

# WONTON 2018

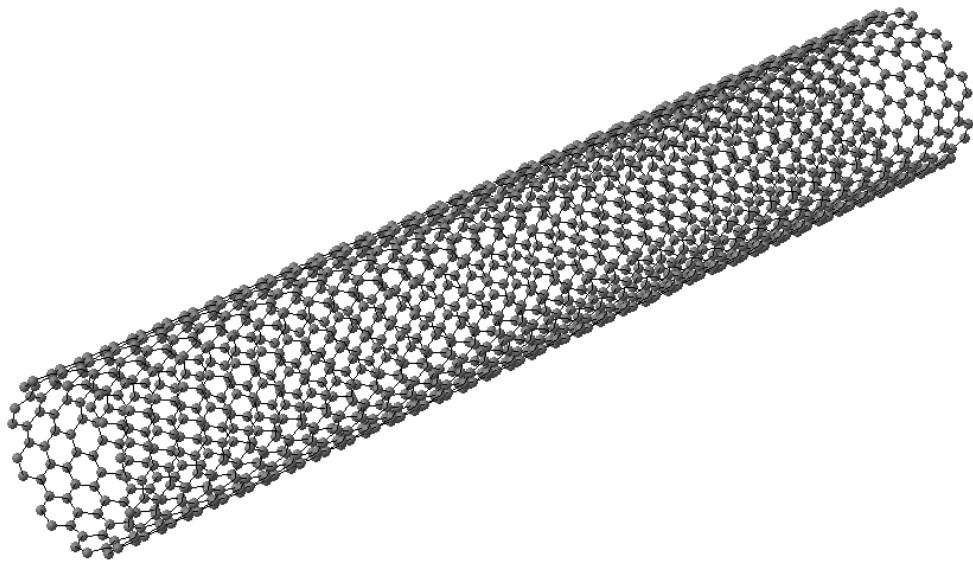
## 7th Workshop on Nanotube Optics and Nanospectroscopy



Sunday, 8 July 2018 - Thursday, 12 July 2018  
The Prince Hakone Lake Ashinoko

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RIKEN

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# Time Table

	Sunday 08 July	Monday 09 July	Tuesday 10 July
09:00		Junichiro Kono (Rice U.)	Feng Wang (UC Berkeley)
09:30		Yuhei Miyauchi (Kyoto U.)	Yoshikazu Homma (Tokyo U. of Science)
10:00		Matt Graham (Oregon State U.)	Riichiro Saito (Tohoku U.)
10:20		Coffee Break	Coffee Break
10:40		YuHuang Wang (U. of Maryland)	Jana Zaumseil (U. of Heidelberg)
11:10		Tomohiro Shiraki (Kyushu Univ.)	Michael Arnold (U. of Wisconsin-Madison)
11:40		Antonio Setaro (Freie Univ. Berlin)	Ken-ichi Sasaki (NTT Basic Research Lab.)
12:00		Lunch	Lunch
14:00		Ralph Krupke (KIT)	Free Discussion
14:30		Taishi Takenobu (Nagoya U.)	
15:00		Alexandre Plaud (CNRS)	
15:20		Coffee Break	
15:40		Christophe Voisin (CNRS)	
16:10		Alexander Högele (LMU München)	
16:40		Akihiro Ishii (RIKEN)	
17:00			
18:00	Welcome Reception & Registration	Poster Session: 1	
19:00		Dinner	Dinner
20:00			

## Time Table

	Wednesday 11 July	Thursday 12 July
09:00	Yoshihiro Iwasa (U. of Tokyo)	R. Bruce Weisman (Rice U.)
09:30	Liu Kaihui (Peking U.)	Stephen Doorn (Los Alamos)
10:00	Maja Feierabend (Chalmers U. of Technology)	Andreas Sperlich (JMU Würzburg)
10:20	Coffee Break	Coffee Break
10:40	Daniel Heller (MSKCC)	Jeffrey Blackburn (NREL)
11:10	Ming Zheng (NIST)	Hiromichi Kataura (AIST)
11:40	Yutaka Takaguchi (Okayama U.)	
12:00	Lunch	Lunch
14:00	Tobias Hertel (JMU Würzburg)	
14:30	Laurent Cognet (U. of Bordeaux)	
15:00	Achim Hartschuh (LMU München)	
15:20	Coffee Break	
15:40	Etienne Gauffrès (CNRS)	
16:10	Sofie Cambré (U. of Antwerp)	
16:40	Shigeo Maruyama (U. of Tokyo)	
17:00		
18:00	Poster Session: 2	
19:00	Dinner	
20:00		

# Sunday 08 July 2018

18:00-20:00

Welcome Reception & Registration

# Monday 09 July 2018

09:00-09:30	KONO, Junichiro : Optics and Photonics of Aligned Carbon Nanotube Films
09:30-10:00	MIYAUCHI, Yuhei : Mid- and high-temperature exciton photophysics of carbon nanotubes and their applications
10:00-10:20	GRAHAM, Matt : Tunable Interlayer Excitons in Folded & Twisted Graphene
10:20-10:40	Coffee Break
10:40-11:10	WANG, YuHuang : Trions at a Trapping Defect
11:10-11:40	SHIRAKI, Tomohiro : Molecular design for photoluminescence modulation of locally functionalized single-walled carbon nanotubes
11:40-12:00	SETARO, Antonio : Nonperturbing, conjugation-preserving covalent functionalization of single-walled carbon nanotubes
12:00-13:30	Lunch
14:00-14:30	KRUPKE, Ralph : Electroluminescence from carbon nanotubes
14:30-15:00	TAKENOBU, Taishi : Electrochemically doped light-emitting devices of transition metal dichalcogenide monolayers
15:00-15:20	PLAUD, Alexandre : Probing exciton-exciton annihilation in hBN with cathodoluminescence experiments
15:20-15:40	Coffee Break
15:40-16:10	VOISIN, Christophe : Bright and tunable single-photon emission with a carbon nanotube embedded in a fiber micro-cavity
16:10-16:40	HÖGELE, Alexander : Spectroscopy of localized excitons in cryogenic carbon nanotubes
16:40-17:00	ISHII, Akihiro : Room-temperature single photon emission from carbon nanotubes
17:00-19:00	Poster Session: 1
19:00-20:30	Dinner



# Poster Session 1

	Poster No.
[2] UMEYAMA, Tomokazu : Photophysical properties of porphyrin–single walled carbon nanotube linked systems with various spacer lengths	P-1
[6] JANAS, Dawid : Thin films from carbon nanotubes of highly tuned structure and properties	P-3
[8] NUTZ, Manuel : Cryogenic spectroscopy of $sp^3$ defect states in carbon nanotubes	P-5
[12] FUKAZAWA, Yusuke : High-Speed and integrated graphene blackbody emitters	P-7
[14] KAWABE, Rintaro : Photon antibunching in single-walled carbon nanotubes at telecommunication wavelengths and room temperature	P-9
[16] FÖRG, Michael : Cavity-control of bright and dark interlayer excitons in van der Waals heterostructures	P-11
[20] SHIRAISHI, Tomonari : Evaluation of substituent effects on the potential levels of locally-functionalized single-walled carbon nanotubes using <i>in situ</i> photoluminescence spectroelectrochemistry	P-13
[22] ORCIN-CHAIX, Lucile : Optical properties of core-shell systems based on carbon nanotubes	P-15
[24] OHFUCHI, Mari : Optical Properties of Oxidized Single-Wall Carbon Nanotubes	P-17
[28] MÜLLER, Kerstin : Kinetics of diazonium functionalization of carbon nanotubes	P-19
[30] MAEDA, Yutaka : Effect of functionalization and subsequent thermal treatment on photoluminescence properties of single-walled carbon nanotubes	P-21
[46] KOMATSU, Natsumi : Modulation-Doped Multiple Quantum Wells of Aligned Single-Wall Carbon Nanotubes	P-23
[54] GOMULYA, Widianta : Enhanced Raman scattering of graphene using double resonance in silicon photonic crystal nanocavities	P-25
[56] OTSUKA, Keigo : Tracing individual growth process of single-walled carbon nanotubes by digitally coding isotope labels	P-27
[60] PU, Jiang : Monolayer $WSe_2$ - $MoS_2$ Lateral Heterojunction Light-Emitting Diodes	P-29

## Tuesday 10 July 2018

09:00-09:30	WANG, Feng : Luttinger liquid in carbon nanotubes
09:30-10:00	HOMMA, Yoshikazu : Single SWNT spectroscopy for nano-metrology
10:00-10:20	SAITO, Riichiro : Conservation law of angular momentum in Raman spectroscopy using circularly polarized light
10:20-10:40	Coffee Break
10:40-11:10	ZAUMSEIL, Jana : Exciton-Polaritons, Plexcitons and Trion-Polaritons in Single-Walled Carbon Nanotube Thin Films and Devices
11:10-11:40	ARNOLD, Michael : Excitons in Coupled Nanotube Photovoltaic Thin Films
11:40-12:00	SASAKI, Ken-ichi : Theory of a carbon-nanotube polarization switch
12:00-13:30	Lunch
13:30-19:00	Free Discussion
19:00-20:30	Dinner

## Wednesday 11 July 2018

09:00-09:30	IWASA, Yoshihiro : Transition metal dichalcogenide nanotubes
09:30-10:00	KAIHUI, Liu : Stacking-dependent Interlayer Couplings in 2D Materials
10:00-10:20	FEIERABEND, Maja : Controlling the optical fingerprint of transition metal dichalcogenides via molecules, strain and disorder
10:20-10:40	Coffee Break
10:40-11:10	HELLER, Daniel : Carbon Nanotube Optical Bandgap Modulation for Cancer Research and Diagnosis
11:10-11:40	ZHENG, Ming : DNA-wrapped carbon nanotubes for sorting and multiplex optical sensing
11:40-12:00	TAKAGUCHI, Yutaka : H <sub>2</sub> -evolving SWCNT Photocatalysts for Effective Use of Solar Energy
12:00-13:30	Lunch
14:00-14:30	HERTEL, Tobias : Killer defects in semiconducting SWNTs
14:30-15:00	COGNET, Laurent : Nanoscale Imaging in, of & with Luminescent Single Walled Carbon Nanotubes
15:00-15:20	HARTSCHUH, Achim : Antenna-Controlled Antibunching in the Photoluminescence of Single Carbon Nanotubes
15:20-15:40	Coffee Break
15:40-16:10	GAUFRÈS, Etienne : Optical properties of dyes confined into carbon and boron nitride nanotubes
16:10-16:40	CAMBRÉ, Sofie : Diameter-dependent optical absorption and energy transfer from encapsulated dye molecules to single wall carbon nanotubes
16:40-17:00	MARUYAMA, Shigeo : Synthesis and properties of single-walled carbon nanotubes co-axially wrapped with mono – and few-layer BN nanotubes
17:00-19:00	Poster Session: 2
19:00-20:30	Dinner

## Poster Session 2

	Poster No.
[5] TANAKA, Yuichiro : Phonon Assigning of G-band from Suspended Single walled Carbon Nanotubes	P-2
[7] NOÉ, Jonathan : Environmental electrometry with luminescent carbon nanotubes	P-4
[9] FLAVEL, Benjamin : Photocurrent Spectroscopy of Dye Sensitized Carbon Nanotubes	P-6
[19] SHIGA, Tamehito : Post modification approach for photoluminescence modulation of locally functionalized single-walled carbon nanotubes	P-8
[21] MACHIYA, Hidenori : Spectral tuning of optical coupling between air-mode nanobeam cavities and individual carbon nanotubes	P-10
[23] CIESIELSKI, Richard : Probing the optical dipole transition and vibrational coherences in individual (5,4) carbon nanotubes by femtosecond pulse shaping	P-12
[35] ROSKOS, Hartmut : Dielectric properties of vertically aligned carbon nanotubes in the mid-IR and THz spectral range	P-14
[45] TANAKA, Shunsuke : Molecular screening effects on trion binding energies and electronic band gaps in air-suspended carbon nanotubes	P-16
[47] NISHIHARA, Taishi : Narrow-band thermal exciton radiation in individual suspended single-walled carbon nanotubes	P-18
[55] FURUTA, Hiroshi : Reflectance of Carbon Nanotube Forest metamaterials	P-20
[59] CHIASHI, Shohei : Photoluminescence from Single-walled Carbon Nanotubes on hexagonal Boron Nitride Substrates	P-22
[65] SIMPSON, Jeffrey R. : Resonance Raman Signature of Intertube Excitons in Compositionally-Defined Carbon Nanotube Bundles	P-24
[67] JEON, Il : Achieving 20% Efficiency Perovskite Solar Cells with High Stability by using Semiconducting Single-walled Carbon Nanotube Grain Bridges	P-26
[68] INABA, Takumi : Effects of Chirality and Defect Introduction on the Intermediate Frequency Mode	P-28
[69] WURSTBAUER, Ursula : Long-lived direct and indirect interlayer excitons in van der Waals heterostructures	P-30

## Thursday 12 July 2018

09:00-09:30	WEISMAN, R. Bruce : Photo-induced interactions between SWCNTs and oxygen
09:30-10:00	DOORN, Stephen : Environmental Effects on Photoluminescence Properties of Carbon Nanotube $sp^3$ Defects
10:00-10:20	SPERLICH, Andreas : Direct Determination of Chemically Induced Doping Concentrations in (6,5)- Single-Wall Carbon Nanotubes by EPR
10:20-10:40	Coffee Break
10:40-11:10	BLACKBURN, Jeffrey : Long-lived Charge Separation Across Interfaces with Semiconducting Single-walled Carbon Nanotubes
11:10-11:40	KATAURA, Hiromichi : PL quantum yield of SWCNTs: photon reabsorption effect
12:00-13:30	Lunch

# Invited Talks

# Optics and Photonics of Aligned Carbon Nanotube Films

W. Gao,<sup>1</sup> N. Komatsu,<sup>1</sup> F. Katsutani,<sup>1</sup> X. Li,<sup>1</sup> K. Yanagi,<sup>2</sup> and J. Kono<sup>1</sup>

<sup>1</sup> Department of Electrical & Computer Engineering, Rice University, Houston, Texas, U.S.A.

<sup>2</sup> Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, Japan

We have recently developed a controlled vacuum filtration technique (Fig. 1a) to fabricate wafer-scale films (1 inch [1] and 2 inches [2] in diameter, as shown in Figs. 1b and 1c, respectively) of aligned and packed single-wall carbon nanotubes (SWCNTs); see Figs. 1d-1g. We can further build unique architectures and devices through stacking and doping (Fig. 1c). Here, we summarize some of our recent accomplishments using these unique samples.

We have made the first observation of intersubband plasmons (ISBPs) in gated aligned films [3]. For parallel polarization (Fig. 1h), the  $S_{11}$ ,  $S_{22}$ , and  $M_{11}$  transitions disappear as carriers are injected; for perpendicular polarization (Fig. 1i), a new peak due to ISBP appears and grows as the carrier density increases. We have also made the first direct observation of the  $E_{12}/E_{21}$  peak in the optical absorption of an aligned (6,5) film (Fig. 1j). We further built an exciton-polariton architecture by incorporating such films inside a Fabry-Pérot microcavity [4]. This system displayed a continuous transition from the strong-coupling to the weak-coupling regime through facile polarization control (Figs. 1k-1m). The obtained dispersion surfaces revealed the existence of exceptional points and two equienergy arcs (Fig. 1n). Furthermore, the vacuum Rabi splitting exhibited cooperative enhancement (Fig. 1o).

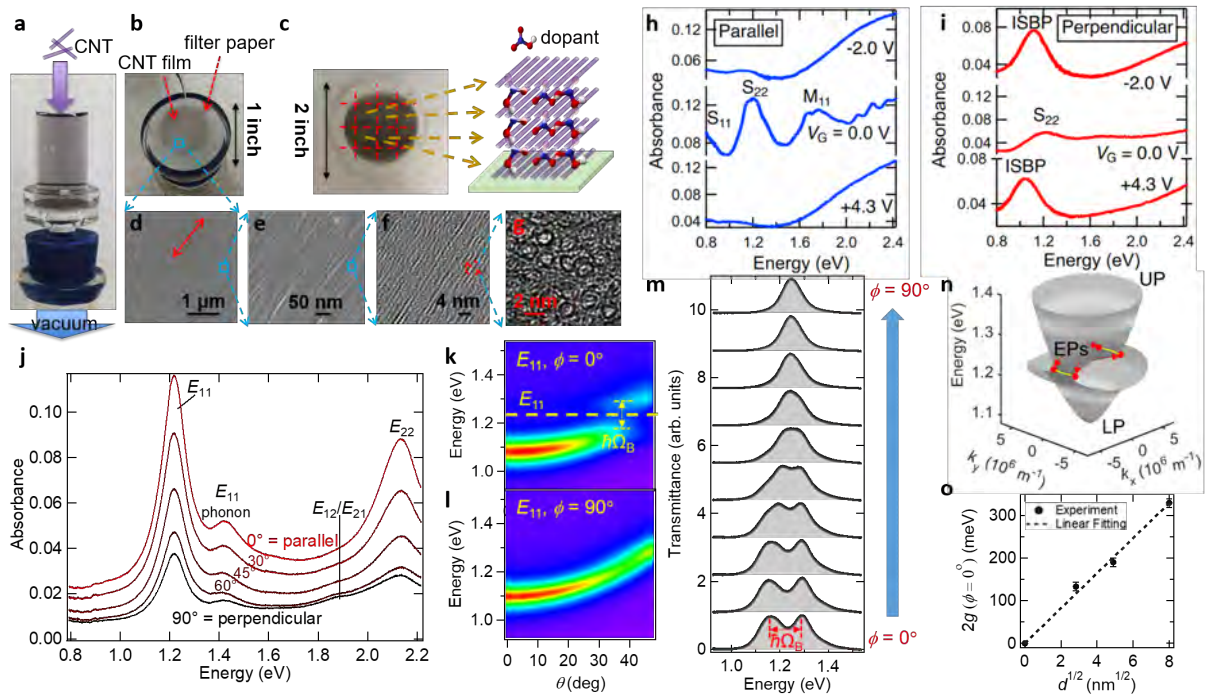


Fig. 1 (a) Vacuum filtration system to produce (b) 1-inch films, (c) 2-inch films and architectures of aligned CNTs; see (d, e) SEM and (f, g) TEM images. (h) Parallel- and (i) perpendicular-polarization absorption spectra for gated and aligned CNTs. (j) Polarization-dependent absorption spectra for an aligned (6,5) CNT film. Transmittance spectra of an exciton-polariton device for (k)  $\phi = 0^\circ$  and (l)  $\phi = 90^\circ$ . (m) Transmittance spectra for varying  $\phi$ . (n) Dispersion surfaces for the device. (o) Vacuum Rabi splitting versus the square root of the film thickness.

- [1] X. He *et al.*, Nat. Nanotech. **11**, 633 (2016).
- [2] N. Komatsu *et al.*, Adv. Func. Mater. **27**, 1606022 (2017).
- [3] K. Yanagi *et al.*, Nat. Commun., accepted for publication.
- [4] W. Gao *et al.*, Nat. Photon., accepted for publication.

# Mid- and high-temperature exciton photophysics of carbon nanotubes and their applications

Yuhei Miyauchi<sup>1,2,3</sup>

<sup>1</sup>*Institute of Advanced Energy, Kyoto University, Uji, 611-0011, Japan*

<sup>2</sup>*Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan*

<sup>3</sup>*JST-ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Chikusa, Nagoya 464-8602, Japan*

Optical properties of single-walled carbon nanotubes (SWNTs), dominated by correlated electron-hole bound states known as excitons [1-3], have been intensively studied for exploring fundamental photophysics in nearly ideal quasi-one-dimensional systems and their applications in the fields ranging from optoelectronics to bioimaging. Because of the strong Coulomb interaction resulting from 1D quantum confinement and weak dielectric screening, excitons in semiconducting SWNTs have binding energies on the order of 0.5 eV. Thus, SWNTs have offered a unique system for the study of excitons and their applications at high temperatures even much more than room temperature. Here we discuss our recent studies on exciton photophysics in SWNTs and their applications at mid- and high-temperatures. These include intrinsic high-temperature radiation properties of individual structure-defined semiconducting and metallic SWNTs at more than 1000 K [4], and applications of efficient phonon-assisted up-conversion luminescence phenomena [5,6] of SWNTs around living body temperatures for probing distribution of individual SWNTs trapped in mice liver tissues [7], autofluorescence-free real-time anatomical imaging of mice using a silicon-based image sensor, and for deep-tissue luminescence thermometric imaging toward realization of non-contact in vivo local temperature measurement for biomedical applications [8].

- [1] T. Ando, *J. Phys. Soc. Jpn.* 66, 1066 (1997).
- [2] F. Wang, G. Dukovic, L. E. Brus, and T. F. Heinz, *Science* 308, 838 (2005).
- [3] J. Maultzsch, R. Pomraenke, S. Reich, E. Chang, D. Prezzi, A. Ruini, E. Molinari, M. S. Strano, C. Thomsen, and C. Lienau, *Phys. Rev. B* 72, 241402(R) (2005).
- [4] T. Nishihara, A. Takakura, Y. Miyauchi, and K. Itami, submitted.
- [5] N. Akizuki, S. Aota, S. Mouri, K. Matsuda, and Y. Miyauchi, *Nat. Commun.* 6, 8920 (2015).
- [6] S. Aota, N. Akizuki, S. Mouri, K. Matsuda, and Y. Miyauchi, *Appl. Phys. Express* 9, 045103 (2016).
- [7] S. Okudaira, Y. Iizumi, M. Yudasaka, T. Okazaki, K. Matsuda, and Y. Miyauchi, the 51<sup>st</sup> Fullerenes-Nanotubes-Graphene General Symposium, September 7-9, 2016, Hokkaido, Japan.
- [8] K. Hachiya, S. Okudaira, Y. Konno, Y. Maeda, K. Matsuda, and Y. Miyauchi, the 54<sup>th</sup> Fullerenes-Nanotubes-Graphene General Symposium, March 10-12, 2018, Tokyo, Japan.



# Trions at a Trapping Defect

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<sup>2</sup> *Maryland NanoCenter*

Trions—or charged excitons—are quasi-particles composed of two electrons and one hole (or vice versa). Particularly a negative trion may be seen as an analog to the anions of hydrogen and positronium. In contrast to excitons, a trion features a net charge and half integer spin, which allow for the manipulation of electron spin and optically probing local electrostatic fluctuations. Governed by optical selection rules different from those of excitons, trions can also significantly impact the dynamics of optically forbidden dark excitons. Because of their unique properties, trions have been intensively explored for a broad range of potential applications, including quantum information, sensing, energy harvesting, lasing, and light-emitting devices. The existence of trions was experimentally confirmed only recently, first in quantum wells and more recently in carbon nanotubes. In SWCNTs, trions have been generated by high power laser excitation [1, 2] and doping [3-6] of the host material. However, in the few previous cases in which trions have been observed, trion PL is rather weak. One of the key factors that fundamentally limits trions to rise as a dominant species is their low binding energy.

In this talk, we will discuss experimental evidence of trions that are trapped at chemical defects synthetically introduced into semiconducting SWCNT hosts. [7, 8] By co-localizing charges with excitons at these emissive defect centers we show that it is possible to produce ultrabright trions. The trap-localized trions fluoresce brightly at room temperature, even with weak excitation. We experimentally determined the binding energy of the defect-localized trions to be as large as 119 meV in (6,5)-SWCNT, which are significantly larger than that of mobile trions in the same host (54 meV), 0D quantum dots (2–25 meV), and also 2D materials (15–45 meV), and can even be compared to the 327 meV binding energy of positronium anions. The trapped trions have a photoluminescence lifetime that is more than two-order of magnitude larger than “free” trions in the same host material. Our defect dependence studies and magnetoluminescence spectroscopy suggest that unlike native excitons and free trions, these trapped trions are intrinsically bright.

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- [2] B. Yuma, S. Berciaud, J. Besbas, J. Shaver, S. Santos, S. Ghosh, R. B. Weisman, L. Cognet, M. Gallart, M. Ziegler, B. Hönerlage, B. Lounis, P. Gilliot, *Phys. Rev. B* **87**, 205412 (2013).
- [3] J. S. Park, Y. Hirana, S. Mouri, Y. Miyauchi, N. Nakashima, K. Matsuda, *Journal of the American Chemical Society* **134**, 14461-14466 (2012).
- [4] F. Jakubka, S. B. Grimm, Y. Zakharko, F. Gannott, J. Zaumseil, *ACS Nano* **8**, 8477-8486 (2014).
- [5] T. Koyama, S. Shimizu, Y. Miyata, H. Shinohara, A. Nakamura, *Phys. Rev. B* **87**, 165430 (2013).
- [6] R. Matsunaga, K. Matsuda, Y. Kanemitsu, *Phys. Rev. Lett.* **106**, 037404 (2011).
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- [8] H. Kwon, M. Kim, M. Nutz, N. F. Hartmann, V. Perrin, B. Meany, M. S. Hofmann, C. W. Clark, H. Htoon, S. K. Doorn, A. Högele, Y. Wang, *under review* (2018).

# Molecular design for photoluminescence modulation of locally functionalized single-walled carbon nanotubes

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<sup>2</sup> *International Institute for Carbon-Neutral Energy Research (WPI-I<sup>2</sup>CNER), Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan*

Near infrared photoluminescence (NIR PL) of semiconducting single-walled carbon nanotubes (SWNTs) is highly functionalized through chemical reactions of the tube walls, in which local functionalization is a key for partial doping of the sp<sup>2</sup> carbon network structures. Oxygen atom doping and sp<sup>3</sup> defect doping have been conducted, and the resulting locally functionalized SWNTs (lf-SWNTs) show PL intensity enhancement with wavelength shifts. Recent studies are revealing that doped site structures are closely related to the PL functions of the lf-SWNTs. Based on our chemistry background, we synthesize new diazonium molecules for local functionalization of SWNTs, by which the doped site structures are molecularly designed towards modulation and functionalization of the NIR PL properties.

For example, bisdiazonium compounds (2Dz) were synthesized and the modification of (6,5) SWNTs using the 2Dz (lf-SWNTs/2Dz) provided new red-shifted PL.[1] Namely, the emission peak appeared at 1256 nm which was significantly red-shifted than those of pristine SWNTs (985 nm) and mono-functionalized SWNTs (lf-SWNTs/1Dz, 1129 nm). In another project, substituted aryl isomers were introduced as a moiety of the doped site structures of lf-SWNTs. The observed PL was varied with strong dependence on the isomeric substituent positions.[2, 3] Thus, these molecular structure-dependent spectral changes are expected to develop the lf-SWNTs whose PL appears in the wide wavelength range of NIR regions.

As another developed function of the lf-SWNTs, dynamic wavelength shifting is achieved through creation of the doped sites that selectively bind molecules and ions, etc. The local binding occurred by employing molecular recognition motives for the doped site design. The first example was phenylboronic acid-modified lf-SWNTs that showed PL wavelength shifts by attachment of saccharide molecules at the doped sites.[4] More recently, the modification of crown ether groups, which can capture cations such as metal ions, provided unique PL wavelength shifts depending on the difference in the bound cationic species. Therefore, the local events at the doped sites create PL shifting functions on the basis of the molecular systems that are driven by molecular interactions with selectivity and flexibility.

As described above, molecular design approaches are quite useful for modulation and functionalization of the NIR PL of the lf-SWNTs. The resultant functions are applicable to develop advanced applications such as bio/medical imaging and sensing, and nanodevices for telecommunication.

[1] T. Shiraki, T. Shiraishi, G. Juhász and N. Nakashima, *Sci. Rep.* **6**, 28393 (2016).

[2] T. Shiraki, S. Uchimura, T. Shiraishi, H. Onitsuka and N. Nakashima, *Chem. Commun.* **53**, 12544-12547 (2017).

[3] T. Shiraishi, T. Shiraki and N. Nakashima, *Nanoscale* **9**, 16900-16907 (2017).

[4] T. Shiraki, H. Onitsuka, T. Shiraishi and N. Nakashima, *Chem. Commun.* **52**, 12972-12975 (2016).

# Electroluminescence from carbon nanotubes

Ralph Krupke<sup>1,2</sup>

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<sup>2</sup> *Technische Universität Darmstadt, 64287 Darmstadt, Germany*

Electrically generated light emission from carbon nanotubes is of great interest for the development of nanoscale on-chip electro-optical transducers and single-photon sources [1,2], operating in the telecom band and at GHz frequency [3]. To further advance device performance, reproducibility and reliability we need to better understand and control the mechanism of light generation, tailor the interface between the nanotube and environment and to locally modify nanotube properties with nanoscale precision. In my presentation I will report on our current efforts in this direction and present latest results.

[1] S. Khasminkaya et al., *Nature Photonics* **10**, 727 (2016).

[2] F. Pyatkov et al., *Nature Photonics* **10**, 420 (2016).

[3] F. Pyatkov et al., *Beilstein J. Nanotechnol.* **8**, 38 (2017).

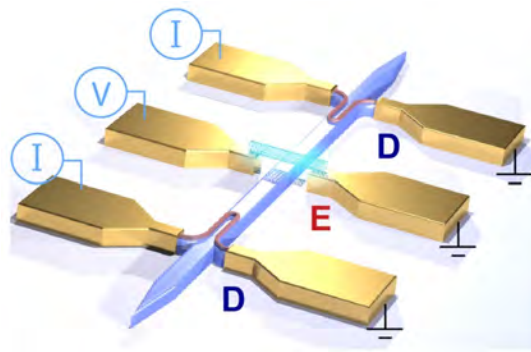


Fig.1 Quantum photonic circuit comprising of carbon nanotube emitter (E) and superconducting detectors (D).

# Electrochemically doped light-emitting devices of transition metal dichalcogenide monolayers

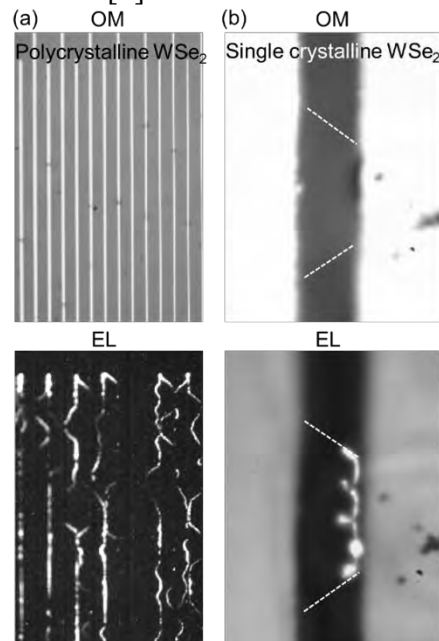
Taishi Takenobu

*Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan*

Recently, 2D layered materials have attracted much attention for exploring new electronic, optoelectronic, and photonic applications. Particularly, direct bandgap and unique electronic structure in monolayer transition metal dichalcogenides (TMDCs) provides a platform for exploring novel optoelectronic functionalities and devices [1,2]. One of the most interesting properties of TMDCs is topological features, such as a non-centrosymmetric two-dimensional crystal and spin-valley coupling [3], and circularly polarized light emission has been demonstrated [4,5].

Although the optical properties of TMDCs are very promising, light-emitting devices require intentional doping techniques to form p-n junction. However, reliable doping methods for TMDCs have not yet been fully established. Therefore, the fabrication of TMDC light-emitting devices are still limited, and this fundamental barrier has made investigating electroluminescence (EL) properties of TMDCs inevitably difficult [2].

To overcome this issue, we recently developed the electrochemical method to dope both holes and electrons [6-10], and proposed a simple approach to form p-n junction universally in TMDCs [11,12]. Here, we apply this method into various forms of TMDCs, such as monolayer polycrystalline films (Fig. 1(a)) and single crystalline flakes (Fig. 1(b)), to achieve EL emission. Particularly, using single crystal samples, we have performed temperature and position dependent measurements of EL and investigated their optical properties. Very interestingly, we observed robust circularly polarized EL emission, arising from spin-valley coupling in TMDCs. Our approach paves a versatile way for using TMDCs in discovering new functional optoelectronic devices.



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# Bright and tunable single-photon emission with a carbon nanotube embedded in a fiber micro-cavity.

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Single-photon sources (showing a vanishing probability to emit more than one photon at a time) are a key building block for secured quantum telecommunications or for future quantum optical information processing. In order to bring high speed operation, this source is required to be on-demand and to have high brightness and large anti-bunching purity. In addition, further integration in long range telecommunication networks requires near infrared operation. Room temperature operation together with electrical injection would also be highly valuable for large scale integration.

Carbon nanotubes have strong assets in this perspective since they were shown to have excellent single-photon emission properties (both at low-temperature and room temperature for chemically grafted nanotubes) and high polarization purity. In addition, their emission wavelength can be chosen over a wide range by selecting appropriate chiral species. Electrically induced luminescence has been reported by several teams [1]. Nevertheless, their reported luminescence quantum efficiency is consistently small and their spectral properties may be deteriorated by interactions with phonons or local environment fluctuations.

Here, we show that these latter limitations can be drastically improved by coupling a nanotube to a small volume, high-finesse micro cavity, through the so-called Purcell effect [1].

In order to tackle the so-called spatial and spectral mode matching issues (that become especially critical in high Q applications), we used a tunable cavity designed at the apex of an optical fiber for further integration in telecom networks. We show that the emission rate of the nanotube can be enhanced by a factor 60 leading to an effective luminescence quantum yield of about 40% and a coupling factor close to 100% [2].

In addition, the original tuning capability of our cavity, allows us to exploit the spectral broadening of the nanotube excitonic line and to achieve a widely tunable single-photon source, possibly valuable for multiplexing applications in telecom or for indistinguishability engineering from remote nano-sources for quantum computing. We show how an original asymmetric energy exchange between a phonon broadened 1D emitter and a cavity can serve as a new handle to bypass the intrinsic spectral efficiency limit of a symmetrically broadened emitter [4].

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# Spectroscopy of localized excitons in cryogenic carbon nanotubes

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Semiconducting single-wall carbon nanotubes feature exciton localization by unintentional disorder or chemically tailored potential traps with peculiar consequences for their photophysical properties including non-classical light emission statistics [1] up to room temperatures [2,3]. In our most recent experiments, we used cryogenic photoluminescence spectroscopy to study (i) unintentionally localized excitons exhibiting interactions with the electrostatic environment via their permanent dipole moment [4,5] and (ii) the competition for the photogenerated population between discrete excitonic states of chemically engineered sp<sup>3</sup>-defect traps [6]. Our results shed light on internal and external parameters of localized carbon nanotube excitons with implications for their potential applications as single-photon sources and all-optical electrometers.

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# **Luttinger liquid in Carbon Nanotubes**

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Single Walled carbon nanotubes provide the ideal platform to explore Luttinger liquid physics due to the strong one-dimensional quantum confinement. I will discuss out combined electrical and optical studies to correlate the unusual electron tunneling and plasmon excitations of a Luttinger liquid. I will also show that distinctly different plasmon behavior in electrically gated metallic and semiconducting carbon nanotubes, which are described by the linear Luttinger liquid and nonlinear Luttinger liquid, respectively.

# Single SWNT spectroscopy for nano-metrology

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A single-walled carbon nanotube (SWNT), suspended between micro-structures, is an excellent system for probing responses to molecular adsorption/encapsulation, optical/thermal excitation, etc., because of the quasi 1D electronic structure of the SWNT allowing highly resonant optical transitions, and sensitivity to the surrounding environment with the outer surface and the inner space. We have developed techniques for fabrication of a perfectly isolated SWNT, as long as 10  $\mu\text{m}$ , between a pair of silica pillars as shown in Fig. 1, and for selective detection of photoluminescence (PL) and/or Raman scattering from it [1].

In this talk, we will focus on two topics: phase analyses of water confined in an SWNT [2] and thermal conductivity measurements of SWNTs [3]. Water molecules confined in the inner space of SWCNT affect the optical transition energy in the SWNT depending on the dielectric constant of water that varies with its phase. Thus, the phase diagram of water confined inside of an SWNT could be constructed from the temperature and water vapor pressure dependent spectra. The water in an SWNT is one dimensional, thus the phase change is of interest. The thermal conductivity of an SWNT is difficult to measure because of a small diameter and low heat capacity. With the spectroscopic PL imaging, we could obtain the temperature distribution along the tube axis under laser irradiation based on the temperature dependent PL spectrum change. From the temperature distribution, the temperature dependence of thermal conductivity was derived by solving heat equation. The single SWNT spectroscopy provides fruitful information on molecules on/in an SWNT as well as the properties of SWNTs.

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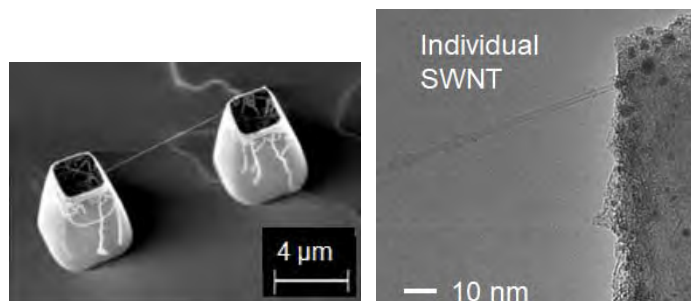


Fig.1 Scanning electron micrograph (left) and transmission electron micrograph (right) of a singly suspended SWNT between micropillars.



# Exciton-Polaritons, Plexcitons and Trion-Polaritons in Single-Walled Carbon Nanotube Thin Films and Devices

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Exciton-polaritons are mixed light-matter quasiparticles that form upon strong coupling between electronic excitations of a material and photonic states of a surrounding microcavity. Highly purified, monochiral (6,5) single-walled carbon nanotubes (SWCNTs) exhibit optical and electronic properties that make them ideal for strong light-matter coupling in combination with fast charge transport, thus enabling optically and electrically pumped near-infrared exciton-polaritons at room temperature [1,2]. While exciton-polaritons can be observed in simple metal-clad or high-quality distributed Bragg reflector microcavities, coherent coupling of carbon nanotube excitons with hybrid plasmon-photonic modes (supported by plasmonic crystals formed by diffractive coupling of periodically arranged gold nanorods) results in plasmon-exciton polaritons ('plexcitons') [3] that can propagate over 20-30 micrometers during their short lifetime (~100 fs).

Further, doped (6,5) SWCNTs also exhibit stable trions (positively or negatively charged excitons) at room temperature with red-shifted absorption and emission. We demonstrate the formation of emissive trion-polaritons (indicated by splitting of the lower polariton mode into a new lower and middle polariton, see Fig. 1) via electrochemical hole-doping of a thick film of (6,5) SWCNTs in a suitable metal-clad microcavity [4]. These charged trion-polaritons might be interesting for enhanced charge transport due to their low effective mass.

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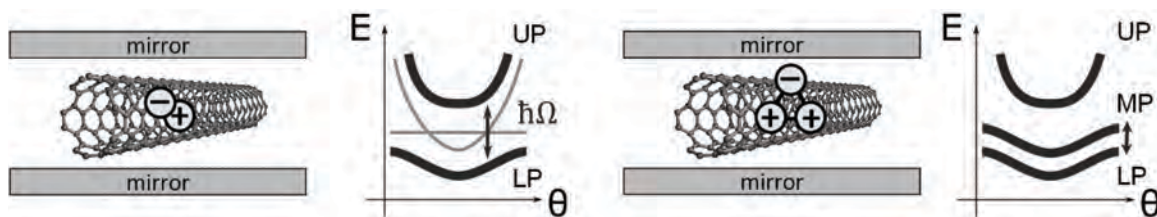


Fig.1 Schematic illustration of (6,5) SWCNT excitons in a simple microcavity leading to exciton-polariton formation (UP: upper polariton, LP: lower polariton), corresponding schematic for nanotube trions resulting in additional splitting of the LP mode (MP: middle polariton) and thus formation of charged trion-polaritons.

# Excitons in Coupled Nanotube Photovoltaic Thin Films

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We have previously reported on the efficient harvesting of excitons from photoexcited, semiconducting nanotube thin films. The films are interfaced with C<sub>60</sub> fullerenes to form a type-II heterojunction with band offsets that exceed the exciton binding energy. Excitons photogenerated near the heterointerface are dissociated into separable electrons (which transfer to C<sub>60</sub>) and holes (which remain on the nanotubes) with quantum efficiency  $\approx 90\%$ . This behavior has promise for creating nanotube photoabsorber-based photovoltaic solar cells and photodetectors. However, the efficiency by which excitons can be dissociated remains high only when the nanotube films are thin (5 nm in thickness). The efficiency rapidly decreases as the nanotube film thickness increases, due to poor inter-nanotube exciton migration.

Here, we present on recent work designed to understand and improve exciton migration in coupled nanotube films via theory [1] and experiments [2-4]. We have calculated exciton transfer rates due to Coulomb coupling between nanotubes of varying orientations considering both first- and second-order (phonon-assisted) processes. Second-order dark-to-bright inter-nanotube transfer is as fast as both first and second order bright-to-bright transfer. This important result shows that dark excitonic states are able to efficiently and directly transfer between nanotubes in films.[1] We have tested the hypothesis that poor inter-nanotube exciton migration in films can be attributed to quenching by defects via experiments in which (i) diazonium defects are intentionally added to nanotubes at known concentrations [2] and in which (ii) nanotubes are prepared via three different processes of decreasing harshness: extended ultrasonication, brief ultrasonication, and shear force mixing [3]. Inter-nanotube exciton transfer is then characterized via photoluminescence-, transient absorption-, and device photocurrent spectroscopies. Our results show that poor out-of-plane exciton diffusion depth can be attributed in large part due to losses that arise from the trapping and quenching of excitons by defects induced during processing. Other photovoltaic parameters including fill-factor and open-circuit voltage also improve with decreasing processing harshness.

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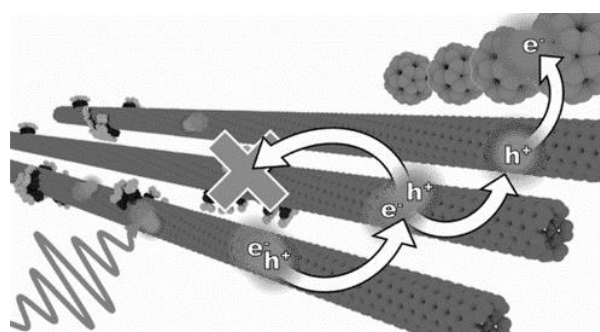


Fig.1. Photogeneration, intra- and inter-nanotube migration, quenching, and dissociation of excitons in coupled nanotube thin films.

# Transition metal dichalcogenide nanotubes

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Due to their favorable and rich electronic and optical properties, group-VI-B transition-metal dichalcogenides (TMDs) have attracted considerable interest. They have earned their position in the materials portfolio of the spintronics and valleytronics communities. The electrical performance of TMDs will be enhanced by rolling up the two-dimensional (2D) sheets to form quasi-one-dimensional (1D) tubular structures. Actually, the TMD nanotubes were first synthesized back in 1992 [1], but only recently device related researches have been conducted [2]. In this presentation, we discuss transport and optoelectronic properties ranging from field effect transistor (FET) operation to solar cell actions in tungsten disulfide multiwalled nanotubes (WS<sub>2</sub>-NT).

We first fabricated electric double layer transistor (EDLT) of an individual WS<sub>2</sub>-NT and found an ambipolar operation, in sharp contrast to the solid gated FET devices which exhibits only n-type conduction. Furthermore, we found that gating with KClO<sub>4</sub>/polyethylene glycol electrolyte, induce superconductivity at  $T_c = 5.8$  K. This is the first superconductivity in the individual nanotube structure. Importantly, this superconductivity of gated WS<sub>2</sub> exhibited peculiar transport properties arising only from tubular and chiral structure [3].

Using the EDLT devices, we were able to fabricate a p-n junction in an individual WS<sub>2</sub>-NT, and found that this p-n junction shows current-driven light emission, and photovoltaic actions. Both of these actions are linearly polarized along the NT axis, and more importantly, the *external* quantum efficiency for the photovoltaic effect reaches a value as high as 4.8%, exceeding by far that of 2D TMDs and even approaching the internal quantum efficiency of the 2D TMDs [4].

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# Stacking-dependent Interlayer Couplings in 2D Materials

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

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# Carbon Nanotube Optical Bandgap Modulation for Cancer Research and Diagnosis

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The measurement of biomarkers, drugs, and metabolites in live cells and organisms would allow for improvements in disease detection, drug development, and biomedical research. Single-walled carbon nanotubes have suitable optical properties for application as sensors for use in live cells and in vivo, including narrow, near-infrared emission bands with sensitivity to the local environment. To develop them into sensors for bioanalytes, we devised new methods to probe single-walled carbon nanotube optical properties, including near-infrared hyperspectral imaging[1] and live-tissue excitation/emission spectroscopy[2]. We also harnessed a mechanism of carbon nanotube photoluminescence optical bandgap modulation, whereby electrostatic charges mediate spectral shifts[2]. We believe that this effect is consistent with carbon nanotube solvatochromic behavior and found that this mechanism facilitates the measurement of multiple classes of bioanalytes, such as nucleic acids[3, 4], drugs[5], and proteins[6], enabling the development of in vivo implantable sensors[3, 6] for the study and detection of cancer (Fig. 1).

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Fig 1. Near-infrared photoluminescence image of microRNA-responsive DNA-encapsulated single-walled carbon nanotubes within a membrane implanted into a live mouse.

# **DNA-wrapped carbon nanotubes for sorting and multiplex optical sensing**

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Many fundamental studies and technology development rely on structurally well-defined carbon nanotubes as well as corresponding coating layers. DNA-wrapped carbon nanotube (DNA-CNT) library has been used successfully to select structurally well-defined hybrids. In this talk, I will present our recent work in developing new aqueous two-phase separation systems for the selection of structurally defined DNA-CNTs, as well as our effort in revealing DNA sequence selection rules for CNT sorting. The utility of DNA coating goes well beyond CNT sorting, for it provides a means to control CNT interaction with other molecules. To elaborate on this point, I will present a “molecular perceptron” proposal based on the optical response from  $\sim 10^3$  independent DNA-CNT structures to sense the metabolome of a biofluid in its entirety.

# Killer defects in semiconducting SWNTs

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The doping of semiconductors is key for providing electronic and photonic devices with their desired functionality. This comes with the realization, that the failure to successfully dope certain classes of materials “is an important bottleneck for the technological utilization of these materials” in electronic or photonic devices, as succinctly expressed by Zunger [1]. This concern also pertains to the doping of semiconducting single-wall carbon nanotubes (s-SWNTs) where our ability to provide stable and measured concentrations of surplus carriers remains a major challenge.

Current approaches to doping of s-SWNTs are mostly designed around redox chemistry or covalent modification with electron pulling or pushing side-chain functionalities while the use of substitutional impurities has hardly been explored for the purpose of electronic enhancement. Despite the importance of doping for device technologies, however, it appears that our ability to quantify the concentration of impurity site concentrations or their effectiveness in providing surplus free carriers is still rather limited.

To address these shortcomings we have performed spectroscopic investigations of redox- and electrochemically doped (6,5) s-SWNT samples using fluorescence and absorption spectroscopy [2]. Spectroscopically, there appears to be no noticeable difference between these two approaches. In both cases, exciton bands are found to broaden, become asymmetric and shift to higher energies when the electrochemical potential is shifted toward valence or conduction band edges. These observations are consistent with confinement of excitons by a stochastic distribution of impurities, suggesting that doping is in-homogeneous rather than homogeneous. Moreover, our analysis suggests that the interaction of minority carriers with external counterions can provide deep traps in the band gap which act as ‘killer defects’, capturing free charge carriers and effectively preventing the desired homogenous doping.

We also discuss how the analysis of exciton absorption bands can be applied to quantify impurity level concentrations. In the context of optical spectroscopy this allows to define and clearly distinguish between intrinsic-, weak-, moderate- and heavy-doping regimes. The onset of degenerate s-SWNT doping is determined to be at about  $\pm 0.1 e \text{ nm}^{-1}$ .

The observed generation of deep charge traps by adsorbed counterions can largely be attributed to weak dielectric screening of Coulomb interactions by SWNTs or their environment, a common characteristic of low-dimensional systems. We take this as evidence for serious fundamental challenges which may have far reaching and possibly broader implications for the successful fabrication of functional semiconductor devices from nanoscale materials.

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# Nanoscale Imaging in, of & with Luminescent Single Walled Carbon Nanotubes

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Sub-wavelength localization of single nano-emitters allows super-resolution imaging and subtle probing of their spatio-temporal nano-environments. This can be applied to reveal exciton localization in luminescing carbon nanotubes[1] which is subject of intense investigations due to its impact on nanotube emission properties. I will present our current efforts to map luminescent defect localization in ultra-short carbon nanotube having controlled chemical and morphological properties [2].

I will also present that video-rate tracking of luminescent biocompatible carbon nanotubes allows imaging of local live brain tissue architecture and viscosity at the nanoscale[3-5]. Specific features are uncovered near identified brain structures [6] (e.g synapses) and in neurodegenerative disease animal models [7].

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# Optical properties of dyes confined into carbon and boron nitride nanotubes

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The inner cavity of nanotubes has been used as a template for the encapsulation of elongated dyes molecules, such as polythiophenes (6T). The 1D confinement of the nanotube wall drives the stacking of the molecules and induces original aggregation effects in their optical properties [1,2]. When confined inside a carbon nanotube, the organics dyes exhibit for instance a surprisingly strong Raman signal clear of its luminescence emission due to an efficiently quenching effect from the nanotube [3]. Here we show that boron nitride nanotubes ( $E_g \sim 5$  eV) having inner diameters between 1 nm to 5 nm provide similar 1D confinement effects with the difference that they preserve the luminescence of the dyes. The resulting 1D nanohybrids (dye@BNNT) shows in photoluminescence imaging experiments strong and tunable luminescence emissions depending on the dyes used. Experiments on individual dyes@BNNT demonstrate that the BNNT protect the dyes against oxidation and reduce significantly the dyes photobleaching under continuous photo-excitation. Preliminary results on *Daphnia Pulex* colored with dyes@BNNT suggest that these dye@BNNT nanoprobe have reduced toxicity for multimodal imaging based on Raman and luminescence and that they can be adapted to work in the NIR I window to study biological materials.

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[2] S. Cambré *et al* Nature Nano. **10**, 248-252 (2015)

[3] E. Gaufres *et al* ACS Nano, **10**, 11 (2016)

# Diameter-dependent optical absorption and energy transfer from encapsulated dye molecules to single wall carbon nanotubes

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The hollow core and well-defined diameters of single-walled carbon nanotubes (SWCNTs) allow for creation of unique one-dimensional hybrid structures by encapsulation of various molecules. For instance, we previously demonstrated that in this way dipolar dye molecules can be naturally aligned in an ideal head-to-tail arrangement to create assemblies with a giant total nonlinear optical response.[1]

Here, we encapsulated specific dye molecules inside the SWCNTs and demonstrate that the optical absorption of the encapsulated dye molecules and subsequent excitation energy transfer (EET) from encapsulated dyes to the SWCNTs is strongly modulated by the SWCNT diameter, implying a diameter-dependent stacking of the molecules inside the SWCNTs. The dye filling and EET are thoroughly characterized by optical absorption, resonant Raman, two-dimensional infrared photoluminescence excitation (PLE) spectroscopy and transient absorption spectroscopy.

In addition, we find that SWCNT filling does not limit the selectivity of subsequent separation protocols (including polyfluorene polymers for isolating only semiconducting SWCNTs and aqueous two-phase separation for enrichment of specific SWCNT-chiralities). The design of these functional hybrid systems, with tunable dye absorption, fast and efficient EET, and possibilities for subsequent separation, demonstrates potential for implementation in photo-conversion devices.

[1] S. Cambré *et al.*, Nature Nanotechnol. **10**, 248 (2015)

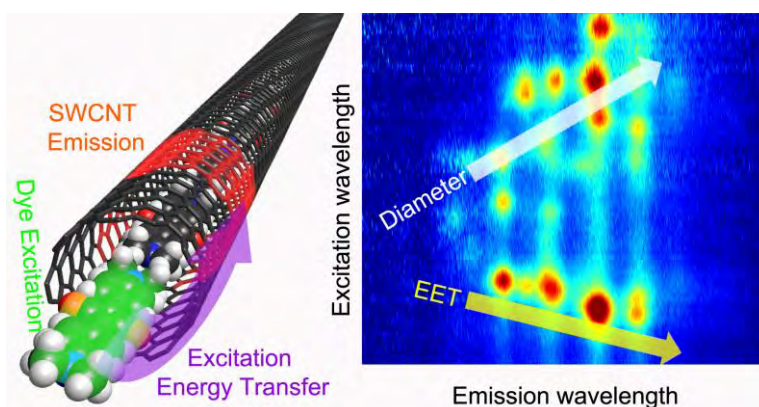


Fig.1 Excitation energy transfer from encapsulated dyes to SWCNTs probed by wavelength-dependent PLE spectroscopy.

# Photo-induced interactions between SWCNTs and oxygen

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We will report new investigations of photophysical and photochemical interactions involving single-walled carbon nanotubes (SWCNTs) and oxygen. These processes differ from our earlier discovery that SWCNTs can be covalently doped with O atoms through reaction with oxygen's reactive allotrope, ozone (O<sub>3</sub>) [1]. A fully reversible, non-covalent interaction of aqueous surfactant-coated SWCNTs with dissolved O<sub>2</sub> is revealed by partial quenching of the nanotube fluorescence [2]. The extent of this quenching is found to vary with surfactant coating, reflecting how completely the SWCNT surface is protected. When the SWCNTs are suspended by single-stranded DNA oligomers, the extent of fluorescence quenching reveals selective affinities between specific ssDNA sequences and specific SWCNT structures. By contrast, we have found that a covalent photochemical reaction with dissolved oxygen occurs when SWCNTs are strongly irradiated at their E<sub>11</sub> absorption peaks. The result is persistent and spectrally localized fluorescence quenching resulting from an optically directed photochemical reaction with the SWCNT sidewall. This process holds promise for allowing the optical properties and possibly the composition of mixed SWCNT samples to be tailored by targeted photochemistry. Recent evidence will also be presented that SWCNT triplet excited states can be formed through solution-phase energy transfer from O<sub>2</sub> in its singlet excited state. The key observation is weak delayed SWCNT fluorescence, which apparently comes from thermal excitation of long-lived SWCNT triplet excitons to emissive singlet states. Finally, we will show novel fluorescence signatures from ssDNA-wrapped SWCNTs exposed to singlet O<sub>2</sub>. This process leads to a covalent sidewall reaction involving one nucleotide base in the ssDNA. The resulting reaction product displays intense nanotube fluorescence with (*n,m*)-dependent spectral shifts and broadening, modified absorption spectra, and intriguing temperature dependences. This reaction class may offer a new path for chemically modifying SWCNT optical properties.

[1] S. Ghosh, S. M. Bachilo, R. A. Simonette, K. M. Beckingham, R. B. Weisman, *Science* **330**, 1656 (2010).

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# Environmental Effects on Photoluminescence Properties of Carbon Nanotube $sp^3$ Defects

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Photoluminescent defect states introduced by low-level covalent functionalization of single wall carbon nanotubes (SWCNTs) are of growing interest as routes to enhanced photoluminescence (PL) quantum yields and new functionality [1,2]. In particular, exciton localization in deep traps at the defect sites gives rise to single photon emission at room temperature that is tunable to telecom wavelengths [3,4]. We present results exploring the effects of varying dielectric environments on PL spectroscopic and dynamic behaviors of  $sp^3$  defects introduced via aryl diazonium functionalization chemistry. Changes in PL relaxation times with dielectric constant of various solvents will be discussed as evidence for an electronic to vibrational energy transfer from the defect-trapped exciton to the solvent degrees of freedom. Solvent interactions are thus seen to be an important component of relaxation that also includes multi-phonon decay processes [5]. Strategies for tailoring the SWCNT environment to extend defect-state PL lifetimes (to nanoseconds) and optimize linewidths will also be presented. Environmental impacts on dephasing times will also be discussed.

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## Long-lived Charge Separation Across Interfaces with Semiconducting Single-walled Carbon Nanotubes

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Semiconducting single-walled carbon nanotubes (s-SWCNTs) are attractive absorbers for use in solar energy harvesting schemes because of their strong and energetically tunable optical absorption, and high charge carrier mobilities due to the delocalized nature of the  $\pi$ -electron system. Beyond their technological potential, s-SWCNTs offer attractive properties for fundamental studies of charge generation in strongly confined nanoscale systems and photoinduced electron transfer (PET) processes. For example, strong quantum confinement and low dielectric screening impart single-walled carbon nanotubes with exciton-binding energies substantially exceeding  $k_B T$  at room temperature. Additionally, the energetically narrow and distinct spectroscopic signatures for excitons and charges within s-SWCNT thin films enables the unambiguous temporal tracking of fundamental photophysical processes occurring at important photoactive heterojunctions designed for charge separation.

In this presentation, I will discuss recent studies that probe the generation and recombination of long-lived charges in samples consisting of heterojunctions between s-SWCNTs and various electron acceptors, both organic and inorganic. I will focus on the roles of important interfacial properties that can influence the kinetics and efficiency of the interfacial PET process and recombination of the resulting separated charges. These properties include the energetic driving force for exciton dissociation, the amount of residual wrapping polymer on the highly enriched s-SWCNTs, the local dielectric environment, the presence or absence of an electric field, and geometrical factors of the interface that can be modified *via* structural properties of the acceptors. Better fundamental understanding of these model interfaces can inform the design of more efficient solar energy harvesting systems, photodetectors, and other opto-electronic devices.

# PL quantum yield of SWCNTs: photon reabsorption effect

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Atsushi Hirano, and Takeshi Tanaka

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Photoluminescence (PL) from single-wall carbon nanotube (SWCNT) has been often used for its structural identification without consideration of reabsorption of the emission. In order to derive the correct content rate of the species of specific chirality, it is at least necessary to know the quantum yield of each chirality. In the PL of SWCNT, furthermore, since Stokes shift is small, the photon reabsorption effect is dominant and the apparent PL spectrum shape and emission intensity are greatly modified depending on its concentration in the used SWCNT dispersion. This problem makes quantitative identification of SWCNT by PL intensity difficult. In this study, concentration dependence of the PL of SWCNT separated into a few chirality was analyzed in detail including the effect of the photon reabsorption [1]. Surprisingly, all changes in the PL spectrum occurring in the high SWCNT concentration range can be explained simply by the reabsorption effect and there were no further influences caused by interaction between SWCNTs that were suggested in the previous studies. We have obtained PL quantum yield derived from the emission intensity corrected from the photon reabsorption effect. They varied highly depending on the chirality of SWCNT, which agreed well with theoretical report [2] where the LO phonon relaxation process from  $E_{22}$  to  $E_{11}$  is dominant.

[1] X. Wei *et al.* in preparation.

[2] Y. Oyama *et al.* Carbon **44**, 873 (2006).

# Contributed Talks

# Tunable Interlayer Excitons in Folded & Twisted Graphene

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We demonstrate how resonantly-excited interlayer electronics in twisted bilayer graphene (*t*BLG) form a carrier relaxation bottleneck that enables weak photoluminescence (PL) emission and enhanced photocurrent (PC) extraction potential. Similar interlayer electronic properties are also seen in  $\sim 50$  nm graphene folds that we resolve optically by selective fluorination (see Fig. 1). After resonant two-photon excitation of twisted bilayer graphene (*t*BLG), we show in Fig. 2ab, weak light emission that is spectrally tunable with the stacking angle,  $\theta$ . These signals are best ascribed to PL associated with stabilized bound interlayer exciton states[1].

The exciton binding energy and long-lived kinetics of individual *t*BLG domains are estimated through two-photon PL excitation spectra and intraband transient absorption spectra. Spectral peaks from both two-photon photoluminescence and transient spectrum of intraband exciton transition independently suggest interlayer exciton binding energies ranging from  $\sim 0.5$  to  $0.7$  eV for stacking angles of  $8^\circ$  to  $17^\circ$ [1,3]. This report of resonant PL from twisted bilayer graphene materials under ambient conditions is best explained by a transient coexistence of strongly-bound interlayer excitons and metallic graphene continuum states. Such  $\theta$ -tunable interlayer excitons states may permit new optoelectronics by directing energy and charge.

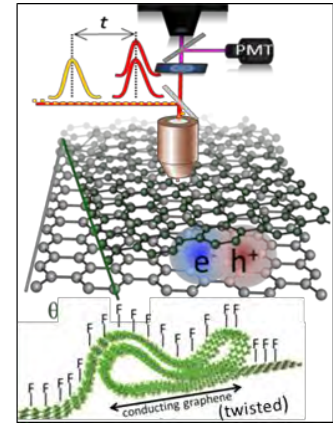


Fig. 1- Resonantly excited interlayer *e-h* pairs are measured in *t*BLG and twisted graphene nanofolds by 2-photon PL & intraband TA.

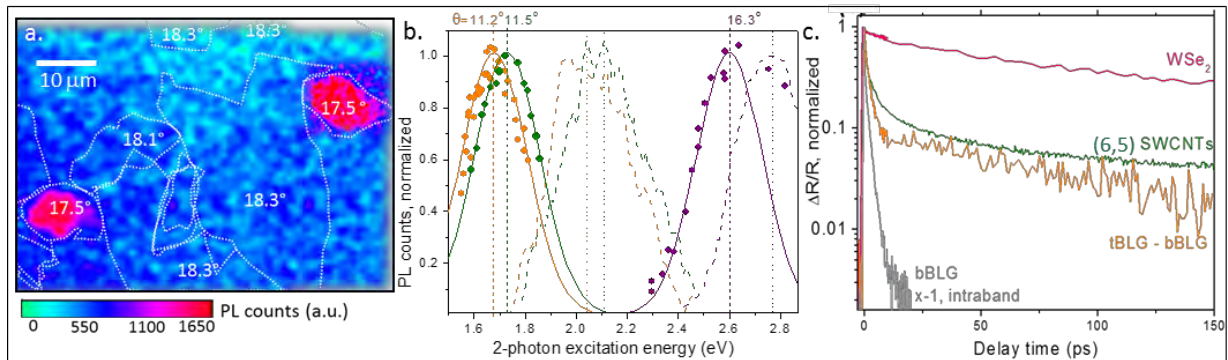


Fig. 2 – (a) Spatial PL map of *t*BLG for resonant 2-photon excitation of the  $17.5^\circ$  domains. (b)  $\theta$ -tunable 2-photon PLE spectra (*circles*) for three stacking angles show a dark state lying below the linear absorption spectra (*dashed*,  $\sigma_{\text{tBLG}} - 2\sigma_{\text{G}}$ ). (c) Comparative TA relaxation kinetics[2] of resonantly excited *t*BLG,  $0^\circ$  *b*BLG, (6,5) SWCNTs, and few-layer  $\text{WSe}_2$  show an initial electronic relaxation bottleneck for twisted bilayer materials.

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- [3] Y. Liang *et al.*, *Phys Rev B*, 90, 115418 (2014)



# Nonperturbing, conjugation-preserving covalent functionalization of single-walled carbon nanotubes

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The most common outcome of covalent treatments of carbon nanotubes is the conversion of  $sp^2$  carbon atoms into their  $sp^3$  hybridization state. Even mild approaches interrupt the conjugation of the carbon network with detrimental effects on their optoelectronic properties. Cycloaddition reactions establish covalent bonds through  $\pi$ -electrons to bridge targeted functionalities onto the tubes. The carbon atoms below the bridge are converted into the  $sp^3$  state (closed configuration, Fig. 1a) or, if the C-C bond below the bridge is released, keep their  $sp^2$  character (open configuration, Fig. 1b) and preserve the overall conjugation of the extended network. We have recently demonstrated that the outcome of a triazine-based [2+1] cycloaddition reaction results in the open configuration (Fig. 1c) and preserves the intrinsic properties of the tubes, even at high degrees of functionalization (4%) [1]. Here we will highlight some of the benefits of this approach, such as the preservation of their radiative emission (Fig. 1d) or the fine-tuning of the position of their Fermi levels.

We will moreover discuss how the functionalized tubes can be exploited as starting platform for advanced materials. We show how the attachment of molecular systems makes them integrating part and in electronic communication with the conjugated network of the tubes, yielding new ways to non-perturbatively tailor, control, and alter the optical response of the tubes for novel applications. The conjugation of the molecular switch spyropiran-merocyanine, for example, enables controlled on-off switching of the tubes' emission to be exploited for nanotubes-based super-resolution microscopy.

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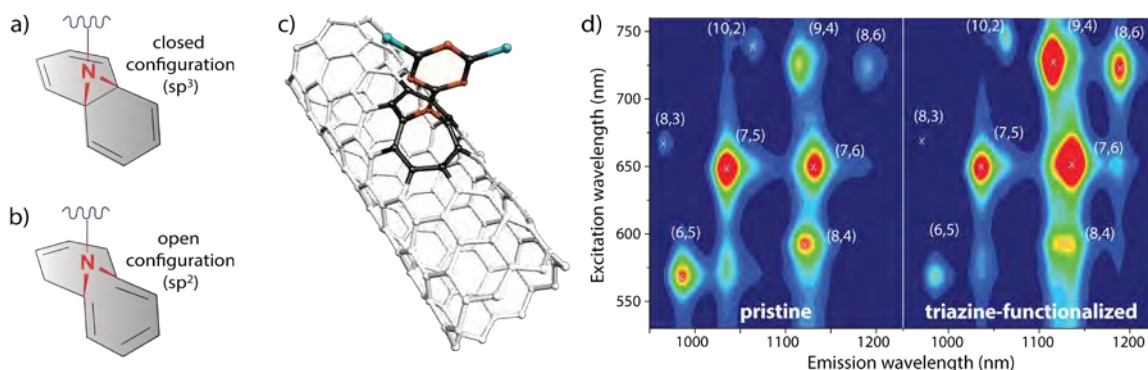


Fig.1 As a product of a [2 + 1] cycloaddition reaction bridging a triazine molecule, the two carbon atoms underlying the bridge can be in (a) their  $sp^3$  state in the closed configuration, or (b) their  $sp^2$  state in the open configuration. (c) Quantum chemical calculations show that the open configuration is the stable one. (d) Comparison between the PLE chart of pristine and triazine functionalized tubes.

# Probing exciton-exciton annihilation in hBN with cathodoluminescence experiments

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Hexagonal boron nitride (hBN) is a wide bandgap semiconductor of about 6.4 eV. It is considered as a promising insulating substrate for 2D crystals: preserving the high carrier mobility of graphene [1], enhancing the luminescence properties of transition metal dichalcogenides [2], or decreasing exciton-exciton annihilations in WS<sub>2</sub> [3]. As a key material for prospective devices based on 2D heterostructures, it is crucial to better understand hBN intrinsic properties, in particular luminescence ones that exhibit deep UV emissions governed by tightly-bound excitons.

In this work, we present exciton-exciton annihilation (EEA) experiments in hBN by using cathodoluminescence (CL), following our previous studies on the impact of defects [4,5] and on the thermal stability of excitons [6]. A control of the exciton density in continuous CL is achieved by tuning the focus and the current of the electron beam. Fig. 1 evidences a strong quenching of the luminescence at high exciton densities. In focused conditions, the quenching follows a square root dependence as a function of the beam current, evidencing a bimolecular and non-radiative process attributed to the EEA phenomena. Besides, a significant EEA rate of about  $1.7 \times 10^{-6} \text{ cm}^3/\text{s}$  is estimated thanks to CL experiments as a function of the defocusing. The impact of these results for atomic layers is discussed.

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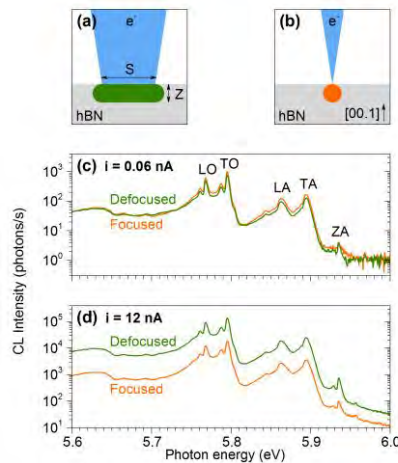


Fig.1 Schematic diagram of defocused (a) and focused (b) electron beams. CL spectra obtained at 10 K, 5 keV and a beam current equal to (c) 0.06 nA or (d) 12 nA. For each current, focused or defocused conditions are compared.

# Room-temperature single photon emission from carbon nanotubes

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H. Htoon<sup>4</sup>, S. K. Doorn<sup>4</sup>, Y. K. Kato<sup>1,2</sup>

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Single-walled carbon nanotubes are a promising material as quantum light sources at room temperature and as nanoscale light sources for integrated photonic circuits on silicon. Here we discuss the use of carbon nanotubes as room-temperature single photon emitters from two different approaches. The first is where efficient exciton-exciton annihilation process [1] is used to reduce the number of mobile excitons. We investigate photon statistics in as-grown individual air-suspended carbon nanotubes and perform theoretical analysis to show that diffusion-driven annihilation of mobile excitons can produce high-purity single photons [2]. In the second approach where exciton trapping sites are created to localize excitons [3], we demonstrate integration of carbon nanotube dopant states to silicon photonic crystal microcavities [4]. The coupling of the dopant emission to the microcavity results in an increase of photoluminescence by a factor of  $\sim 100$ , corresponding to a single-photon emission rate of  $1.7 \times 10^7$  Hz which is the highest reported for room-temperature operation of nanotube single photon sources. Our results show that both diffusive (1D) and localized (0D) excitons in carbon nanotubes can produce high quality single photons at room temperature, opening up a pathway to quantum light sources with additional functionality and flexibility.

Work supported by JSPS (KAKENHI JP16H05962, JP16K13613, JP17H07359) and MEXT (Photon Frontier Network Program, Nanotechnology Platform). A.I. acknowledges support from MERIT, and H.M. is supported by RIKEN Junior Research Associate Program. We thank Advanced Manufacturing Support Team at RIKEN for their assistance in machining. This work was conducted in part at the Center for Integrated Nanotechnologies, a US Department of Energy, Office of Science user facility and supported in part by Los Alamos National Laboratory Directed Research and Development funds.

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# Conservation law of angular momentum in Raman spectroscopy using circularly polarized light

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In Raman scattering of two-dimensional material, it is known that the helicity of circularly polarized light (left- or right-handed circularly polarized light) becomes opposite for incident and scattered light for some Raman active modes such as the in-plane optical IMC mode of transition metal dichalcogenides and the G band of graphene [Nano Lett. **15**, 2526 (2015) and Phys. Rev. B **95**, 165417 (2017)]. Since circularly polarized light has an angular momentum,  $\pm\hbar$ , the angular momentum of a photon is transferred to the material when the helicity of the scattered light is changed from that of incident light after the Raman scattering.

In the first-order Raman scattering, since a phonon is emitted in the Raman process, it may be natural to think that the angular momentum of the incident photon is transferred to the emitted phonon. L. Zhang *et al.* discuss the angular momentum of phonon and they show that the degenerated  $\Gamma$ -point phonon can have an angular momentum  $\pm\hbar$  by making the superposition of two degenerate eigenvectors of the phonon [Phys. Rev. Lett. **115**, 115502 (2015)]. However, if the angular momentum of a photon changes from  $+\hbar$  to  $-\hbar$ , the change of angular momentum of a photon is  $2\hbar$  which cannot transfer to a phonon with  $\pm\hbar$ .

In this presentation, we discuss the conservation law of angular momentum for first-order Raman scattering by considering the  $N$ -fold and  $N\nu$ -fold rotational symmetries of crystal and phonon, respectively [1]. H. J. Simon and many reseachers discussed the conservation law of angular momentum of crystal for 3-fold rotational symmetry. [Phys. Rev. **171**, 1104 (1968)]. Here we give a general conservation law for  $N = 1, 2, 3, 4$ , and 6 of the crystal for Raman and Rayleigh scattering. Further, we calculate the Raman and Rayleigh spectra for circularly polarized light by using the first principles calculations [2]. The calculated results explain all existing experiments and theories and predict some phonon modes in general  $N$ -fold rotational symmetry. We hope that the predicted, helicity exchanged Raman spectra that is not observed yet will be observed by experiment.

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# Theory of a Carbon-Nanotube Polarization Switch

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Recently, it was suggested that the polarization dependence of light absorption into a single-walled carbon nanotube (CNT) is altered by carrier doping [1]; a CNT absorbs light whose linear polarization is parallel to the tube's axis, but not when the polarization is perpendicular to it. This is a well-known property of an undoped CNT, which enables aligned CNTs to function as an optical polarizer [2]. Charge doping of a CNT inverts the polarization dependence; a doped CNT transmits parallel polarized light and absorbs perpendicular polarized light (Fig. 1). To change the polarization direction of light transmitted through a typical Polaroid lens, it is necessary to rotate the lens itself. However, according to the theory of doping dependence, a CNT polarizer can invert the polarization of the transmitted light by 90° without having to spatially rotate the polarizer; in other words, it is expected to function as a polarization switch.

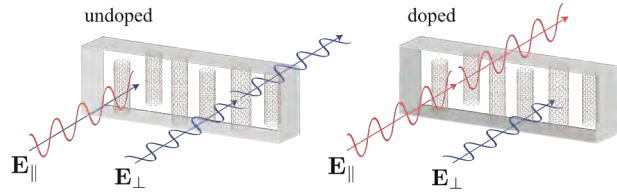


Fig.1 (left figure) Undoped CNTs transmit only perpendicular polarized light. (right figure) Doped CNTs transmit only parallel polarization. Since the polarization of the transmitted light rotates 90 degrees by doping, the aligned CNTs function as a polarization switch.

We specify theoretically the doping level at which the polarization anisotropy is reversed by plasmon excitation (Fig. 2) [3]. The plasmon energy is mainly determined by the diameter of a CNT, because pseudospin makes the energy independent of the details of the band structure. We argue that the effect of doping on the Coulomb interaction appears through the screened exchange energy, which can be observed as changes in the absorption peak positions ( $S_{22}$  and  $S_{33}$ ).

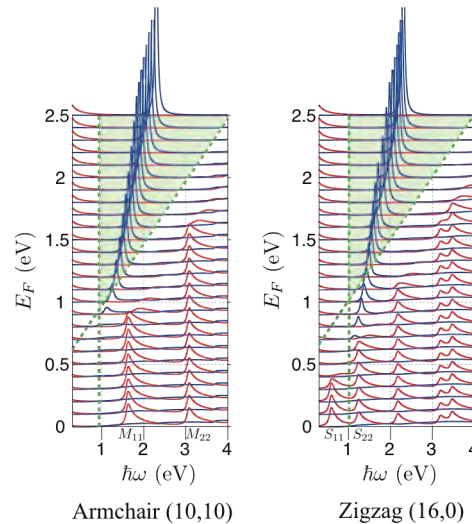


Fig.2 Doping with approximately 1 eV creates a transient region where the polarization anisotropy starts to be reversed. The green area shows the region where single particle excitation does not exist.

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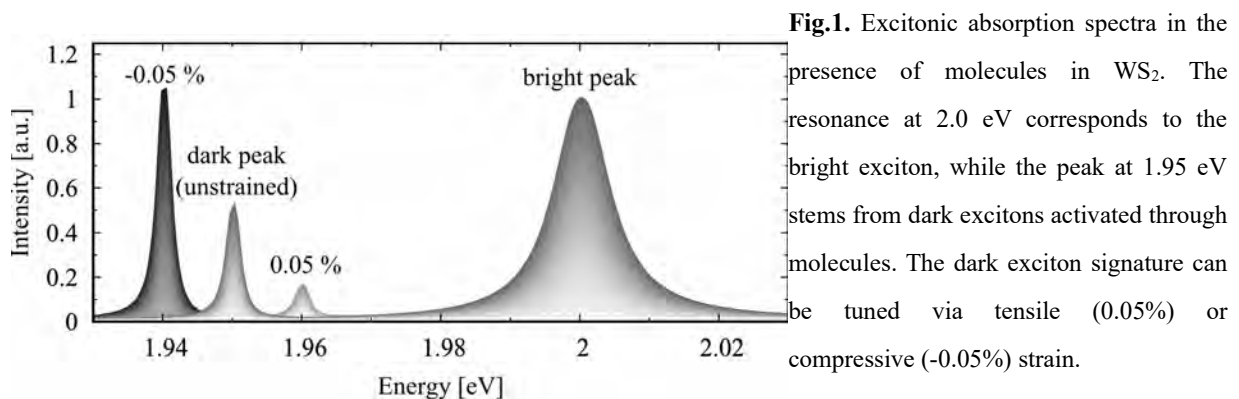
# Controlling the optical fingerprint of transition metal dichalcogenides via molecules, strain and disorder

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Atomically thin transition metal dichalcogenides (TMDs) have been in focus of current research due to their efficient light-matter interaction and the remarkably strong Coulomb interaction leading to tightly bound excitons. Beside bright excitons, TMDs also show a variety of dark (optically inaccessible) excitons. Moreover, as TMDs are atomically thin, they are very sensitive to changes in their surrounding which opens up the possibility of externally tailoring their optical properties.

Here, based on a fully quantum-mechanical approach, we present different strategies to control the optical fingerprint of different TMD monolayers via molecules, strain or impurities. We show that the coupling of excitons to specific molecules can activate momentum-forbidden dark exciton states resulting in an additional well pronounced peak in the optical spectra [1,2] (Fig. 1). Moreover, we find that these dark excitonic states are very sensitive to strain, leading to crucial energy shifts and intensity changes of dark exciton signatures (Fig. 1). Based on these findings, we suggest a novel optical sensing method for molecules and strain through activation of dark excitons. Finally, we also investigate which impact disorder has on the formation of localized excitonic states including their excitonic binding energies, phonon-assisted capture processes and thermalization as well as their photoluminescence including the possibility of single-photon emission [3].



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# H<sub>2</sub>-evolving SWCNT Photocatalysts for Effective Use of Solar Energy

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Visible and near-infrared (NIR) light-induced water splitting has received considerable attention in terms of solar energy conversion and hydrogen energy storage. Single-walled carbon nanotubes (SWCNTs) are potentially strong optical absorbers with tunable absorption wavelengths depending on their chiral indices ( $n,m$ ). In order to make SWCNTs act as a H<sub>2</sub>-evolving photocatalyst, we have developed coaxial p-n heterojunction systems consisting of a SWCNT and fullerodendrons, such as SWCNT/fullerodendron [1], SWCNT/fullerodendron/SiO<sub>2</sub> [1], SWCNT/fullerodendron/ Pt(II) [2,3,5], and SWCNT/fullerodendron/TiO<sub>x</sub> [4]. Moreover, we have found SWCNT/dendrimer that does not contain C<sub>60</sub> acts as a photosensitizer for H<sub>2</sub> evolution in the presence of methyl viologen dication (MV<sup>2+</sup>) [6]. By the use of these SWCNT-photocatalysts, we can effectively use solar energy since the mixture of SWCNTs with different helicities exhibits satisfiable efficiency of H<sub>2</sub> evolution from water. Recently, we fabricated SWCNT-photocatalyst based on dye-encapsulated SWCNTs in order to challenge the enhancement of light-absorbing ability [7].

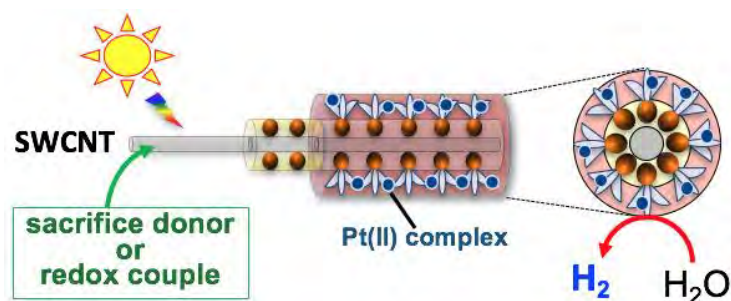


Fig.1 A schematic illustration of H<sub>2</sub> evolution reaction using a SWCNT-photocatalyst, SWCNT/fullerodendron/Pt(II).

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# Antenna-Controlled Antibunching in the Photoluminescence of Single Carbon Nanotubes

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Since its first report in 2008 [1], photon antibunching in the photoluminescence (PL) from semiconducting single-walled carbon nanotubes (SWCNTs) attracted considerable attention because of potential applications of SWCNTs as single-photon-sources. Known for single point-like quantum systems, the observed antibunching from a 1D nanomaterial also raised fundamental questions regarding the underlying mechanism. In general, antibunching is thought to require the efficient localization of the excited state energy at local minima in the exciton energy landscape or at chemical dopant sites and was reported for different nanotube materials and configurations upon optical as well as electrical excitation [2-5].

We performed photon-correlation experiments in a Hanbury-Brown-Twiss setup. A sharp laser-illuminated metal tip operated in a scanning probe scheme acted as optical antenna providing near-field PL enhancement with a spatial range around 20 nm [6,7]. In the near-field of the tip, the second order correlation at zero delay  $g^{(2)}(0)$  was found to be substantially reduced (Fig. 1). Stronger PL antibunching resulting from the antenna-induced localization of the light-matter interaction has the potential to reach the single-photon-regime ( $g^{(2)}(0) < 0.5$ ) for nanotubes on glass. We discuss possible mechanisms of antenna-controlled antibunching including localized exciton-exciton annihilation [5] and applications to other low-dimensional materials.

- [1] A. Högele, C. Galland, M. Winger, A. Imamoğlu, *Phys. Rev. Lett.* **100**, 217401 (2008)
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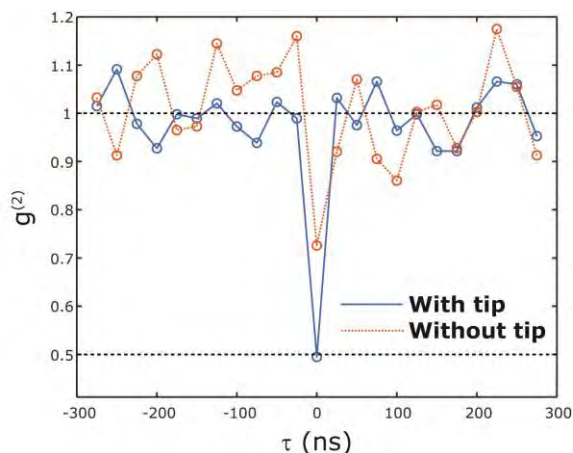


Fig.1 Second order correlation  $g^{(2)}(\tau)$  of the PL emission from a single (6,5) SWCNT with and without optical tip antenna.



# Synthesis and properties of single-walled carbon nanotubes co-axially wrapped with mono- and few-layer BN nanotubes

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

Part of this work was supported by JSPS KAKENHI Grant Numbers JP25107002 and JP15H05760.

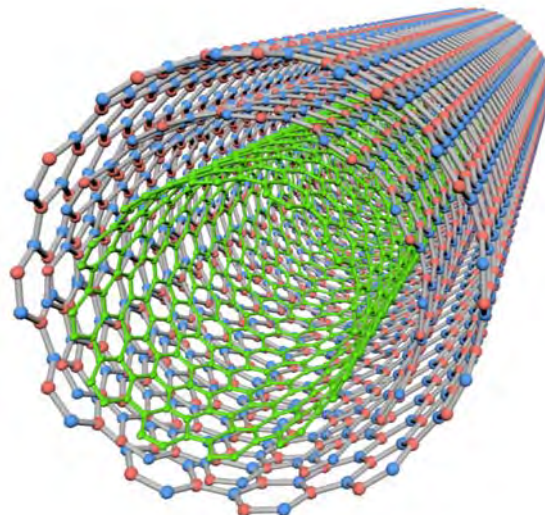


Fig.1 Schematic structure of an SWNT wrapped with a bilayer BN nanotube.

# Direct Determination of Chemically Induced Doping Concentrations in (6,5)- Single-Wall Carbon Nanotubes by EPR

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Control over doping of semiconducting Single-Wall Carbon Nanotubes (SWNTs) by (electro-) chemical methods and intrinsic impurities are considered to be crucial for future applications of SWNTs in carbon-based electronics and photonics. Previous indirect all-optical techniques hypothesize charge carrier localization in semiconducting (6,5)-SWNTs following redox chemical AuCl<sub>3</sub> doping, which is indicated by spectral and dynamical changes of the S<sub>1</sub> exciton band [1].

Here, we present direct quantitative investigations of chemical impurities by means of electron paramagnetic resonance (EPR). For the as-produced (6,5)-SWNT samples we detected very low signal intensities stemming from two separate radical-like, isolated spin contributions that we assign to defects or residual impurities and which may be associated with what is sometimes referred to as intrinsic p-doping. Their concentration indicates exceptional nanotube quality with only few paramagnetic species per μm nanotube. Upon addition of the doping agent (AuCl<sub>3</sub>)<sub>2</sub> we observe a linear increase of the EPR signal intensity which we ascribe to localized p-type impurities on the nanotube. However, at higher doping concentrations, the observed signal saturates, before decreasing again and finally vanishing at the highest AuCl<sub>3</sub> concentrations. This seemingly puzzling result can be understood in terms of the formation of EPR silent, diamagnetic bi-radicals which start to appear at moderate doping concentrations. We model this behaviour with a stochastic formation of impurity sites in a 1D lattice, yielding good agreement with experimental data. In conclusion, we can confirm charge carrier confinement at low impurity concentrations in SWNTs with potentially far reaching implications for future device applications.

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# Note

# Posters

# Photophysical properties of porphyrin–single-walled carbon nanotube linked systems with various spacer lengths

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Although the precise understanding of the intrinsic nature of the exciplex state with both excited state and charge-transfer characters is crucial for efficient formation of the long-lived charge-separated state, the information is extremely limited in comparison with the charge-separated state because of lack of suitable model systems and difficulty in creating such model systems.

We report herein unprecedented long-range observation of both formation and decay of the exciplex state in donor (D)–bridge (B)–acceptor (A) linked systems. Zinc-porphyrins (ZnP) as a donor were tethered to single-walled carbon nanotube (SWNT) as an acceptor through oligo(*p*-phenylene)s (ZnP-ph<sub>*n*</sub>-SWNT) or oligo(*p*-xylene)s (ZnP-xy<sub>*n-1*</sub>-ph<sub>1</sub>-SWNT) with systematically varied lengths (*n* = 1–5) to address the issue (Figure 1). Exponential dependencies of rate constants for the exciplex formation (*k*<sub>FEX</sub>) and decay (*k*<sub>DEX</sub>) on the edge-to-edge separation distance between ZnP and SWNT through the bridges were unambiguously derived from time-resolved spectroscopies. Distance dependencies (i.e., attenuation factor, β) of *k*<sub>FEX</sub> and *k*<sub>DEX</sub> in ZnP-ph<sub>*n*</sub>-SWNT were found to be considerably small (β = 0.10 for *k*<sub>FEX</sub> and 0.12 Å<sup>-1</sup> for *k*<sub>DEX</sub>) compared to those for charge separation and recombination (0.2–0.8 Å<sup>-1</sup>) in D–B–A systems with the same oligo(*p*-phenylene) bridges. The small β values may be associated with the exciplex state with mixed characters of charge-transfer and excited-states. In parallel, the substantially non-conjugated bridge of oligo(*p*-xylene)s exhibited larger attenuation values (β = 0.12 for *k*<sub>FEX</sub> and 0.14 Å<sup>-1</sup> for *k*<sub>DEX</sub>). These results provide deep insight into the unique photodynamics of electronically strongly coupled D–B–A systems involving exciplex.

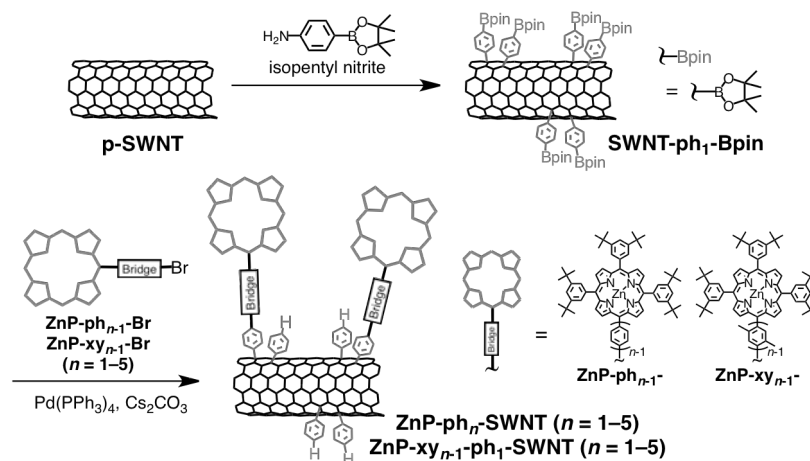


Figure 1. Synthesis of ZnP-ph<sub>*n*</sub>-SWNT and ZnP-xy<sub>*n-1*</sub>-ph<sub>1</sub>-SWNT (*n* = 1 – 5).

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## Phonon Assigning of G-band from Suspended Single-walled Carbon Nanotubes

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Generally, phonon symmetry of Raman peaks is assigned by polarized Raman spectroscopy because polarization dependence of Raman intensity is affected by phonon symmetry. However, as for a single-walled carbon nanotube (SWCNT), polarization dependence is affected by the selection rule of light absorption and antenna effect [1] as well as the phonon symmetry. Thus, determining phonon symmetry of Raman peaks from SWCNT by polarized Raman spectroscopy was difficult especially for G peaks. Moreover, it is known that six G peaks could exist in SWCNT [2] while only two G peaks ( $G^+$ ,  $G^-$ ) are detected from isolated SWCNT [3]. The problem is that it is unknown which of six G peaks could be assigned to  $G^+$ ,  $G^-$  peaks.

In this study, we tried to determine phonon symmetry of  $G^+$ ,  $G^-$  peaks from measurements of suspended SWCNTs considering the selection rule of light absorption and antenna effect. In polarization measurements, Raman scattering was detected only when its polarization was parallel (VV) or perpendicular (VH) to that of incident laser beam. Because the intensity of Raman scattering depends on incident and scattered polarization and phonon symmetry, phonon symmetry could be determined from polarization dependence by fixing polarization configurations. The result of polarization dependence of  $G^+$ ,  $G^-$  peaks in VV configuration is shown in Fig. 1. The solid line in Fig. 1 is the fitting result. The fitting was succeeded by using equations presumed that both  $G^+$ ,  $G^-$  peaks have  $A$  symmetry considering the selection rule of light absorption and antenna effect. Raman tensor elements of  $A$  symmetry were calculated by the result of fitting parameter in  $G^+$ ,  $G^-$  peaks, respectively.

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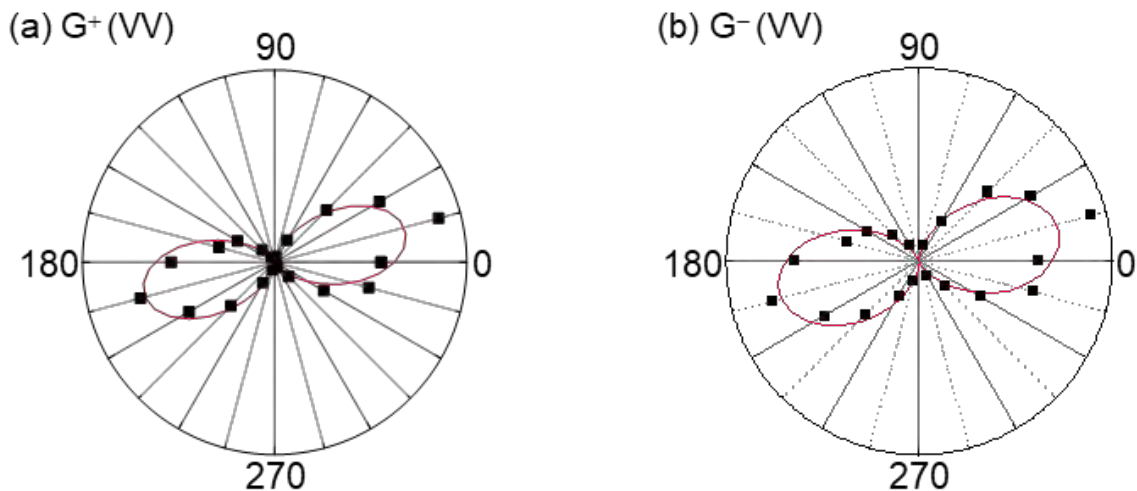


Fig. 1. Polarization dependence of the intensity of (a)  $G^+$  and (b)  $G^-$  peaks from (9,8) suspended SWCNT in VV configuration.

## **Thin films from carbon nanotubes of highly tuned structure and properties**

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Due to remarkable electrical, thermal, optical and other properties of carbon nanotubes they have attracted significant interest from research groups all over the world. However, to implement them in the real life, we still need better methods to control their structure at the nanoscale and also techniques to turn these highly defined materials into macroscopic ensembles. In this contribution, I will present results of our work how we have attempted to solve these problems. I will share our recent advances on the front of sorting CNTs by electrical character and chirality [1,2]. I will also show a method developed by us, which enables formation of free-standing thin films from any type of CNTs including that of monochiral nature [3,4]. The obtained materials are very promising for a wide range of electrical and optical applications.

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[4] D. Janas, G. Stando, Sci. Rep. **7**, 12274 (2017)

## **Environmental electrometry with luminescent carbon nanotubes**

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We demonstrate that localized excitons in luminescent carbon nanotubes can be utilized to study electrostatic fluctuations in the nanotube environment with sensitivity down to the elementary charge. By monitoring the temporal evolution of the cryogenic photoluminescence from individual carbon nanotubes grown on silicon oxide and hexagonal boron nitride we characterize the dynamics of charge trap defects for both dielectric supports. We find a one order of magnitude reduction in the photoluminescence spectral wandering for nanotubes on extended atomically flat terraces of hexagonal boron nitride. For nanotubes on hexagonal boron nitride with pronounced spectral fluctuations our analysis suggest proximity to terrace ridges where charge fluctuators agglomerate to exhibit spatial densities exceeding those of silicon oxide. Our results establish carbon nanotubes as sensitive probes of environmental charge fluctuations and highlight their potential for applications in electrometric nanodevices with all-optical readout.



## Cryogenic spectroscopy of $sp^3$ defect states in carbon nanotubes

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Photoactive defect states in semiconducting single-walled carbon nanotubes (CNTs) have the potential to enable novel applications in quantum photonic technologies. While early experiments have established cryogenic CNTs as quantum light emitters [1], more recent work has identified luminescent defect states as sources of single photons up to room temperature [2,3]. For chemically-engineered CNTs,  $sp^3$  functionalization offers means to deterministically influence the corresponding trap state properties *via* the characteristics of the covalent side chains. Recent findings show that the incorporation of  $sp^3$  alkyl defects into the  $sp^2$  lattice of narrow-diameter CNTs promotes the formation of both neutral and charged localized excitons [4] with unexpectedly high quantum efficiency. Here, we report the results of our cryogenic photoluminescence studies carried out on individual nanotubes functionalized with  $sp^3$  side-wall chemistry.

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## Photocurrent Spectroscopy of Dye-Sensitized Carbon Nanotubes

Asiful Alam<sup>1,2</sup>, Simone Dehm<sup>2</sup>, Frank Hennrich<sup>1,4</sup>, Yuriy Zakharko<sup>3</sup>, Arko Graf<sup>3</sup>, Moritz, Pfohl<sup>1,2</sup>, Ihteaz M. Hossain<sup>5</sup>, Manfred M. Kappes<sup>1,4</sup>, Jana Zaumseil<sup>3</sup>, Ralph Krupke<sup>1,2</sup> & Benjamin S. Flavel<sup>1,2</sup>

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Monochiral (7,5) single walled carbon nanotubes (SWCNTs) are integrated into a field effect transistor device in which the built-in electric field at the nanotube:metal contact allows for exciton separation under external light bias. Variable wavelength spectroscopy and 2D surface mapping of devices consisting of 10 – 20 nanotubes is performed in the visible, and a strong correlation between the nanotube's second optical transition ( $S_{22}$ ) and the photocurrent is found. Subsequently, the SWCNTs are non-covalently modified with three different fluorescent dye molecules with off-resonant absorption maxima at 532, 565, and 610 nm. Energy transfer from the dyes onto the SWCNTs allows for the optical properties of the nanotube to be tailored and holds promise for the development of photo-detectors and for applications in photovoltaics and biosensing

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## High-Speed and integrated graphene blackbody emitters

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<sup>2</sup> *Faculty of Electrical Engineering and Information Technology, RWTH Aachen University, Aachen, 52074, German*

<sup>3</sup> *Global Innovation Center (GIC), Kyushu University, Fukuoka, 816-8580, Japan*

<sup>4</sup> *JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*

Nanocarbon-based optoelectronic devices are promising candidates for the high-speed, uncooled and on-chip optical communication devices [1-3]. Here, we report highly integrated, high-speed blackbody emitters based on graphene in near-infrared region including telecommunication wavelength and these application to optical communications [4].

We fabricated blackbody emitters with single-layer, few-layer and multi-layer graphene. By applying bias voltage to these devices, we heated graphene by Joule heating and obtained light emission following Planck's law in near-infrared region including telecommunication wavelength. Under a rectangular voltage, a fast response time of ~ 100 ps, corresponding to ~ 10 GHz modulation, has been experimentally demonstrated for single and few-layer graphene. Their emission responses are strongly affected by the graphene contact with the substrate depending on the number of graphene layers. The ultra-high-speed emission can be understood by remote quantum thermal transport via surface polar phonons of the substrates. We also confirmed by time resolved measurement that these graphene light sources can emit optical pulse with full width at half maximum of 200 ps. We also demonstrated real-time optical communications, integrated two-dimensional array emitters, capped emitters operable in air, and the direct coupling of optical fibers to the emitters. These results indicates that the graphene light source is a new candidate for high speed light source for on silicon-chip optical communication.

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

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## Post modification approach for photoluminescence modulation of locally functionalized single-walled carbon nanotubes

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<sup>1</sup> Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motoka, Nishi-ku, Fukuoka, 819-0395, Japan

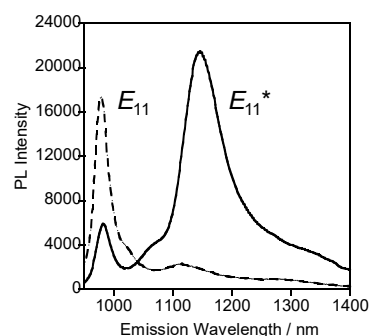
<sup>2</sup> WPI-I2CNER, Kyushu University, 744 Motoka, Nishi-ku, Fukuoka, 819-0395, Japan

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Single-walled carbon nanotubes (SWNTs) show photoluminescence (PL) in the near infrared (NIR) region and, are applicable to a wide range of applications including optoelectronic devices and imaging materials. Recently, local chemical functionalization of SWNTs has been reported to create red-shifted PL ( $E_{11}^*$ ) with enhanced quantum yields compared to  $E_{11}$  PL [1-5]. The PL properties emerge by the formation of new emissive sites that have narrower band gaps and can trap excitons generated on the tubes. We have been synthesizing molecularly-designed modifiers to modulate the  $E_{11}^*$  PL and, recently have succeeded in a selective  $E_{11}^*$  wavelength shift of the locally functionalized SWNTs (lf-SWNTs) based on binding of a specific molecule on the modified sites through a molecular recognition technique [2].

In this study, as a new modulation technique using molecular systems, a post modification approach is developed for  $E_{11}^*$  PL modulation, in which the post modification occurs locally at the chemically-modified sites on lf-SWNTs. Herein, we employ imine bond formation, which is based on a condensation reaction between aldehyde and amine groups, at the modified site by using the synthesized aromatic aldehyde-modified lf-SWNTs (**PhCHO-SWNTs**) and their post modification upon addition of amine compounds.

Fig. 1 shows PL spectra of pristine SWNTs and **PhCHO-SWNTs**. For **PhCHO-SWNTs**, a new PL peak appeared at 1140 nm ( $E_{11}^*$ ) which was red-shifted than  $E_{11}$  PL at 980 nm. When *p*-methylaniline, *p*-bromoaniline or *p*-nitroaniline was mixed with **PhCHO-SWNTs**, peak shifts of the  $E_{11}^*$  PL were observed, resulting in different wavelength shift values ( $\lambda(E_{11}^*) - \lambda(E_{11})$ ) of 154, 163 and 165 nm, respectively. The results indicate that the wavelength shift occurs with strong dependence on the chemical structures of the added aniline derivatives. Our present technique, therefore, is expected to achieve versatile modulation of the wavelength of  $E_{11}^*$  PL.



**Fig. 1** PL spectra of pristine SWNTs and **PhCHO-SWNTs** ( $\lambda_{\text{ex}} = 570$  nm).

[1] Y. Wang, *et al.*, Nat. Chem. **5**, 840 (2013). [2] T. Shiraki, *et al.*, Chem. Commun. **52**, 12972 (2016). [3] T. Shiraki, *et al.*, Sci. Rep. **6**, 28393 (2016). [4] T. Shiraki, *et al.*, Nanoscale, **9**, 16900 (2017). [5] T. Shiraki, *et al.*, Chem. Commun. **53**, 12544 (2017).

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

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Toward the spread of quantum information technology such as quantum communications to the general public, the development of quantum light sources, which can operate at room temperature and telecommunication wavelength, are required. In this study, we measured the photoluminescence (PL) of individual air-suspended SWNTs over the telecommunication wavelength range and a range of temperatures and investigated the time-resolved PL and photon antibunching properties. Air suspended SWNTs were grown on a line-and-space patterned silicon substrate, and the PL was measured from 6 to 300 K. We carried out photon correlation measurements with a Hanbury-Brown-Twiss setup, and observed the first photon antibunching in the telecommunication wavelength range at room temperature [1]. This high-temperature photon antibunching can be explained by the exciton diffusion in a suspended SWNT taking into account exciton-exciton annihilation (EEA) and end quenching investigated by Monte Carlo simulation, which was recently reported in Ref. 2. We expect that future developments will see the application of this antibunching behavior of SWNTs for high-efficiency single photon emitters at telecommunication wavelength and room temperature [3,4].

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

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## Spectral tuning of optical coupling between air-mode nanobeam cavities and individual carbon nanotubes

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We design high quality factor air-mode nanobeam cavities by finite-difference time-domain simulations, and utilize the cavities to enhance the emission of air-suspended carbon nanotubes [1]. The cavities are fabricated from silicon-on-insulator wafers, and nanotubes are synthesized over the cavities by chemical vapor deposition. Photoluminescence spectroscopy is performed on the devices, where we observe optical coupling when the nanotube emission energy is close to the cavity resonance. Taking advantage of laser-heating-induced blueshifts of the nanotube emission, we can reduce the detunings [2]. We derive and numerically calculate the generalized expression for the spectral overlap, and good correlation to the enhancement factors is obtained.

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## Cavity-control of bright and dark interlayer excitons in van der Waals heterostructures

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Monolayer transition metal dichalcogenides integrated in optical microcavities host exciton-polaritons as a hallmark of the strong light-matter coupling regime [1]. Analogous concepts for hybrid light-matter systems employing spatially indirect excitons with a permanent electric dipole moment in heterobilayer crystals promise realizations of exciton-polariton gases and condensates with immanent dipolar interactions. Here, we identify optical signatures of spatially indirect momentum-bright and momentum-dark interlayer excitons in vertical MoSe<sub>2</sub>-WSe<sub>2</sub> heterostructures and implement cavity-control of both exciton manifolds. To this end we employ a tunable open-access cavity with one curved fiber-based mirror [2] and one planar mirror with extended MoSe<sub>2</sub>-WSe<sub>2</sub> heterobilayer flakes on top. The configuration of controlled intermirror spacing and lateral scanning capabilities is used to explore the light-matter coupling of excitons as a function of the cavity length at representative positions of heterobilayers selected by two-dimensional cavity imaging. Our experiments quantify the strength of interlayer excitons and demonstrate Purcell enhancement in cavity-modified photonic environments [3].

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# Probing the optical dipole transition and vibrational coherences in individual (5,4) carbon nanotubes by femtosecond pulse shaping

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Optical detection and coherent control of quantum interferences in nanostructures have attracted considerable attention both as tools to study ultrafast photo-induced phenomena and for their possible application in novel nanophotonic devices. Here, we perform experiments on individual semiconducting single-walled carbon nanotubes (SWCNTs) using femtosecond laser pulse shaping microscopy. Single (5,4) SWCNTs [1] excited with a pair of phase-locked 20 fs laser pulses [2] exhibit beating patterns in their photoluminescence intensity resembling Rabi oscillations in a two-level system. We show that these oscillations can be controlled within the first approximately 100 fs by varying the delay of the pulses and by tuning their relative carrier envelope phase.

Whereas the observed signal variations can be interpreted in terms of coherent control [4-6], they could also be understood in terms of a spectral interference effect because the experiments were carried out mainly in the linear response regime [3]. On the basis of our measurements we discuss the limits of the coherent control approach in pulse shaping microscopy.

For longer pulse separations, coherent radial breathing mode excitations with a period of 90 fs are observed, matching the well-known radial breathing mode in these nanotubes. We show that the onset of these nanoscopic oscillations is deterministic for the (5,4) nanotubes.

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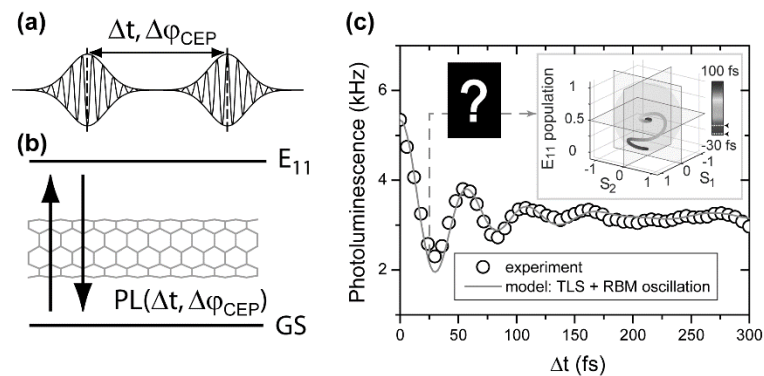


Fig. 1 (a) Two phase-locked femtosecond laser pulses excite (b) a carbon nanotube resonantly. (c) Autocorrelation scans show distinct beating patterns which can be explained in the context of coherent control and Rabi oscillations, but this interpretation depends on the exact circumstances in a critical fashion.



## Evaluation of substituent effects on the potential levels of locally-functionalized single-walled carbon nanotubes using *in situ* photoluminescence spectroelectrochemistry

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Recently, single-walled carbon nanotubes (SWNTs) with local chemical functionalization were reported to produce the photoluminescence (PL) with red-shifted PL wavelengths by over 100 meV and enhanced quantum yields compared to those of pristine SWNTs [1]. Interestingly, the PL wavelengths of locally-functionalized SWNTs (lf-SWNTs) shift based on the difference in the chemical structures of the modified groups on the lf-SWNTs [2]. As another structural factor, we reported the proximal modification using bisdiazonium compounds for the synthesis of the lf-SWNTs and observed a largely red-shifted PL by 250 meV from  $E_{11}$  PL of the pristine SWNTs [3]. These findings are of importance in view of the new PL phenomena of the SWNTs but the effect of the defect structures on the lf-SWNTs has been mainly discussed based on the optical band gaps of the SWNTs and their PL dynamics.

In this study, we conduct an *in situ* PL spectroelectrochemical analysis to evaluate potential levels (HOMO and LUMO) of the lf-SWNTs [4]. Four types of lf-SWNTs with aryl groups that had different substituents (-MeO, -H, -Br and -NO<sub>2</sub>) were synthesized and characterized in order to investigate the substituent effect on their electronic states. As shown in Fig. 1, the HOMO and LUMO levels shifts occurred by the local functionalization and a substituent dependence was observed specifically in the HOMO level. The observed negative potential shift in the HOMO level largely occurred according to the increase in the electron-accepting natures of the substituents. Regarding the LUMO level, on the other hand, negligible change was observed. In this presentation, we will discuss more details in terms of factors of the level shifting and, differences in chiral indices and family patterns of the nanotubes.

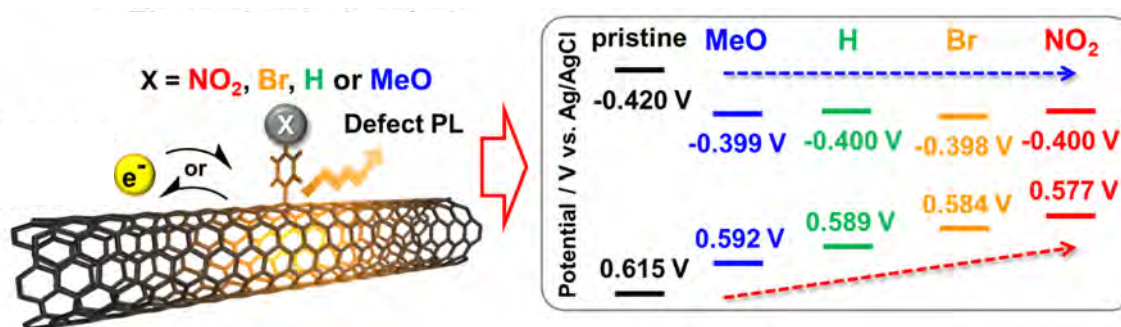


Fig. 1 (Left) Schematic illustration for the reduction/oxidation of lf-SWNTs using the *in situ* PL spectroelectrochemical method. (Right) The evaluated HOMO and LUMO levels of the pristine and lf-SWNTs with different substituents.

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## Dielectric properties of vertically aligned carbon nanotubes in the mid-IR and THz spectral range

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Vertically aligned carbon nanotubes (VACNT) are interesting candidates as chemo-physical sensors. The reason lies not only in their huge surface-to-volume ratio, but also the low carrier dimensionality which suggests that an adsorption of molecules should lead to a measurable change of the conductivity. Here, we explore the use of THz radiation to probe for such conductivity changes in a contactless manner.

In preparation of sensing measurements, we first investigated the dielectric properties of VACNT of different tube lengths in the THz/mid-IR spectral range (0.1-100 THz) [1], because the data found in the literature are highly disparate and their interpretation is conflicting. Our measurements with the radiation impinging vertically onto the sample yield a rather featureless optical density with a broad peak around 24 THz.

We employ for the first time a fit of such data with a *Bergman*-type effective medium theory which takes the morphology of the tubes into account via depolarization factors which can be understood as representing the capacitive coupling between neighboring tubes respectively the internal capacitance of each tube. The intrinsic conductivity of the tubes is assumed to be of conventional Drude type. With this model, we can fit our measure data very satisfactorily if we allow for a weak additional axial conductance manifesting at low THz frequency and arising because the tubes are not perfectly vertical. The fits yield a plasma frequency  $\nu_p = 42 \pm 2$  THz, a carrier momentum scattering time  $\tau = 3.5 \pm 0.3$  fs and a residual axial conductivity of  $\sim 0.3$  ( $\Omega\text{cm}$ )<sup>-1</sup>. Our analysis suggests that the responses of plasmonic, phononic, Drude-Smith, Drude-Lorentz or even more exotic type resorted to in the literature in order to explain the THz or IR spectra may in most cases not be needed and may only mimic the depolarization effects imposed by the nanostructure of the tubes and their microscopic arrangements.

We also show first THz gas sensing measurements which reveal doping effects of NH<sub>3</sub> and SO<sub>2</sub> adsorbed in the VACNT “forest” [2]. Fig. 1 displays results from our THz transmission measurements of VACNT in either air or NH<sub>3</sub> atmosphere. The presence of NH<sub>3</sub> reduces the conductivity. This can be understood – consistent with the literature – by the donor character of the NH<sub>3</sub> molecules. VACNT are a statistical mixture of metallic and semiconducting tubes with an overall p-type conductivity. The interaction with the NH<sub>3</sub> molecules reduces the hole density and with it the conductivity. This suggests that THz read-out of VACNT may be useful for gas-sensing.

The VACNT samples were provided by the group of J. Schneider, TU Darmstadt. The project was funded by the Hessian excellence initiative LOEWE, project *Sensors Towards THz*.

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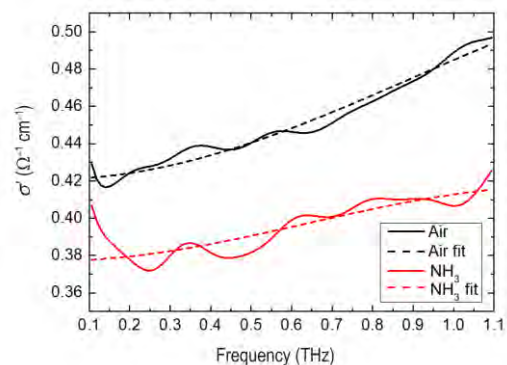


Fig.1 Decrease of the THz conductivity of VACNT upon exposure to NH<sub>3</sub> gas at ambient pressure. The upper curve (black online) is for VACNT in air, the lower one (red online) for VACNT in NH<sub>3</sub> atmosphere.

## Optical properties of core-shell systems based on carbon nanotubes

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Single-walled carbon nanotubes exhibit unique physical properties. In particular, single-photon emission at room temperature has been recently reported ([1], [2]). This has been achieved by surface chemistry that creates point-like defects that localize the nanotube's exciton. The design of these defects allows creating potential well with deepness far above  $kT$  leading to the antibunching at room T. The last achievement reports  $g^2(0) < 0.01$  at room T and in the telecom wavelength bands ([2]). Concomitantly, first Cavity Quantum Electrodynamics experiments have been carried out using nanotubes as the quantum emitter. These experiments exhibit Purcell effect and cavity feeding ([3], [4]). These results pave the way to the use of nanotubes as emitters in quantum devices.

Nevertheless, efforts have to be made on the material side in order to integrate nanotubes in devices. Nanotubes being only made of surface atoms, they show an uncontrolled sensitivity to their local environment. One of the main problems for the use of nanotubes as quantum emitters is the degradation of the purity of the source due to blinking and spectral diffusion processes. Here, we report on a strategy that consists in protecting carbon nanotubes from their close environment to improve the stability of their emission while being suitable materials for incorporation in real devices. To do so, we synthesize core/shell nanostructures: the nanotube is the active core, while a double polymer layer acts as protective shell [5]. In this poster, we discuss our preliminary results about the influence of a double shell structure on the emission properties of single nanotubes investigated by microphotoluminescence experiments at low temperature.

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## Molecular screening effects on trion binding energies and electronic band gaps in air-suspended carbon nanotubes

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The quasi-one-dimensional geometry of single-walled carbon nanotubes results in enhanced Coulombic interactions. The strong electron-hole attractive force leads to a formation of tightly bound excitons and trions. These optical properties are sensitive to environmental screening, which causes the reduction of the Coulombic interactions. For air-suspended nanotubes, the excitons are known to be affected by screening of adsorbed molecules [1,2]. However, the effect of the adsorbed molecules on the trion binding energies and electronic band gaps still remain unclear.

Here, we investigate the molecular screening effects on trion binding energies and electronic band gaps in air-suspended carbon nanotubes within field-effect transistor configuration. Measurements of gate voltage dependence on photoluminescence from nanotubes before and after the molecular adsorption show that the molecules significantly modify the trion binding energies as well as the electronic band gaps. We further observe large influence of the excitation power on the gate dependence of photoluminescence, which could be a signature of the band gap renormalization induced by excitonic screening.

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## Optical Properties of Oxidized Single-Wall Carbon Nanotubes

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Optical properties of oxidized single-wall carbon nanotubes (SWCNTs) have attracted much attention because of the greater luminescence quantum yield than that of pristine CNTs [1]. To advance the fundamental understanding of the optical properties of oxidized SWCNTs, we theoretically investigated the energetics and the optical transitions for complex oxygen (O) adsorption structures on (6,5) CNTs, including adsorption of two O atoms [2]. Further O diffusion simulations considering the energetics provide a possible mechanism for significant emission at lower energy in recent bioimaging experiments.

As shown in Fig. 1, we obtained four groups of optical transition levels below  $E_{11}$  for CNTs adsorbed by isolated O atoms, including the levels known as  $E_{11}^*$  and  $E_{11}^{*-}$ . The most stable O-adsorption structure is ether structure, which corresponds to the  $E_{11}^*$  level; however the epoxy structure that produces the  $E_{11}^{*-}$  level is much less stable than the ether structure, which is unlikely to explain the experimentally observed  $E_{11}^{*-}$  emission. To address this issue, we considered adsorption of two O atoms. The most stable adsorption structure for two O atoms is two parallel ether structures, whose transition energy appear between  $E_{11}^*$  and  $E_{11}^{*-}$ , and more stable than two isolated ether structures. The second most stable structure is neighboring ether and epoxy structures, whose O-adsorption energy is also much stronger than the sum of those of isolated ether and epoxy structures. The transition energy is only 0.02eV lower than the  $E_{11}^{*-}$  level that is produced by the isolated epoxy structure. According to the O diffusion simulations considering the energetics we had found, we found that a certain number of O atoms maintain the epoxy structure at higher O concentrations, providing a possible mechanism for significant brightening of  $E_{11}^{*-}$  in the recent bioimaging experiments.

These results explain the multiple emission peaks in the low-temperature PL measurements of SWCNTs oxidized by  $O_3$  and those in the PL spectra of SWCNTs oxidized by  $O_2$  molecules during single chirality separation processes. Our comprehensive understanding is essential for further applications of oxidized SWCNTs.

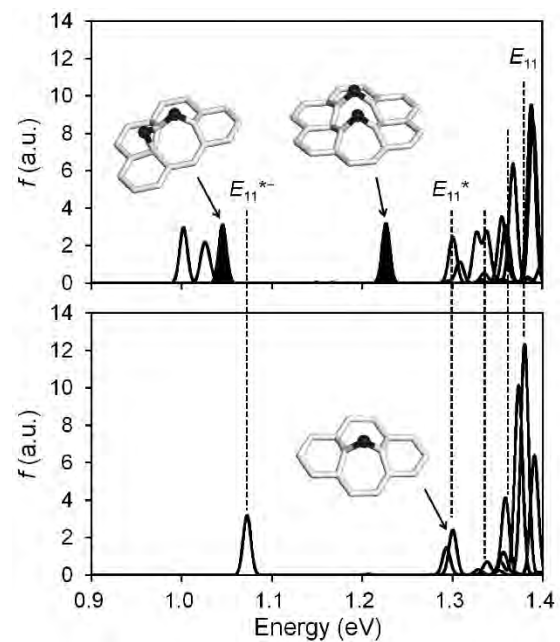


Fig.1: Optical transitions for (6,5) CNTs adsorbed by one O atom (lower panel) or two O atoms (upper panel). The oscillator strengths are plotted with 5-meV width around the transition energies. The insets are the schematic diagrams for the related O-adsorption structures. The gray sticks and black spheres represent C-C bonds and O atoms, respectively.

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## Narrow-band thermal exciton radiation in individual suspended single-walled carbon nanotubes

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A number of intriguing phenomena arising from many-body quantum correlations have been discovered in single-walled carbon nanotubes (hereafter referred to as nanotubes); their understanding and control are intensively studied from the viewpoint of the fundamental physics and device applications. Majority of these experimental works have been conducted below room temperature, and it has been revealed that their optical properties are dominated by excitons and/or exciton complexes. In contrast to these properties, thermal radiation, which is one of the fundamental optical properties, remains unclear because of technical difficulties. Although some pioneering studies reported light emission spectra consisting of broad peaks from nanotubes under Joule-heating conditions [1,2], the carrier doping and current injection required to heat the nanotubes may considerably modify their one-dimensional quantum correlation effects [3], and the origin of the peak features (whether they are band-to-band or excitonic transitions) remains debatable [1,2]. In addition, the possibility of competing electroluminescence mechanisms, including ambipolar carrier injection and impact excitation, further complicates the interpretation of light emission phenomena during current injection.

In this work, we show the fundamental thermal radiation properties of intrinsic semiconducting and metallic nanotubes suspended in a vacuum [4]. We employed continuous-wave (cw) laser irradiation for heating nanotubes, which provided non-contact local heating while retaining the neutral charge balance of the nanotubes throughout the measurements. In addition, it enabled temperature measurement using Raman spectroscopy of the in-plane carbon stretching mode (*G*-mode) [5]. At 1,000–2,000 K, an intrinsic semiconducting nanotube emitted linearly polarized, narrow-band near-infrared radiation, in contrast to its broadband metallic counterpart. We unambiguously confirmed that this narrow-band radiation was enabled by the thermal generation of excitons using the distinctive spectral difference between semiconducting and metallic nanotubes, the temperature dependence of the radiation intensities, and simultaneous observation of the radiation spectra and the optical susceptibilities. In the presentation, universal features of thermal radiation of one-dimensional structures will be discussed.

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## Kinetics of diazonium functionalization of carbon nanotubes

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Impurities in semiconductors play a key role for enabling device functionality, for example by acting as donors or acceptors for the generation of free charge carriers or by modifying photophysical properties in beneficial ways. Accordingly, the introduction of defect states in covalently functionalized semiconducting single-wall carbon nanotubes (s-SWNTs) has led to the realization of single photon sources at room-temperature and at telecom wavelengths [1]. The mechanism underlying such functionalization has been proposed to consist of two steps, an initial charge transfer followed by covalent bond formation between nanotube and the diazonium radical [2].

However, this two-step mechanism continues to be debated controversially and additional investigations are needed to clarify its nature. This may help to obtain a greater degree of control over reaction outcomes and kinetics.

To further elucidate the reaction mechanism we have thus measured the kinetics of s-SWNT functionalization on a timescale from seconds to days using absorption and photoluminescence (PL) spectroscopy. The samples investigated are mixtures of aryl-diazonium salt solution and nanotube suspension. The latter consist of chirality-selected organic PFO:BPY polymer- or aqueous SDS surfactant-stabilized s-SWNTs.

In aqueous suspensions we observe that the kinetics are characterized by a quasi instantaneous initial decrease of the first subband ( $S_1$ ) exciton PL signal, followed by a slower recovery of the exciton PL signal from minutes to hours. In addition, we also observe the slow increase of a familiar, red-shifted defect-induced emission band [3]. In contrast, no such defect induced increase of a defect related PL band is observed for organic solvent based nanotube suspensions.

We will discuss these findings in light of prior studies of s-SWNT functionalization and doping [1-4].

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## Reflectance of Carbon Nanotube Forest metamaterials

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CNT forest of high emissivity, nearly ideal “black-body absorber[1]”, is attracting researchers as a candidate material for the future application of high-sensitive sensor, thermal energy storage device[2], and so on. Recently, metamaterials, electro-magnetic circuit to the incident EM-wave, opened a method to design desired optical properties. We recently reported CNT forest metamaterial in infrared and visible region in order to increase optical and thermal absorbance utilizing FIB nanofabrication [3, 4].

In this paper, metamaterials composed by 1D anisotropic refractive index material of CNT Forests, and the effect of nano-sized patterning on the optical and thermal properties are discussed. Figure 1 shows calculated UV-Vis-IR spectra of vertical- and parallel-aligned metal-nanorod CNT forests to the Electric field ( $E_z$ ) of incident EM wave propagating in the x direction, showing good correspondence to the experimental results[5] in Fig. 1(d-g). Components of perpendicularly aligned CNTs, which were parallel to the  $E_z$  of EM wave, increased reflectance in longer wave length region. Alignment of CNTs had an important role to improve absorption on the metamaterial patterns. Patterning shape effect of CNT forest metamaterials[3-5] will be also discussed in detail.

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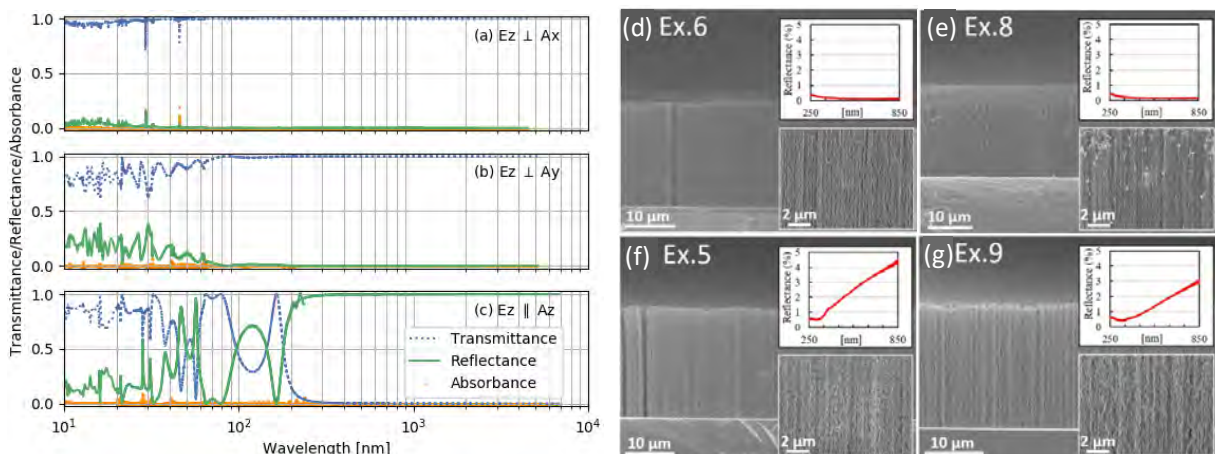


Fig.1 (a-c) Calculated Transmittance, reflectance and absorbance spectra by meep FDTD program for the metal-nanorod CNT forests.  $E_z$  of EM wave was perpendicular to (a) x-axis and (b) y-axis of CNT alignment, and (c) parallel to z-axis of CNT alignment. (d, e) Highly vertically aligned CNT forests exhibiting low reflectance in 10-degree specular reflectance [5]. (f, g) Low-degree aligned (wavy) CNT forests showing higher reflectance in longer wavelength [5].



## Effect of functionalization and subsequent thermal treatment on photoluminescence properties of single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWNTs), because of their excellent mechanical and electrical properties, have been studied extensively for numerous potential applications. In 2002, near-infrared (NIR) photoluminescence (PL) of semiconducting SWNTs was observed in individually dispersed SWNTs by Weisman et al.<sup>1</sup> Since the structure of SWNTs can be assigned based on its excitation and emission wavelength, NIR PL spectra of SWNTs are used as useful analysis tools in, for example, synthesis and separation of SWNTs. The PL of SWNTs has received significant attention for application in biological imaging because NIR light from 1000 to 1400 nm, which is known as the second NIR window, has high transparency in biological tissues.<sup>2</sup> Recently, considerable effort has been focused on SWNTs functionalization to induce bright red-shifted PL peaks, such as oxidation and arylation reactions using ozone and aryl diazonium compounds, respectively.<sup>3,4</sup> It has been reported that the functionalization degree of SWNTs influence the PL efficiencies emerged after functionalization.

Here we report our recent results on control functionalization degree and NIR PL properties of SWNTs by bulk scale preparation.<sup>5-11</sup> Both steric hindrance of the reagents and subsequent thermal treatment were effective to control functionalization degree of SWNTs and the PL intensities. Additionally, it was revealed that not only the reagents used but also reaction methods influence the amount of Stokes shift observed after the functionalization.

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## Photoluminescence from Single-walled Carbon Nanotubes on hexagonal Boron Nitride Substrates

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Photoluminescence (PL) spectroscopy is one of the important analysis techniques for the optical properties of single-walled carbon nanotubes (SWNTs). However, PL spectra are measured only from surfactant-wrapped SWNTs [1], suspended SWNTs [2], and vertically-aligned SWNTs [3]. For optical and opto-electronic applications of SWNTs, SWNTs which lie on substrates and emit PL signal are needed. In this study, SWNTs were directly synthesized on hexagonal boron nitride (h-BN) substrates and PL spectroscopy was performed. h-BN is a suitable substrate for SWNTs because it has large band gap and its surface is atomically flat [4]. By using mechanical exfoliation technique, multilayered h-BN was obtained on silicon substrates. Iron metal particles and ethanol were used as the catalyst and carbon source of SWNT growth, respectively. Figure 1 shows (A) PL spectrum and (B) PL map obtained from SWNTs on h-BN. Relatively sharp PL emission was measured. It is known that the optical transition energy ( $E_{ii}$ ) of SWNTs depends on the surrounding conditions. The  $E_{11}$  and  $E_{22}$  of SWNTs on h-BN were almost the same as those of surfactant-wrapped SWNTs, and PL map, as shown in Fig. 1(B), exhibited that the chirality was (9,5).

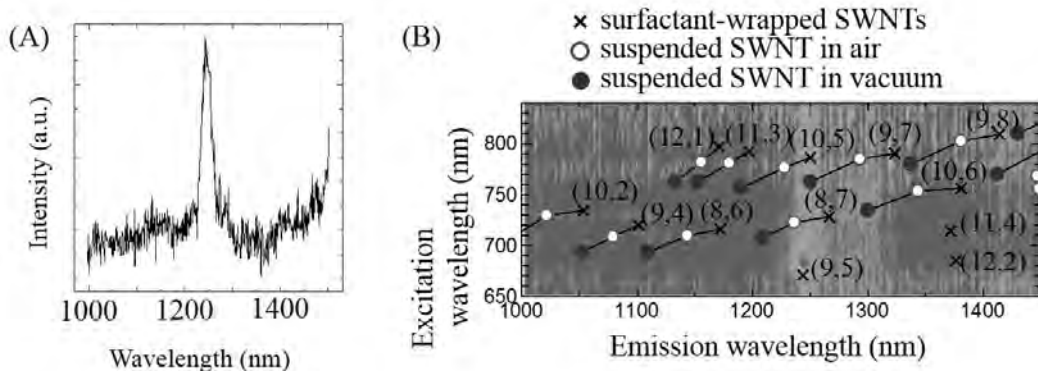


Fig. (A) PL emission spectrum and (B) PL map from SWNT on h-BN substrate. (B) Filled and opened circles correspond to the  $E_{ii}$  of suspended SWNTs in vacuum and air, respectively [5].

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## Modulation-Doped Multiple Quantum Wells of Aligned Single-Wall Carbon Nanotubes

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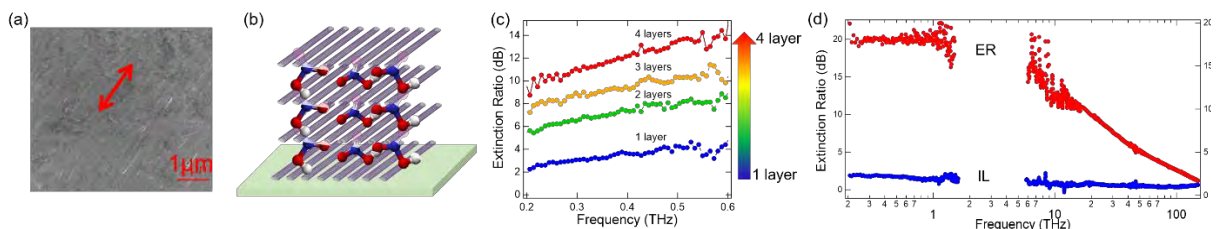
Doping, alloying, and combining traditional semiconductors are at the core of today's technologies, and there is considerable interest in constructing 3D architectures of low-dimensional materials with tailored electrical and optical properties [1]. In this study, we have fabricated a structure consisting of multiple thin layers of aligned single-wall carbon nanotubes (SWCNTs) with dopants inserted between the layers [2]. The individual layers were ~20 nm in thickness and 2 inches in diameter, containing SWCNTs that spontaneously aligned during vacuum filtration [3]. Figure 1a shows a scanning electron microscopy image of highly aligned and packed SWCNTs in a 2-inch-diameter film, demonstrating that the vacuum filtration method is indeed scalable. Multiple films were combined vertically by stacking, while inserting dopants between layers at the same time (Fig. 1b). The extinction ratio (ER) value, defined as  $-\log(T_{\parallel}/T_{\perp})$  where  $T_{\parallel}$  ( $T_{\perp}$ ) is the transmittance for the parallel (perpendicular) polarization, increases linearly with increasing number of layers (Fig. 1c), suggesting that alignment and dense packing are well preserved during the stacking process. Figure 1d shows that this unique 3D architecture of doped SWCNTs works as an excellent terahertz (THz) polarizer with an ultrabroadband working frequency range (from ~0.2 to ~200 THz), a high ER (20 dB from ~0.2 to ~1 THz), and a low insertion loss (<2.5 dB from ~0.2 to ~200 THz), exceeding the performance of previously reported THz polarizers based on aligned SWCNTs [4].

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**Fig. 1** (a) A scanning electron microscopy image of a highly aligned and packed SWCNT film. (b) A schematic of a fabricated structure of aligned and modulation-doped SWCNTs. (c) Effects of stacking on the THz response of aligned SWCNT films. ER value as a function of frequency in THz. (d) ER and insertion loss (IL) of stacked, modulation-doped aligned SWCNT films in the range of 0.2–200 THz. The frequency axis is on a logarithmic scale.

## Resonance Raman Signature of Intertube Excitons in Compositionally-Defined Carbon Nanotube Bundles

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Electronic interactions in low-dimensional nanomaterial heterostructures can lead to novel optical responses arising from exciton delocalization over the constituent materials. Similar phenomena have been suggested to arise between closely interacting semiconducting carbon nanotubes of identical structure. Such behavior in carbon nanotubes has potential to generate new exciton physics, impact exciton transport mechanisms in nanotube networks, and place nanotubes as one-dimensional models for such behaviors in systems of higher dimensionality. Here we use resonance Raman spectroscopy to probe intertube interactions in (6,5) chirality-enriched bundles. Raman excitation profiles for the radial breathing mode and G-mode display a previously unobserved sharp resonance feature. We show the feature is evidence for creation of intertube excitons and is identified as a Fano resonance arising from the interaction between intratube and intertube excitons.[1] The universality of the model suggests that similar Raman excitation profile features may be observed for interlayer exciton resonances in 2D multilayered systems.

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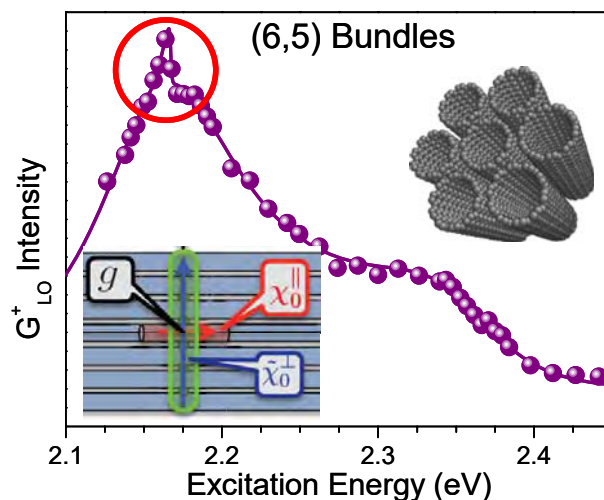


Fig.1 Raman resonant excitation profile of the  $G^+$  mode for the largest bundle size of (6,5)-enriched SWCNTs.[1] Data shown as symbols and fits to the Fano resonance model shown as a solid line. The sharp additional feature at  $\sim 2.16$  eV (circled) appears for bundled samples and increases with bundle size. Lower-left inset shows a bundle cross-section with the intertube exciton (right arrow) and the intratube exciton (upward arrow). Local coupling  $g$  between the two types of excitons at the intercept point gives rise to their scattering. A schematic of bundled SWCNTs is illustrated in the upper-right inset.[2]

## Enhanced Raman scattering of graphene using double resonance in silicon photonic crystal nanocavities

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We demonstrate enhancement of the G' Raman band of graphene by coupling to the L3 silicon photonic nanocavity. The L3 nanocavities have been used to enhance the photoluminescence of carbon nanotubes [1], and monolayer graphene has an advantage of being compatible with cavities in a photonic crystal slab because of its two dimensionality. We utilize a unique mechanism for a double resonance in two-dimensional photonic crystals, which originates from simultaneous enhancements by a localized guided mode (LGM) and a cavity mode [2]. By adjusting the photonic cavity parameters, the double resonance can be tuned to the G' Raman scattering. Excitation wavelength dependence measurements show a large Raman peak enhancement when the excitation and emission wavelengths are simultaneously on-resonance with the LGM and the cavity mode, respectively. Furthermore, spatial imaging measurements are performed to confirm that the enhancement is localized, and we find that the enhanced Raman intensity is more than 50 times larger compared to the on-substrate Raman signal. The observed cavity enhancement of Raman scattering opens new possibilities for the development of graphene-based light sources for silicon photonics.

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## Achieving 20% Efficiency Perovskite Solar Cells with High Stability by using Semiconducting Single-walled Carbon Nanotube Grain Bridges

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Since liquid-junction perovskite solar cells (PSCs), the development of organo-lead halide perovskite photovoltaics research has gained momentum with the achievement of the solid-state PSCs in 2012. High absorption coefficient, long-range diffusion length and high defect tolerance of PSCs enable remarkable certified power conversion efficiencies (PCEs) over 20%. Although PSCs are proven to be promising next-generation solar devices, further breakthroughs in terms of efficiency and stability are necessary to supersede conventional silicon solar cells. With regard to the performance and stability of PSCs, perovskite grain boundaries play a significant role. Structural disorders at these boundaries induce shallow trap states and non-radiative recombination of localised charge carriers which serve as limitations to PSC performance. At the same time, these areas are also responsible for the perovskite degradation, as the reaction with moisture in air has been found to initiate from the grain boundaries. Therefore, technologies aiming at passivating the perovskite grains are highly desired.

Over the last two decades, carbon nanotubes (CNTs) with an exceptional charge carrier property with outstanding chemical and mechanical stability have generated a lot of excitement among researchers for their device applicability. Especially, single-walled carbon nanotubes (SWNTs) with a certain chirality possess a wide range of direct bandgap of up to 2 eV, qualifying for a light-harvesting medium with strong absorption and high carrier mobility. Semiconducting SWNTs (s-SWNTs) are highly conductive along the tube axis and therefore can function effectively as a charge-transporter between perovskite grains. While there have been a few reports on phenyl-C61-butyric acid methyl ester (PCBM) as a charge-transporter at the grain boundaries of perovskite films, fullerenes have inherently low carrier mobility and low stability compared to SWNTs. It has also been demonstrated that hydrophobic and air-stable SWNTs can protect the perovskite layer successfully from the oxygen and moisture.

Here, we fabricated PSCs in a configuration of glass/ITO/SnO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/spiro-MeOTAD/Au in which the perovskite grains are passivated and connected by s-SWNTs. s-SWNTs here are functioning as a charge-transporter, light-harvester, and protector from the moisture in air. By incorporating a small amount of s-SWNTs in deionised water, 18.0% efficiency of the reference PSCs increased to 20% with reduced hysteresis. due to the increased perovskite grain size arising from favourable vapour pressure of the solvent. Upon addition of s-SWNTs, the PCE further increased beyond 20% with improved hysteresis and air/light stability. Ultimately, s-SWNTs added PSCs showed superior stability over the reference devices.

# Tracing individual growth process of single-walled carbon nanotubes by digitally coding isotope labels

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Arrays of purely semiconducting single-walled carbon nanotubes (SWNTs) attract a significant attention as alternative materials of silicon for high-performance electronics. Despite recent progress in controlled synthesis of SWNTs [1], the growth process leaves some mysteries due to their size, variety and system complexity. Although thermodynamic and kinetic control is important for the chirality-controlled synthesis, it is controversial, for example, whether the growth rate of SWNTs depends on their chirality [1,2]. Usual *in situ* and *ex situ* measurements often missed a variation of grown SWNTs and the time evolution of the growth, respectively. Here we present a method to analyze the growth behavior, *e.g.* growth rate, incubation and lifetime, of individual SWNTs with various lengths by embedding digitally coded isotope labels.

SWNTs were grown from iron nanoparticles patterned in stripes on quartz substrates [2]. During the synthesis of SWNTs, binary-like codes of isotopic carbon were incorporated by periodically introducing the pulse of <sup>13</sup>C ethanol with three different ratios (Fig. 1a), and then detected by Raman mapping. A Raman intensity map along an SWNT (Fig. 1b) shows G-band downshifts in three different levels. We found that after various lengths of incubation, most SWNTs monotonically elongated until abrupt termination (Fig. 1c). This indicates the catalytic activity of nanoparticles did not change with time. Digital coding of isotope labels also offered opportunities to link modulation of growth conditions, such as temperature and carbon concentration (Fig. 1d), with changes in growth behavior along individual SWNTs. Similar analyses for the growth with a variety of catalysts and conditions would significantly improve the synthesis of SWNTs once combined with other characterization methods.

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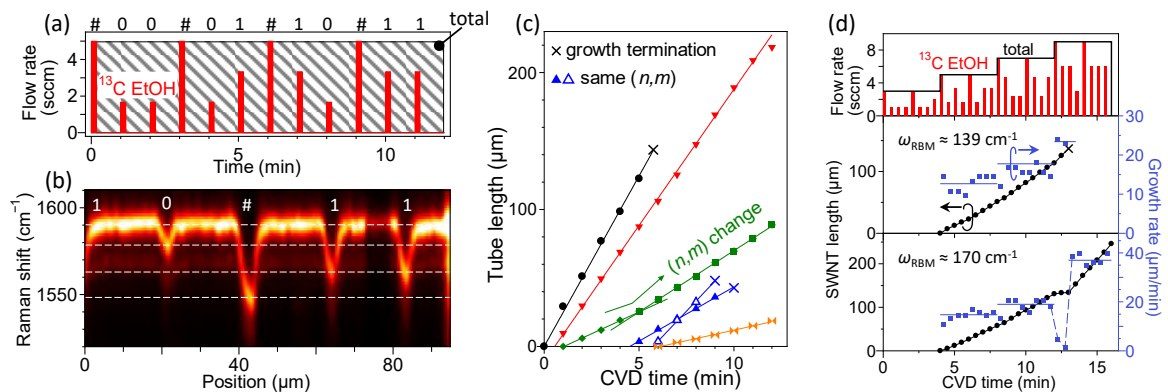


Fig.1 (a) Flow rate of <sup>13</sup>C ethanol (bars) for digital isotope coding with constant flow rate (5 sccm) of total ethanol. (b) G-band intensity map along an SWNT. (c,d) Time evolution of SWNT lengths with a constant growth condition (c), and with elevated ethanol flow rates (d).

## Effects of Chirality and Defect Introduction on the Intermediate Frequency Mode

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An intermediate frequency mode (IFM) of single-walled carbon nanotubes (SWCNTs) has intriguing properties. The IFM originates from a phonon branch that has acoustic nature in graphene, and has non-zero momentum. Phonons with these properties are usually not analyzable with photons. However, the IFM of SWCNTs was successfully observed in prior reports [1, 2]. Remarkable features of the IFM may provide new insights into Raman spectroscopy of SWCNTs. Although the effects of chirality and defect density on the peak position was well explained in these reports, what determines the IFM intensity is not clear. We will show our recent analysis of the IFM intensity with focusing on the effects of chirality and defect density.

Intensities of the IFM, the D-mode, and the G-mode are shown in Figure 1a as functions of a duration time of defects introduction into an air-suspended SWCNT. Defects were introduced by using photoinduced bleaching in air [3]. The G-mode intensity decreased as results of the defect introduction. On the other hand, the IFM intensity increased along with the D-mode intensity. Furthermore, fluctuations of the IFM intensity was clearly following that of the D-mode intensity, which implies that the IFM originates from K-momentum phonons similar to the D-mode. From the results shown in Figure 1a, we suggest the intensity ratio  $I_{IFM}/I_D$  as a good representation to understand the physics underlying K-momentum phonons. Figure 1b shows effects of chirality on the  $I_{IFM}/I_D$ , as well as  $I_{RBM}/I_G$ , obtained from 5 kinds of SWCNTs; (12,1), (11,3), (10,5), (9,7), and (9,8). Although the chiral angle dependence of the  $I_{IFM}/I_D$  is less significant than the  $I_{RBM}/I_G$ , the ratios decrease with an increase of the chiral angle.

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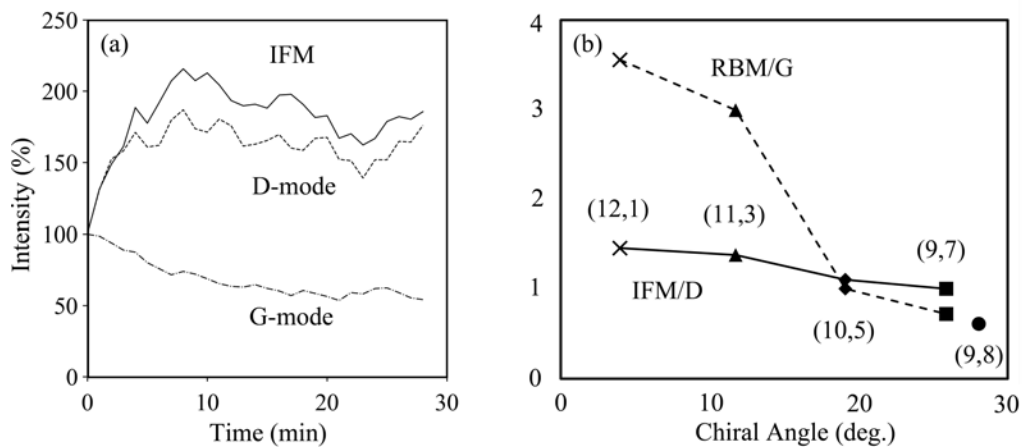


Figure 1 (a) Raman intensities of an individually suspended SWCNT as functions of a duration time of defects introduction. (b) Intensity ratios of Raman peaks generated from 5 types of individually suspended SWCNTs.



## Monolayer WSe<sub>2</sub>-MoS<sub>2</sub> Lateral Heterojunction Light-Emitting Diodes

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Recent advances of heterostructure fabrications based on transition metal dichalcogenides (TMDCs) yield atomically regulated interfaces due to their intrinsically passivated surfaces, allowing us to explore unusual electrical and optical phenomena and to make outstanding improvements to device performance [1]. Although, numerous experimental demonstrations of vertically stacked heterostructures have been realized using scotch-tape approach, the investigation of physical properties of lateral heterojunctions, in which dissimilar TMDCs are artificially stitched together, has been still limited. In particular, lateral heterojunctions are easier to tune band offset for designing p-n junction because of their spatial separation. Moreover, compared with manual transfer of vertical heterostructures, lateral heterojunctions is ideally adopted for the scalable approach of chemical vapor deposition (CVD) for creating atomically sharp heterojunctions [2]. Here, we developed a scalable fabrication process for WSe<sub>2</sub>-MoS<sub>2</sub> lateral heterojunction films and firstly realized its light-emitting device arrays.

WSe<sub>2</sub>-MoS<sub>2</sub> lateral heterojunction films were synthesized by two-step CVD process. As shown in Fig. 1, W electrodes were firstly patterned for the subsequent location-selective growth of WSe<sub>2</sub> monolayers. And then, epitaxial growth of MoS<sub>2</sub> monolayers was performed to form heterojunctions. Finally, additional Mo pads were deposited, followed by spin-coating ion gel films for building light-emitting device [3-5]. As applying voltage, holes (electrons) are injected and accumulated in WSe<sub>2</sub> (MoS<sub>2</sub>) mediated by electric double layers to form p-n junction (Fig.1). Figure 2 obviously indicates electroluminescence (EL) image generating along junction interface. Interestingly, the comparison between photoluminescence (PL) and EL spectra shown in Fig. 3 revealed inconsistent behavior. Although both contributions of WSe<sub>2</sub> and MoS<sub>2</sub> were observed in PL, EL only showed MoS<sub>2</sub> luminescence. This suggests band structure evolution at junction interface; thus we will discuss this physical picture based on recent scanning tunneling spectroscopy study. Importantly, we firstly realized lateral heterojunction light-emitting devices and achieved the improvements of their external quantum efficiency compared to reported homojunction devices, providing a new platform for high-performance optoelectronic device applications.

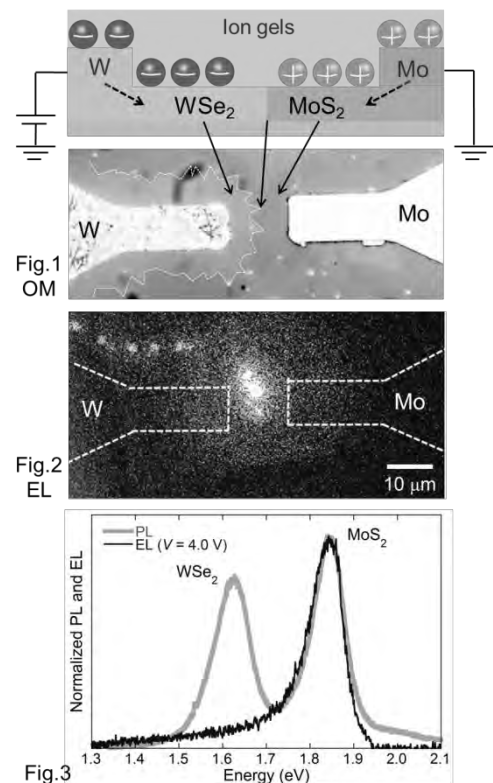
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## Long-lived direct and indirect interlayer excitons in van der Waals heterostructures

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Ensembles of indirect or interlayer excitons (IXs) are intriguing systems to explore classical and quantum phases of interacting bosonic ensembles. IXs are composite bosons that feature enlarged lifetimes due to the reduced overlap of the electron-hole wave functions resulting in dense IX ensembles thermalized to the lattice temperature. Besides IX ensemble in III-V heterostructures [1,2], transition metal dichalcogenides exhibit superior potential for studying interacting IX ensembles due to a strong light matter interaction together with a large exciton binding energy in these 2D materials [3]. Hetero-bilayers from these materials have a type II band alignment driving an efficient charge transfer between the two layers that results in the formation of spatially separated electron hole pairs or interlayer excitons.

We report the observation of a doublet structure in the low-temperature photoluminescence of interlayer excitons in heterostructures consisting of monolayer MoSe<sub>2</sub> and WSe<sub>2</sub>. Both peaks exhibit long photoluminescence lifetimes of several tens of nanoseconds up to 100 ns verifying the interlayer nature of the excitons. The energy and line width of both peaks show unusual temperature and power dependences. While the low-energy peak dominates the spectra at low power and low temperatures, the high-energy peak dominates for high power and temperature. We explain the findings by two kinds of interlayer excitons being either indirect or quasi-direct in reciprocal space. Our results provide fundamental insights into long-lived interlayer states in van der Waals heterostructures with possible bosonic many-body interactions [4].

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