thin film

Zhao Chenyi<sup>1</sup>, Zhong Donglai<sup>2</sup>, Zhiyong Zhang, Lianmao Peng

<sup>1</sup> Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China

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With outstanding electrical properties, semiconducting carbon nanotube (CNT) is considered as an excellent channel material to build high-performance field effect transistor (FETs). From the point of material development, solution processed CNT film reached high semiconducting purity and capability of mass production. However, most of them are applied in flexible or transparent circuit, and suffering in poor performance. To improve the performance of circuits based on CNT network thin film, we explored the vertical and horizontal scaling behavior of individual device, the density of CNT film and length of contact. The CNT thin film FETs exhibited both high transconductance and low subthreshold slope that provide high speed and low power dissipation. The transconductance are 30-80mS/µm, and the subthreshold slope can be as low as 60-80mV/dec. Our high performance devices demonstrates the possibility to fabricate high performance circuits in large scale that can complement or extend silicon based ICs. Simulation also was carried out to analysis factors influencing performance in CNT thin film FETs.

#### Self-introduction



My name is Zhao Chenyi. I was born in 1992, in Hubei province in China. Now I'm in my third year as a PhD candidate in Peking University. I'm major in Nano science and device. I like reading and running in my spare time. I also like movies and music.

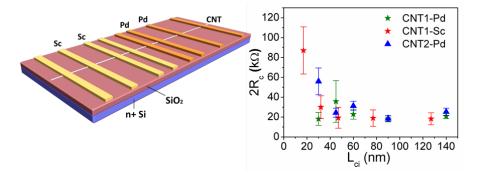
#### Scaling down contact length in complementary carbon nanotube field-effect

#### transistors

Lijun Liu\*, Zhiyong Zhang, Lian-Mao Peng

Key Laboratory for the Physics and Chemistry of Nanodevices and School of Electronics Engineering and Computer Science (EECS), Peking University, Beijing 100871, China. \*E-mail: liulijun@pku.edu.cn

Carbon nanotube (CNT) has long been considered as a desirable replacement material for the channel of high performance field-effect transistors (FETs). However, there has been concern regarding the contact resistance  $(2R_c)$  of nanotube/metal limiting the performance especially at scaled contact length and for both n-FETs and p-FETs. Here, we performed an experimental investigation on contact length (L<sub>c</sub>) scaling of carbon nanotube (CNT) complementary field-effect transistors (FETs).  $2R_c$  of Sc-contacted (for n-type) and Pd-contacted (for p-type) CNT FETs are respectively retrieved based on experimental data through transfer length method (TLM). The performance of L<sub>c</sub> scaling of Sc/CNT is proved to be comparable to that of Pd/CNT contact with L<sub>c</sub> larger than approximately 40 nm, but degrades sharply when further scaling down L<sub>c</sub> mainly owing to the surface oxidation of Sc film. After decoupling the effect of oxide thickness, the intrinsic contact scaling behavior of Sc-contacted CNT FET is found to be as good as that of Pd-contacted one, which can further satisfy the requirement of developing complementary CNT FET technology scaled down to 14 nm node.



#### **Self-introduction**



My name is Lijun Liu (in simplified Chinese: 刘力俊), BS and currently a PhD candidate in department of Electronics and school of EECS, Peking university. I was born in province of Guizhou, a mountainous state with beautiful and diverse scenery. Apart from the research I'm up to, watching movie is one of my favorite. Traveling is another major interest of mine.

# Measuring Complex Dielectric Function of Individual Carbon Nanotubes

Fengrui Yao<sup>1</sup>, Can Liu<sup>2</sup>, Cheng Chen<sup>1</sup>, Kaihui Liu<sup>1\*</sup>

<sup>1</sup> Peking University, School of Physics, State Key Laboratory for Mesoscopic Physics, Center for Nanochemistry, Beijing 100871, China

<sup>2</sup> Peking University, School of Physics, Academy for Advanced Interdisciplinary Studies, Center for Nanochemistry, Beijing 100871, China
\* fengruiyao@pku.edu.cn @ Fengrui Yao

Determining carbon nanotubes (CNTs)' complex dielectric function is of great importance for characterizing their light-matter interactions and for their emerging applications in electronics and optoelectronics. Despite its central role, a general optical characterization technique that permits noninvasive measurements of complex dielectric function of individual nanotubes has been lacking. The main difficulty lie in the individual CNTs, with only diameters of nanometers, does not even reflect light. Therefore, conventionally methods, like ellipsometer, which based on the analysis of material's reflection, is no longer applicable. Here, we report a determination of the complex dielectric function of chirality-defined single-walled nanotube (SWNTs) for photon energies from 1.45 to 3 eV. The real and imaginary part of complex dielectric function can be extract by varying the phase between an external reference field and CNT's scattered field. We also provide a comparison of the dielectric function for the monolayers graphene.

#### **Self-introduction**



My Fengrui name is Yao, 24 year old. born in Shandong province, where is also hometown of Confucius. I come from Peking University, school of physics, my supervisor is prof. Kaihui Liu. This is my second year of postgraduate education, I will get my doctor's degree in 2020 if everything goes well. My main research is the novel physical phenomena in nanoscale structures by using in-situ Nano-optics technique, especially for 1D carbon nanotubes. In my spare time,

I have broad interests, like listening music, and playing tennis. I am an optimistic, cheerful girl, like all the wonderful things, hope to make more friends! That's all. Thanks.

# Helical Conformations of Poly(3,5-disubstituted phenylacetylene)s Tuned by Nanomaterials

Meng Wang<sup>1</sup>, Sheng Wang<sup>2</sup>, Juan Yang<sup>1</sup>, Xinhua Wan<sup>2\*</sup>, Yan Li<sup>1\*</sup>

<sup>1</sup> Department of Inorganic Chemistry, College of Chemistry and Molecular Engineering, Peking University; <sup>2</sup> Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University

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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 in this report. 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<sub>60</sub>, Au NPs, SiO<sub>2</sub> 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 being added the above-mentioned nanomaterials, and about 60 nm red-shift of peak position of Cotton effects when added carbon nanomaterials. On the basis of the experimental data, we suppose that the helical transitions of the polyene backbone is related to the spatial configuration of pyrene group, which dependent on the nanomaterials.

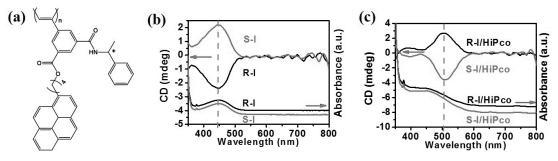


Figure: (a) Chemical structures of **R-I** and **S-I**; CD spectra of (b) 0.01mg/mL R-I/S-I in NMP and (c) 0.05mg/mL **R-I/S-I** HiPCO in NMP

#### Self-introduction



Hello! I'm Meng Wang( $\pm \pm$ ), a PhD candidate of Chemistry. Graduating from Shandong University in 2014, I became a student of Peking University. I like reading, calligraphy and badminton. My research interest is the purification and separation of SWNTs. Expect to be friends with you!

# Saturable absorber based on graphene and its application to mode-locked laser

Yuki Shirakura<sup>1</sup>, Sze Y. Set<sup>1</sup>, Shinji Yamashita<sup>1</sup> <sup>1</sup>The University of Tokyo, Research Center of Advanced Science and Technology shirakura@cntp.t.u-tokyo.ac.jp

Atomic layer materials like graphene or molybdenum disulfide have many unique properties, and saturable absorption is one of them. Saturable absorption is third-order nonlinear photonic phenomena that high intensity light is less absorbed in material, and low intensity light is more absorbed in it [1]. When a light pulse goes through saturable absorber (SA), the pulse gets sharp because peak of the pulse doesn't decay and other parts of the pulse decay (Fig 1). Passive mode-locked laser, that is spontaneous pulse oscillating laser, is realized by inserting SA in optical cavity with gain medium (Fig 2).

SA mirror is one way to insert SA in laser cavity. SA is attached on mirror, and the mirror is used as end of cavity. However mirror works as fixed end for light wave, thereover electric field of light near the SA mirror is standing wave. Hence the distance SA and mirror of the SA mirror should effect its property. We calculated its absorption change.

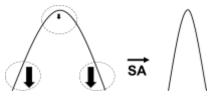


Fig.1 SA effect on pulse

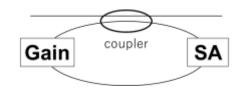


Fig2. passive mode-locked laser

Reference

[1] Shinji Yamashita, J. Lightwave Technol. 30, 427-447 (2012)

#### **Self-introduction**

## CNT Based Saturable Absorber and Its Application on 2µm Modelocked Fiber Laser

<u>Hongbo Jiang<sup>1</sup></u>, Sze. Y. Set<sup>1</sup>, Shinji Yamashita<sup>1</sup> <sup>1</sup>RCAST, The University of Tokyo hbjiang@cntp.t.u-tokyo.ac.jp

The research effort to design and operation mode-locked fiber lasers in the 2  $\mu$ m spectral region can now be said to be an essential preparation for so many promising future areas such as atmospheric sensing and laser imaging detection and ranging (LIDAR). In this report, we demonstrate an all-fiber passively mode-locked ring laser using carbon nanotube as saturable absorber. Carboxymethyl cellulose (CMC) is used as a host polymer for the CNTs because it has a flat absorption spectrum in the 1-2  $\mu$ m wavelength region. The thulium (Tm3+) doped fiber is regard as gain media in 2  $\mu$ m. The experiment setup is shown in figure 1.

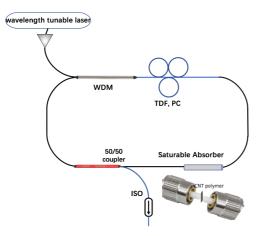


Fig 1. Experiment Setup. The concentration of the CNT-CMC mixture is further condensed via ultracentrifugation before the formation of the CNT polymer film

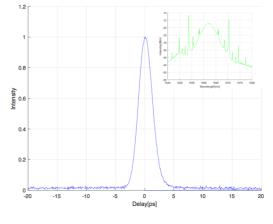


Fig 2. autocorrelation trace and soliton in subplot

The pulse shape and spectral from optical analyzer is shown in figure 2, Which indicates that CNT can be regard as a good mode locker for 2  $\mu$ m picosecond pulse trains generation and has great potential application for mid-ir.

#### Self-introduction



I am Jiang Hongbo, Master year one student from UTokyo, Yamashita-Set laboratory. Graduated from

the BUPT (2012). My hometown is Lanzhou, China.

### Thermal Dependence of Power Generation by Reverse Electrodialysis with Silica Nanopores

<u>Tatsuki Sekimoto<sup>1</sup></u>, Junho Hwang<sup>1</sup>, Wei-Lun Hsu<sup>1</sup>, Hirofumi Daiguji<sup>1</sup> <sup>1</sup>Department of Mechanical Engineering, The University of Tokyo, Japan sekimoto@thml.t.u-tokyo.ac.jp

The power generation with ion-selectivity nanopores is expected to be used as a power source of miniaturized electric devices and sensors because of its high energy density and conversion efficiency. In particular, the nanofluidic-based power generator by concentration-gradient-driven ion-selective transport, which is also known as a reverse electrodialysis (RED) power generator, as shown in Fig. 1, has been intensively investigated to enhance its performance characteristics. In this study, we investigated the thermal dependence of the power generation by reverse electrodialysis with silica nanopores.

As the temperature increases, the surface charge density of silica nanopores generally increases owing to an increase in the zeta potential of the pore walls, which in turn increases the concentration of counter-ions in the electrical double layer and the open circuit voltage. However, as the temperature increases further, the open circuit voltage decreases [1]. In the simulation study, assuming that the surface charge density decreases with

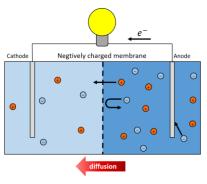


Fig. 1 RED power generator

increasing temperature, we could successfully reproduce this thermal dependence of power generation. We concluded that an increase in temperature induces bubble nucleation at silica surface, and thus the effective surface charge density decreases.

[1] J. Hwang, T. Sekimoto, W. Hsu, S. Kataoka, A. Endo, and H. Daiguji, "Thermal Dependence of Nanofluidic Energy Conversion by Reverse Electrodialysis", submitted.

#### Self-introduction



My name is Tatsuki Sekimoto. I'm 22 years old, a Masters student at the University of Tokyo. My hometown is Kyoto, which is famous for historic temples like Kinkaku-ji. I like listening to music on weekends. I'm glad to participate in this summer camp, so please feel free to talk to me!

# Dissociation of CO molecule on Fe catalyst: *Ab initio* molecular dynamics simulation

Satoru Fukuhara<sup>1</sup>, Masaaki Misawa<sup>2</sup>, Fuyuki Shimojo<sup>2</sup>, Yasushi Shibuta<sup>1</sup> <sup>1</sup>Department of Materials Engineering, The University of Tokyo <sup>2</sup>Department of Physics, Kumamoto University

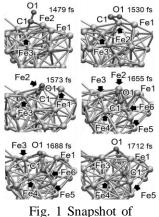
fukuhara@mse.mm.t.u-tokyo.ac.jp

For the application of carbon nanotubes (CNTs), various features of CNTs are required to be controlled. HiPCO process is one method to synthesize high quality CNTs [1]. CO molecules are used as carbon source in HiPCO process. Thus, understanding the mechanism of CO dissociation is important. Up to now, the activation energy and the active site on structure-fixed catalyst have been studied by a static calculation [2]. However, the dynamics of the reaction including the structural change of the catalyst is not well understood yet. In this study, the dynamics of CO dissociation on Fe catalyst is investigated by *ab initio* molecular dynamics. Within the 2 ps calculation at 1500 K, one dissociation of the CO molecule

on the Fe cluster is observed (Fig.1). The mechanism of the CO dissociation is as following. First, the oxygen atom (labeled O1) of adsorbed CO makes bond with Fe atom (labeled Fe1). Consequently, the carbon atom (C1) gets into the hollow site constructed by five Fe atoms (Fe1 to 5). After both C1 and O1 make bonds with Fe atoms, CO bond dissociates. The initial bonding of oxygen atom to Fe atom is considered to be an important process for the dissociation.

[1] M.J. Bronikowski, et al., J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.

19 (2001) 1800. [2]G. Lanzani, et al., J. Phys. Chem. C. (2009) 12939.



CO dissociation.

#### Self-introduction



I'm Satoru Fukuhara, born in Okayama, Japan. Now I am in the second year of the master course and studying the dissociation process of carbon source molecules in the initial stage of CNT synthesis by using *ab initio* molecular dynamics simulation.

I'm interested in Zen-meditation and belong to Zen-meditation team in the University of Tokyo. I also like drinking.

# Synthesis of Vertically Aligned Single-Walled Carbon Nanotube from sputtered Co catalyst at low temperature

Ming Liu, liuming@photon.t.u-tokyo.ac.jp

D1, Department of Mechanical Engineering, The University of Tokyo Supervising Professor: Shigeo Maruyama (professor)

Vertically aligned single-walled carbon nanotubes (VA-SWNTs) with high specific surface area and high conductivity have exponentially increase in research interest in the past decades years, which are perfect candidates for many applications especially for energy storage and heat dissipation.[1] In this work, forest-like VA-SWNT was controllable synthesized from monometallic catalyst cobalt at 600 °C on silicon substrate with uniform dense and height. Temperature dependent growth mechanism was investigated by a systematic study which revealed that low temperature synthesis process provided the highest growth efficiency and smaller diameter carbon nanotube. Meanwhile, in-plane transmission electron microscope technique unambiguously identified the structure of catalyst and the diameter of carbon nanotube, which shed some lights to the underlying low temperature growth mechanism. Tammann temperature [2] and sintering theory [3] were utilized to support the theoretical explanation of this growth mechanism.

#### Reference

- 1. Murakami, Y., et al., *Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy.* Chemical Physics Letters, 2004. **385**(3): p. 298-303.
- Baker, R., The relationship between particle motion on a graphite surface and Tammann temperature. Journal of Catalysis, 1982. 78(2): p. 473-476.
- Hansen, T.W., et al., Sintering of catalytic nanoparticles: particle migration or Ostwald ripening? Accounts of chemical research, 2013. 46(8): p. 1720-1730.

#### Self-introduction



My name is Ming Liu, from Dandong, Liaoning Province, China. I got my bachelor degree in Material Physics from Sun Yat-sen University and master degree in Mechanical Engineering from University of Tokyo. Now, I am the first-year PhD student in Department of Mechanical Engineering, the University of Tokyo. I like jogging, hiking, table tennis and billiards.

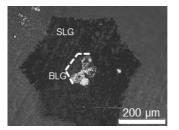
## Growth of Single-Crystal Single-Layer and Bi-Layer Graphene **Using Alcohol Catalytic CVD**

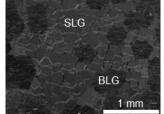
Kotaro Kashiwa<sup>1</sup>, Naomasa Ueda<sup>1</sup>, Hayato Arai<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, The University of Tokyo kashiwa@photon.t.u-tokyo.ac.jp

Graphene, an sp<sup>2</sup>-bonded single-layer honeycomb lattices, is a promising material due to its extraordinary mechanical, thermal, and electrical properties. Whereas single-layer graphene (SLG) has no bandgap, several groups reported that a bandgap up to 250 meV can be induced in AB-stacked bi-layer graphene (BLG) by an external electric field [1]. Therefore, the synthesis of BLG is essential for electronic applications of graphene.

In my group, we synthesize single-crystal SLG and BLG using the alcohol catalytic CVD (ACCVD) [2]. We use copper foil as the catalyst and before synthesis, we oxidize and fold it into a pocket. The processes are performed at 1065 °C with various pressures of Ar/H<sub>2</sub> and ethanol. We found that single-crystal BLG can be grown by low pressure of the CVD condition. Figure 1 is a dark field (DF) optical image of graphene on copper foil, which shows the crystal orientation of single-crystal BLG matches that of SLG. Figure 2 shows large-size flakes of single-crystal BLG and many of them have the same orientation. This indicates BLG are epitaxially grown on SLG in the ACCVD. Now there is a problem that the size of the single-crystal BLG is still not large.





[1] Y. Zhang et al. Nature, 459, 820 (2009). [2] X. Chen et al. Carbon, 107, 852 (2016).

SLG and BLG.

Self-introduction

Fig. 1 DF optical image of Fig. 2 DF optical image of large flakes of single-crystal BLG.

Nice to meet to you! I am Kotaro Kashiwa. I am 24 years old and in my second year for my master's in mechanical engineering. Last year, I came to Maruyama-Chiashi lab and started to study about graphene.

My home town is Sendai, which has many beautiful places and delicious foods. On weekends, I like listening to music. Especially, I love classical guitar.

#### Synthesis and characterization of SWNTs using sputtered W-Co

<u>Shun Yamamoto<sup>1</sup></u>, Kazuma Yamauchi<sup>1</sup>, Bunsho Koyano<sup>1</sup> yamamoto@photon.t.u-tokyo.ac.jp

Chirality controlled growth of SWNTs is highly expected toward the applications of SWNTs. Recently, it was reported that W<sub>6</sub>Co<sub>7</sub> alloy catalyst realized the growth of single-chirality SWNTs with purity over 90% through pretreatment and growth at high temperature [1]. In order to investigate the controlled-growth mechanism and to conduct the experiment safely, we grew SWNTs using W-Co catalyst via ethanol CVD under much lower pressure conditions. Owing to a narrow growth window of SWNTs at high temperature, we varied the growth parameters to search for appropriate conditions. Moreover, it was reported that sputtered W-Co catalysts can also control the growth of SWNTs [2]. But the mechanism of the selectivity is not revealed and the selectivity is insufficient. We focused on the reduction condition and pressure at the growth, and the result is that high temperature and high pressure than the previous work have an effect on growth of SWNTs with small diameter and narrow chirality distribution.

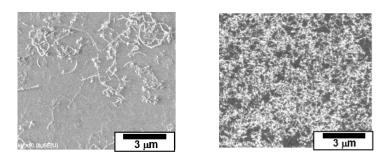


Fig. growth at higher pressure(Left) and at higher reduction temperature(Right) than previous work [2].

F. Yang *et al.*, *Nature* **510**, 522 (2014).
 H. An, *et al.*, *Nanoscale*, **8**, 14523 (2016).

#### Self-introduction



Name : Shun Yamamoto(山元隼) Age: 22 Hometown: Tokyo Interests: Guitar, Band, any kind of Music, Movie

### Optical measurement of single walled carbon nanotubes using Rayleigh scattering and photoluminescence

<u>Tatsurou Ogamoto<sup>1</sup></u>, Shun Kamakura<sup>1</sup>, Satoshi Yotsumoto<sup>1</sup> ogamoto@photon.t.u-tokyo.ac.jp

Because SWNTs are nano-materials and have large specific surface, the interaction between SWNTs and the environments sometimes changes the electronic property. This change need to be studied because it may influence the quality and reliability of SWNT devices. We study various SWNT's electronic property by focusing on both Rayleigh scattering [1], which is easy to take images but hard to take spectra and on photoluminescence, which is easy to take spectra but hard to take images. For measuring Rayleigh scattering and photoluminescence, we have been constructing the optical system in which continuum laser (the range of wavelength is 400 – 2500 nm) was used as the excitation light. Although the overall construction has been finished it is still hard to get the precise spectra of SWNTs, so the system should be refined. The samples we have tried to measure are suspended SWNTs, SWNTs on a Si substrate, dispersed SWNTs in the surfactant solutions [3] and dry-deposited SWNT films [4]. We will discuss the influence on the electronic structures of SWNTs lead by environmental conditions based on experimental results.

[1] M. Y. Sfeir et al., Science 306, 1540 (2004).

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

[3] A. Kaskela et al., Nano Lett. 10, 4349 (2010).

#### Self-introduction



I'm Tatsurou Ogamoto aged 22 and have majored mechanical engineering for 3 years at University of Tokyo in Japan. I like to ride a sports-bicycle and I make it a rule to ride 150 km every week.

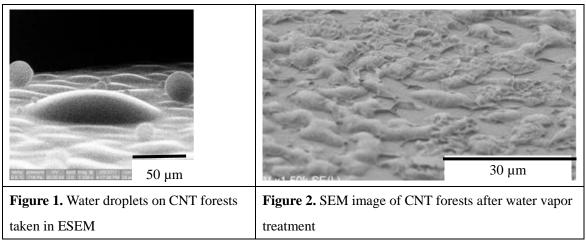
When I was 18 years old, I made a goal. The goal is that during my college days, I would ride 40000 km which corresponds to one round of the earth. Finally, I accomplished this goal before I graduated my university.

# Structural change mechanism of carbon nanotube films by dropwise condensation and evaporation

Koichi Isomura<sup>1</sup>, Sou Sugiyama<sup>1</sup>, An Hua<sup>1</sup>, Takuma Hori<sup>1</sup>, Yuta Yoshimoto<sup>1</sup>, Taiki Inoue<sup>1</sup>, Ikuya Kinefuchi<sup>1</sup>, Shohei Chiashi<sup>1</sup>, Shu Takagi<sup>1</sup>, Shigeo Maruyama<sup>1</sup>, <sup>1</sup>Department of Mechanical Engineering The University of Tokyo isomura@fel.t.u-tokyo.ac.jp

Carbon Nanotube (CNT) forests is a promising materials as a low price and flexible transparent conductive film. CNT forests forms a microhoneycomb network by exposuring water vapor and drying many times. This structure exhibits lower sheet resistance and higher optical transmittance compared with original CNT forests. However, the mechanism of this structure change is not fully understood. Therefore, we investigate the mechanism by using Environmental Scanning Electron Microscope (ESEM).

So far we have found that there are two types of water droplets on CNT forests using (Figure 1). Also, we observed details of CNT after water vapor treatment (Figure 2). Based on these results, it can be indicated that the state of structural deformation of CNT forests has changed depending on the types of water droplets.



#### **Self-introduction**



Koichi Isomura is 24 years old and lives in Kanagawa Prefecture. He is in the 2<sup>nd</sup> year of a Master's degree. He is in the laboratory of fluid engineering and focusing on deformation of CNT with water. In free time, Koichi plays tennis and ski.

#### Fabrication of S-CNT electrodes for lithium-sulfur batteries

Keisuke Hori<sup>1</sup>, Kei Hasegaw<sup>1</sup>, Suguru Noda<sup>1</sup>

<sup>11</sup>Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

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The lithium-sulfur battery has been expected for next generation electrochemical energy storage due to its high gravimetric energy density (2600 Wh kg<sup>-1</sup>), which is three to five times higher than commercialized batteries ( $\text{Li}_x\text{C}_6$  -  $\text{Li}_{1-x}\text{CoO}_2$ : 430–570 Wh kg<sup>-1</sup>). Although sulfur cathode has high theoretical capacity (1675 mAh  $g_{\text{sulfur}^{-1}}$ ), it suffers from the low sulfur loading in the cathode. In recent years, 3D current collector such as metal and graphene foams has been used to increase sulfur areal loading. Carbon nanotube (CNT) is also a candidate for 3D current collector. However, the up-to-date electrodes do not satisfy practical criteria (simple fabrication process and high gravimetric, volumetric, and areal capacities).

In this work, we realized S-CNT electrodes with high capacity via simple fabrication process. Submillimeter-long few-wall CNTs were dispersed with surfactant solution. Then, the solution was vacuum filtrated, and CNT paper was fabricated. S-CNT electrodes with 30–80 wt% sulfur

content were prepared by the sublimation method. The fabricated electrode with 60 wt% S-40 wt% CNT showed a high initial discharge capacity of 1060 mAh  $g_{sulfur}^{-1}$ . Furthermore, the electrode showed a capacity over 900 mAh  $g_{sulfur}^{-1}$  after the 100 cycles.



#### Self-introduction



I am Keisuke Hori from Department of Applied Chemistry, Waseda University. Please call me Keisuke. I am now in the first year of doctor course, and my research theme is about application of carbon nanotubes for electric devices such as battery. I like to watch moves, read books and so on. I lived in Beijing when I was a child (not good at speaking Chinese, though) I hope to share wonderful time with you in this summer camp.

# CO<sub>2</sub>-assisted chemical vapor deposition for large-area synthesis of carbon nanotube arrays

Toshihiro Sato<sup>1</sup>, Hisashi Sugime<sup>2</sup>, Suguru Noda<sup>1</sup>

 <sup>1</sup> Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
 <sup>2</sup> Waseda Institute for Advanced Study, Waseda University, 1-6-1 Nishiwaseda, Shijuku-ku, Tokyo 169-8050, Japan

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A small addition of water vapor at 50–200 ppmv level realized millimeter-tall carbon nanotube (CNT) arrays [1]. Its drastic effect is scientifically interesting, however it is practically uneasy to feed the H<sub>2</sub>O vapor at the level closed to the background for large-area substrates uniformly. CO<sub>2</sub> can also be an effective additive to remove the excess carbon by the reaction of C+CO<sub>2</sub>  $\rightleftharpoons$  2CO. Because CO<sub>2</sub> is milder for oxidation, we propose CO<sub>2</sub> at high concentrations instead of H<sub>2</sub>O at low concentrations.

First, we systematically compare the effect of  $H_2O$  and  $CO_2$  on the CNT growth with a wide range of Fe thickness (0.20–5.0 nm) using the combinatorial masked deposition (CMD) method [2] on 15 nm  $Al_2O_x$  [3]. From the threshold Fe thickness (0.20–1.0 nm) for millimeter-tall CNTs (red dotted lines in Figure 1),  $CO_2$  at 0.3–1 vol% proves to have similar effect as  $H_2O$  at 50 ppmv. The  $CO_2$  concentration can be roughly 200-fold higher than the  $H_2O$  concentration.

Next, we examine the possibility for scale-up of the CNT growth using 50 ppmv H<sub>2</sub>O and 1.0 vol% CO<sub>2</sub>. 18 substrates (10 mm×10 mm) with 0.80 nm Fe on 15 nm Al<sub>2</sub>O<sub>x</sub> were loaded in one batch from the inlet to outlet of the reactor. Figure 2 shows change of CNT areal yield with the distance from the inlet. With 50 ppmv H<sub>2</sub>O, CNT areal yield decreased dramatically to 0.20 mg/cm<sup>2</sup> for the 4rd substrate (6.0 cm from the inlet). On the other hand, 1.0 vol% CO<sub>2</sub> retained the CNT areal yield at ~1.0 mg/cm<sup>2</sup> for 16 substrates (2–17 cm from the inlet). Therefore, the CO<sub>2</sub> addition at high concentrations is more feasible for the scale-up synthesis of CNT arrays than the H<sub>2</sub>O addition at low concentrations.

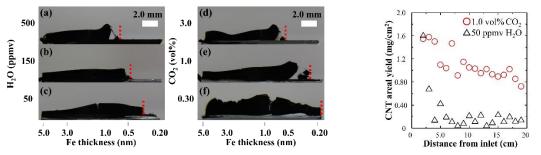


Figure 1. Side-view photographs of CNT forest grown by the gradient  $Fe/Al_2O_x$  catalyst with  $H_2O$  (a-c) and  $CO_2$  (d-f).

Figure 2. CNT yield vs distance from the inlet ( $\Delta$ 50 ppmv H<sub>2</sub>O,  $\circ$ 1.0 vol% CO<sub>2</sub>)

[1] K. Hata et al., Science **306**, 1362 (2004). [2] S. Noda et al., Carbon **44**, 1414 (2006). [3] S. Noda, et al., Jpn. J. Appl. Phys. **46**, L399 (2007).

#### Self-introduction



I am Toshihiro Sato, a 24-year-old, 1st-year master-course student in Noda-Hanada laboratory. I am from Nagasaki, Japan, which has many islands, slopes, and attractive places. I like drinking coffee, skiing, and watching TV.

# Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries

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Lithium (Li) metal has been strongly considered as a critically important substitution of graphite anode to further boost the energy density of Li ion batteries. However, Li dendrite growth during Li plating/stripping induces safety concern and poor lifespan of Li metal batteries (LMB). Herein, fluoroethylene carbonate (FEC) additives were employed to form a LiF-rich solid electrolyte interphase (SEI). The FEC induced SEI layer is compact and stable, thus beneficial to obtain a uniform morphology of Li deposits. This uniform and dendrite-free morphology renders a significantly improved Coulombic efficiency of 98 % within 100 cycles in a Li | Cu half-cell. When the FEC-protected Li metal anode matched high loading  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  (NMC) cathode (12 mg cm<sup>-2</sup>), a high initial capacity of 154 mAh g<sup>-1</sup> (1.9 mAh cm<sup>-2</sup>) at 180.0 mA g<sup>-1</sup> was obtained. This LMB with conversion-type Li metal anode and intercalation-type NMC cathode affords an emerging energy storage system to probe the energy chemistry of Li metal protection and demonstrate the material engineering of batteries with very high energy density.

#### Self-introduction



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