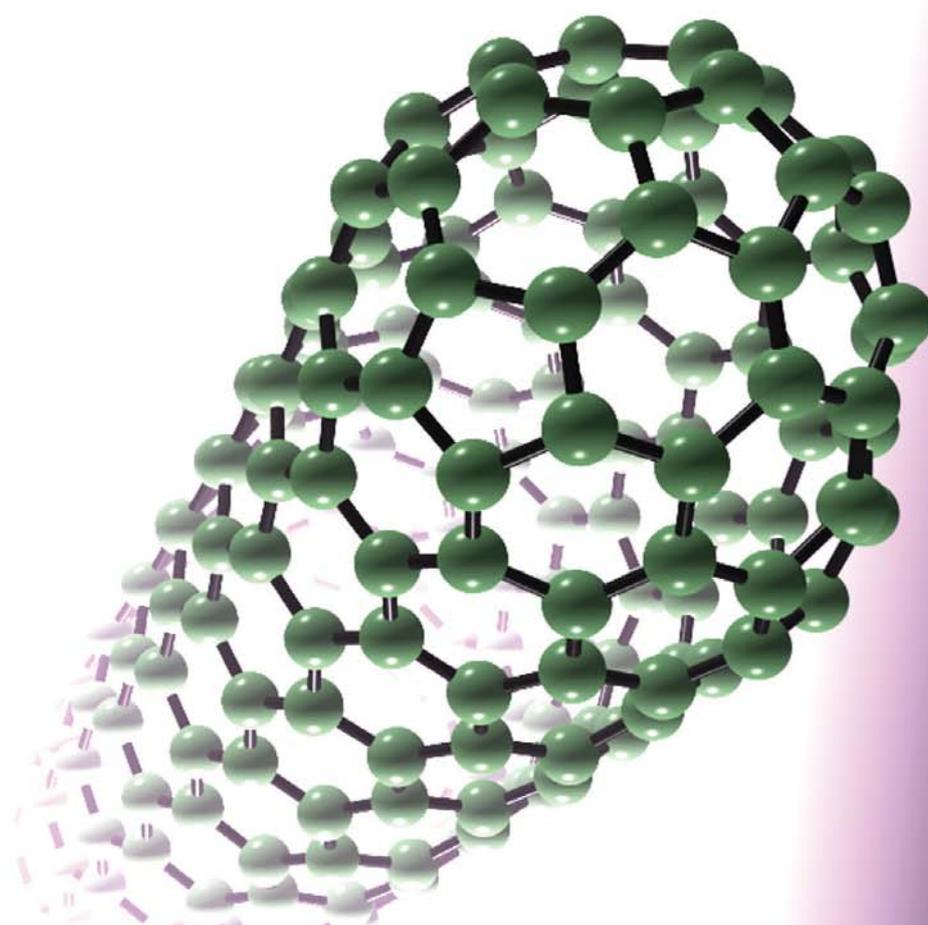


# WONTON '09

3rd Workshop on Nanotube  
Optics & Nanospectroscopy

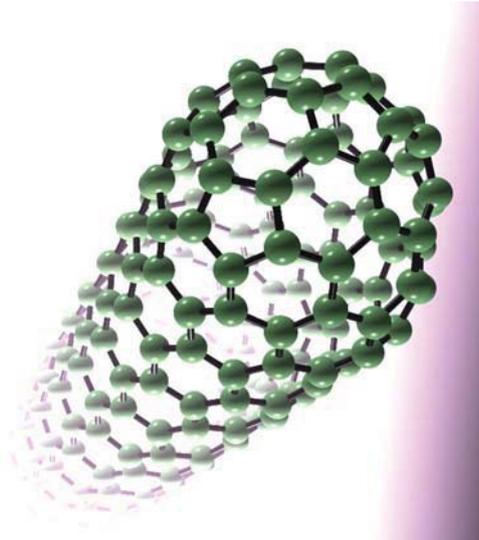


June 7 - 10, 2009  
Matsushima, Japan

**Program and Book of Abstracts**

# WONTON '09

## 3rd Workshop on Nanotube Optics and Nanospectroscopy



June 7 – 10, 2009      Matsushima, Japan

<http://www.photon.t.u-tokyo.ac.jp/~WONTON/>

### Venue:

Hotel Matsushima Taikanso  
10-76 Inuta Matsushima, Matsushima-machi,  
Miyagi-gun, Miyagi, Japan  
Phone: (81) 22-354-2161  
FAX: (81) 22-353-3431  
<http://www.taikanso.co.jp/eg/>

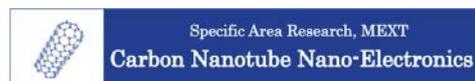
### Organizers:

Shigeo Maruyama (The University of Tokyo)  
Riichiro Saito (Tohoku University)  
Kazunari Matsuda (Kyoto University)  
Yutaka Ohno (Nagoya University)  
Junichiro Shiomi (The University of Tokyo)

### Sponsored by:



Japan Society for the Promotion  
of Science (JSPS)  
"International Scientific Meeting  
in Japan"



'Carbon Nanotube Nano-Electronics',  
Specific Area Research, MEXT

## Scope & Format:

The recent advances in the field of nanotube spectroscopy have not only broadened our horizon regarding their optical properties and their potential towards new applications, they have also stimulated intense discussions regarding issues of fundamental interest. The previous workshops in the series have been held in Telluride, USA (2005), and Ottawa, Canada (2007). Following those successful and stimulating workshops, we are happy to organize the *3rd Workshop on Nanotube Optics and Nanospectroscopy*, WONTON '09, in Matsushima, Japan, from 7 to 10 June, 2009. We believe that this is the time to bring colleagues together for a concentrated four-day workshop on nanotube optics and spectroscopy.

Topics to be covered at the meeting include:

- Light absorption, emission, and Raman scattering spectroscopy
- Carrier interactions, band structure and optical spectra
- Excitons in carbon nanotubes
- Spectroscopy individual nanotubes
- Magneto- and electro-optics
- Nanotube-based optoelectronic devices and electroluminescence
- Growth, purification and separation of nanotubes for optical studies
- Spectroscopy of graphene

The meeting will host a maximum of 90 participants. It will feature 33 invited talks by distinguished researchers as well as 36 contributed poster presentations. We believe that the size of this meeting with a clear focus on nanotube optics and spectroscopy will provide an ideal forum for fruitful and

stimulating interactions among young and established researchers.

## Poster Sessions:

We have accepted many excellent contributed papers. Instead of squeezing them as selected oral talks, we have decided to have enough poster session time, total 5 hours. All posters will be displayed from opening on 7th through lunch time on 10th with devoted poster sessions on 7th and 8th. Please enjoy detailed discussion!

The poster size is recommended be A0 size: 841W x 1189H. The panel size is 1200W x 1800H

## Joint Program:

International Symposium on Carbon Nanotube Nanoelectronics (CNTNE2009) will be held at the same location during June 9-12, 2009. WONTON and CNTNE2009 will be jointly programmed on June 9 (afternoon) and June 10. Registered participants in WONTON'09 can freely attend full CNTNE2009 meeting. For more information of CNTNE2009 see the web. site: <http://133.6.66.95/tokutei/workshop/>

## Registration:

Registration fees are 40,000 Yen for each participant (20,000 Yen for students) and 10,000 Yen per accompanying person. They should be paid only in cash at the registration desk at the workshop. The registration desk at the workshop site will be open

from 14:00 to 18:00 on June 7  
 from 8:00 to 18:00 on June 8  
 from 8:30 to 16:00 on June 9  
 from 8:30 to 12:00 on June 10

### Location and Access:

The meeting will be held in the Hotel Matsushima Taikanso, near Sendai (<http://www.taikanso.co.jp/eg/>). All participant will stay the same hotel. The summer in Matsushima features pleasant daytime temperatures 25 °C. Very beautiful sea scene in Matsushima, which is one of the most beautiful three scenes in Japan, provides a very attractive environment for informal discussions among colleagues. In the afternoon on June 9, we are planning to have a sightseeing cruise.



Matsushima is located at 350km north from Tokyo.



Access: by JR (Japan Railway)

Tokyo Narita Airport → JR Tokyo Station

(1 hour by NEX Narita Express)

→ Sendai Station

(2 hours by Tohoku Shinkansen )

→ Matsushima-kaigan Station

(1 hour by JR Senseki line)

→ Hotel Taikanso (12min on foot or taxi).



### Contact:

WONTON'09 Organizers:

wonton@photon.t.u-tokyo.ac.jp

WONTON'09 Web. Page:

<http://www.photon.t.u-tokyo.ac.jp/~WONTON/>

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Tohoku University

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## WONTON 2009 Program Outline

Start at.	Sunday, June 7	Start at.	Monday, June 8	Start at.	Tuesday, June 9	Start at.	Wednesday, June 10
		8:30	Tobias Hertel	8:30	Tony F. Heinz	8:30	Mildred Dresselhaus
		9:05	Manfred M. Kappes	9:05	Jay Kikkawa	9:05	Tsuneya Ando
		9:40	Nobutsugu Minami	9:40	Christian Thomsen	9:40	Andrea C. Ferrari
		10:15	<i>Coffee Break</i>	10:15	<i>Coffee Break</i>	10:15	<i>Coffee Break</i>
		10:35	Sumit Mazumdar	10:35	Luiz Gustavo Cancado	10:35	Steven G. Louie
		11:10	Ji Ung Lee	11:10	Zi Kang Tang	11:10	Yoshikazu Homma
		11:45	Yutaka Ohno	11:45	<i>Lunch</i>	11:45	Atac Imamoglu
		12:20	<i>Lunch</i>	13:00	<i>CNTNE2009 Opening</i>	12:20	<i>Lunch</i>
		13:35	Riichiro Saito	13:10	Marcus Freitag	13:35	Arao Nakamura
		14:10	Jacques Lefebvre	13:45	Junichiro Kono	14:10	Naotoshi Nakashima
		14:45	Michael S. Strano	14:20	Kazunari Matsuda	14:45	Susumu Saito
15:00	<b>Opening</b>	15:20	<i>Coffee Break</i>	15:10	<i>Tour</i>	15:20	<i>Coffee Break</i>
15:15	R. Bruce Weisman	15:40	Masao Ichida			15:40	Yohji Achiba
15:50	Hirromichi Kataura	16:15	Ado Jorio			16:15	Shigeo Maruyama
16:25	Stephen K. Doorn	16:50	Poster Session (All Posters)				
17:00	<i>Break</i>						
18:00	<i>Evening Reception</i>	18:00	<i>Dinner</i>				
19:30	Evening Poster Session <small>(19:30~20:30 Odd Numbered) (20:30~21:30 Even Numbered)</small>	19:30	Evening Poster Session <small>(19:30~20:30 Odd Numbered) (20:30~21:30 Even Numbered)</small>			19:00	<i>Banquet</i>
~21:30		~21:30		~21:30			

# WONTON 2009 Program

## Sunday, June 7

- 15:00 *Opening*
- 15:15 **Recent Applications of Single-Walled Carbon Nanotube Fluorescence**  
R. Bruce Weisman  
*Department of Chemistry and R. E. Smalley Institute for Nanoscale Science and Technology, Rice University Houston, Texas 77005 USA*
- 15:50 **Squeezing Metallic SWCNTs from Thawed out Black Agarose**  
Hiromichi Kataura, Takeshi Tanaka, Shunjiro Fujii, Daisuke Nishide, Kazuhiro Yanagi, Yasumitsu Miyata, Ye Feng, Kiyoto Matsuishi, Yutaka Maniwa  
*Nanotechnology Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, JST, CREST, Kawaguchi, Saitama, Japan, University of Tsukuba, Tsukuba Japan, Tokyo Metropolitan University, Tokyo, Japan*
- 16:25 **Modulation of Surfactant/Nanotube Interfacial Behavior: Enhanced Separations and Spectroscopy**  
Stephen K. Doorn, Sandip Niyogi, Crystal G. Densmore, Erik H. Haroz, Donny Magana, Junichiro Kono  
*Chemistry Division, Los Alamos National Laboratory and Department of Electrical and Computer Engineering, Rice University*

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17:00 *Coffee Break*

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18:00 *Evening Reception*

19:30 *Evening Poster Session*  
 19:30-20:30 *Odd numbered posters should be presented.*  
 20:30-21:30 *Even numbered posters should be presented.*

## Monday, June 8

- 8:30 **When size does matter: Exciton diffusion and Brownian motion of carbon nanotubes**  
Tobias Hertel, Thomas Ackermann, Jared Crochet, Sabine Himmelein, Dominik Stich, Larry Luer, Guglielmo Lanzani  
*Institute for Physical Chemistry, Am Hubland, Julius-Maximilians University Wurzburg, 97076 Wurzburg, Germany*
- 9:05 **Photoluminescence studies and separation of single-walled carbon nanotubes**  
 Sergei Lebedkin, Oliver Kiowski, Frank Hennrich, Stefan Jester, Ninette Sturzl, Lea Burger, Zhong Jin, Yan Li and Manfred M. Kappes  
*Institute of Physical Chemistry, Universitaet Karlsruhe and Institute of Nanotechnology, Forschungszentrum Karlsruhe, Germany*
- 9:40 **Absorption, Photoluminescence and Photoconductivity of Highly Purified Semiconducting Single-wall Carbon Nanotubes**  
Nobutsugu Minami, Y. Futami, Said Kazaoui and Nicolas Izard  
*Nanotechnology Research Institute and Nanotube Research Center, AIST*

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10:15 *Coffee Break*

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- 10:35 **The Mott-Hubbard Interaction and Exciton Binding Energies in Semiconducting and Metallic Single-Walled Carbon Nanotubes**  
S. Mazumdar, D. Psiachos and Z. Wang  
*Department of Physics, University of Arizona, Tucson, AZ 85721, USA*
- 11:10 **Optical Spectroscopy of Carbon Nanotube P-N Diodes**  
Ji Ung Lee  
*College of Nanoscale Science and Engineering, The University at Albany-SUNY, 255 Fuller Road, Albany, NY, USA*
- 11:45 **Direct comparison of photoluminescence intensity with (n,m) abundance of single-walled carbon nanotubes**  
Yutaka Ohno, Atsushi Kobayashi, and Takashi Mizutani  
*Department of Quantum Engineering, Nagoya University, Japan*
- 
- 12:20 *Lunch*
- 
- 13:35 **Exciton effect and phonon softening effect in the Raman spectroscopy of single wall carbon nanotubes**  
Riichiro Saito  
*Tohoku University*
- 14:10 **Luminescence spectroscopy of individual SWNTs and elemental bundles**  
Jacques Lefebvre and Paul Finnie  
*IMS/National Research Council*
- 14:45 **Biological applications of near-infrared fluorescent sensors based on single-walled carbon nanotubes**  
Michael S. Strano  
*M.I.T. Dept. of Chemical Engineering*
- 
- 15:20 *Coffee Break*
- 
- 15:40 **Nonlinear Optical Properties and Phase Relaxation Processes in Semiconducting Single-Walled Carbon Nanotubes**  
Masao Ichida, Tadashi Nakano, Singo Saito, Yasumitsu Miyata, Hiromichi Kataura, and Hiroaki Ando  
*Department of Physics, Konan University*
- 16:15 **Probing Disorder in Graphene with Raman Spectroscopy**  
Ado Jorio, Marcia M. Lucchese, Fernando Stavale, Erlon H. M. Ferreira, Cecilia Vilani, Rodrigo B. Capaz, Carlos. A. Achete  
*Departamento de Fisica, UFMG, Belo Horizonte, MG and Divisao de Metrologia de Materiais, metro, Duque de Caxias, RJ, Brazil*
- 16:50 *Poster Session (All posters)*
- 18:00 *Dinner*
- 19:30 *Evening Poster Session*  
*19:30-20:30 Odd numbered posters should be presented.*  
*20:30-21:30 Even numbered posters should be presented.*

Tuesday, June 9

- 8:30        **Optical Spectroscopy of Single and Multilayer Graphene**  
Tony F. Heinz  
*Departments of Physics and Electrical Engineering, Columbia University, New York, NY 10027, USA*
- 9:05        **Optical and Magnetic Anisotropy in Graphene Oxide**  
Jay Kikkawa  
*The University of Pennsylvania*
- 9:40        **Vibrational modes in graphene and semiconductor nanorods**  
Christian Thomsen  
*Institut für Festkörperphysik, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany*
- 
- 10:15       *Coffee Break*
- 
- 10:35       **Theory of Near-field Raman Enhancement in Carbon Nanotubes**  
Luiz Gustavo Cancado, Ado Jorio, Achim Hartschuh, E. Joselevich, and Lukas Novotny  
*The Institute of Optics, University of Rochester*
- 11:10       **Optical properties of ultra-thin single-walled carbon nanotubes aligned in the nano channels of zeolite AEL single crystals**  
Z. K. Tang, J. P. Zhai, and R. Saito  
*Department of Physics and the Institute of Nano Science & Technology, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*
- 
- 11:45       *Lunch*
- 
- 13:00       *CNTNE2009 Opening (T. Mizutani)*
- 13:10       **Electrical power dissipation, phonon populations, and substrate effects in carbon nanotubes and graphene**  
M. Freitag  
*IBM Watson Research Center, Yorktown Heights, NY 10598, USA*
- 13:45       **Terahertz Dynamics in Carbon Nanotubes**  
Junichiro Kono  
*Rice University*
- 14:20       **Exciton Fine Structures and Dynamics Studied by Single Carbon Nanotube Spectroscopy**  
Kazunari Matsuda  
*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
- 15:10       *Tour*
- 19:00       *Banquet*

## Wednesday, June 10

- 8:30 **Our Recent Advances in Nanotube and Graphene Research**  
Mildred Dresselhaus and Jing Kong  
*Massachusetts Institute of Technology*
- 9:05 **Optical properties of monolayer and bilayer graphene**  
Tsuneya Ando<sup>1</sup>, Mikito Koshino<sup>1</sup>, and Kenichi Asano<sup>2</sup>  
<sup>1</sup>*Department of Physics, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan*  
<sup>2</sup>*Department of Physics, Osaka University, 1-1 Machikaneyama, Toyonaka 560-0043, Japan*
- 9:40 **Raman, Photoluminescence and Saturable Absorption in Graphene**  
Andrea C. Ferrari  
*Engineering Department, Cambridge University, Cambridge, UK*
- 
- 10:15 *Coffee Break*
- 
- 10:35 **Electronic and Optical Properties of Nanotubes, Graphene, and Graphene Nanostructures**  
Steven G. Louie  
*Department of Physics, University of California, Berkeley, California 94720, USA*
- 11:10 **Effects of Environment and Defects on Photoluminescence of Single Wall Carbon Nanotube**  
Yoshikazu Homma, Shohei Chiashi, Ryota Mitobe, and Kotaro Nagatsu  
*Department of Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*
- 11:45 **Quantum optics with carbon nanotubes**  
C. Galland, A. Hoegeler, and A. Imamoglu  
*ETH Zurich*
- 
- 12:20 *Lunch*
- 
- 13:35 **Third-Order Nonlinear Optical Response in Fullerene-Peapods**  
A. Nakamura<sup>1</sup>, D. Hosooka<sup>1</sup>, T. Koyama<sup>1</sup>, H. Kishida<sup>1</sup>, K. Asaka<sup>1</sup>, Y. Saito<sup>1</sup>, and T. Saito<sup>2</sup>  
<sup>1</sup>*Department of Applied Physics, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan,*  
<sup>2</sup>*Research Center for Advanced Carbon Materials, AIST, 1-1-1 Higashi, Tsukuba, 305-8565, Japan*
- 14:10 **Direct Determination of Precise Electronic States of SWNTs Based on Soluble Carbon Nanotubes**  
Naotoshi Nakashima  
*Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395 Japan*
- 14:45 **Electronic and Geometrical Properties of Carbon Nanotubes: A First-Principles Study**  
Susumu Saito  
*Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan*
- 
- 15:20 *Coffee Break*
-

- 15:40      **Production of (5,4) and (6,4) Enriched Single-Walled Carbon Nanotubes Grown Using a Platinum Catalyst**  
Naoko Takamizu<sup>1</sup>, Keisuke Urata<sup>1</sup>, Toshiya Okazaki<sup>2</sup>, and Yohji Achiba<sup>1</sup>  
<sup>1</sup> *Department of Chemistry, Tokyo Metropolitan University, Tokyo 192-0397, Japan*  
<sup>2</sup> *Nanotube Research Center, AIST, Tsukuba 305-8568, Japan*
- 16:15      **Spectral features due to dark exciton in photoluminescence map of single-walled carbon nanotubes**  
Shigeo Maruyama<sup>1</sup>, Yuhei Miyauchi<sup>2</sup> and Yoichi Murakami<sup>3</sup>  
<sup>1</sup> *Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan,* <sup>2</sup> *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan,* <sup>3</sup> *Global Edge Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

## Poster Presentations

*All posters will be displayed from opening on 7th through lunch time on 10th.*

*For Evening Poster Sessions, during 19:30-21:30 in June 7 and 8,*

*Odd-numbered posters should be presented during 19:30-20:30*

*and even-numbered posters should be presented during 20:30-21:30 for better access to the presenter.*

- P1 **Enrichment of Armchair Carbon Nanotubes via Density Gradient Ultracentrifugation: Raman Spectroscopy Evidence**  
Erik H. Haroz, William D. Rice, Benjamin Y. Lu, Robert H. Hauge, Saunab Ghosh, R. Bruce Weisman, Pavel Nikolaev, Sivaram Arepalli, Donny Magana, Stephen K. Doorn, and Junichiro Kono
- P2 **Quantitative Purity Evaluation of Single-Wall Carbon Nanotubes using Resonance Raman Spectroscopy**  
Daisuke Nishide, Yasumitsu Miyata, Kazuhiro Yanagi, Takeshi Tanaka, and Hiromichi Kataura
- P3 **Optical Active Single-Walled Carbon Nanotubes**  
Naoki Komatsu, Xiaobin Peng, Feng Wang, Ajoy Bauri, A. F. M. M. Rahman, Takahide Kimura, and Atsuhiko Osuka
- P4 **Optical characterization of Length-Separated DNA-Wrapped Double-Wall Carbon Nanotubes**  
Yuki Asada, Shota Kuwahara, Toshiki Sugai, Ryo Kitaura, and Hisanori Shinohara
- P5 **Resonance Raman Spectra of Optical Purified (6,5) Nanotubes Sorted by Density Gradient Ultracentrifugation**  
Pei Zhao, Theerapol Thurakitserree, Erik Einarsson, Junichiro Shiomi, Shigeo Maruyama
- P6 **Diameter distribution analysis of sorted double wall carbon nanotubes by optical absorption spectroscopy and electron transmission microscopy.**  
Romain Fleurier, Jean-Sebastien Lauret, Emmanuel Flahaut, Annick Loiseau
- P7 **Polarized Raman spectroscopy on vertically aligned single-walled carbon nanotubes**  
Zhengyi Zhang, Yoichi Murakami, Erik Einarsson, Yuhei Miyauchi and Shigeo Maruyama
- P8 **High-Precision Selective Deposition of Catalyst for Facile Localized Growth of Single Walled Carbon Nanotubes**  
Rong Xiang, Tianzhun Wu, Erik Einarsson, Yuji Suzuki, Yoichi Murakami, Junichiro Shiomi, Shigeo Maruyama
- P9 **Raman and optical spectroscopic analysis of single walled carbon nanotubes synthesized by an industrial scale aerosol reactor**  
Ying Tian, Albert G Nasibulin, Hua Jiang, Timur Nikitin, Brad Aitchison, Jan V Pfaler, Leonid Khriachtchev, Jussi O Sarkkinen, David P Brown, Esko I Kauppinen
- P10 **Effects of Bundling and Diameter on the UV Optical Absorption of Single-Wall Carbon Nanotubes**  
Takeshi Saito, Shigekazu Ohmori, Bikau Shukla, Motoo Yumura and Sumio Iijima
- P11 **Fermi energy dependence of radial breathing mode in metallic single-wall carbon nanotubes**  
Jin Sung Park, Kenich Sasaki, Riichiro Saito, Gene Dresselhaus, Mildred S. Dresselhaus
- P12 **Exciton energy Kataura plot and excitonic effect of single wall carbon nanotubes**  
Kentarō Sato, Riichiro Saito and Shigeo Maruyama
- P13 **Pressure-assisted tip-enhanced Raman imaging of carbon nanotubes at the spatial resolution of a few nanometres**  
Taka-aki Yano, Prabhat Verma, Yuika Saito, Taro Ichimura and Satoshi Kawata
- P14 **Resonance Raman scattering of hole-doped metallic and semiconducting carbon nanotubes**  
Yasumitsu Miyata, Kazuhiro Yanagi, Yutaka Maniwa, Hisanori Shinohara and Hiromichi Kataura
- P15 **Coherent Phonon Dynamics in Highly Aligned Single-Walled Carbon Nanotubes**  
Layla G. Booshehri, Erik H. Haroz, Junichiro Kono, Cary L. Pint, Robert H. Hauge, Yong-sik Lim, Ji-Hee Kim, Ki-Ju Yee
- P16 **Photoluminescence Observation of Water Encapsulation in an individual Single-walled Carbon Nanotube**  
Shohei Chiashi, Tataki Hanashima, Ryota Mitobe, Yoshikazu Homma
- P17 **Intrinsic and Extrinsic Factors which Affects the Optical Properties of Individual Single-Walled Carbon Nanotubes**  
Juan G. Duque, Stephen Door, Howard K. Schmidt and Matteo Pasquali Laurent Cognet and Brahim Lounis
- P18 **Electrochemistry and Self-Assembly of Complex Single-Walled Carbon Nanotube (SWNT) Nanostructures**  
Juan G. Duque, Laurent Cognet, Howard K. Schmidt, Matteo Pasquali

- P19 **SEM Observation Effect on Photoluminescence Spectra from Single-Walled Carbon Nanotubes**  
Kotaro Nagatsu, Tomohito Chokan, Takeshi Kitajo, Shohei Chiashi, Yoshikazu Homma
- P20 **Fast Band-Gap Tuning of Carbon Nanotube with Repetitious Uniaxial Strain**  
Hideyuki Maki and Tetsuya Sato
- P21 **An Optical Study of a Single Carbon Nanotube**  
Xu Wang, M. Hadjipanayi, R. J. Nicholas and R. A. Taylor
- P22 **Photoluminescence saturation in an air-suspended SWCNT**  
Y.-F. Xiao, T.Q. Nhan, M.W.B. Wilson, and James M. Fraser
- P23 **Symmetry-Induced Exciton Distribution between the Bright and Dark States in Single Carbon Nanotubes**  
Ryusuke Matsunaga, Kazunari Matsuda, and Yoshihiko Kanemitsu
- P24 **Exciton Dynamics in Carbon Nanotubes and Nonlinear Dependence of Photoluminescence Intensity on Pump Power**  
Maria Hilczner and M. Tachiya
- P25 **Exciton Dephasing Dynamics in Single-Walled Carbon Nanotubes**  
M. W. Graham, Y.-Z. Ma, A. A. Green, M. C. Hersam and G. R. Fleming
- P26 **Exciton Radiative Lifetimes and Coherence Lengths in Single-Walled Carbon Nanotubes**  
Yuhei Miyauchi, Ryusuke Matsunaga, Hideki Hirori, Kazunari Matsuda, and Yoshihiko Kanemitsu
- P27 **Excitons in carbon nanotube within effective-mass approximation**  
Tsuneya Ando and Seiji Uryu
- P28 **Inter-Valley Mixing of Carbon Nanotube Excitons by a Short-Range Impurity**  
Yuh Tomio and Hidekatsu Suzuura
- P29 **Theory of 1D Exciton and its Application to SWNT**  
Seiji Sakoda and Madoka Tokumoto
- P30 **Reflectance spectra of individual metallic single walled carbon nanotubes.**  
Hualing Zeng, Hongbo Zhao, Fu-Chun Zhang, and Xiaodong Cui
- P31 **Magneto-optical Spectroscopy of Metallic Single-Walled Carbon Nanotubes**  
T. A. Searles, J. Kono, J. A. Fagan, Erik K. Hobbie, Y. Imanaka
- P32 **Anisotropic Terahertz Response of Aligned Carbon Nanotubes**  
Lei Ren, Layla G. Booshehri, William D. Rice, Xiangfeng Wang, David J. Hilton, Junichiro Kono, Cary L. Pint, Robert H. Hauge, Aleksander K. Wojcik, Alexey A. Belyanin, Yoshiaki Takemoto, Kei Takeya, Iwao Kawayama, and Masayoshi Tonouchi
- P33 **Finite-length effects on optical absorption in metallic carbon nanotubes**  
Takeshi Nakanishi and Tsuneya Ando
- P34 **Resonant Optical Forces for Nanotube Aggregation in Solution**  
Thomas Rodgers, Satoru Shoji, and Satoshi Kawata
- P35 **Molecular physisorption at the groove and interior of single-walled carbon nanotubes**  
S. Iwata, S. Ogura, S. Lee, K. Fukutani, Y. Sato and K. Tohji
- P36 **Efficient dissociation of carbon nanotube excitons in organic semiconductor / carbon nanotube heterojunctions for photovoltaics and ultrabroadband photodetection**  
Michael S. Arnold, Jeramy D. Zimmerman, Christopher K. Renshaw, Xin Xu<sup>1</sup>, Richard R. Lunt, Christine M. Austin, and Stephen R. Forrest

# **Abstracts**

## **Invited Speakers**

**INVITED TALK**  
**June 7, Sunday**



## Recent Applications of Single-Walled Carbon Nanotube Fluorescence

R. Bruce Weisman

Department of Chemistry and R. E. Smalley Institute for Nanoscale Science and Technology  
Rice University  
Houston, Texas 77005 USA

The intrinsic near-IR fluorescence of semiconducting single-walled carbon nanotubes (SWCNTs) provides a powerful tool for a range of basic and applied investigations. One particularly valuable approach involves the use of near-IR microscopy to acquire images and spectra of individual SWCNTs. We have used this approach to extend our calibrated measurements of absolute fluorescence action cross sections to additional  $(n,m)$  species not previously reported. These fluorescence action cross sections are the products of  $E_{22}$  peak absorptivity times fluorescence quantum yield for pristine SWCNTs in aqueous SDBS suspension. The data reveal strong structure-dependent patterns for smaller diameter nanotubes, from which general empirical patterns can be deduced. The results provide calibration factors for deducing  $(n,m)$  concentration distributions from bulk fluorimetric measurements. In another project, an efficient new method has been developed for measuring SWCNT length distributions. Dilute samples in liquid suspension are imaged by near-IR fluorescence videomicroscopy at frame rates high enough to resolve the Brownian motions of the nanotubes. Custom image analysis software then identifies all of the SWCNTs in the frame, tracks their individual trajectories, deduces the corresponding translational diffusion coefficients, converts diffusion coefficients into lengths, and compiles the histogram of nanotube lengths. Data acquisition and analysis in this method are much quicker than for AFM length analysis. In the third application, a variety of bulk and single-particle methods have been used to investigate the apparent inner shell near-IR emission from samples of DWCNTs. We have studied the spectroscopy, chemical quenching, mechanical rigidity, density, and TEM structures of the near-IR emitters in DWCNT samples. The findings show that genuine inner shell fluorescence from DWCNTs is weaker than SWCNT fluorescence by a factor of at least 10,000, and that the observed near-IR emission is attributable to the presence of residual SWCNTs.

## Squeezing Metallic SWCNTs from Thawed out Black Agarose

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Kazuhiro Yanagi<sup>1,2</sup>, Yasumitsu Miyata<sup>1</sup>, Ye Feng<sup>2,3</sup>, Kiyoto Matsuishi<sup>3</sup>,  
and Yutaka Maniwa<sup>2,4</sup>

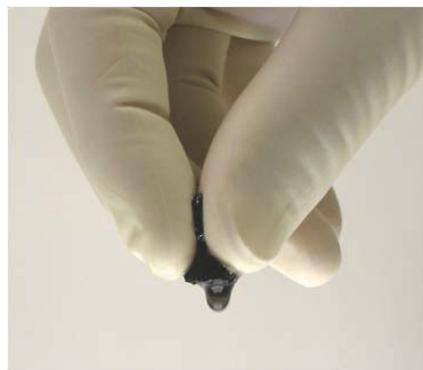
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It is well known that there are three electronic types of single-wall carbon nanotubes (SWCNTs), metal, narrow gap, and wide gap semiconductors, depending on their chiral indices. Metal-semiconductor separation is now indispensable for practical applications of SWCNTs, such as thin film transistors and transparent conducting films. After the great works by Arnold *et al.* [1], now we can obtain high-purity (up to 99 %) metallic and semiconducting SWCNTs using density gradient ultracentrifugation (DGU) [2]. Although DGU gives us high quality separation, we have to reduce time and cost of the separation for the industrial applications. Recently, we found the agarose gel can separate SWCNTs-SDS solution into metallic and semiconducting phases without any special treatment. [3,4] This new method can separate SWCNTs with high purity, high efficiency, and totally low cost. In this presentation, we will show our recent progress in the separation and some device applications.



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## **Modulation of Surfactant/Nanotube Interfacial Behavior: Enhanced Separations and Spectroscopy**

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Current advances in density-based separations of carbon nanotubes rely on modulation of surfactant interactions at the nanotube surface. We have studied how these interactions can be tuned via addition of electrolyte to surfactant suspensions of nanotubes. Addition of metal chloride salts will selectively aggregate nanotubes in a diameter-dependent fashion [1]. Use of salt concentrations below this aggregation threshold can act to enhance the density differences between nanotubes of similar diameter and/or metallicity. Use of this phenomenon to separate nanotubes into highly enriched metallic and semiconductor fractions in a diameter-dependent fashion will be discussed [2]. It will also be shown how electrolyte modulation of photoluminescence behavior, paired with the separations results, can act as a probe of the surfactant structure at the nanotube surface. Additionally, examples of how access to such enriched samples enables new fundamental measurements will be discussed. In particular, results will be presented that demonstrate generalized G-band behavior in armchair metallic nanotubes. Recent UV-Raman measurements of enriched samples will also be presented.

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**INVITED TALK**  
**June 8, Monday**



## When size does matter: exciton diffusion and Brownian motion of carbon nanotubes

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We have studied exciton diffusion in SWNTs and carbon nanotube diffusion in aqueous environments using optical and colloidal techniques for the characterization of excited state- and particle kinetics. The character of exciton diffusion in semiconducting carbon nanotubes is governed by the mean electron-hole separation, which has been determined experimentally using femtosecond time-resolved pump-probe spectroscopy. The finite length of tubes and the electronic structure of their ends likewise have an effect on exciton dynamics by providing additional pathways for non-radiative decay and by limiting the range that excitons can explore before decaying non-radiatively. Finite tube length has moreover been found to severely limit the achievable photoluminescence quantum yields for tubes shorter than about 100 nm. The resulting length dependence of photoluminescence quantum yields allows a determination of exciton diffusion lengths. In combination with time-resolved photoluminescence studies this can be used to infer exciton diffusion constants which are here found to be on the order of  $0.1 \text{ cm}^2 \text{ s}^{-1}$ . The effect of the environment on non-radiative exciton decay has been studied by systematically varying the surfactant coating. In addition we discuss the outcome of recent efforts with the preparation of length selected SWNTs using zonal fractionation in density gradients and asymmetric-flow field-flow fractionation. Nanotube diffusion and its dependence on tube length plays a crucial role for both these techniques and is studied by a combination of fluorescence correlation microscopy and zonal fractionation.

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## Photoluminescence studies and separation of single-walled carbon nanotubes

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We will present our recent results on the photoluminescence (PL) spectroscopy and imaging of semiconducting single-walled carbon nanotubes (SWNTs). These include studies of individual, millimeter-long nanotubes grown by chemical vapor deposition on pre-patterned silicon substrates and characterized by PL before and after micro-manipulation with an atomic force microscope. PL provides information about the local nanotube surroundings (air-suspended vs. on-silicon nanotube sections), the axial and torsional strain generated in the nanotube, as well as shows characteristic changes at a nanotube rupture site. Complimentary to photophysical studies on individual nanotubes we have also carried out ensemble measurements of SWNT dispersions which are highly enriched in a specific nanotube species. Nearly monodisperse (up to ~90% purity) samples of several semiconducting nanotube species could be obtained by using a relatively simple and readily scalable procedure based on dispersion in non-polar solvents/organic polymers. Finally, we have found that SWNTs are efficient and extremely robust quenchers of singlet oxygen.

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## Absorption, Photoluminescence and Photoconductivity of Highly Purified Semiconducting Single-wall Carbon Nanotubes

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Highly pure semiconducting single-wall carbon nanotubes (s-SWNTs) with selective chiralities can be extracted by the use of polyfluorene (PFO) as a dispersant dissolved in toluene [1,2], yielding sharp and well-resolved optical spectra. Moreover, the absorption background supposedly ascribed to carbonaceous impurities can be considerably suppressed. Thus simplified spectral shape has expanded the applicability of optical spectroscopy to the study of electronic processes in s-SWNTs. Here we applied absorption (Abs), photoluminescence (PL), and photoconduction spectroscopy for the study of various properties of selectively extracted s-SWNT. We stress that the successful fabrication of highly pure s-SWNT thin films has enabled the straightforward measurement and analysis of the photoconductivity with minimal disturbance due to dark conduction in residual metallic SWNTs.

Figure 1 shows changes in Abs and PL spectra induced by the addition of tetrafluorotetracyanoquinodimethane (TCNQF<sub>4</sub>), a p-dopant, into a HiPco/PFO/toluene solution. It is remarkable that, for Abs, isosbestic points are clearly observed with the increase in TCNQF<sub>4</sub> concentration and only the low-energy (9,7) peak shows a considerable decrease in Abs intensity. On the other hand, PL decrease by doping is much larger for all chiral indexes (n, m), implying that the underlying mechanisms are different. Stern-Volmer plot of PL quenching revealed good correlation between the position of LUMO and a Stern-Volmer constant for each (n, m). Implications of these results will be discussed in relation to charge transfer between TCNQF<sub>4</sub> and ground/excited states in s-SWNTs.

Photocurrent and Abs spectra are compared in Fig. 2 for a thin film prepared from highly purified s-SWNT dispersion. The observation of clearly separated peaks each assigned to different chiral indexes (n, m) has made it possible to extract information about the photoconduction process. Specifically, it can be seen that the relative

photocarrier generation efficiency depends on (n,m) and the type (**I** or **II**) of s-SWNT. Also, the efficiency tends to increase with tube diameters, reflecting smaller exciton binding energies for larger diameters. The effect of electric field on photocurrent spectra was also studied.

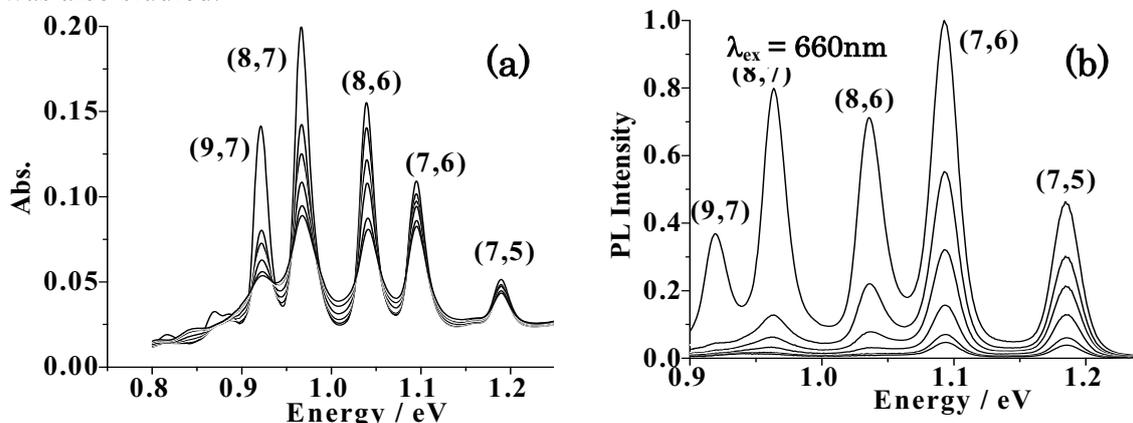


Fig.1 Decrease in Abs (a) and PL (b) intensity by the addition of TCNQF<sub>4</sub> (0-150 $\mu$ g/mL) into a HiPco/PFO/toluene solution.

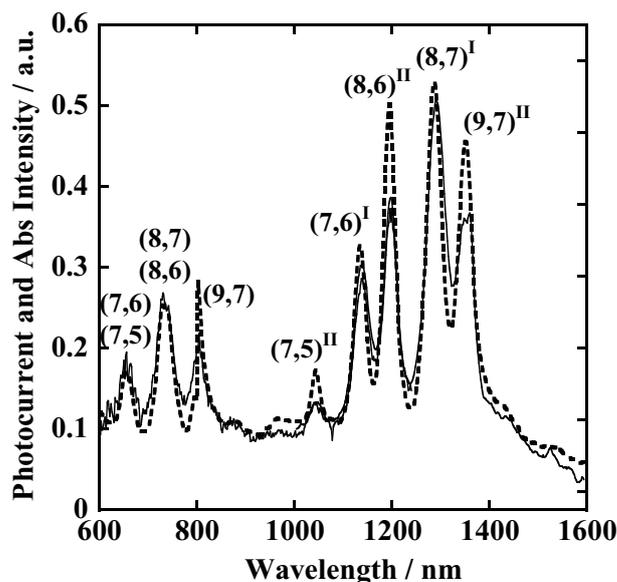


Fig.2 Photocurrent (solid line) and Abs (dotted line) spectra of a highly purified s-SWNT thin film prepared from a polyfluorene dispersion of HiPco SWNT.

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## The Mott-Hubbard Interaction and Exciton Binding Energies in Semiconducting and Metallic Single-Walled Carbon Nanotubes

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DFT-based ab initio calculations, and the quantum chemical configuration interaction method as applied to the molecular Pariser-Parr-Pople (PPP) model, have both been used to estimate exciton binding energies in semiconducting and metallic single-walled carbon nanotubes (S-SWCNTs and M-SWCNTs.) Ab initio exciton binding energies for S-SWCNTs with diameters of 1 nm are 1 eV or even larger. In contrast the PPP exciton binding energies are 0.3 - 0.4 eV [1], close to what have been estimated from the experimentally determined energy location of the two-photon exciton above the optical exciton [2,3]. It has been claimed that the ab initio exciton binding energies are for single nanotubes, and the experimental quantities reflect screening of Coulomb interactions in bulk materials. It has also been claimed that in one-dimension the true exciton binding energies are much larger than the energy difference between the lowest two-photon state and the optical exciton. We examine both these issues critically, and conclude that screening affects nonlinear absorption measurements weakly, and that the two-photon exciton is indeed close to the continuum threshold, in agreement with PPP calculations [3]. We ascribe the discrepancy between the experimental binding energies and the ab initio predictions to the difficulty of treating the Mott-Hubbard interaction within DFT-based theories.

We discuss M-SWCNTs also within the PPP model [5]. Standard theories of screening do not apply to systems with strong short-range Coulomb interactions. As with the semiconductors, theoretical fits to the experimental absorption spectra in M-SWCNTs are excellent (see Fig. 1). Our calculated exciton binding energies for M-SWCNTs are only slightly smaller than in the S-SWCNTs. For the (21,21) NT, we calculate a binding energy of 0.12 eV for the E22 exciton [4]. We make verifiable predictions about optical absorptions in M-SWCNTs

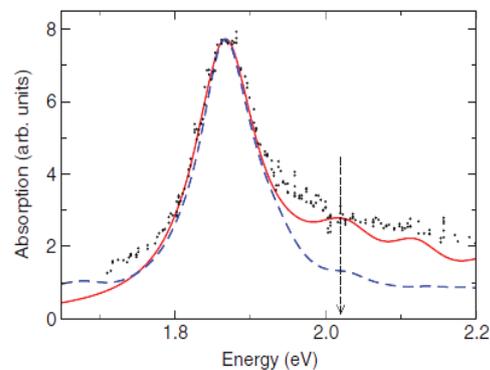


Fig. 1 Calculated absorption spectrum (red curve) in the E22 region of the (21,21) M-SWCNT, superimposed on the experimental data (black dots) [4].

[5].

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## Optical Spectroscopy of Carbon Nanotube P-N Diodes

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The p-n diode is an ideal device for probing optical properties of semiconductors. Here, we demonstrate that p-n diodes formed along individual nanotubes can probe the excited states of single-walled carbon nanotubes. The p-n diodes are formed using a split gate structure that electrostatically dopes the two ends of a single nanotube. These devices are fabricated at CNSE's advanced 300mm wafer processing facility which allows large numbers of devices to be fabricated on a single die. This allows a large design variation to be examined, including devices with additional gates for further doping control.

In the photocurrent spectroscopy, a series of peaks are observed. These correspond to exciton and exciton photon peaks, for the lowest and higher sub-bands, providing specific signature of the nanotube chirality. Here, we will report on the observation of two new sets of fine structures. For suspended nanotubes, a fine-structure associated with the lowest exciton peaks can be seen. For those resting on a SiO<sub>2</sub> surface, a large set of narrow (~2meV) peaks can be seen. We will discuss the origin of these peaks and, when applicable, discuss them in the context of the diode current-voltage characteristics.

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## Direct comparison of photoluminescence intensity with $(n,m)$ abundance of single-walled carbon nanotubes

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The abundances of single-walled carbon nanotubes (SWNTs) grown on a periodic trench structure [1] have been investigated for 20 species by counting the number of luminous spots by means of the micro-photoluminescence (PL) spatial distribution measurements. The abundance was estimated from the length and the number of SWNTs. We obtained featureless  $(n,m)$  distributions of the length and number of SWNTs in the growth condition used in this study. From the direct comparison of photoluminescence intensity with  $(n,m)$  abundance, the  $(n,m)$  dependence of PL efficiency has been investigated experimentally. The PL efficiencies of type-I [ $2n+m \bmod 3 = 1$ ] were slightly higher than those of type-II [ $2n+m \bmod 3 = 2$ ], and the higher PL efficiency was obtained in the smaller diameter. In addition, the PL efficiency also seemed to follow the energy gap law [2], indicating that the nonradiative relaxation attributed to G-band phonon was dominant in the relaxation process from the first excited state of exciton to the ground state, possibly via nonradiative recombination centers.

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## Exciton effect and phonon softening effect in the Raman spectroscopy of single wall carbon nanotubes

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Recent Raman measurements of single wall carbon nanotubes (SWNTs) have been provided the detailed Raman spectra as function of the surrounding materials or the Fermi energy. The modifications of such conditions change the dielectric response of the exciton states of SWNTs and phonon self energy for the electron-phonon interaction, which are known as the environmental effect and the Kohn anomaly effect, respectively. By comparing with the experiments, we can discuss physics of the exciton and phonons of SWNTs. For the environmental effect, the dielectric response for an exciton is important for determining the transition energies as a function of SWNT diameter (exciton Kataura plot), which is a subject of the talk [1]. Electro-chemical doping makes it possible to change the Fermi energy in which each Raman active phonon has a finite life time as a function of the Fermi energy because of the electron-phonon interaction. When we discuss the Raman intensity, two kinds of the life time in a Raman process should be considered. One is the life time for the photo-excited carrier to emit a phonon, which is relevant to the resonance width in the Raman excitation profile. Another life time is the phonon coherent time in which the vibration of phonon can be defined which is relevant to the spectra width of the Raman spectra. In the presence of electron-phonon (exciton-phonon) interaction, the virtual excitation of e-h pair in the metallic energy sub band makes either softening or hardening of phonon frequencies in the metallic SWNTs. We show in this presentation that the Kohn anomaly effect generally occurs for all Raman active modes which show different chiral angle dependence [2]. Analytical expression of the electron-phonon interaction can reproduce the specific measurement of the single nanotube spectroscopy as a function of the Fermi energy.

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## Luminescence spectroscopy of individual SWNTs and elemental bundles

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We have demonstrated that photoluminescence imaging at the single SWNT level is a powerful tool to access detailed information about SWNT optical properties. Luminescence from isolated SWNTs shows high spatial uniformity and high quantum efficiency [1] and the excitonic excited states spectrum has been observed [2, 3]. In this presentation, I will review our photoluminescence excitation studies that led to a definite assignment of new spectral features to exciton excited states of transverse and longitudinal nature [2, 3]. The binding energy for the lowest bright exciton and its diameter dependence is determined and the self-energy correction can also be estimated. Building on the known spectral signature of individually isolated SWNTs, I will report on recent studies of elemental bundles made of two, three and even four semiconducting SWNTs. When SWNT components of bundles are of different lengths we separately resolve bundled and unbundled sections both spatially and spectrally (in PL as well as in PLE mapping).[4] In agreement with previous near field and ensemble measurements, exciton energy transfer is observed from *donor* to *acceptor* nanotube. However, the reverse process of transfer from *acceptor* to *donor* is also important. The persistent luminescence of donor SWNTs is understood as a consequence of thermalization of excitons within bundles.

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- 4 Lefebvre, J.; Finnie, P. to be published.

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Title: Biological applications of near infrared fluorescent sensors based on single walled carbon nanotubes

Nanoscale sensing elements offer promise for single-molecule analyte detection in physically or biologically constrained environments for the first time. Single-walled carbon nanotubes (SWNT), as optical sensors, offer unique advantages such as photostable near-infrared (n-IR) emission for prolonged detection through biological media, single-molecule sensitivity, as we have recently documented, nearly orthogonal optical modes for signal transduction that can be used to identify distinct classes of analytes. Selective binding to the SWNT surface is difficult to engineer, but we have shown that even a pair of single-walled carbon nanotubes provides at least four optical modes that can be modulated to uniquely fingerprint chemical agents by the degree to which they alter either the emission band intensity or wavelength. We validate this identification method in vitro by demonstrating detection of six genotoxic analytes and their chemical kinetics in NIH-3T3 cells, including chemotherapeutic drugs and reactive oxygen species (ROS), which are spectroscopically differentiated into four distinct classes. We also demonstrate single-molecule sensitivity in detecting hydrogen peroxide, one of the most common genotoxins. An array of such sensors has allowed us to study a new signaling pathway of the Epidermal Growth Factor Receptor (EGFR) involving biocatalyzed  $H_2O_2$  production on the membrane protein receptor itself in response to ligand binding. We show the detection of single molecule  $H_2O_2$  at the membrane surface for the first time, and map the kinetics of the receptor in the bound and unbound state while on the live cell surface. The platform is promising for extending single molecule kinetic analysis to traditionally difficult biological systems.

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## Nonlinear Optical Properties and Phase Relaxation Processes in Semiconducting Single-Walled Carbon Nanotubes

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Since the discovery of single-walled carbon nanotube (SWNT), many theoretical and experimental works have been done in nonlinear optical properties. We have reported that the absolute value of figure of merit  $|\text{Im}\chi^{(3)}/\alpha|$  increases with an increase in tube diameter[1]. In general, third-order nonlinear optical susceptibility  $\chi^{(3)}$  depends on transition dipole moment  $\mu$ , population ( $T_1$ ) and phase relaxation ( $T_2$ ) times. The  $T_1$  in film sample estimated from pump-probe measurements is about 1 ps and it becomes longer in a tube with larger diameter[2]. The  $T_2$  which has been directly measured by time-resolved two-beam degenerate four-wave mixing (DFWM) method is less than 1 ps, and it becomes shorter at a higher excitation intensity, a higher temperature[3], and a smaller tube diameter. These results can be explained by the enhancement of phase relaxation due to frequent exciton-exciton and exciton-phonon scattering[3]. Although the experimental trends of diameter dependence in lifetimes ( $T_1$  and  $T_2$ ) and figure of merit  $|\text{Im}\chi^{(3)}/\alpha|$  are similar, but the power of diameter in  $|\text{Im}\chi^{(3)}/\alpha|$  can not be explained by only the diameter dependence of lifetimes. This fact suggests that the diameter dependence of  $\chi^{(3)}$  are mainly governed by the transition dipole moment  $\mu$ .

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## Probing Disorder in Graphene with Raman Spectroscopy

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We induced disorder in graphene systems with low energy Ar<sup>+</sup> bombardment and probe the effects in the real and momentum spaces, as obtained by scanning tunneling microscopy and Raman spectroscopy measurements, respectively. We study the details of each Raman feature, and the evolution of the intensity ratio between the graphite-like (G band) and disorder-induced (D band modes)  $I_D/I_G$ . We discuss the effects based on the electronic and vibrational properties of graphene, correlating crystalline and localized processes, addressing the coherence parameters for the resonance Raman spectroscopy.

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**INVITED TALK**  
**June 9, Tuesday**



## Optical Spectroscopy of Single and Multilayer Graphene

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Optical spectroscopy provides a powerful tool to probe the structure and dynamics of electronic excitations in graphene. We first present results on the optical absorption of monolayer graphene in the infrared and visible spectral regions. Like the Manchester group, we find a flat absorption spectrum from 0.5 eV to the visible. The magnitude of the absorbance is given by  $\pi\alpha = 2.3\%$ , where  $\alpha$  is the fine structure constant, as predicted by a simple theory of interband transitions. At lower photon energies, however, we can see clear departures from this universal absorption associated with the effect of finite carrier concentration.

We also have performed measurements on few-layer graphene samples. For low photon energies, we see the development of a more complex band structure and the onset of new interband transitions. We can understand the spectra in terms of a zone-folding scheme applied to the 3-D band structure of graphite. The case of bilayer samples is of particular interest. We show from spectroscopic measurements that the application of a strong dc field across the bilayer can significantly alter its band structure, giving rise to a band gap as large as 200 meV. The possibility of producing graphene with a band gap is of considerable importance both for fundamental studies and applications.

Optical spectroscopy with femtosecond pulses also permits one to probe the dynamics of these excitations. After creation of electron-hole pairs by an ultrafast pump pulse, equilibration of the carriers among themselves and with strong-coupled optical phonons is found to occur on a sub-picosecond time scale, while full thermalization occurs on the picosecond time scale. On a still slower time scale, we observe heat flow from excited graphene layers into the substrate.

## Optical and Magnetic Anisotropy in Graphene Oxide

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We report broad band visible photoluminescence (PL) from solid (drop cast) graphene oxide, and modifications of the emission spectrum by progressive chemical reduction.<sup>1</sup> The data suggest a gapping of the two-dimensional electronic system by removal of  $\pi$ -electrons. We discuss possible gapping mechanisms, and propose that a Kekule pattern<sup>2</sup> of bond distortions could account for the observed behavior. To further explore the origins of this PL, we perform additional studies of optical and magnetic anisotropy. Using angle- and polarization-dependent PL we are able to determine uniaxial anisotropy tensors for absorptive and emissive processes and to establish the extent of their two-dimensional nature. We also discuss magnetic field dependent alignment measurements, which probe the disruption of aromatic diamagnetism and can thereby indicate the fraction of C6 hexagons over which the  $\pi$ -network remains intact.

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## Vibrational modes in graphene and semiconductor nanorods

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We investigated the vibrational properties of graphene nanoribbons and semiconductor nanorods by means of first-principles calculations on the basis of density functional theory. We confirm that the phonon modes of graphene nanoribbons with armchair and zigzag type edges can be interpreted as fundamental oscillations and their overtones. These show a characteristic dependence on the nanoribbon width. Furthermore, we demonstrate that a mapping of the calculated  $\gamma$ -point phonon frequencies of nanoribbons onto the phonon dispersion of graphene corresponds to an "unfolding" of nanoribbons' Brillouin zone onto that of graphene. We consider the influence of spin states with respect to the phonon spectra of zigzag nanoribbons and provide comparisons of our results with past studies. We also investigated the electronic structure of graphene under uniaxial strain and compare to available experiments. We present experimental and theoretical results on the radial breathing vibration of CdSe nanorods. In particular, we find that  $\omega_{\text{RBM}}=91 \text{ cm}^{-1}\text{nm}/d$ , which is useful for the determination of the diameter of such nanorods.

## Theory of Near-field Raman Enhancement in Carbon Nanotubes

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Many experimental works have recently shown that near-field Raman is an useful optical technique for the study of carbon nanotubes on the nanometric scale [1,2,3,5,6]. The high-resolution achieved in these experiments (~10-30 nm) made it possible to resolve local variations in the Raman spectrum along an isolated single-wall carbon nanotube, which would otherwise be hidden in far field measurements.

In spite of the great potential of near-field Raman on the development of the science of carbon nanotubes, a careful analysis taking in account its theoretical basis still missing. This manuscript presents a theory describing the near-field Raman enhancement of carbon nanotubes. The theory predicts that the near-field Raman intensity is inversely proportional to the 11<sup>th</sup> of the tip-sample distance. Supporting the theory, experimental results of near-field Raman measurements performed on distinct serpentines carbon nanotubes (with different chiralities) is presented. The experimental data show that distinct peaks present in the near-field Raman spectra originated from an specific tube present the same enhancement for a given tip-sample distance. These results indicate that the near-field enhancement does not dependent considerably on the symmetry of the Raman mode, but mainly on the field enhancement factor intrinsic from the near-field probe used in the experiment.

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## **Optical properties of ultra-thin single-walled carbon nanotubes aligned in the nano channels of zeolite AEL single crystals**

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Nano-porous single crystals can serve as ideal nano-reactors and assume variety of nano-structures those are usually not stable in free space. Their mono-dispersed porous with a macro-size of crystal, their optical transparency and electrical insulating properties, all make them attractive hosts for numerous applications. The periodic array of crystal porous makes it possible to build a quasi-3D structure for carbon nanotubes which is of importance for making optical and transport devices as it is. Using aluminophosphate porous single crystal of  $\text{AlPO}_4\text{-11}$  (AEL) as the template, we fabricated ultra-thin single wall carbon nanotubes (SWNTs) with a diameter of only 0.3 nm. Raman spectra, with excitation wavelengths in the range from 457.9 to 647.1 nm, show excellent agreement with the density functional calculations of the Raman-active vibrational modes from the armchair (2,2) SWNTs. Calculated imaginary part of the dielectric function also displays qualitative agreement with the resonant Raman data. The polarizability of the Raman modes agrees well with the calculated intensities for non-resonant Raman scattering, although the resonant Raman scattering plays a key role in the process. Interestingly, the (2,2) SWNT has two meta-stable ground states corresponding to two slightly different lattice constants in the axial direction, one state is metallic and the other is semiconducting. Because of strong curvature effect, the 0.3nm SWNTs are not stable in free space, the unstable structure is stabilized by the confinement of the SWNTs in the nano-channels.

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## Electrical power dissipation, phonon populations, and substrate effects in carbon nanotubes and graphene

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When a high current is passed through a carbon nanotube transistor, the kinetic energy of electrons is transferred to optical phonons by inelastic scattering, leading to current saturation. We use resonant Raman scattering to measure the population of specific phonons under a high current and find a non-equilibrium phonon population even in supported carbon nanotubes. The primarily pumped zone-boundary and G-band phonons become “hot” because their decay pathway is slowed-down at a long-lived intermediate frequency phonon. Acoustic phonons as represented by the radial breathing mode have significantly lower effective temperatures. We need to include remote-scattering of electrons by polar surface phonons of the SiO<sub>2</sub> substrate to explain the I-V characteristics that does not show negative differential conductance.

Substrate effects are investigated by partially suspending carbon nanotubes and measuring their resonant Raman scattering profiles, fluorescence excitation profiles, and spectral lineshapes in the suspended and supported parts. The observed energy shifts and broadenings are explained by energy differences of free and bound excitations, as well as substrate-induced symmetry breaking.

Finally, I will give an overview of our efforts in graphene FET electro-optics, which includes spatially-resolved Raman spectroscopy and photoconductivity. The former is used to differentiate between heat-flow into the metal contacts vs. the underlying substrate, and the latter is used to detect metal-induced pn-junctions, which are responsible for an electron-hole asymmetry in I-V<sub>G</sub> characteristics of graphene FETs.

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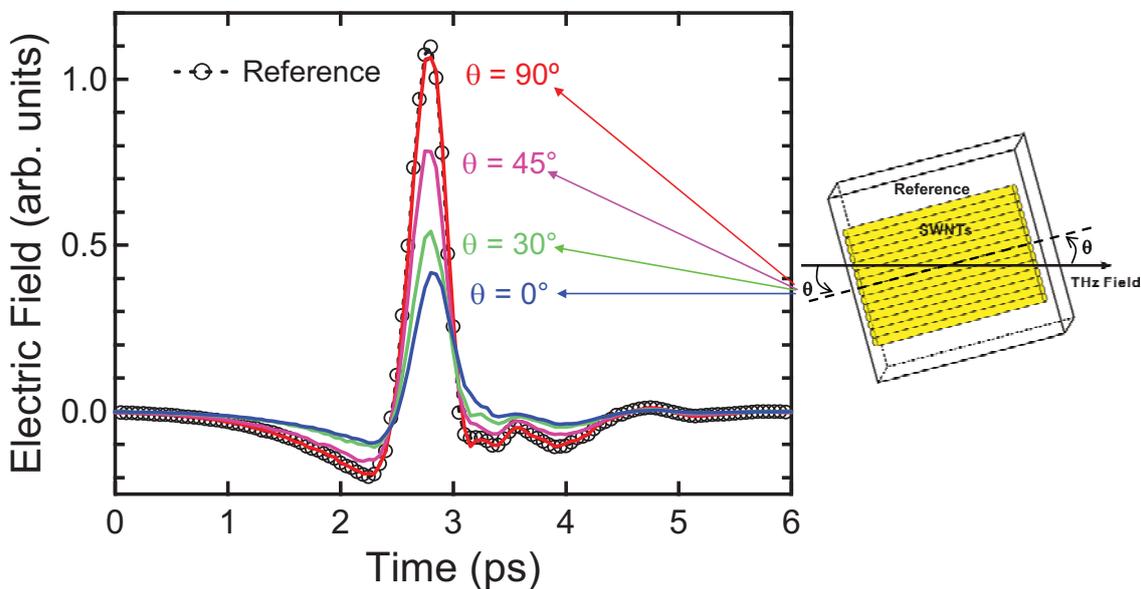
## Terahertz Dynamics in Carbon Nanotubes

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This talk will summarize our recent advances in the spectroscopy of single-walled carbon nanotubes (SWNTs) using the techniques of magneto-optics, ultrafast optics, and nonlinear optics [1-7]. In particular, as described below, results of our time-domain terahertz (THz) spectroscopy of SWNTs [7] will be reported.

Using polarization-dependent time-domain THz spectroscopy, we have studied the anisotropic conduction properties of free carriers in a thin film of highly aligned SWNTs. When the THz polarization was parallel to the nanotube alignment direction, there was strong absorption, while virtually no absorption was observed when the THz polarization was perpendicular to the nanotube alignment axis. See Fig. 1, where we present transmitted time-domain waveforms for various angles between the THz polarization and the nanotube alignment direction.



**Figure 1:** Transmitted THz electric field signals for the reference sapphire substrate (dashed curve with circles) and for the nanotube film for different polarization angles (colored solid curves) [7]. There is virtually no attenuation (strong absorption) when the terahertz polarization is perpendicular (parallel) to the nanotube axis.

The sample was synthesized via chemical vapor deposition and transferred onto a sapphire substrate through a high temperature water etching process [8]. Through a proper model, the THz complex dynamic conductivity of the SWNTs was extracted and showed a non-Drude-like frequency dependence, with the real part monotonically increasing with increasing frequency. In addition, the real part of the dielectric constant showed negative values, indicating the highly metallic nature of carrier conduction along the nanotube direction. The degree of polarization in terms of absorbance was calculated to be 1, and the reduced linear dichroism was calculated to be 3 using the theory of linear dichroism for an ensemble of anisotropic molecules, which demonstrates the nematic order parameter of the SWNTs in the film to be 1. This indicates that the alignment of the nanotubes is “perfect” and any misalignment must have characteristic length scales much smaller than the wavelengths used in these experiments (1.5 mm – 150  $\mu\text{m}$ ). All these findings suggest that this type of aligned SWNT film performs as an ideal linear polarizer in the THz frequency range.

This work was performed in collaboration with Lei Ren, Layla G. Booshehri, William D. Rice, Xiangfeng Wang, David J. Hilton, Takashi Arikawa, Cary L. Pint, Robert H. Hauge, Aleksander K. Wojcik, Alexey A. Belyanin, Yoshiaki Takemoto, Kei Takeya, Iwao Kawayama, and Masayoshi Tonouchi.

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# Exciton Fine Structures and Dynamics Studied by Single Carbon Nanotube Spectroscopy

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## §1 Introduction

The electronic properties of single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention because of their degenerated band structures in momentum-space and enhanced Coulomb interaction. The enhanced Coulomb interaction leads to the formation of excitons with large binding energies of 200–400 meV. The novel optical properties in SWNTs arise from characteristics of the excitons [1,2]. Recently, there are several studies about optically-forbidden (dark) exciton states in SWNTs [3,4]. The dark exciton state near the lowest optically-allowed (bright) state has great influence on the optical properties. Here, we study the exciton fine structures and dynamics between the bright and dark states by single nanotube spectroscopy.

## §2 Experimental

The samples used in this work were suspended SWNTs synthesized on Si substrates using an alcohol catalytic chemical vapor deposition method [5-7]. The photoluminescence (PL) spectroscopy of a single carbon nanotube was carried out using a variable-temperature confocal microscope. The samples were mounted in a cryostat under a superconducting magnet with fields up to 7 T.

## §3 Results and Discussion

We studied diameter and temperature dependence of PL spectra of single SWNTs. The PL linewidth of a single carbon nanotube (homogeneous linewidth) at room temperature depends on the diameter. Furthermore, the value of the homogeneous linewidth almost linearly decreases with a decrease of temperature from 300 to 5 K. The temperature dependence of the homogeneous linewidth implies that the exciton decoherence is dominated by the diameter dependent exciton-phonon interaction [6,7]. The very narrow PL spectra of single SWNTs at low temperatures allow us to observe small spectral changes under low magnetic fields. A single PL peak arising from the bright exciton is observed at zero magnetic field. With increasing the magnetic field parallel to the tube axis, we have observed another PL peak a few meV below the bright

exciton PL peak at low temperatures [8]. The additional peak arises from the dark exciton due to the symmetry breaking caused by the Aharonov-Bohm effect. We have also investigated temperature and magnetic field dependence of the PL intensity ratio of the dark to bright exciton, and found that excitons are nonequilibriumly distributed (nonBoltzmann distribution) between the bright and dark exciton states.

#### §4 Conclusion

We studied temperature and magnetic field dependence of PL spectra of a single carbon nanotube. The experimental results indicate that the exciton decoherence is dominated by the diameter dependent exciton-phonon interaction. Direct observation of the dark exciton PL peak under magnetic field by single nanotube spectroscopy revealed a non-equilibriumly exciton distribution between the bright and dark state.

#### Acknowledgement

The author thanks Mr. R. Matsunaga, Dr. Y. Miyauchi, and Prof. Y. Kanemitsu for collaboration of the study. This study was supported by a Grant-in-Aid for Scientific Research on Priority Area of the MEXT of Japan (Nos. 20048004, and 20340075).

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**INVITED TALK**  
**June 10, Wednesday**



## Our Recent Advances in Nanotube and Graphene Research

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A report is presented on recent advances in the Dresselhaus-Kong group at MIT on several topics relevant to Nanotube and Graphene Photophysics research. First we review progress with studies of the Raman spectra of individual double wall carbon nanotubes (DWNTs), making comparisons between the work in our group and by others doing similar measurements at the single DWNT level, making comparisons between individual SWNTs and individual DWNTs, between individual DWNTs and bundled DWNTs, and between CVD-derived DWNTs and peapod-derived DWNTs as bundles and at the individual level. Recent results are reported for several features in the Raman spectra of metallic tubes as a function of gate voltage in an electrochemical cell, with comparisons made between experiment and theory. Results from a study of the resonance window for members of  $(2n+m)$  families of SWNTs are reported for both metallic and semiconducting families with a discussion of the implications of this work. The use of Raman spectroscopy to characterize large area graphene films grown on a (111) Nickel polycrystalline substrate is discussed with particular reference made to the number of graphene layers. Comparisons are made with the Raman spectra obtained by other methods of growing few layer graphene. The use of Raman spectroscopy to study the large differences between edges in graphene ribbons when prepared by joule heating under far from equilibrium conditions and under near equilibrium conditions is also discussed.

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## Optical properties of monolayer and bilayer graphene

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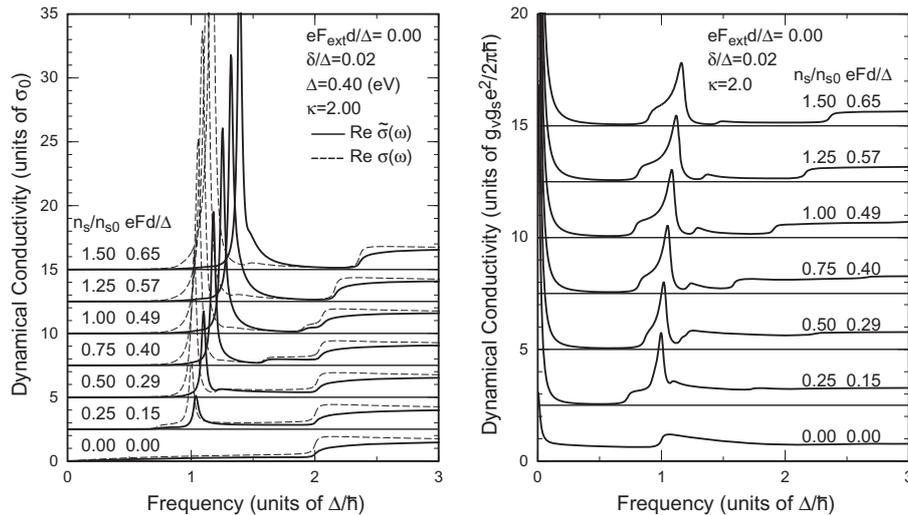
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Recently, graphene consisting of the monolayer graphite sheet was fabricated [1], and the conductivity modulation by the gate was demonstrated and the quantum Hall effect was observed [2,3]. Actually, graphene has been a subject of theoretical study prior to the experimental realization because of the peculiar electronic structure also responsible for intriguing properties of carbon nanotubes [4,5]. The purpose of this paper is to give a brief review on recent theoretical study on optical properties of monolayer and bilayer graphene. The topics include a singular dynamical conductivity and effects of electron-electron interaction on cyclotron resonance in monolayer graphene, and optical absorption for perpendicular and parallel polarization in bilayer graphene.

The dynamical conductivity  $\sigma(\omega)$  consists of the Drude conductivity determined by states in the vicinity of the Fermi level and the interband conductivity determined by interband optical transitions. In a conventional Boltzmann-type approximation, the frequency dependence of  $\sigma(\omega)$  in monolayer graphene is completely scaled by Fermi energy  $E_F$ , i.e.,  $\sigma(\omega, E_F) = \sigma(\hbar\omega/|E_F|)$ , and the interband conductivity becomes universal  $\sigma(\omega) = g_v g_s e^2 / 16\hbar$ . This leads to a singular behavior of  $\sigma(\omega)$  in the vicinity of  $E_F = 0$  called the Dirac point, which is removed by the inclusion of level broadening effect in a self-consistent Born approximation [6].

According to Kohn's theorem, the conventional two-dimensional electron systems do not show interaction effects in cyclotron resonance, where the system is homogeneous and all the electrons have the same parabolic energy dispersion. This Kohn's theorem is, however, inapplicable for graphene, since the electrons have a linear dispersion. We investigate interaction effects based on the method of exact diagonalization in finite-size systems taking into account a few relevant Landau levels. For transitions from the  $n=0$  to 1 Landau level, in particular, the obtained spectra show double peaks, i.e., a dominant peak in the low energy side and a sub-peak in the high energy side. The peak splitting is attributed to coupling between two excitation modes, the optically allowed excitation from the  $n=0$  to 1 Landau level and the optically forbidden transition from  $n=-1$  to 0 level. The energy splitting is most enhanced in the limit of vanishingly small filling of the  $n=0$  level, but is suppressed with increasing filling factor. In spite of the fact that graphene is in the strong nonparabolicity limit, interaction effects manifest themselves as a surprisingly small modification of the spectra for transitions involving



**Fig. 1** Absorption for perpendicular (left) and parallel polarization (right).

level  $n=0$  in the presence of broadening. This situation changes for other transitions such as those from  $n=-1$  to  $n=2$ .

Graphene bilayer has a unique band structure distinct from monolayer graphene, where the conduction and valence bands with quadratic dispersion touch at zero Fermi energy [7,8]. An important property is that an electric-field applied perpendicularly to the layers modifies its low-energy band structure by opening an energy gap between the electron and hole bands [9,10]. Another interesting feature is that optical transitions can be induced by light polarized both parallel and perpendicular to the layer.

For the perpendicular polarization, in particular, the effective dynamical conductivity giving the absorption is calculated with inclusion of the depolarization effect associated with induced charge redistribution between two layers. Spectral features, characterized by peaks and edges associated with specific transitions between subbands, are quite different between perpendicular and parallel polarizations, because each of transitions can be allowed or prohibited depending on the polarization direction. For the perpendicular light, the absorption energy is considerably shifted by the dynamical screening effect, while that is absent for parallel polarization.

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## Raman, Photoluminescence and Saturable Absorption in Graphene

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I will review some recent advances in optoelectronic and photonics of graphene layers. Raman spectroscopy is one of the most powerful tools for graphene characterisation [1] I will first focus on the effects of uniaxial strain on its Raman spectrum [2]. The doubly degenerate  $E_{2g}$  optical mode splits in two components, one polarized along the strain and the other perpendicular to it. This leads to the splitting of the G peak into two bands, which we call  $G^+$  and  $G^-$ , by analogy with the effect of curvature on the nanotube G peak. Their relative intensities depend on light polarization, which allows one to determine the graphene crystallographic orientation with respect to the applied strain [2]. I will then discuss the dependence of the 2D peak intensity on doping [4-6] and show that this is determined by a combination of electron-phonon and electron-electron scattering [6]. Under full resonance, the generated electron-hole pairs can scatter not just with phonons, but also with electrons and holes, and this affects the 2D peak intensity [6]. This explains quantitatively the experimental doping dependence of the 2D peak and can be used to determine its Electron Phonon Coupling, which is higher than previously predicted by density-functional theory, as a consequence of the renormalization by Coulomb interactions [6]. Finally I will discuss how to induce significant photoluminescence in graphene [8], and how to exploit Pauli blocking to realise an ultrafast laser based on graphene as saturable absorber [9]. The latter examples show the viability of graphene for optoelectronics.

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## Electronic and Optical Properties of Nanotubes, Graphene, and Graphene Nanostructures

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The low-energy electronic states in graphene behave like those of two-dimensional (2D) massless Dirac fermions with pseudospin character. Many of the unusual electronic, transport and optical properties of carbon nanotubes and graphene and graphene-based nanostructures originate from this unique electronic structure. *Ab initio* calculations further showed that, because of reduced dimensionality, electron-electron interaction effects are very important in the quasiparticle and optical excitations in these systems. In this talk, we illustrate these effects with results from several recent theoretical studies. Single-walled carbon nanotubes (SWCNTs) exhibit highly unusual exciton excited-state spectra owing to a 1D anti-screening effect. First-principles calculations on excitonic effects in the nonlinear optical properties of SWCNTs will also be presented. For graphene-based nanostructures, we show that they possess further fascinating properties. Graphene nanoribbons are semiconductors with novel electronic, magnetic and optical properties. For example, the existence of magnetic edge-state excitons is predicted for zigzag-edged nanoribbons. Owing to the chiral nature of the electronic states, the carrier dynamics in graphene exhibits anomalous anisotropy when subjected to an external periodic potential of nanometer dimensions (called graphene superlattices). Under appropriate conditions, these graphene superlattices are predicted to be electron supercollimators and new generation of 2D massless Dirac fermions may be created.

## Effects of Environment and Defects on Photoluminescence of Single Wall Carbon Nanotube

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### §1 Introduction

Single wall carbon nanotubes (SWNTs) are promising materials for nano-electronics applications. In addition to peculiar electric properties originated from one dimensionality of SWNTs, semiconducting SWNTs exhibit intense photoluminescence (PL) owing to a direct bandgap and high densities of singular electronic states. However, since all the carbon atoms are in the surface layer, PL of SWNTs suffers from strong influence by the surrounding materials. They become unluminescent when lying on a substrate. Investigation into the effect of adsorbates is thus important for elucidating the PL quenching mechanism. Defects on the wall should also affect the PL properties. We have studied the effects of adsorbates and defects using individual SWNTs suspended between micropillars.

### §2 Investigation of Adsorbate Effect

We have used an environmental chamber to control the gas (ethanol or water vapor) ambience surrounding suspended SWNTs. Both PL excitation and emission energies of a suspended SWNT rapidly change at a transition pressure [1]. The transition pressure shows clear diameter dependence: the transition pressure decreases with an increase in the tube diameter. This phenomenon is quantitatively described by adsorption and desorption of molecules on the SWNT surface. Condensation of gas molecules on the SWNT surface causes change in the dielectric constant, which affects the binding energy of exciton.

Deposition of carbon, on the other hand, causes formation of satellite peaks only in the emission spectrum. The excitation energy remains the same after carbon deposition, while the emission intensity decreases with increasing the amount of carbon deposited. The carbon deposits on the SWNT wall induce new electronic levels.

Deposition of non-wetting metals, such as gold and iron, on a SWNT shows a different effect on PL. Metal deposits induce tensile strain on the nanotube, thus the emission energy shifts depending on the family-type of nanotube.

### §3 Investigation of Defect Effect

We are now studying the effect of defect creation by irradiating a SWNT with an electron beam in a scanning electron microscope (SEM). SEM observation is known to cause sizable damage in SWNTs [2]. However, it was difficult to distinguish between the defect creation and contamination deposition effects. Thus, we use electron irradiation at elevated temperatures, which can reduce contamination deposition during SEM observation.

For the investigation of defect effects, observation of PL in a microscopic scale is useful. Thus, we are developing a high-spatial resolution PL system using a near-field scanning optical microscope (NSOM) combined with the laser-excited PL system. Suspended SWNTs formed on narrow-gap grooves can be imaged with the scanning probe. We expect spatial resolution on the order of 10 nm.

### Acknowledgement

This work was supported by Grant-in-Aid for Scientific Research on Priority Area of the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

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## Quantum optics with carbon nanotubes

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Semiconducting carbon nanotubes (CNT) constitute a new paradigm for solid-state quantum optics. I will discuss recent experiments where we have used photon correlation measurements to demonstrate that unintentional exciton localization could lead to strong photon antibunching in a single CNT [1]. Our experiments also demonstrated that the confined exciton photoluminescence (PL) lineshape could be highly asymmetric [2]. The independent boson model that we use to describe the confined exciton-phonon interactions reproduce with very high accuracy the broad and asymmetric PL lines observed in these experiments. A principal goal of future experiments is the demonstration of all-optical spin manipulation in CNTs [3].

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## Third-Order Nonlinear Optical Response in Fullerene-Peapods

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### §1 Introduction

It is known that quasi-one-dimensional exciton effects near the fundamental absorption edge in single-walled carbon nanotubes (SWNTs) enhance optical nonlinearities in the near-infrared region[1,2]. Fullerene-peapods are also of interest to investigate optical properties because of the unique structure consisting of one- and zero-dimensional systems. The theoretical study has predicted significant modification of electronic states in peapods due to hybridization between  $\pi$  states of fullerenes and nearly free electron states of SWNTs [3]. In this presentation, we report on third-order nonlinear optical susceptibilities in carbon peapods encapsulating C<sub>60</sub>, C<sub>70</sub> and C<sub>84</sub> studied by femtosecond pump-probe spectroscopy.

### §2 Experiments

SWNTs with the average diameter of  $1.9 \pm 0.4$  nm were produced by the direct injection pyrolytic synthesis method using colloidal solutions of metal nanoparticles containing Co and Mo. Peapods were made by heating a quartz ampoule containing a dry mixture of C<sub>60</sub> (C<sub>70</sub> or C<sub>84</sub>) and SWNT at 650 C. After the heat treatment the mixture was washed with toluene to remove any excess fullerene molecules from the outside of the SWNTs. For comparison of optical properties of the fullerene-peapods with those of SWNTs, we also prepared SWNT samples without containing fullerenes with the same procedures. Pump-probe measurements were carried out using a 120 fs-width pump pulse with the photon energy of 2.5–3.1 eV and a white continuum probe pulse.

### §3 Results and discussion

Figure 1(a) shows the absorption spectra of C<sub>84</sub>-peapods (solid curve) and reference-SWNTs (dashed curve). Two absorption bands due to the E<sub>22</sub> excitonic transition ( $\sim 0.9$  eV) of semiconductor tubes and the M<sub>11</sub> transition ( $\sim 1.3$  eV) of metal

tubes are observed. The absorption peaks for the C<sub>84</sub>-peapods are shifted to the lower energy side by ~20 meV compared with those for the reference SWNTs. The difference absorption spectrum between the C<sub>84</sub>-peapods and the reference-SWNTs in Fig. 1(b) shows the absorption component due to the encapsulated C<sub>84</sub> in the photon energy range of 1.0–1.5 eV. Third-order nonlinear optical susceptibilities  $\text{Im}\chi^{(3)}$  were measured by the pump-probe method with the pump-photon energy of 2.50 eV. Closed squares and open squares in Fig. 1(a) show the  $\text{Im}\chi^{(3)}$  spectra for the C<sub>84</sub>-peapods and the reference SWNTs, respectively. The  $\text{Im}\chi^{(3)}$  spectra exhibit peaks at the corresponding absorption peaks of the E<sub>22</sub> and M<sub>11</sub> transitions, which indicates the resonance enhancement of each transition.

Interestingly, the  $\text{Im}\chi^{(3)}$  value of the E<sub>22</sub> transition in the C<sub>84</sub>-peapods is larger than in the reference-SWNTs. This situation is more clearly seen in the difference  $\text{Im}\chi^{(3)}$  spectrum (closed circles) in Fig. 1(b), indicating a peak at the E<sub>22</sub> transition. Therefore, we have found that the nonlinear optical response in the C<sub>84</sub>-peapods is enhanced compared with that of the SWNTs because of the existence of encapsulated C<sub>84</sub>. Similar experiments were done for the C<sub>60</sub>- and C<sub>70</sub>-peapods. No enhancement has been observed for the E<sub>22</sub> transition, but instead in the energy range of 1.5–3.0 eV we have observed the  $\text{Im}\chi^{(3)}$  component corresponding to the component seen in the C<sub>60</sub> (C<sub>70</sub>) film. These results suggest that hybridization between the  $\pi$  states of C<sub>84</sub> and the electronic states of the SWNTs causes the enhancement of the nonlinear optical response in C<sub>84</sub>-peapods.

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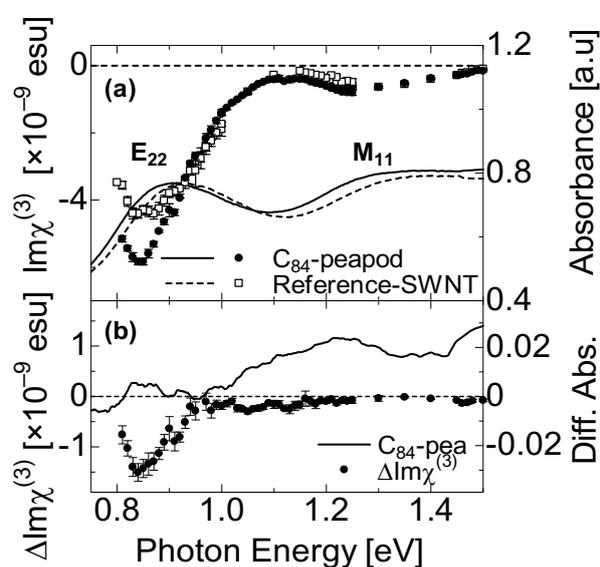


Fig. 1 (a) Absorption and  $\text{Im}\chi^{(3)}$  spectra in C<sub>84</sub>-peapods (solid curve and closed squares) and reference-SWNTs (dashed curve and open squares). (b) difference spectra of absorption and  $\text{Im}\chi^{(3)}$ . The redshift by 20 meV is considered.

## Direct Determination of Precise Electronic States of SWNTs Based on Soluble Carbon Nanotubes

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Since the discovery of carbon nanotubes (CNTs), many groups have endeavored to understand the fundamental properties of the CNTs and explored their applications in nanomaterials science and engineering. Electronic structures of CNTs, one of the most fundamental features of nanotubes, strongly depend on the chirality of the nanotubes.

We have discovered that we can determine the precise electronic states of isolated SWNTs having their own chirality indices by *in situ* near-IR photoluminescence spectroelectrochemistry at the fabricated modified ITO electrode. This has been achieved by using this modifying film that retains the isolated SWNTs and the spectroelectrochemical results analyzed by Nernst equation. Table 1 summarized the results of fifteen individual SWNTs having chirality indices of (6,5), (8,3), (7,5), (8,4), (10,2), (7,6), (9,4), (10,3), (8,6), (9,5), (12,1), (11,3), (8,7), (10,5), and (9,7).

Details including direct determination of precise electronic states of SWNTs, as well as fundamental and applications of “soluble carbon nanotubes”<sup>1</sup> will be reported at the meeting.

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**Table 1.** Experimentally Determined Electronic States of Fifteen Isolated SWNTs.

chirality index (n,m)	nanotube diameter (nm)	$E_{ox}^{0'}$ (V vs. vacuum)	$E_{red}^{0'}$ (V vs. vacuum)	Fermi level ( $E_f$ ) (V vs. vacuum)	bandgap (eV)
(6,5)	0.757	5.08	4.01	4.55	1.07
(8,3)	0.782	5.03	3.95	4.49	1.08
(7,5)	0.829	4.98	3.97	4.48	1.01
(8,4)	0.840	4.96	4.05	4.50	0.91
(10,2)	0.884	4.93	3.95	4.44	0.98
(7,6)	0.895	4.94	4.03	4.49	0.91
(9,4)	0.916	4.92	4.01	4.47	0.91
(10,3)	0.936	4.89	4.09	4.49	0.81
(8,6)	0.966	4.90	4.05	4.47	0.85
(9,5)	0.976	4.89	4.09	4.49	0.79
(12,1)	0.995	4.93	4.03	4.48	0.90
(11,3)	1.014	4.87	4.05	4.46	0.82
(8,7)	1.032	4.88	4.09	4.49	0.79
(10,5)	1.050	4.86	4.08	4.47	0.78
(9,7)	1.103	4.85	4.10	4.47	0.75

# Electronic and Geometrical Properties of Carbon Nanotubes: A First-Principles Study

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## §1 Introduction

Electronic properties of carbon nanotubes (CNTs) have been studied intensively so far. One of their most important electronic properties, the topology-dependent metallic versus semiconducting transport properties, were predicted theoretically based on the tight-binding approximation [1,2]. From the viewpoint of the next-generation nanoelectronics materials, so-called armchair nanotubes are of high interest as metallic nanowires to be used in the nanometer-scale devices, partly due to the high maximum electric current density they can host, and partly due to their high thermal conductivity because the appropriate heat treatment is the key to miniaturizing the electronics devices further and further in the future. On the other hand, carbon nanotubes which are either moderate-gap or narrow-gap semiconductors can be even more important than metallic armchair nanotubes as materials to be used to construct central functional part of the next-generation nanodevices [3]. Therefore, predicting the precise electronic structure of each individual carbon nanotube is highly important at present.

In addition to the study of pristine carbon nanotubes, studying the effect of doping into semiconductor nanotubes are equally very important since, as in the case of bulk materials, doping should be the key technology to be used in realizing both n-type and p-type semiconductor units with nanometer scale. We have addressed these important issues using a variety of predictive theoretical methods including the local density approximation (LDA) in the framework of the density-functional theory, the transferable tight-binding models which can reproduce either LDA energetics or LDA electronic properties, and the Green-function based GW approximation [4]. Also the production of new nanometer-scale carbon materials using carbon nanotubes by utilizing external pressure and/or thermal effect have been theoretically studied in detail.

## §2 Workfunction of metallic nanotubes

In the case of C60, it has been shown that the geometry optimization is of essential importance to predict its electronic structure [4]. The simple assumption of its

interatomic distances of graphite value is found to give as much as 0.3 eV smaller gap between the highest-occupied state and the lowest-unoccupied state than that of C60 with complete geometry optimization. Therefore, at least in the case of thin carbon nanotubes with diameters similar to or smaller than that of C60 (about 7 Å), the geometry optimization should be important as well to predict their electronic properties. We have optimized systematically the geometry of armchair nanotubes, and actually its effect is confirmed to be important to predict, for example, their workfunction values [5].

### §3 Doping into semiconductor nanotubes

In the previous work, we studied the energetics and the positions of the impurity-induced states in substitutionally B-doped carbon nanotubes [6]. The N-doped carbon nanotubes should be equally important and we have studied them comparatively with previous B-doped case using the LDA. Interesting differences between B and N doped cases including the exceptionally shallow N-induced impurity state in the case of thin nanotubes is revealed.

### §4 New nanocarbon phases

An atomistic process of the carbon-nanotube formation from C60 fullerenes inside the outer nanotube via thermal treatment is simulated using the variable-cell molecular dynamics [7]. Also the formation of various new phases from various crystalline nanotube samples under external pressure is studied in detail [8].

### Acknowledgements

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# Production of (5,4) and (6,4) Enriched Single-Walled Carbon Nanotubes Grown Using a Platinum Catalyst

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## §1 Introduction

Since the electronic and optical properties of single-wall carbon nanotubes (SWNTs) very much depend on the tube structure<sup>1)</sup>, one of the most important issues of SWNTs is to control the distribution of nanotube diameters and chiralities in the product. For methods in which nanotubes are grown from gaseous precursors on metallic catalyst particles, the selection of metal catalyst is of particular importance, because the product compositions are strongly influenced by the kinds of metallic nanoparticle materials. For example, the CoMoCAT catalyst system has been known to give rise to thin and narrow diameter distribution<sup>2)</sup>, but HiPco, very broad abundance profile. Here, in the present work, we will demonstrate the production of the SWNTs with narrow and very small diameter distribution in comparison with the CoMoCAT system by use of platinum particle as a catalyst and will show the presence of the (4,2) tube with 0.47 nm in diameter as the smallest diameter carbon nanotube.

## §2 Experimental

The SWNT sample was synthesized by alcohol CVD method using ethanol as carbon precursor, and platinum was used as a catalyst deposited on PG (porous glass with average pore size of 20-30nm<sup>3)</sup>). The furnace temperature and an inner pressure of ethanol were systematically changed with the aim of synthesizing the smaller and the narrower diameter distributions of SWNTs. The obtained as-grown SWNT sample was characterized by TEM, Raman scattering spectroscopy, and absorption and fluorescence measurements were carried out for the sample after the conventional dispersion and isolation procedures of the SWNTs in SDBS/water solution.

## §3 Results and Discussion

It is well known that the furnace temperature, carbon source materials, and the kind of catalyst are important parameters for controlling the compositions of the grown SWNTs. For the purpose of production of SWNTs with the diameter distribution as

narrow and small as possible, we have examined the dependence of temperature, alcohol gas density as well as the pore size of the porous glass. In Figs. 1,2, Raman scattering and absorption spectra of the sample prepared at different temperature are shown, demonstrating how the furnace temperature gives influence on the diameter distribution of SWNTs. The 488 nm excitation Raman spectra (Fig.1) are interpreted in

terms of the presence of both the metallic tubes with about 0.7 nm in diameter and the semiconducting tubes with the smaller or the larger diameters than the metallic ones. By decreasing the temperature, it is noticed that the abundance of the smaller diameter tubes increases (see also Fig.2). The diameter of the smallest tube detected by Raman was found to be about 0.41 nm with  $506\text{ cm}^{-1}$  as a radial breathing mode.

Examining the excitation energy (488nm) and the frequency of the RBM, the  $506\text{ cm}^{-1}$  Raman peak is strongly suggested the formation of (4,2) tube. From absorption spectra, it is also suggested that at low temperature, the major product of the sample consists of (5,4) and (6,4) tubes.

#### Acknowledgement

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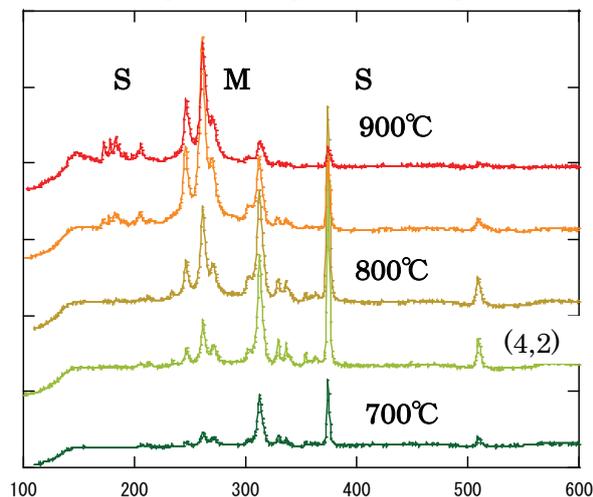


Fig.1 Raman spectra of SWNTs ( $\text{cm}^{-1}$ )

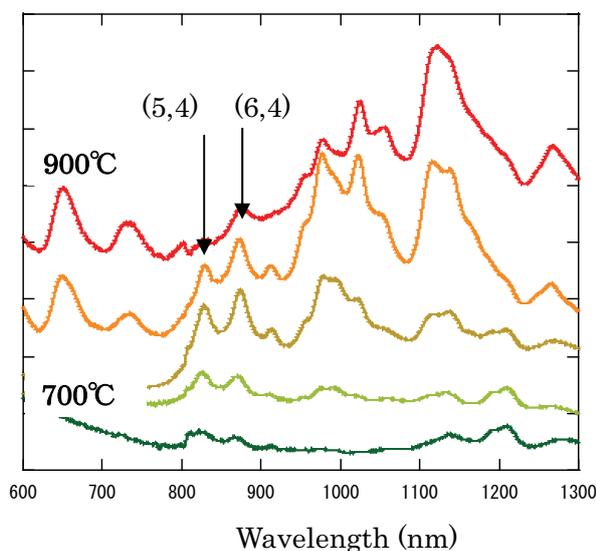


Fig.2 Absorption spectra of SWNTs prepared at different temperature

## Spectral features due to dark exciton in photoluminescence map of single-walled carbon nanotubes

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**Features in Photoluminescence Map of SWNTs** Over the past seven years photoluminescence (PL) spectroscopy has emerged as an important characterization tool for determining the (n, m) chirality and population of semiconducting SWNTs. This technique is essential for the chirality selective growth and/or the separation depending on chirality. Under excitation with the appropriate wavelength of light, SWNTs exhibit characteristic peaks with well-defined emission from their corresponding excitonic states. Besides the quantum yield of the photoluminescence, sound understanding of extra features mainly due to dark exciton are necessary, in order to use this PL map for the determination of chirality population of SWNTs. Such features are shown in Fig. 1, where the sample contains only (7,5) and a trace of (6,5); at least within PL spectroscopic measure. Optical absorption by excitonic phonon sideband due to mixing of dark exciton and K phonon (marked as  $E_{11}+K$  and  $E_{22}+K$ ) is well discussed [1]. And, the cross-polarized absorption marked as  $E_{12}^+$  is confirmed [2]. Here, the phonon sideband in emission ( $E_{11}-K$ ) and quasi-dark exciton in cross-polarized excitation ( $E_{12}^-$ ) are discussed.

**Phonon Sideband in Absorption and Emission** We performed detailed PL spectroscopy studies of three different types of

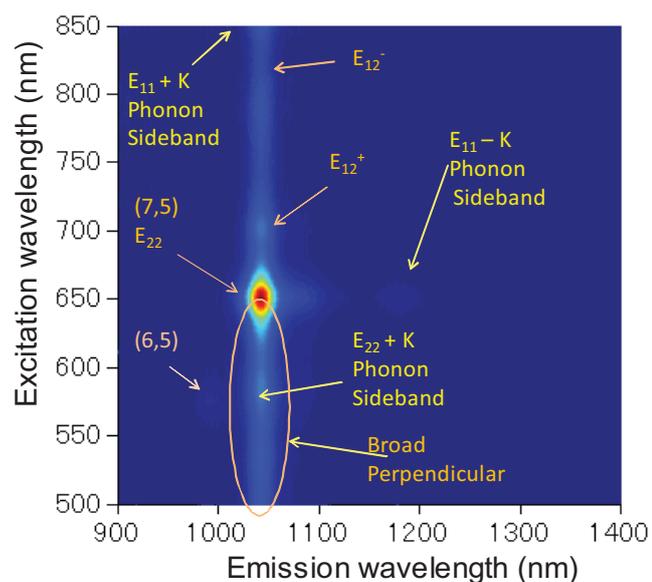


Fig. 1 Various features in photoluminescence map

single-walled carbon nanotubes (SWNTs) by using samples that contain essentially only one chiral type of SWNT, (6,5), (7,5), or (10,5). The observed PL spectra unambiguously show the existence of an emission sideband at  $\sim 145$  meV below the lowest singlet excitonic ( $E_{11}$ ) level. We find that the energy separation between the  $E_{11}$  level and the sideband is almost independent of the SWNT diameter. Based on this, we ascribe the origin of the observed sideband to coupling between K-point phonons and dipole-forbidden dark excitons [3].

### Quasi-Dark Exciton in Cross-Polarized Absorption

We performed the direct observation of the spin-singlet transverse dark excitons in SWNTs through the polarized photoluminescence excitation spectroscopy as shown in Fig. 2. We studied the exciton optical absorption polarized transverse to the nanotube axis. The intrinsic asymmetry between valence and conduction bands lifts the degeneracy of the spin-singlet transverse excitons at two equivalent K and K' valleys in momentum space, leading to "brightening" of transverse dark exciton states. The energy splitting between transverse bright and dark states were about 200-300 meV, much larger than the bright-dark splitting of longitudinal excitons. The chirality-dependent spectral weight transfers to the transverse dark states from the bright states were clearly observed.

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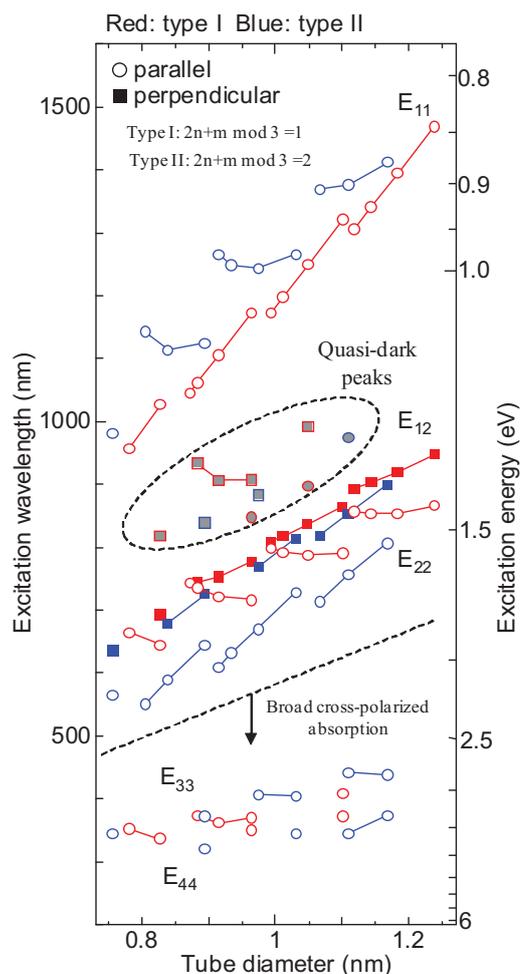


Fig. 2 Kataura plot including cross-polarized absorption.

# **Abstracts**

## **Poster Session**



## Enrichment of Armchair Carbon Nanotubes via Density Gradient Ultracentrifugation: Raman Spectroscopy Evidence

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We have performed resonant Raman scattering studies of single-walled carbon nanotubes (SWNTs), enriched in metallic  $(n,m)$  species [or  $(n-m) \bmod 3 = 0$ ] by the density gradient ultracentrifugation (DGU) technique. Through these studies, we provide evidence for a ***strong enrichment in armchair and near-armchair  $(n,m)$  species*** not previously observed optically. These measurements were carried out over a broad range of excitation wavelengths (440-850 nm) such that all  $(n,m)$  species remaining in the enriched material were identified. When compared to pristine, as-produced SWNT material, Raman results indicate the almost complete suppression of semiconducting [or  $(n-m) \bmod 3 = \pm 1$ ] SWNTs, confirming observations by absorption and photoluminescence excitation spectroscopy. Additionally, clear Raman excitation profiles (REPs) of the radial breathing mode (RBM) were generated for all armchair  $(n,n)$  nanotubes from (6,6) through (12,12). A comparison between the REPs of armchair SWNTs and the other metallic species over such a broad range of diameters indicates a *strong enrichment in  $(n,m)$  species of large chiral angle and, in particular, armchair SWNTs* as well as a *lack of diameter dependence* in DGU-based, metallic  $(n,m)$  enrichment. Furthermore, we were able to measure REPs of the G-band mode and observe how the longitudinal and transverse optical phonons evolve in peak position, linewidth, and intensity as different metallic nanotubes are resonantly excited. By combining results from such data, we have gained valuable insight into metallic nanotubes as well as the phenomenological nature of type separation based on DGU.

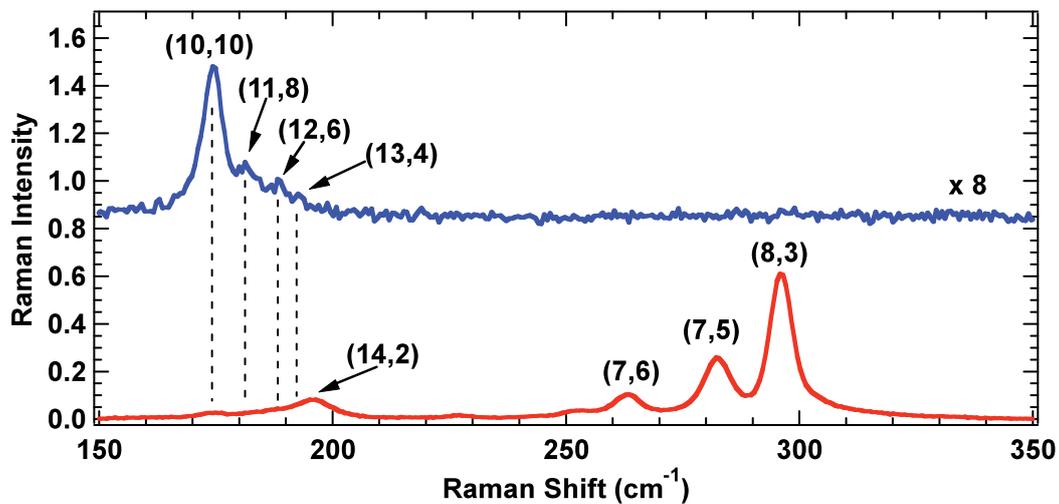


Figure: Resonant Raman spectra, excited at 655 nm, taken for pristine HiPco SWNT material (red, bottom) and metallic SWNT-enriched HiPco material (blue, top).

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## Quantitative Purity Evaluation of Single-Wall Carbon Nanotubes using Resonance Raman Spectroscopy

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We propose a new method for the purity evaluation of single-wall carbon nanotubes (SWCNTs). Here, we have defined a purity evaluated by Raman intensity of pristine and ultracentrifuged topping of SWCNTs as PERIPUTOS that is named after the initial letters. For the quantitative evaluation of the purity of SWCNTs, resonance Raman spectra of isolated SWCNTs solution were used as the probing signal, because the Raman intensity of the isolated SWCNTs should be proportional to the amount of SWCNTs. A purified SWCNTs solution prepared by ultracentrifugation [1,2] was used as 100%-SWCNTs, namely an impurity-free standard sample. Optical absorbance of pristine-, and 100%-SWCNTs were set to be same at the wavelength of excitation laser, and Raman spectra of the solutions were measured. Here, resonance condition of SWCNTs was not changed, because diameter distribution of SWCNTs was not modified before/after ultracentrifugation. From the Raman intensity ratio of 100%-, and pristine-SWCNTs, the purity of pristine-SWCNTs was evaluated. In the presentation, we will report the detailed experimental protocols for the PERIPUTOS method. Moreover, by using the present method, some case studies for the purity evaluation of commercial available SWCNTs will be presented.

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## Optical Active Single-Walled Carbon Nanotubes

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Since SWNTs were first prepared in 1993, much effort has been directed toward selective synthesis and separation of SWNTs with limited structures or specific properties. However, optical activity originating from carbon nanotubes themselves has been elusive. Here we designed and synthesized chiral diporphyrins **1** – **3** shown in Fig. 1 to obtain optically active SWNTs through molecular recognition of the helical isomers of SWNTs [1-3].

The solutions of SWNTs extracted by (*R*)- and (*S*)-diporphyrins (**1** – **3**) showed symmetrical CD spectra, indicating that two stereoisomers (*R* and *S*) of each diporphyrin preferentially extract SWNTs with opposite helicities (*M* and *P*) [2] and that the SWNTs extracted are optically active. The two prominent CD peaks are found at 374 and 639 nm and are assigned to E<sub>33</sub> and E<sub>22</sub> transitions of (7,5)-SWNTs (Fig. 2). These spectral features suggest much higher discrimination ability of **3** to the helicities of (7,5)-SWNTs [3].

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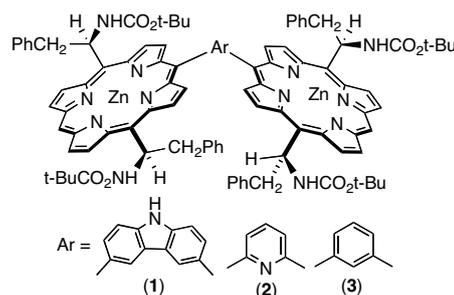


Fig. 1 Structures of (*R*)-diporphyrins.

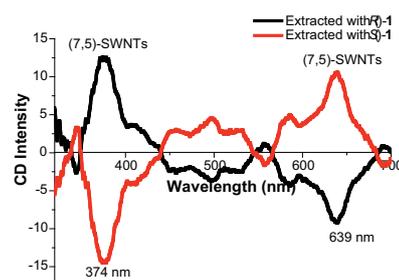


Fig. 2 CD spectra of SWNTs extracted with (*R*)- and (*S*)-diporphyrins **3**.

## Optical characterization of Length-Separated DNA-Wrapped Double-Wall Carbon Nanotubes

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Carbon nanotubes (CNTs) have unique structural, electronic and mechanical properties. Recently, double-wall carbon nanotubes (DWNTs) have attracted much attention because of their unique properties compared to single-wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs). DNA-wrapped CNTs (DNA-CNTs) have been known to exhibit unique characteristics in their structures as well as the high solubility in pure water, and separations on the chirality and length have been achieved. Separation of CNTs by structure is very important for their utilization. We have reported the synthesis and characterization of isolated DNA-SWNTs by using natural DNA from salmon in aqueous solutions [1]. Here, we report detailed studies on the separation and the optical characterization of length separated DNA-CNTs, and we compare the dependence on the length and layer-layer interaction between SWNTs and DWNTs.

DNA-CNTs were separated by high performance liquid chromatography (HPLC) with COSMOSIL CNT (SEC 300, 1000 and 2000) columns. Fractions were collected at 1 min intervals and the lengths of DNA-CNTs were determined by AFM observation.

Fig. 1 shows the AFM images of DNA-DWNTs after separation. The average lengths of each image are  $378 \pm 54$ ,  $202 \pm 34$ ,  $100 \pm 20$  and  $51 \pm 15$  nm. PL and Raman spectra of the separated DNT- DWNTs will also be presented.

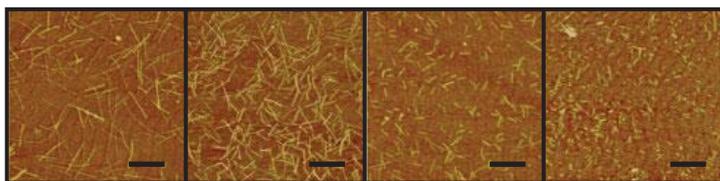


Fig. 1 AFM images of variety lengths of the DNA-DWNTs. The scale bars: 500  $\mu\text{m}$

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## Resonance Raman Spectra of Optical Purified (6,5) Nanotubes Sorted by Density Gradient Ultracentrifugation

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We present a protocol to selectively isolate single-walled carbon nanotubes (SWNTs) with a chirality of (6,5) using density gradient ultracentrifugation (DGU)<sup>[1]</sup>. Starting with SWNTs synthesized by the alcohol catalytic chemical vapor deposition (ACCVD) method, we used sodium deoxycholate (DOC), sodium dodecyl sulfate (SDS) and sodium cholate (SC) as co-surfactant encapsulating agents<sup>[2]</sup> to isolate (6,5) SWNTs. Successful isolation was determined by photoluminescence excitation (PLE) maps, which show only one feature corresponding to (6,5). However, additional spectroscopic data (Fig. 1) such as resonance Raman spectra (488 nm laser excitation) and optical absorbance, as well as transmission electron microscopy (TEM) observation before and after the DGU process show that the sample contained a high relative purity of (6,5) SWNTs, but other chiralities were still present at low concentrations. Some evidence of their existence can be seen in optical absorbance spectra, but resonance Raman spectra using different excitation energies clearly reveal the existence of these minority species. This shows that resonance Raman spectroscopy is a more sensitive tool for determining the purity of optically isolated SWNT samples, and we hope that iterated refinement of our DGU process can lead to successful extraction of single-chirality SWNTs.

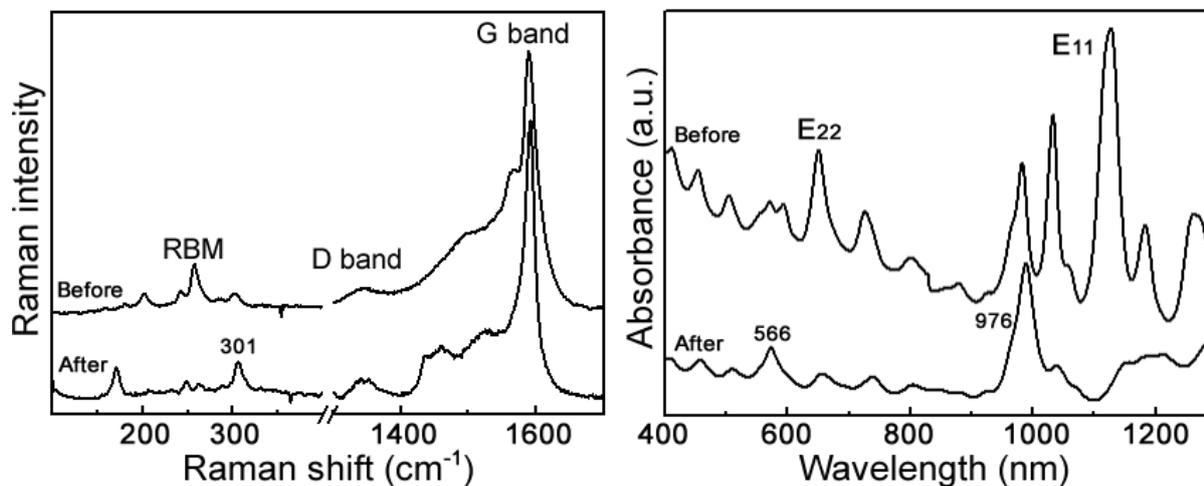


Figure 1: Resonance Raman spectra (left, 488 nm laser excitation) and optical absorbance spectra (right) before and after DGU process showing selective isolation of optically purified (6,5) SWNTs from pristine ACCVD samples.

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## **Diameter distribution analysis of sorted double wall carbon nanotubes by optical absorption spectroscopy and electron transmission microscopy.**

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Carbon nanotubes and also other nanostructures can be now separated by gradient density ultracentrifugation methods. These techniques offer a unique opportunity to improve our understanding of optical properties of species which are not very well separated as synthesized and to relate them quantitatively to their structural characteristics such as helicity and diameter. This knowledge will in turn open the possibility to use optical spectroscopy as a reliable tool for evaluating the structure distribution of a macroscopic sample. However optical response can be biased by several effects such as surfactants and its relationship to the tube structure needs a independent and direct determination of this latter.

Transmission electron microscopy, on the counterpart, provides direct measurements of the tube characteristics such as diameter distribution, number of walls and helicity (1).

In this presentation, we propose TEM analyses as a convenient and reliable way to evaluate and quantify the structural sorting of both single- (SWNT) and double (DWNT)-walled nanotubes. We show that thanks to a statistical analysis of high resolution images, one can determine the tube diameter distribution and its standard deviation (1). In particular, we have applied the gradient centrifugation technique to a sample containing SWNT and DWNT of different diameters and have evaluated the efficiency of the technique for separating both kinds of tubes as well as the diameter sorting of each kind. We will discuss how these data are related to optical absorption spectra recorded on the same sorted samples in order to evaluate the response of this technique to a known sample.

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## Polarized Raman spectroscopy on vertically aligned single-walled carbon nanotubes

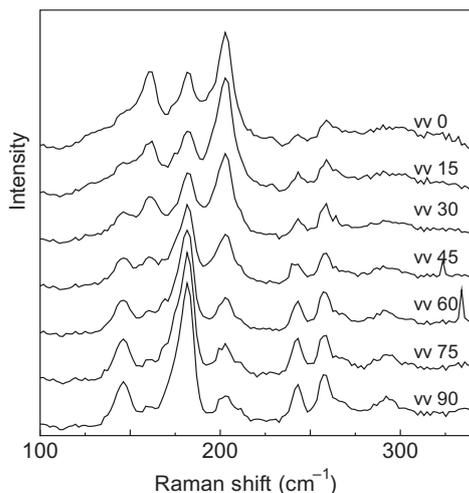
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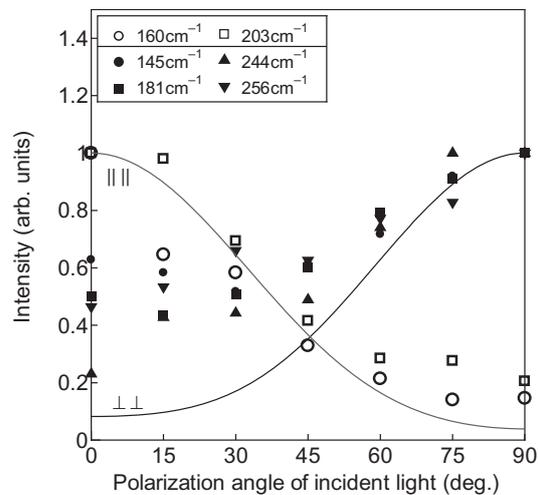
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Vertically aligned single-walled carbon nanotube (VA-SWNT) films with high purity have been prepared up to 30  $\mu\text{m}$  thick by the alcohol catalytic chemical vapor deposition (CVD) method[1][2]. In a previous polarized Raman spectroscopy study, we found anomalous anisotropic peaks such as at  $180\text{ cm}^{-1}$  for the excitation by 488 nm laser and explained them as perpendicularly polarized excitation [3]. However, recent high resolution Raman spectrum shows that the strong  $180\text{ cm}^{-1}$  peak is comprised by four fine sharp peaks which might be from isolated SWNTs. To clarify its origin, polarized Raman experiment is carried out using two configurations, where the orientation of the polarizer for inspecting the scattered light was parallel to (VV) and perpendicular to (VH) the polarization of the incident light. By changing the incident light orientation with respect to the VA-SWNT growth direction, two different polarization dependences were found for the radial breathing mode (RBM) peaks. The peaks at  $160$  and  $203\text{ cm}^{-1}$  behave consistently with the parallel excitation, while peaks at  $145$ ,  $181$ ,  $244$ , and  $256\text{ cm}^{-1}$  exhibit the opposite behavior in the VV configuration. Although the selection rules for Raman scattering process allow perpendicularly polarized excitation in RBM (A mode) [4],  $181\text{ cm}^{-1}$  group peaks deviate much from the theoretical calculation assuming the orientation distribution by the order parameter obtained from absorption measurements[5]. The  $181\text{ cm}^{-1}$  group intensities were further revised by taking into account of laser heating effect, which show that they tend to be constant and independent for different polarization angles. Moreover, it is observed from high resolution SEM image that some isolated tubes distribute among the array which may correspond to the abnormal behaviors in CNTs.



**Fig. 1.** Raman spectra of a VA-SWNT film in the VV configuration, and changing the incident polarization from  $0^\circ$  (along alignment direction) to  $90^\circ$  (perpendicular to the alignment direction).



**Fig. 2.** Normalized RBM Peak intensity changes for incident light polarization from  $0^\circ$  to  $90^\circ$  with respect to the VA-SWNT growth direction (VV configuration).

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## High-Precision Selective Deposition of Catalyst for Facile Localized Growth of Single Walled Carbon Nanotubes

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In the liquid-based dip-coating, hydrophilicity of Si/SiO<sub>2</sub> substrate is found to be critical for the successful deposition of catalyst and hence the growth of single-walled carbon nanotubes (SWNTs). When the surface is functionalized by self-assembly monolayer (SAM) and becomes hydrophobic, no catalyst remains and no SWNT grows. This concept can be utilized to localize the growth of SWNTs at designed regions where SAM were selectively removed by, e.g. UV or electron beam. The advantage of the proposed technique comparing to conventional M/NEMS technique (e.g. lift-off) is as followings. Firstly, the resolution can be expected to be very high, and a SWNT pattern with the line-wide of 50 nm can be easily obtained. Secondly, the ability of damaging SAM by electron beam in an SEM makes the localization process visible, which facilitates the fabrication of devices basing on as-grown high-quality SWNTs. Examples will be demonstrated.[1]

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## Raman and optical spectroscopic analysis of single walled carbon nanotubes synthesized by an industrial scale aerosol reactor

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**Abstract** Carbon nanotubes, and in particular Single walled carbon nanotubes (SWCNTs), have attracted a great interest due to their remarkable properties, which have been utilized in many different applications such as sensors, transistors, optoelectronic devices, composites with enhanced properties and for energy storage. It is well known that the properties of SWCNTs can significantly vary depending on their diameters and chiral angles. Therefore, it is crucial to tailor the size distribution of the SWCNTs to fit the requirement for specific applications.

In this work, detailed parametric analysis of SWCNTs synthesized in an industrial scale aerosol method was carried out. The sample morphology, mean diameter, diameter distribution as well as the relative nanotube abundance of the SWCNTs were analyzed by a combined study of transmission electron microscopy, Raman and optical absorption spectroscopy. The results show that increased growth temperature results in an increase in SWCNT mean diameter. The CO<sub>2</sub> plays an essential role in the SWCNTs growth process as an etching agent. The addition of small amounts of CO<sub>2</sub> increases the mean diameter of SWCNTs and improves the purity of SWCNTs. Moreover, the resident time and the concentration of catalyst were varied by changing the flow rate of CO, which also affects the diameter distribution of the SWCNTs production. These results show that the SWCNTs diameter, diameter distribution and purity can be varied as a function of reactor conditions, which is important to meet requirements of various applications.

## Effects of Bundling and Diameter on the UV Optical Absorption of Single-Wall Carbon Nanotubes

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**Introduction:** Optical absorption spectroscopy has been frequently used as one of the most powerful tool for the characterizations of purity [1], metal/semiconductor ratio [2], and diameters of single-wall carbon nanotubes (SWCNTs) [3]. In general, peaks analyzed for these characterizations are observed in near infrared (NIR) region and can be assigned to the interband transitions between van Hove singularities. On the other hand, the ultraviolet absorption which is largest part of optical absorption of SWCNTs have not been fully investigated, probably due to the analytical difficulty arisen from overlapped pi plasmon absorption of graphitic impurities. The pi plasmon absorption is extremely broad and is superposed on the NIR absorption peaks as a featureless background in NIR region. It has been pointed out that the intensity ratio between the NIR absorption peaks and the background increases as bundles of SWCNTs are exfoliated, although this mechanism has not yet been clarified.

In this work, we have investigated the variation of UV optical absorption of SWCNTs on the different degree of their bundling. Moreover, we have prepared three samples with different SWCNT diameter ranges and discussed the diameter dependence of UV optical absorptions.

**Experimental:** SWCNTs synthesized by the gas-phase CVD growth, e-DIPS method [3], were dispersed in D<sub>2</sub>O containing 1 wt% of sodium cholate by using a tip ultrasonic homogenizer (SONICS VCX500) equipped with a titanium alloy tip (TI-6AL-4V). Pulsed sonication was applied (on: 1 sec, off: 2 sec) with a power of 200 W for 30 min. In order to prepare SWCNT dispersions with different degree of bundling, each dispersed solution was then centrifuged at 127600 ×g for 0.5, 1.0 and 2.5 hrs (Hitachi CP 100MX with a P56ST swing rotor) and the supernatant of the upper ca. 80 % of the volume was collected and subjected to the optical absorption measurements.

**Results and Discussion:** Optical absorption spectra of SWCNT dispersions prepared by different centrifugation times, 0.5, 1.0 and 2.5 hrs are shown in Figure 1A. Optical absorption observed in NIR region became weaker but sharper as the elongation of centrifugation time, although shapes of that were basically maintained. Because the

centrifugation can precipitate SWCNT bundles and leave isolated SWCNTs in the supernatant in general, these phenomena in NIR absorption peaks can be attributed to the increase in the degree of SWCNT isolation. On the other hand, in UV region two broad components were observed and the shapes of UV absorption spectra were gradually changed by the centrifugation time. Difference spectra with broad peaks at 4.7 eV obtained by subtraction of longer centrifugation spectra from shorter ones are shown in Figure 1B that should be attributed to the precipitates, that is, SWCNT bundles and impurities. Interestingly the shapes of the two difference spectra were approximately agree with each other. Supposing the spectrum shape of background absorption can be expressed by these difference spectrum, the optical absorption originated from perfectly isolated SWCNTs was estimated by subtraction of appropriate background from observed spectrum of 2.5 hrs centrifugation as shown in Figure 1C. Obtained spectrum of isolated SWCNTs clearly shows the two broad peaks at 4.1 and 5.5 eV that are different from the UV peaks of the background in their peak positions. These results suggest that the analysis of the UV optical absorption can be used as the indicator of the degree of SWCNT bundle. In the presentation, we will also discuss about the effect of diameter difference on the optical absorption in detail.

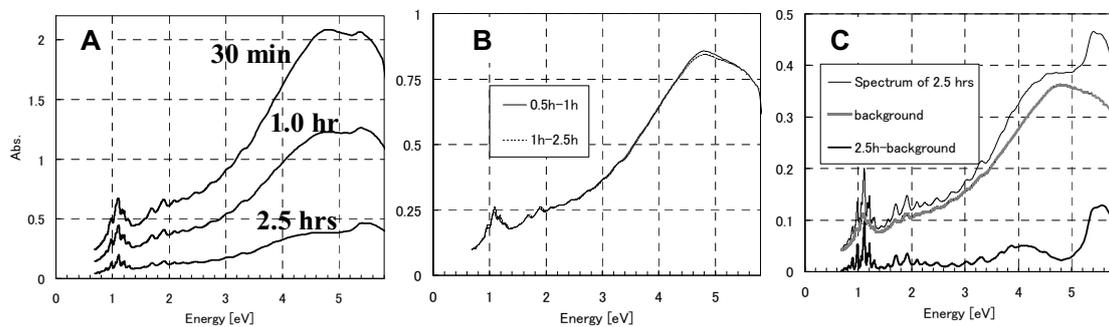


Figure 1. Optical absorption spectra of SWCNT dispersions prepared by different centrifugation times (A), difference spectra calculated by their subtraction attributed to the precipitates (B), and the estimated spectrum of isolated SWCNTs calculated by the subtraction of B (C).

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## Fermi energy dependence of radial breathing mode in metallic single-wall carbon nanotubes

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The radial breathing mode (RBM) of single-wall carbon nanotubes (SWNTs) arises from the first-order, one-phonon and intra-valley Raman scattering process, which is used to assign the diameter and chirality of a SWNT. For metallic SWNTs, the curvature effect induces a small energy gap except for armchair SWNTs. Since the curvature-induced energy gap is similar to the RBM phonon energy for nanotubes with diameter range,  $0.7 < d_t < 2$  nm (15~40 meV), the curvature-induced energy gap may affect the phonon softening of the RBM, so called the Kohn anomaly effect. The Kohn anomaly effect can be explained by the self-energy correction to the RBM phonon mode in which the virtual excitation of an electron-hole pair causes a softening of the RBM phonon frequencies. Recently an experimental group has observed the Fermi energy ( $E_F$ ) dependence of the phonon-softening effect of M-SWNTs by electrochemical doping, and their result clearly shows the RBM phonon softening as a function of  $E_F$  [1]. The frequency shift of the RBM is produced by electron-phonon interaction [2]. The RBM Raman spectrum for the M-SWNTs depends on chirality and diameter. While a zigzag SWNT shows the maximum RBM frequency shift, an armchair SWNT does not show any frequency shift. It has been known that the k-electron-phonon (el-ph) interaction of the RBM gives rise to the chirality dependence [3]. Although the RBM Raman intensity has been calculated by the el-ph and electron-photon (el-op) interactions, the RBM Raman spectrum has not been calculated yet. In this poster, the RBM Raman spectrum will be shown by including the Kohn anomaly effect and the resonance window values [4]. And instead of el-ph and el-op interaction for Raman intensity calculation, we will consider exciton-phonon and exciton-photon interactions. As a result, the chiral angle dependence of the RBM Raman spectrum can be directly compared to the experiment. The gate voltage dependence of the RBM Raman spectra for metallic nanotubes is also directly compared to the experiment in which the Kohn anomaly effect appears by change of the Fermi energy.

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## Exciton energy Kataura plot and excitonic effect of single wall carbon nanotubes

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We calculate exciton energy of single wall carbon nanotubes (SWNTs). The exciton energy depends on the surrounding materials of the SWNT [1]. This environmental effect is expressed by the dielectric constant [2]. In previous paper we used the static dielectric constant in order to reproduce the resonance Raman experiment for bundle samples [3,4]. However, since the dielectric constant depends on the nanotube diameter [5] and the surrounding materials, we need to consider a correction to the environmental effect for other samples. In this paper we discuss the environmental effect of SWNTs. The exciton energy of SWNTs is calculated by solving the Bethe-Salpeter equation in which the one particle energies are given by the extended tight-binding scheme [3]. We also compare our calculation with the resonance Raman experiments in the different environment. From our calculation we show the exciton energy Kataura plot for different samples.

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## Pressure-assisted tip-enhanced Raman imaging of carbon nanotubes at the spatial resolution of a few nanometres

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Tip-enhanced Raman spectroscopy (TERS) has allowed nanoscale observation and characterization of carbon nanotubes. A sharp metallic tip plays an important role in confining and enhancing the incident field in the close vicinity of the tip due to excitation of surface plasmon polaritons at the tip end.

Here we demonstrate that tip-applied pressure enables the TERS technique to be even more powerful in terms of both analytical and spatially-resolving power. When a metallic tip is locally pressed against a carbon nanotube (CNT), the tip interacts with the CNT mechanically by applying a controlled pressure on the CNT. The pressure applied by the tip apex is uniaxial and hence the CNT is anisotropically deformed as depicted in Fig 1(a). This effect shows up in interesting Raman spectral changes such as peak-shift and intensity-change shown in Fig. 1(b), which addresses the nano-mechanical properties of the deformed CNT. Due to the extremely localized nature of the tip-applied pressure, we optically imaged the CNT with a spatial resolution of a few nm, that has been never possible without the pressure effect. The optical image shown in Fig. 1(c) was constructed by sensing the spectral changes while raster-scanning the CNT under the metal tip with a controlled pressure.

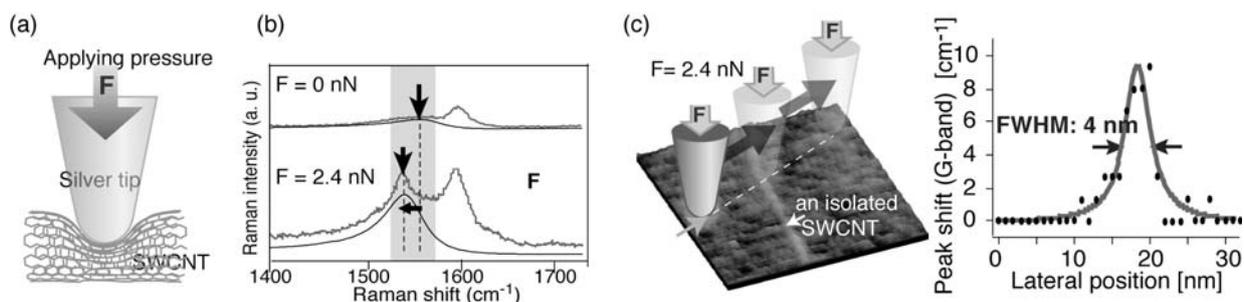


Figure 1 (a) a SWCNT uniaxially-deformed by tip-pressure, (b) tip-enhanced spectral change caused by tip-pressure, (c) optical imaging of an isolated SWCNT by sensing the spectral shift of the G-band.

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## Resonance Raman scattering of hole-doped metallic and semiconducting carbon nanotubes

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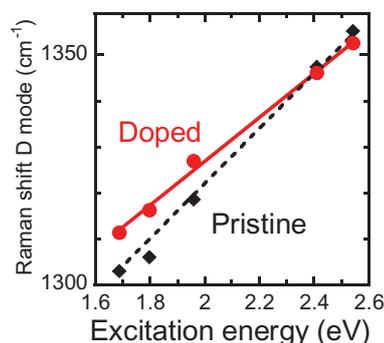
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Electron-phonon (e-p) interaction plays an important role in the transport and optical properties of single-wall carbon nanotubes (SWCNTs). For the detail understanding of e-p interaction, in this study, we have investigated the effect of hole-doping on the phonon dispersions of metallic and semiconducting SWCNTs. It is known that the phonon dispersion around K point can be probed using resonance Raman spectroscopy of the defect-induced Raman mode (D mode). In previous studies, however, the detailed analysis of the D mode has been limited by the mixed Raman signals from the co-existing metallic and semiconducting SWCNTs in as-grown samples. To solve this problem, high purity metallic and semiconducting SWCNT bulk samples were prepared using a density gradient method. Raman spectra of samples before and after hole-doping using sulfuric acid were recorded varying laser energy from 1.7 to 2.7 eV.

Interestingly, it was found that the doping-induced D mode shift significantly depended on resonance conditions. In the case of the semiconducting SWCNTs, the D mode showed an upshift of around  $10\text{ cm}^{-1}$  under the resonance of the  $E_{22}$  optical transition (Fig. 1). On the other hand, such shift was hardly observed under the  $E_{33}$  resonance. Similar tendency was seen for the metallic SWCNTs. The dependence of the shift amount on excitation energy can be explained by the selective hardening of optical phonons near the K point in the Brillouin zone. Our finding suggests the critical role of e-p interaction in the phonon dispersion of SWCNTs.

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**Fig. 1.** D mode frequency of pristine (diamond) and doped (circle) semiconducting SWCNTs plotted as a function of excitation energy.

## Coherent Phonon Dynamics in Highly Aligned Single-Walled Carbon Nanotubes

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Recent ultrafast pump-probe spectroscopy studies of single-walled carbon nanotubes (SWNTs) have successfully detected coherent phonon dynamics, and our previous work on the radial breathing mode (RBM) of coherent phonons provided a powerful method for determining phonon and exciton energies in an ensemble of SWNTs [1,2]. We now extend our previous studies to investigate polarization anisotropy of the RBM of horizontally aligned SWNTs. Using such highly aligned samples, we were able to extract the angular dependence of the RBM as a function of both the angle between the sample and laser polarizations, and the angle between the pump and probe polarization. We observed extreme polarization anisotropy, including a complete quenching of the RBM when the sample alignment is perpendicular to the pump and probe polarization (Fig. 1a). We also determined the angular dependence of the RBM to be a function of  $\cos^4\theta$ , as expected for highly aligned SWNTs (Fig. 1b).

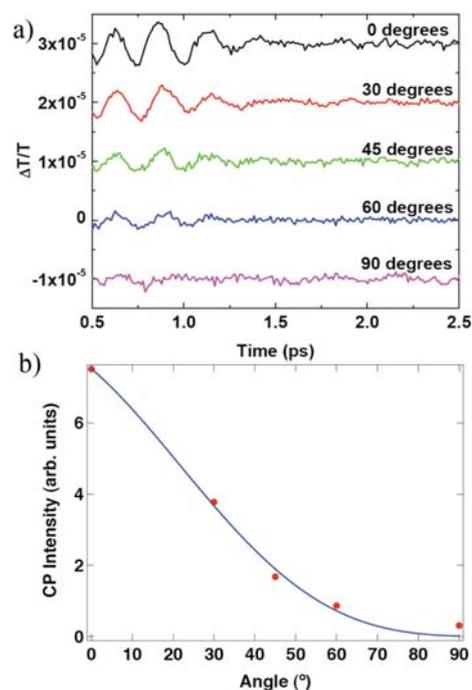


Figure 1 (a) polarization anisotropy of RBM

(b) angular dependence of RBM

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## Photoluminescence Observation of Water Encapsulation in an individual Single-walled Carbon Nanotube

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Encapsulation of water molecules in an individual single-walled carbon nanotube was performed and the incomings and outgoings of water molecules were observed by photoluminescence (PL) measurement. PL spectra were measured in an environmental chamber, which controlled the sample temperature and atmosphere.

The spectra (a, b) in Fig. 1 were measured from as-grown suspended SWNTs in air and in vacuum, respectively. Ethanol gas molecules adsorption increased the dielectric constant surrounding the SWNT and decreased the optical transition energy.<sup>1</sup> Water molecules adsorbed on SWNTs in air and PL peaks red-shifted the same as ethanol. After heating in air at 300 °C, the SWNTs were oxidized and the caps were opened. The PL spectra, which were measured from the oxidized SWNTs (c) in air and (d) in vacuum, showed broadening and red-shift of the peaks, compared to the spectra (a, b). The spectrum (d) gradually blue-shifted and sharpened in vacuum and it agreed with the spectrum (b). It indicated that the broadening and red-shift after oxidation came from the adsorption on the inner surface and the spectrum (d) was the emission from SWNTs encapsulating water molecules. The water molecules both on the inside and outside of SWNTs changed the dielectric constant and the optical transition energies of the SWNTs, but by different extents. Thus, PL spectra can be used for identification of adsorption site.

### Acknowledgement

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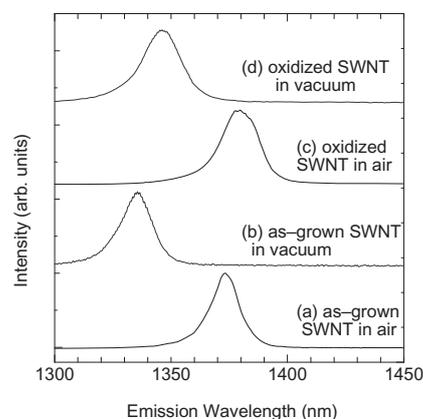


Fig. 1 PL spectra from (a, b) as-grown and (c, d) oxidized SWNTs. The spectra (a, c) and the spectra (b, d) were measured in air and in vacuum, respectively.

## Intrinsic and Extrinsic Factors which Affects the Optical Properties of Individual Single-Walled Carbon Nanotubes

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Multiple studies have shown that the optical properties of single-walled carbon nanotubes (SWNTs) are excitonic in nature.<sup>1-3</sup> However, a complete understanding of how these excitonic states shape the optical properties of SWNTs is lacking. Comparing the results of different published studies is difficult; the luminescence properties of SWNTs are affected by various extrinsic factors originating from synthesis and processing methods which affect the structure, sidewall quality, and environment of SWNTs. Fundamental and applied reports are hindered by poor control over the synthesis and post-processing methods. This is highlighted by the range of reported fluorescence quantum yields and luminescence lifetimes measured from ensembles or single SWNTs – they range between  $10^{-4}$  to 7 %<sup>4-8</sup> and from 5 to 200 ps,<sup>5,8-10</sup> respectively, depending on the report.

Here we use single molecule imaging and time resolved spectroscopy, photoluminescence maps, UV-vis absorbance, and Raman spectroscopy at multiple excitation wavelengths to identify different extrinsic factors which deeply influence the optical properties of SWNT.<sup>11,12</sup> Single molecular studies of individual (6,5) SWNTs showed that SWNT luminescence depends strongly on extrinsic and intrinsic factors such as sample preparation, sample environment, sidewall defects, and tube synthesis methods (HiPco or CoMoCat).<sup>11</sup> More precisely, we showed that surfactant selection and sample medium are crucial factors to obtaining SWNTs with optimum optical properties.

Ensemble measurements showed compelling spectroscopic evidence of substantial differences in chirality and diameter distribution which alter the luminescence properties within different HiPco batches.<sup>12</sup> These variations also affect SWNT solubility both in surfactant suspensions and superacids.

These findings underline the necessity for more standard production and post-processing procedures such that correlations between different reports in the literature can be drawn, and we begin to understand the complex excitonic structure of SWNTs.

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## Electrochemistry and Self-Assembly of Complex Single-Walled Carbon Nanotube (SWNT) Nanostructures

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This work explores the optical and electrochemical properties of surfactant stabilized and individually-suspended SWNTs in aqueous media via application of various external stimuli. As a result, novel nanostructures are obtained, and this allows for the study of the inherent nanotube electronic and optical properties. The goal is to engineer SWNT systems which can be tuned by understanding the mechanism of the electrochemical and environmental reactions so that applications in nanophotonics, photovoltaics, and electronics can be effectively exploited.

A strategy to obtain a surfactant/polymer protective "shell" that improves the stability and luminescence signal of individual SWNTs is presented. We used literature evidence of fluorescence emission shifts to understand the interactions between polymers and surfactants and show how morphological changes induced by extrinsic factors distort the SWNT luminescence. We developed an in-situ polymerization which creates an outer shell around the SWNT micelle that resulted in suspensions with stable luminescence at all pH, in saline buffers, and on the surface of living cells.<sup>1</sup>

Nanoparticle-nanotube structures were also fabricated by exploiting the electrochemical properties of SWNTs upon activation with alternating electromagnetic fields (EM). Under EM, metallic SWNTs will preferentially polarize creating a localized apparent field enhancement at the tips due to their high aspect ratio and electronic properties -antenna behavior. This field enhancement can generate sufficient current densities which drive electron transfer reactions preferentially at their tips, reducing transition metal salts into nanoparticles. The selectivity is assessed using microscopic and spectroscopic techniques such as atomic force microscopy, UV-vis absorbance, and Raman spectroscopy. At the end we obtain a system with tunable reaction conditions where spontaneous particle formations are controlled and selective deposition is obtained to form novel nanostructures.<sup>2</sup>

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## SEM Observation Effect on Photoluminescence Spectra from Single-Walled Carbon Nanotubes

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The optical and electrical properties of SWNTs are affected by SEM observation. During SEM observation, SWNTs are probably damaged by the irradiation of the electron beam or deposited with carbon contamination. The optical transition energies of SWNTs are sensitive to the surface conditions. For example, in ethanol or water vapor, the optical transition energies depended on the gas pressure owing to the gas molecular adsorption and desorption.<sup>1</sup> In this paper, we focused on the effect of the electron beam irradiation during SEM observation by using PL measurement. SWNTs were suspended between the pair of the quartz pillars. Before and after SEM observation, PL spectra were measured by using Ti:sapphire laser (690–830 nm in wavelength) as the excitation laser. Figure 1 shows the PL map from SWNTs after SEM observation. In SEM observation, the exposure time was 5 s, the beam current was 200 pA, the acceleration voltage was 0.5 kV and the working distance was 4 mm. While only one emission peak existed before the SEM observation, a small sub-peak appeared. While the excitation energy of the sub-peak was the same as the main peak, the emission energy of the sub-peak was smaller than that of the main peak. Though the origin of the sub-peak was not so clear, it was speculated that the sub-peak was the emission from an originally-nonradiative state. Because the sub-peak was also measured after amorphous carbon deposition on SWNTs, it was considered that the deposition during SEM observation slightly made one of the non-radiative states radiative.

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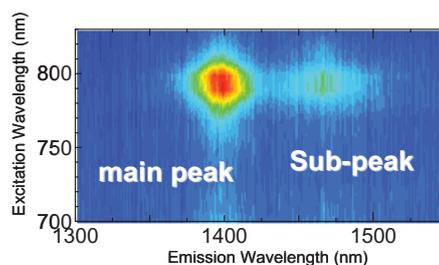


Fig. 1 PL map from (9, 8) SWNTs after SEM observation.

## Fast Band-Gap Tuning of Carbon Nanotube with Repetitious Uniaxial Strain

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It was theoretically reported that the band gap of a SWNT is varied by the strain and the change of the band gap depends on their chirality and deformation mode[1]. In this study, we have fabricated the new devices for applying uniaxial strain to the individual suspended SWNTs by using piezoelectric device. Under uniaxial strain, the emission energy of photoluminescence (PL) from an individual SWNT is shifted due to the bandgap change[2]. Moreover, we also demonstrate the fast band-gap tuning by applying a repetitious piezo voltage.

Figure 1 shows the schematic picture of a device for applying stretch to the suspended SWNTs. Suspended SWNTs were formed over the crack of the substrate. One side of the crack is opened; therefore, extension can be directly applied to the suspended SWNTs by applying piezo voltage ( $V_{piezo}$ ) to the piezoelectric device. PL from individual SWNTs under stretching were detected by a linear-array detector for a spectrum measurement and an avalanche photo-diode (APD) for a time-resolved measurement.

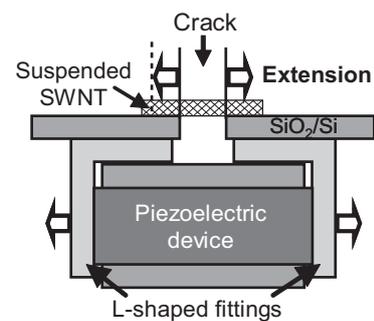


Fig. 1. Fabricated device for applying strain to the suspended SWNTs.

Figure 2(a) shows the PL spectra from a SWNT under applying  $V_{piezo}$ . In this SWNT, the PL peak is shifted to lower wavelength with increasing  $V_{piezo}$ . For this device, rectangular  $V_{piezo}$  is repetitiously applied at 413 Hz, and the time dependence of PL photon counts through a bandpass filter is measured by an APD [Fig. 2(b)]. The photon count is modulated in synchronization with  $V_{piezo}$ ; that is, the fast band-gap tuning of a SWNT with a strain is detected.

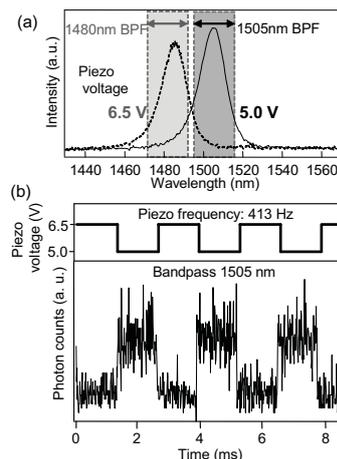


Fig. 2. (a) PL spectra at  $V_{piezo} = 5.0$  and  $6.5$  V. (b) PL counts at  $f = 413$  Hz.

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## An Optical Study of a Single Carbon Nanotube

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**Abstract** We study the photoluminescence from single carbon nanotubes. Single-walled carbon nanotubes (SWNTs) have attracted great interest in the last decade following and great strides have been made in understanding their collective optical properties. However, new approaches are necessary to further the understanding of individual nanotubes. The main difficulties in making these measurements arise from the different diameter and chirality of SWNTs giving rise to spectral overlap; residual bundles of tubes also lead to low quantum yields. Here we report on the progress has made towards the understanding of the optical properties of individual SWNTs.

We prepare different semiconducting polymer-SWNT compound samples [1] and compare the dependence of aqueous suspended SWNTs on the environment. High-density samples show strong spectral peaks at room temperature while a diluted solution is deposited on a hemispherical lens with a mean density below one nanotube per  $\mu\text{m}^2$ . With sensitive optical spectroscopy, fluorescence spectra from single nanotubes are observed, with a Lorentzian lineshape, and the spatial dispersion is confirmed by atomic force microscopy. In order to achieve a good signal to noise, resonant excitation is essential, we have therefore also undertaken photoluminescence excitation mapping so that individual tubes with known diameters and chirality can be chosen for study. Further study is in progress including temperature dependence measurements focusing on single (6,5) nanotubes and the potential application of SWNTs as single photon sources [2].

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## Photoluminescence saturation in an air-suspended SWCNT

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With reduced environmental interactions, single-walled carbon nanotubes (SWCNTs) suspended across trenches are a convenient system to study intrinsic single tube properties [1]. Under low optical excitation (polarized parallel to nanotube axis, resonant to  $E_{22}$ ), we observe linearly polarized photoluminescence (PL) with narrow room-temperature linewidths ( $\sim 12$  meV), large PL action cross-section [2] of 0.002 - 0.01 and high optical quantum efficiency (7 - 20%). Interestingly, with 150 fs duration pulses and pump fluences as low as 100 photon/pulse/SWCNT, PL dramatically saturates (Fig. 1) and does not increase for over a decade increase in pump fluence [3]. The onset of the ‘clamping’ process occurs at very low injected exciton numbers (2 to 6

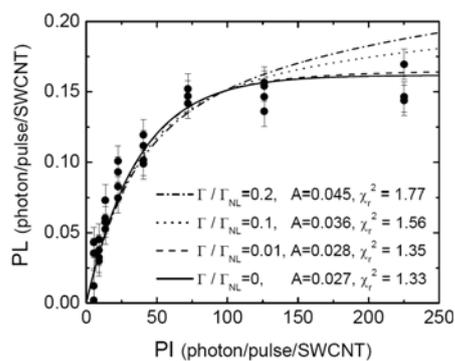


Fig. 1 Single (9,8) SWCNT  $E_{11}$  PL for incident photons (PI) resonant to  $E_{22}$ .

exciton/pulse/SWCNT), as determined through two independent means: application of the previously determined absorption coefficient,  $\sigma_{ab}=10^7$  cm<sup>2</sup>/mol C [2], and comparison of results to a stochastic model of exciton relaxation (including nonlinear exciton-exciton annihilation) [4] (curves in Fig. 1). Reduced chi-square minimization with the model sets two free parameters: the unitless absorption coefficient, A (product of  $\sigma_{ab}$  and carbon surface density [1]), and the ratio between linear and nonlinear exciton-exciton decay rates,  $\Gamma/\Gamma_{NL}$ . A study of several (9,8) and (10,8) single SWCNTs yields values for A of 0.02 - 0.06 (consistent to previous work with similar absorption linewidths [2]) and very fast nonlinear compared to linear decay rates.

Since the above analysis does not allow determination of the nonlinear decay rate independently from the linear rate, we time resolve exciton relaxation through femtosecond excitation correlation spectroscopy (FEC) [5] (Fig. 2). Total PL output is monitored as a function of time delay between two incident pulses, both of which saturate PL (PI > 100 photon/pulse/SWCNT). FEC results are modeled using the same

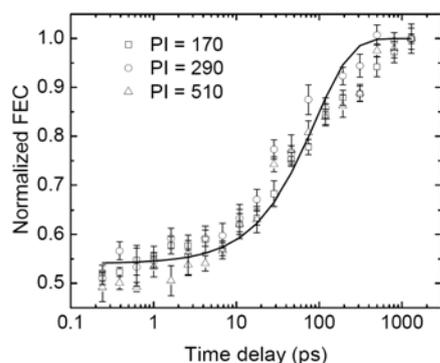


Fig. 2 FEC for a single (9,8) SWCNT with mono-exponential fit (90 ps).

stochastic model as above but for two-pulse excitation. Modeling shows that for exciton decay with two very different time constants, FEC signal is dominated by the slow process (here linear relaxation, with a monoexponential decay of 90 ps) [3]. This explains the observed FEC signal insensitivity to pump fluence (Fig. 2). Relaxation time constants for a number of SWCNTs are  $85 \pm 20$  ps. Combining the analysis results from PL clamping and FEC, we determine the nonlinear exciton decay rate is greater than  $(0.8 \text{ ps})^{-1}$ . Considering the length of the nanotubes under study (2 to 5  $\mu\text{m}$ , measured by PL spatial mapping), the annihilation process is much more efficient than expected based on models developed for encapsulated SWCNTs [6]. Past results were well explained by exciton annihilation interactions limited to diffusion lengths ranging from 6 to 90 nm [7,8]. Application of a diffusion model to our data yields unreasonably high absorption coefficients (orders of magnitude higher than reported here). With no processing or encapsulation, exciton-exciton interaction in an air-suspended SWCNT may be affected by very different microscopic processes than encapsulated SWCNTs. Possibilities include very efficient dipole-dipole interaction due to reduced screening, enhanced transport or coupling due to nonlocalized exciton wavefunction overlap and energy pooling of the excitation to only a few sites on the SWCNT allowing annihilation at very low exciton densities.

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## Symmetry-Induced Exciton Distribution between the Bright and Dark States in Single Carbon Nanotubes

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Although many experimental efforts have been devoted to understanding the optical properties of semiconducting single-walled carbon nanotubes, exciton dynamics and distribution between the exciton fine structures remain unclear. The difficulty arises in both the extrinsic non-radiative decay depending on sample preparations and their multiple exciton states originating from degenerated band structures. Therefore direct information on the optically-forbidden (dark) exciton states is needed to elucidate the intrinsic exciton dynamics.

We have performed photoluminescence (PL) spectroscopy under magnetic fields for as-grown single carbon nanotubes suspended over grooves [1]. Sharp PL spectra of single carbon nanotubes enable us to observe the dark excitons due to the Aharonov-Bohm (AB) effects. The magnetic- and temperature-dependence of the bright and dark exciton PL spectra revealed that the phonon-induced exciton scattering rate from the bright to the dark state is only one order of magnitude larger than the dark exciton recombination rate below 10 K at zero fields [2]. Our results indicate that excitons are nonequilibriumly distributed between the two states due to the different parities of their wave functions [3] and that the AB flux enhances the phonon-induced exciton scattering between these two states. Moreover, our conclusion provides a new insight concerning the non-zero PL intensities at very low temperatures that have been recognized as brightening of the dark excitons induced by defects.

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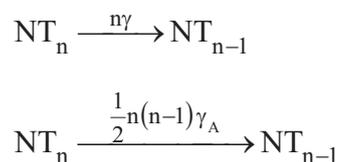
## Exciton Dynamics in Carbon Nanotubes and Nonlinear Dependence of Photoluminescence Intensity on Pump Power

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After the discovery of exciton fluorescence from single-walled carbon nanotubes (SWNT), considerable effort has been devoted to measurements of exciton dynamics in SWNT [1]. The number of excitons produced in a SWNT by photoexcitation is usually very small. Therefore, when one analyzes exciton dynamics in SWNT, one cannot use the conventional deterministic approach which describes exciton decay kinetics by using only the average number of excitons in a SWNT. Instead one has to use a stochastic approach which properly takes into account that the number of excitons in a SWNT is distributed. In the stochastic approach exciton decay kinetics is schematically described by



where  $\text{NT}_n$  stands for a SWNT with  $n$  excitons.  $\gamma$  is the total unimolecular decay constant of an exciton.  $\gamma_A$  is the Auger recombination rate constant in a SWNT which contains two excitons. On the basis of the above model we have derived an analytical expression for the average number  $\bar{n}(t)$  of excitons in a SWNT and explained the experimentally observed fluorescence decay kinetics in SWNT [2].

Recently several groups have measured fluorescence intensity from SWNT as a function of pump power and found a nonlinear dependence [3-5]. The fluorescence intensity is given in terms of the average number of excitons in a SWNT

$$\eta(\infty) = \int_0^\infty \gamma_r \bar{n}(t) dt$$

where  $\gamma_r$  is the radiative rate constant of an exciton. We have calculated the fluorescence intensity as a function of pump power for several values of the ratio  $\gamma_A/2\gamma$  (Fig. 1). On the basis of the present theory we have analyzed the observed dependence of fluorescence intensity on pump power.

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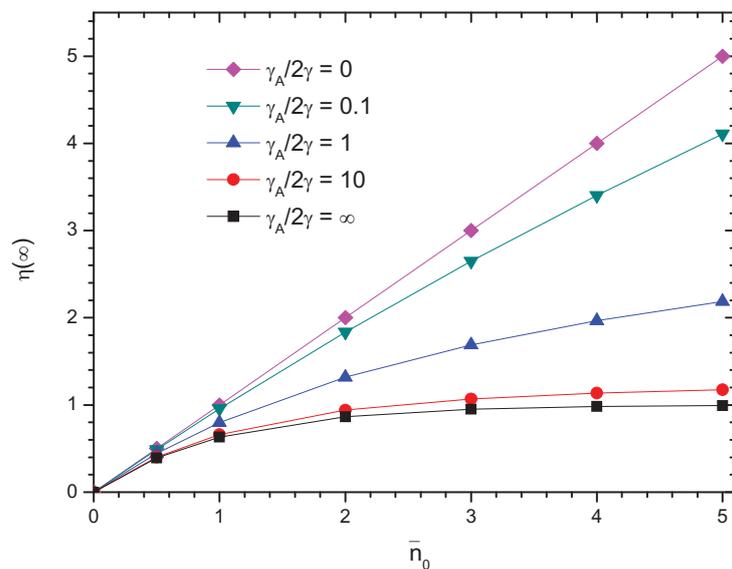


Fig. 1. Dependence of the photoluminescence intensity  $\eta(\infty)$  on the average initial number  $\bar{n}_0$  of excitation produced in a SWNT by an excitation pulse.

## Exciton Dephasing Dynamics in Single-Walled Carbon Nanotubes

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Our recent observation of remarkably long room temperature optical dephasing times ( $T_2$ ) for semiconducting SWNTs demonstrates the important role of coherent excitons in the fundamental photophysics of this quasi-1D nanomaterial. Using femtosecond photon echo measurements collected at different excitation intensities and lattice temperatures (77-294 K) we found that both exciton-exciton and exciton-phonon scattering have profound effects on spectral broadening and exciton dephasing processes [1-3]. Experiments employing three-pulse photon echo peak shift (3PEPS) spectroscopy at room temperature further allowed us to quantify inhomogeneous spectral broadening and to estimate exciton-phonon coupling strength associated with the  $E_{11}$  transition [1]. Collectively, these advanced spectroscopic techniques provide a direct probe of exciton dephasing dynamics through elimination of the population relaxation effects which dominate existing ultrafast measurements [4].

In this contribution, we report our latest results applying both two-pulse photon echo (2PE) and 3PEPS spectroscopies to aqueous and polymer based samples highly enriched in the (6,5) nanotube type. Complimentary fifth order photon echo results are also introduced. These experiments were performed as a function of laser pump fluences for temperatures ranging from 4 to 294 K. With increasing pump fluence, both the photon echo peak shift and the  $T_2$  time decrease by over one fold for a given lattice temperature. Numerical simulations are used to show how increasing exciton density induces optical dephasing owing to enhanced coherent exciton annihilation from one-dimensional confinement.

In recent aqueous phase measurements, a long room temperature dephasing time of 205 fs is extracted for the (6,5) tube species, which is in stark contrast to those found in molecular systems and quantum dots. To understand this effect, we examined our extracted temperature-dependent dephasing times (fig. 1) and the initial 2PE decay profile. Their complex behavior suggests that rapid  $E_{11}$  dephasing is mitigated by delocalized excitons averaging over phonon bath disorder in a confinement enhanced exchange narrowing process. This further suggests the occurrence of remarkable exciton delocalization, and makes nanotubes ideal to study many-body coherent effects in spatially confined systems in real time.

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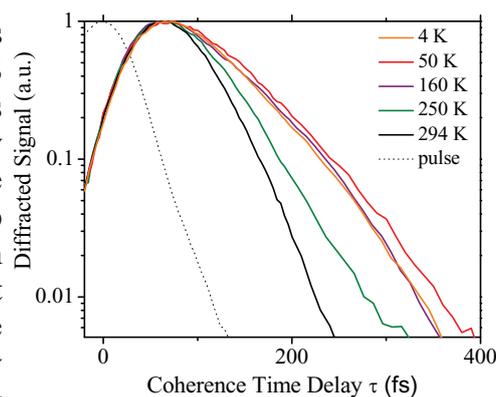


Fig. 1 –Exponential decay of 2PE signal for various temperatures ( $T_2 = 4\tau_{\text{exp}}$ ).

## Exciton Radiative Lifetimes and Coherence Lengths in Single-Walled Carbon Nanotubes

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We have studied the radiative lifetimes of one-dimensional excitons in single-walled carbon nanotubes (SWNTs) from simultaneous measurements of the photoluminescence (PL) lifetimes [1] and the PL quantum yields. A high-quality sample of PFO [poly(9,9-dioctylfluorenyl-2,7-diyl)] dispersed-SWNTs [2] was used for the optical measurements. The PL lifetimes and the PL quantum yields were ~40-60 ps and ~1.5% for small diameter (<1nm) SWNTs, respectively. The evaluated radiative lifetimes were ~3-4 ns for SWNTs with diameters ~0.8-1.0 nm at room temperature. For SWNTs with diameters more than 1 nm, the radiative lifetimes slightly increased with the tube diameter. The exciton spatial coherence lengths were of the order of 10 nm along the tube axis at room temperature, as deduced from the radiative lifetimes. Furthermore, we discuss the dynamics of bright and dark excitons [3] from the temperature dependence of the radiative lifetimes.

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## Excitons in carbon nanotube within effective-mass approximation

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A carbon nanotube is composed of concentric tubes of rolled two-dimensional graphite sheets, on which hexagons are arranged in a helical fashion about the axis. Since the first discovery quite a number of studies have been reported on their electronic properties because of their unique topological structures. The purpose of this talk is to give a brief review on recent theoretical investigations on optical properties of carbon nanotubes in the presence of Aharonov-Bohm magnetic flux (see a recent review [1, 2] and references cited therein).

The topics include an effective-mass description of electronic states and close relationship with neutrino physics, interaction effects on the band structure [3, 4], optical absorption for parallel polarization and strong exciton effect [5, 6], the Aharonov-Bohm (AB) splitting observed recently [7, 8], dark and bright excitons due to the short-range part of the Coulomb interaction causing mixing between K and K' points, and their ordering and relative energy splitting and strong effects of AB flux [9], and two-phonon absorption due to exciton excited states [10]. Without exciton effects, there are no peaks in absorption spectra of light polarized perpendicularly to a tube axis because of strong depolarization effect [11]. However, the strong exciton effect causes absorption peaks for perpendicular light though its intensity is reduced in comparison with that for parallel light [12], as experimentally observed recently [13, 14]. The exciton effect is important also in metallic carbon nanotubes [15]. The family effect can also be understood, in particular for the first semiconducting gap, mostly by considering trigonal warping described by a higher-order  $k \cdot p$  term [16], and by the curvature and associated lattice distortion described by effective magnetic flux [17].

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## Inter-Valley Mixing of Carbon Nanotube Excitons by a Short-Range Impurity

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Optical properties of carbon nanotubes (CN's) have attracted much attention because of, e.g., the strong enhancement of exciton effects arising from the Coulomb interaction and the one-dimensional nature [1]. The valley degeneracy of CN's, which causes the fine structure of excitons, also gives a rich variety of phenomena. In this work, we have examined effects of an impurity potential on excitons in semiconducting CN's within the effective-mass approximation. We clarify how the inter-valley coupling of excitons is generated by impurity scattering and how energy levels of optically active (bright) and inactive (dark) excitons are split.

When the exciton state consisting of an electron in the  $K_1$  valley and a hole in the  $K_2$  valley ( $K_1, K_2=K$  or  $K'$ ) is expressed by  $|K_1K_2\rangle_Q^u$  where  $u=1s, 2p, 2s \dots$  and  $Q$  is the center-of-mass wave number, only bonding state  $|b1\rangle_0^{1s,2s,\dots} = |KK\rangle_0^{1s,2s,\dots} + |K'K'\rangle_0^{1s,2s,\dots}$  is bright and all the others,  $|b1\rangle_{Q\neq 0}^u, |a1\rangle_Q^u$  (anti-bonding state of  $KK$  and  $K'K'$  excitons),  $|b2\rangle_Q^u$  and  $|a2\rangle_Q^u$  (bonding and anti-bonding states of  $KK'$  and  $K'K$  excitons), are dark in the absence of impurity scattering. The presence of a short-range impurity gives rise to mixing between  $KK/K'K'$  and  $KK'/K'K$  excitons due to the inter-valley electron scattering between the  $K$  and  $K'$  valleys. As a result, we can find nonzero transitions between several exciton states as shown in Fig. 1. This reveals two important facts: (i) The bonding and anti-bonding states still remain completely decoupled. (ii)  $|b1\rangle_0^{1s}$  has coupling only to  $|b1\rangle_Q^{2p}$  and  $|b2\rangle_Q^{2p}$  with  $Q \neq 0$ . The former means no any peaks of anti-bonding exciton states in absorption spectra in the presence of a single impurity. The latter also leads to no any peaks of  $2p$  excitons for the weak impurity potential although their mixing contributes to the broadening of spectra.

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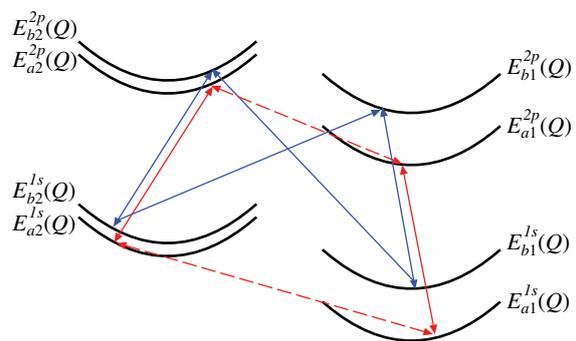


Fig. 1 Schematics of energy levels of 1s and 2p excitons and possible nonzero transitions by impurity scattering.

## Theory of 1D Exciton and its Application to SWNT

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**Motivations** We shall reinvestigate the earlier results [1,2] for one dimensional excitons from the viewpoint of quantum mechanics of singular potentials [3,4].

**Results** We show that the binding energy of the one dimensional exciton remains finite even in the limit of the bare Coulomb potential. In the same limit, wavefunctions of the continuum spectrum with even parity (direct allowed transitions) will not vanish at the origin, but result in non-zero, though suppressed, Sommerfeld factors. We require that we should be able to find a plane wave of the free particle when we switch off the Coulomb interaction, while the one in Ref's [1] and [2] imposes non-trivial boundary condition at the origin. This difference in boundary conditions at the singularity results in different spectrum of exciton states with even parity in addition to the ordinary hydrogen-like spectrum for states with odd parity (Fig. 1). Since even and odd parity states are determined by the poles of the di-Gamma function and the Gamma function, respectively, they appear in an alternate manner. We have made an analysis of the experimental result of Ref. [5] by use of this new exciton spectrum and found that the dielectric constant of SWNT should be about 1.6 times larger than that of Ref. [5].

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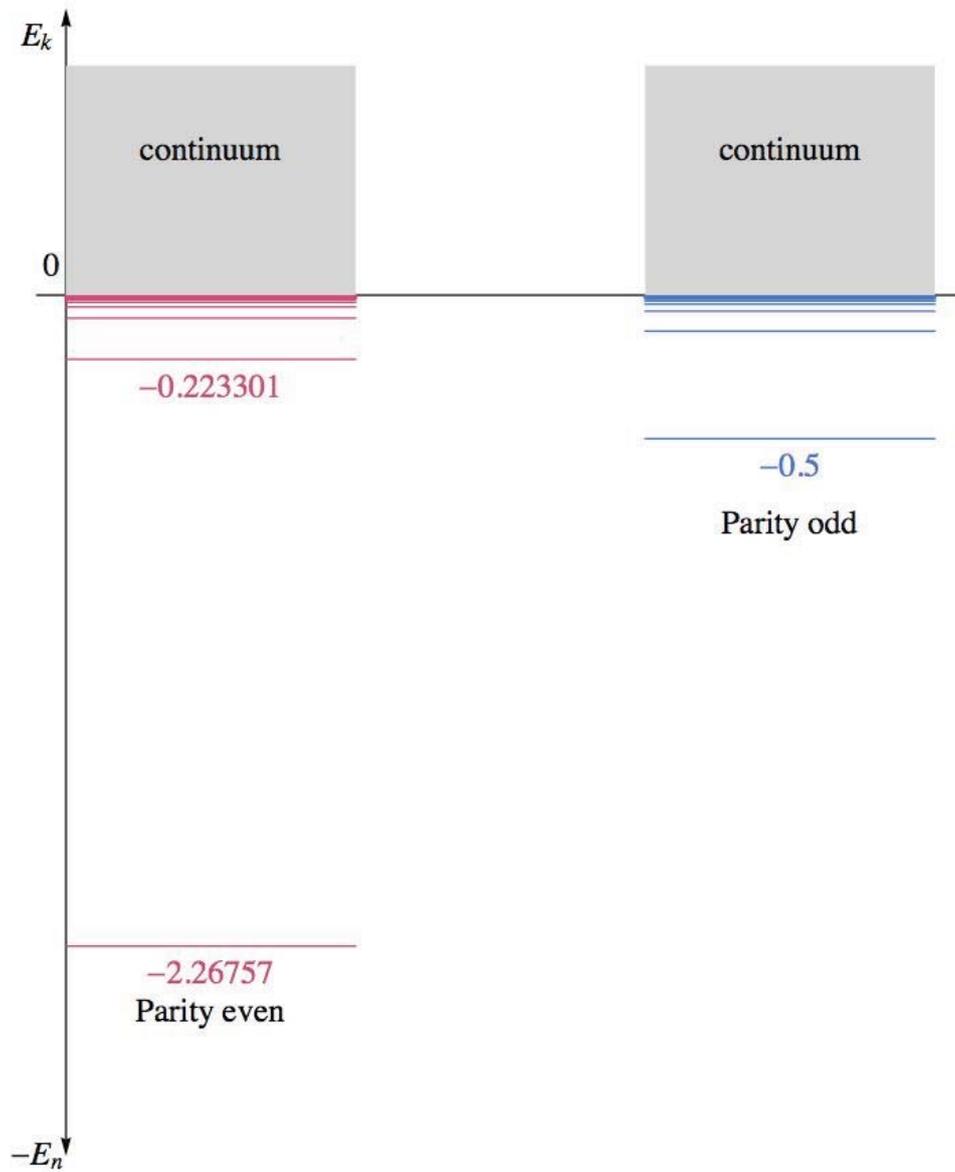


Fig. 1. New spectrum of the 1D exciton

## Reflectance spectra of individual metallic single walled carbon nanotubes.

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### Abstract:

Due to the reduced dimensionality, single-walled carbon nanotubes show strong Coulomb interaction and enhanced electron-phonon interactions. Experimental evidence for both phenomenon in the individual nanotube level is few. We report reflection experiment of an individual single-walled carbon nanotube that shows both.[1] Individual (13,10) metallic nanotube is fabricated cross a slit, focused laser light from near-infrared to visible shine on the nanotube and reflection spectrum is collected. The lower energy part of the spectrum features two well defined peaks separated by 0.2eV. We show that while the lower peak is from the lowest exciton, the higher peak could be the phonon side band of exciton, a result of strong electron-phonon coupling. Our calculation also gives estimation of static dielectric constant.[2]

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## Magneto-optical Spectroscopy of Metallic Single-Walled Carbon Nanotubes

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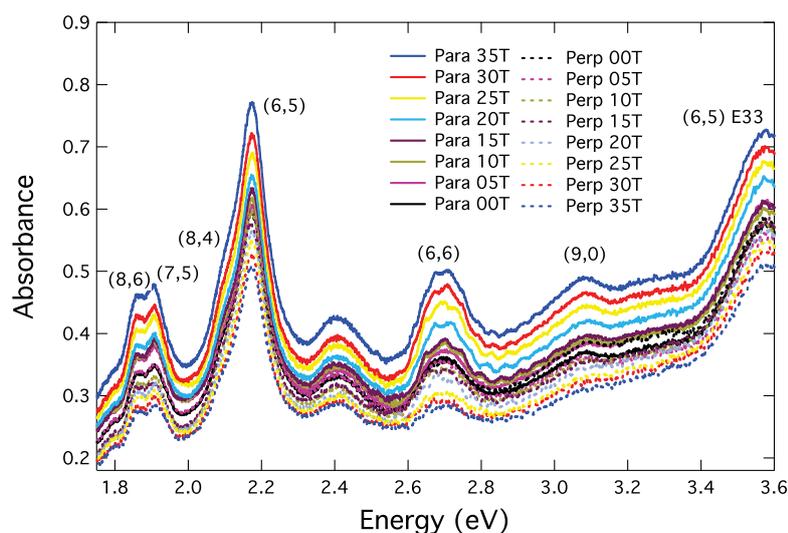
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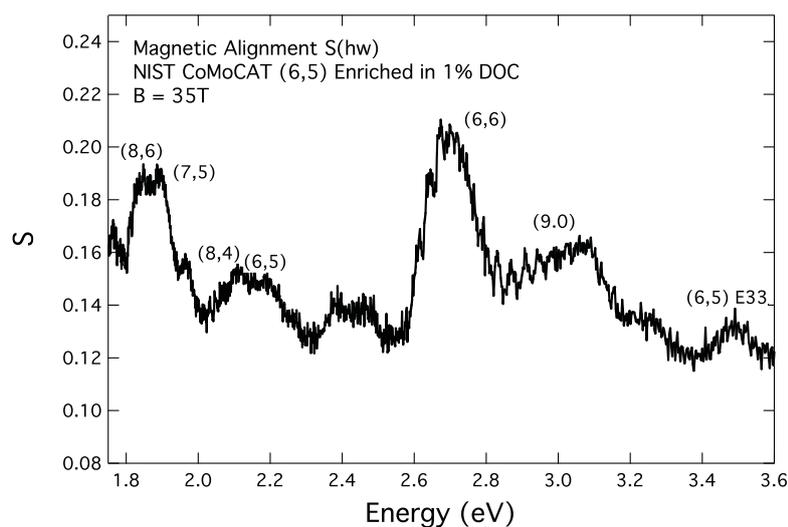
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Through polarization-dependent magneto-absorption spectroscopy, we have extracted the magnetic susceptibility anisotropy for metallic carbon nanotubes and compared it with that of semiconducting carbon nanotubes for the first time. The magnetic properties of carbon nanotubes (both metallic and semiconducting species) change with the direction of the magnetic field with respect to the tube axis, yielding a magnetic anisotropy given by  $\Delta\chi = \chi_{//} - \chi_{\perp}$ . Metallic nanotubes are paramagnetic along the tube axis ( $\chi_{//} > 0$ ) and diamagnetic in the perpendicular direction ( $\chi_{\perp} < 0$ ), whereas semiconducting tubes are diamagnetic in all directions ( $\chi_{//}, \chi_{\perp} < 0$ ) [1]. This anisotropy of magnetic susceptibilities results in the nanotubes in solution aligning as the magnetic field is increased. This, combined with the anisotropic optical absorption properties of carbon nanotubes, allows for the use of polarization-dependent optical absorption to measure the degree of magnetic alignment through magnetic linear dichroism (MLD) spectroscopy. Previous MLD studies on HiPco semiconducting nanotubes found that  $\Delta\chi \approx 1.4 \times 10^{-5}$  emu/mol, but there was no information on  $\Delta\chi$  for metallic nanotubes [2,3].

Our measurements on length-sorted, (6,5)-enriched CoMoCAT single-walled carbon nanotubes were made using the 35 T Hybrid Magnet in the High Magnetic Field Facility of the National Institute of Materials Science in Tsukuba, Japan. We measured absorption with light polarization both perpendicular and parallel to the magnetic field as seen in Fig. 1, to determine the MLD. By relating these values with the nematic order parameter for alignment  $S$  (Fig. 2), we found that the (6,6) nanotube aligns more rapidly with the magnetic field than semiconducting nanotubes [specifically the (6,5) tube].



**Figure 1: Magneto-absorption in UV and visible of (6,5)-enriched CoMoCAT SWNTs. The solid lines represent spectra take with light polarization parallel to the magnetic field and dashed lines are those with light polarization perpendicular to the field.**



**Figure 2: Nematic order parameter  $S$  vs. energy. Alignment is a function of temperature ( $T$ ), diameter, and length ( $L$ ). In our case  $T = 300$  K and  $L \sim 1$   $\mu\text{m}$ . Note that the (6,6) nanotube exhibits the largest alignment.**

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## Anisotropic Terahertz Response of Aligned Carbon Nanotubes

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Using polarization-dependent terahertz (THz) time-domain spectroscopy, we have studied the anisotropic conduction properties of a thin film of highly aligned single-walled carbon nanotubes. When the THz polarization was parallel to the nanotube alignment direction, there was strong absorption, while virtually no absorption was observed when the THz polarization was perpendicular to the nanotube alignment axis. See Fig. 1, where we present transmitted time-domain waveforms as the angle between the THz polarization and the nanotube alignment direction was varied.

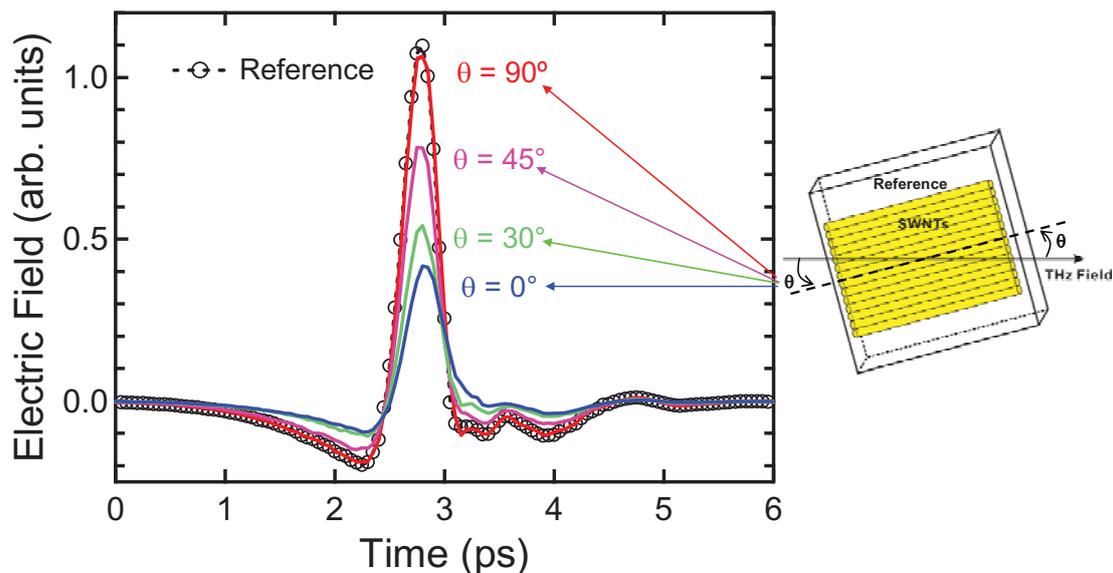


Fig. 1 Transmitted THz electric field signals for the reference sapphire substrate (dashed curve with circles) and for the nanotube film for different polarization angles (colored solid curves).

The sample was synthesized via chemical vapor deposition and transferred onto a sapphire substrate through a high temperature water etching process [1]. Experimental details are described elsewhere [2]. Through a proper model, the THz complex dynamic conductivity of the SWNTs was extracted and showed a non-Drude-like frequency dependence, with the real part monotonically increasing with increasing frequency. The degree of polarization in terms of absorbance was calculated to be 1, and the reduced linear dichroism was calculated to be 3 using the theory of linear dichroism for an ensemble of anisotropic molecules, which demonstrates the nematic order parameter of the SWNTs in the film to be 1. This indicates that the alignment of the nanotubes is perfect and any misalignment must have characteristic length scales much smaller than the wavelengths used in these experiments (1.5 mm – 150  $\mu\text{m}$ ). All these findings suggest that this type of aligned single-walled carbon nanotube film performs as an ideal linear polarizer in the THz frequency range.

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## Finite-length effects on optical absorption in metallic carbon nanotubes

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Carbon nanotubes are a one-dimensional conductor consisting of rolled graphene sheets. Recently, cutting and length selection of single-wall carbon nanotubes have been studied [1-3]. Optical absorption in low-frequency region was recently reported in such nanotubes [4-6]. In short carbon nanotubes with good conductivity, depolarization field in the axis direction becomes important due to the accumulated charge at both ends of nanotubes in optical absorption [7]. The purpose of this paper is to calculate a low-frequency optical response in metallic carbon nanotubes with finite length.

We consider a metallic carbon nanotube with finite length  $l$  under an external electric field in the axis direction. We solve the electrostatic equations instead of full Maxwell's equation, which is justified by the fact that the plasmon velocity in carbon nanotubes is much smaller than the light velocity. The response of the system can generally be described by a nonlocal conductivity. We consider the case that the length of the nanotube is much larger than the mean free path. Thus, we can neglect effects of edges on the conductivity and use the Boltzmann conductivity in infinitely long nanotubes, employing a relaxation-time approximation. In actual numerical calculations, we consider a periodic array of the nanotubes and calculate an effective electric field including effects of polarization charges.

Calculated power absorption oscillates with decreasing  $\sim \omega^{-2}$  in the low frequency region. The frequency of the peaks is inversely proportional to the length of nanotubes. Calculated power absorption is compared with that in a single-mode approximation in which a resonance occurs at frequency  $\omega = v_Q Q_n$  with  $Q_n \approx (2n+1)\pi/l$  ( $n=0, 1, \dots$ ), where  $v_Q$  is a plasmon velocity and a few times larger than the Fermi velocity in carbon nanotubes. We find that the calculated peaks are shifted significantly from those in the single-mode estimation, except for the main peak ( $n=0$ ). Actually, the electric field shows significant mixture of other modes, which are involved to form the induced electric field at the both ends of the nanotubes.

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## Resonant Optical Forces for Nanotube Aggregation in Solution

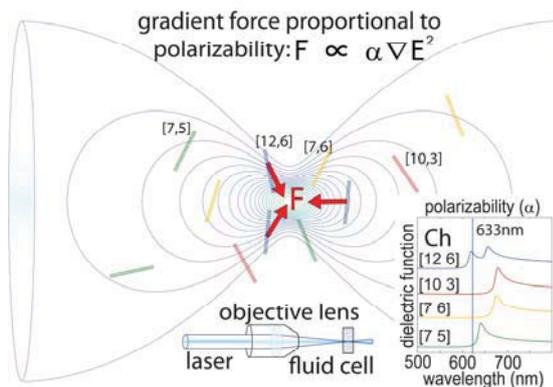
Thomas Rodgers, Satoru Shoji, and Satoshi Kawata

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We present a technique for using tightly focussed light to selectively aggregate chiralities of single walled carbon nanotube (SWCNT) [1,2,3]. The mechanical force of light is well understood in the context of optical trapping [4] and is attributed primarily to unbalanced dipole induction by an electrical field gradient. This force is essentially non-perturbative and non-destructive. As the optical gradient force is directly proportional to the polarizability of the object in the trapping field, the force must vary with wavelength for materials with electronic resonances at optical frequencies. The optical gradient force is written in its simplest form:  $\{F(r) \propto \alpha \nabla E^2\}$  Where  $\alpha$  is the tensor of polarizability of the object for a given optical wavelength,  $\nabla$  is the gradient operator, and  $E$  is the amplitude of the electric field. Here  $\alpha$  is of particular interest due to the highly resonant nature of SWCNTs.

The optical resonances of SWCNTs have been well studied by absorption, resonance Raman and photoluminescence spectroscopy, and these techniques have proven to be reliable measures for determining which SWCNTs are present in a sample of randomly distributed chiral species [5]. We use time-resolved Raman spectroscopy to analyse the aggregation of nanotubes by a laser focussed through a high numerical aperture objective lens. The dynamics suggests a chiral selectivity of the optical gradient force. This result is a step towards the arbitrary, all-optical sorting of nanotube chiralities.



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## Molecular physisorption at the groove and interior of single-walled carbon nanotubes

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Physical and chemical properties of single-walled carbon nanotubes (SWCNTs) are sensitive to defects. However, the methods to characterize the defects of SWCNTs have been limited to observation of the local structure by electronic microscope and scanning probe microscope. To explore the evaluation method, we presented an experimental study of H<sub>2</sub> physisorption on SWCNTs using the cryogenic thermal-desorption spectroscopy (TDS) [1]. The desorption peaks indicate that H<sub>2</sub> adsorbed to the groove site, inside and interstitial channel of the SWCNTs.

In this presentation, we investigated the adsorption site of molecules on SWCNTs by changing the molecular size of adsorbents. SWCNTs were produced by an arc discharge method with Fe and Ni catalysts. We produced defects by heating the samples in air. After the samples were exposed to H<sub>2</sub> or N<sub>2</sub> at a sample temperature of 10K, we performed TDS for SWCNTs.

Fig.1 shows TD spectra of N<sub>2</sub> from SWCNTs, which reveal three distinct desorption peaks at 27, 45 and 59K. While the peak at 27K is attributed to N<sub>2</sub> desorption from the multilayer, the other two peaks correspond to N<sub>2</sub> adsorbed at either groove, interstitial or inside of the tubes. By comparison with the H<sub>2</sub> TDS data, we regard the peak at 45K as N<sub>2</sub> desorption from the groove site. Since the diameter of the N<sub>2</sub> molecule is larger than the interstitial channel size, N<sub>2</sub> can not access the interstitial channel. Thus, the peak at 59K is assigned to N<sub>2</sub> adsorbed at the inside of the tubes.

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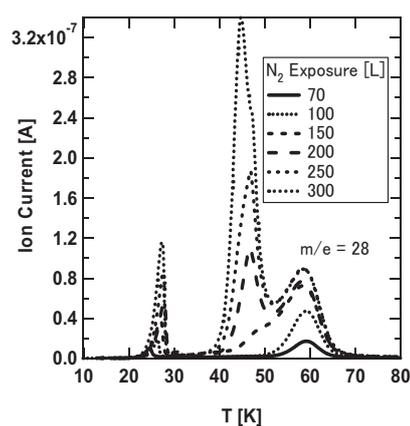


Fig1. Thermal desorption spectra of N<sub>2</sub>.

## Efficient dissociation of carbon nanotube excitons in organic semiconductor / carbon nanotube heterojunctions for photovoltaics and ultrabroadband photodetection

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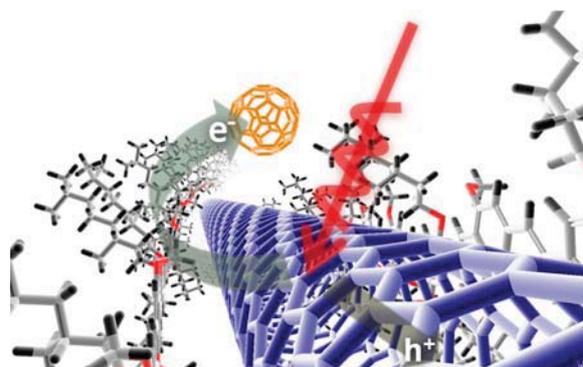
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Semiconducting single-walled carbon nanotubes are intriguing materials for the optically absorptive components of photovoltaic solar cells and photodetectors because of their tunable optical band gap in the near-infrared, strong optical absorption coefficient  $> 10^5 \text{ cm}^{-1}$ , and excellent charge transport characteristics.<sup>1,2</sup>

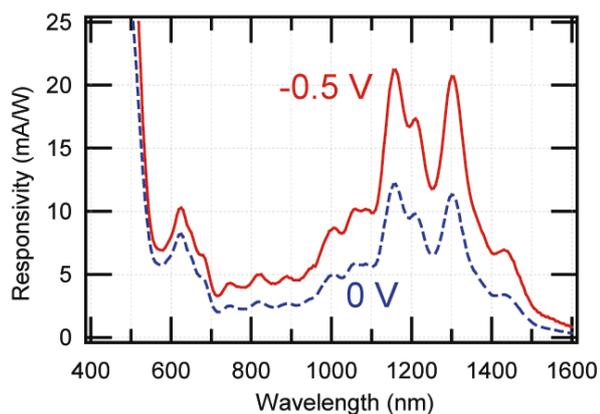
Yet, despite their outstanding materials properties, carbon nanotubes have had limited impact as the optically absorptive components of photosensitive devices. Single (one) nanotube-based photodetectors have been demonstrated but have small absolute absorbance which limits their practicality, and photovoltaics and photodetectors based on bulk films of many nanotubes have been hindered by the large exciton binding energy in nanotubes  $> 0.1 \text{ eV}$ .

Here, we demonstrate that photogenerated excitons in bulk films of carbon nanotubes can be efficiently dissociated by interfacing the carbon nanotubes with electron-withdrawing organic semiconductors such as C<sub>60</sub> (Fig. 1), resulting in a photovoltaic effect.<sup>3</sup> Specifically, we show that heterojunctions between bulk films of carbon nanotubes and thin films of C<sub>60</sub> exhibit a photocurrent even in the absence of an applied bias and exhibit a photovoltage under open-circuit condition in response to near-infrared illumination at the E<sub>11</sub> optical band gap of semiconducting carbon nanotubes (Fig. 2).

The external quantum efficiency (fraction of incident photons resulting in separated electrons and holes at the cathode and anode) is  $>2\%$  for optical excitation at the E<sub>11</sub> transition and is absorption limited. The internal quantum efficiency (fraction of *absorbed* photons resulting in dissociated and separated carriers at the anode and cathode)  $> 40\%$ , indicating that the driving force for exciton dissociation and charge



**Fig. 1.** Schematic depicting dissociation of a photogenerated exciton in a semiconducting single-walled carbon nanotube and electron transfer to C<sub>60</sub>.



**Fig. 2.** Spectral responsivity of HiPCO nanotube/C<sub>60</sub> heterojunction diode at 0 V and -0.5 V applied bias (dashed and solid line, respectively). Peak external and internal quantum efficiency at 1155 nm  $> 2\%$  and  $> 40\%$ , respectively.

separation at the nanotube/C<sub>60</sub> interface is very efficient.

These experimental observations are unique from previous work in which carbon nanotubes have been utilized as optically *inactive* transparent anodes and cathodes and as charge transport adducts in organic solar cells in which near-infrared band gap sensitivity has not reported.

The discovery of efficient exciton dissociation and a photovoltaic effect in our nanotube/C<sub>60</sub> heterojunctions opens the door for new and unique architectures for solar cells and ultrabroadband photodetectors that exploit the exceptional electrical, optical, and materials properties of carbon nanotubes.

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