

Poster Session 2

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Giant nonlinear optical response from dye-filled carbon nanotube hybrids

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Asymmetric dipolar molecules, acting as electric ‘rectifiers’ with a large second-order nonlinear optical (NLO) response (first hyperpolarisability β), find applications in ultrafast electro-optic switches for optical telecommunication networks and wavelength conversion of lasers.^[1] In 3D bulk systems, however, such dipolar molecules tend to align in a pairwise anti-parallel way, thus cancelling each other’s directional properties, such as the NLO response. Parallel alignment is traditionally achieved by electric field poling in a polymer matrix, but long term stability of this alignment remains problematic.

Here we show that by encapsulating such elongated dipolar molecules in the 1D internal channel of single-wall carbon nanotubes (SWCNTs), Coulomb interactions naturally favor a polar head-to-tail alignment of the molecular dipoles, leading to a cooperative enhancement of their second-order NLO responses. This principle is demonstrated for a prototypical dipolar molecule encapsulated in various SWCNT samples. The encapsulation is evidenced by extensive wavelength-dependent fluorescence-excitation^[2] and resonance Raman^[3] experiments on bile-salt solubilized^[4] dye-filled SWCNTs, revealing the effect of encapsulation on the vibrational and electronic properties of the SWCNTs and the encapsulated molecules. Wavelength-dependent hyper-Rayleigh scattering^[5,6] (i.e. second harmonic light scattering) experiments effectively show that these organic-SWCNT nanohybrids possess giant NLO responses ($\beta = 68800 \times 10^{-30}$ esu at resonance; $\beta_0 = 9770 \times 10^{-30}$ esu in the static limit; corresponding to ~ 70 identically aligned chromophores, depending on the SWCNT diameter range). Their equally giant dipole moment and size promises a good and stable alignment of the nanohybrids in a polymer film, which opens up an entirely new route to the rational design of solution-processible yet stable NLO materials.

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S-SWNT interaction with microring resonators

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Semiconducting Single Wall Carbon Nanotubes (s-SWNT) are a promising material for silicon photonics, due to their ability to emit, modulate and detect light. Indeed, Silicon is an indirect bandgap material, unable to efficiently emit photons, thus light emitters are strongly desirable for optical devices on silicon.

Recent work showed integrability of s-SWNT on silicon waveguide, either coupling nanotubes photoluminescence (PL) ^[1] or thermal emission ^[2] with the optical mode of the waveguide. In order to enhance interaction of s-SWNT with the silicon photonics device, the use of microcavities was proposed.^[3,4,5] The main drawback of these cavities designs is the difficulty to efficiently couple them with access waveguides in order to build realistic devices.

We propose the use of silicon microring resonator covered with s-SWNT to address this issue. Microrings are fabricated by e-beam lithography and covered with PFO-extracted s-SWNT. Nanotubes' PL interacts with the microcavity mode, leading to very narrow emission peaks, with quality factors as high as 4000.^[6] Both far-field emission and integrated PL are studied, and we show that mainly photons coupled to the microcavity mode are observed at the waveguide output, with well-defined polarization.

This is the first demonstration of cavity-enhanced PL coupled to a silicon waveguide, which is an important milestone in the area of 'Carbon Nanotube Photonics', and for future realistic applications using this nanomaterial.

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Carbon nanotube integration strategies with silicon photonics

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Semiconducting carbon nanotubes (s-SWNT) constitute a fascinating material, with unique optical properties due to their unidimensionality. They have the ability to emit, modulate and detect light in the wavelength range of silicon transparency which make them an emerging material for nanophotonics. Indeed, the indirect band-gap of silicon prevents efficient light emission at these wavelengths, and s-SWNT are envisioned as an active material in silicon photonics technology.

We have developed several years ago an efficient method to selectively extract s-SWNT displaying strong optical properties.^[1,2] It is therefore particularly attractive to couple s-SWNT with optical resonators. Previous results make use of photonic crystal cavities^[3] or silicon microdisk resonators^[4] but the lack of access waveguides make these designs poorly adapted for silicon photonics. On the other hand, we recently proposed the use of silicon microring resonators to address this issue.^[5]

These different approaches all struggle with the difficulty to integrate 1D nanomaterials such as carbon nanotubes with planar, silicon based, photonic devices. Here, we discuss about strategies to efficiently couple s-SWNT PL with silicon waveguides, using either strip or slot waveguides, and their efficient integration within a photodetector. Additionally, residual metallic nanotubes strongly affect the performance of the structures. We present Monte Carlo simulations and their analysis which allow us estimating acceptable proportions of metallic nanotubes for our applications. All these results allow us advancing the credibility of nanotubes as an active material for silicon photonics.

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Radial Deformation of Single-Walled Carbon Nanotubes on Quartz Substrates and the Resultant Anomalous Diameter-Dependent Reaction Selectivity

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Owing to the unique conjugated structure, chemical reaction selectivity of single-walled carbon nanotubes (SWNTs) has attracted great attentions. By utilizing the radial deformation of SWNTs caused by the strong interactions with the quartz lattice, we achieve an anomalous diameter-dependent reaction selectivity of quartz lattice-oriented SWNTs in treatment with iodine vapor, which is distinctly different from the widely reported and well accepted higher reaction activity in small-diameter tubes over the large ones. The radial deformation of SWNTs on quartz substrate is verified by detailed Raman spectra and mappings in both G band and RBM. Due to the strong interaction between SWNTs and the quartz lattice, large-diameter tubes present larger degree of radial deformation and more delocalized partial electrons are distributed at certain sidewall sites with high local curvature. It is thus easier for the carbon-carbon bonds at those high curvature sites on large-diameter tubes to break down upon reaction. This anomalous reaction activity offers a novel approach for selective removal of small-bandgap large-diameter tubes.

Optical Properties of Single Chirality (5,4) SWCNTs

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Although more than 20 years have passed after the discovery of single-wall carbon nanotubes (SWCNTs), still we don't know well about their detailed structures due to lack of the single-crystal of SWCNT that enables us to analyze its precise structure. Because current SWCNT products are mostly composed of various structures, structure sorting of SWCNTs is necessary for the single crystal growth.

Previously, Liu et al. succeeded to separate 13 kinds of single chirality SWCNTs using multicolumn gel chromatography method.^[1] In this work, we have improved the method and optimized it for thin SWCNTs. Here (5,4) SWCNTs, which have the smaller diameter than C60 are successfully separated for the first time. In the Raman spectrum, single radial breathing mode peak at 373 cm^{-1} and highly softened TO phonon peak at 1497 cm^{-1} were observed. Interestingly, some bright photoluminescence (PL) peaks corresponding to the oxygen doped SWCNTs^[2] were observed probably due to high chemical reactivity of highly curved side wall. Moreover, higher order excitations corresponding to E_{33} and E_{44} of (5,4) SWCNTs were clearly observed in an excitation spectrum using CCD detector. Good agreement between the excitation spectrum and the absorption spectrum indicates successful separation of high purity (5,4).

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Strained graphene nanoribbons and hexagonal quantum rings under external magnetic fluxes

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The coupling between geometrical and electronic properties is a promising avenue to engineer conduction features in graphene. External magnetic fields and electronic confinement added to strain effects allow a rich interplay of different transport mechanisms with potential device applications. In particular, we explored the transport properties of graphene nanoribbons and hexagonal zigzag quantum rings coupled to left and right leads given by semi-infinite zigzag nanoribbons. Electronic density of states and conductance are obtained using the tight-binding approximation and following the Green's function formalism and real space renormalization techniques. We investigate the individual sublattice contributions to the local density of states that should be individually scanned by a STM image.^[1] The electronic mapping shows regions exhibiting trigonal structure even in the absence of buckling or taking into account staggered potentials.

The localization effects on the physical responses of the ring were considered as a consequence of the finite-size confinement of the central part of the nanostructure and due to the applied magnetic field and the presence of tension giving origin to pseudofields. When the magnetic flux is considered, the conductance results exhibit clear Fano-like resonances. The peculiar null conductance states are pinned at the same energy values independently of the magnetic field intensity. We highlight that strain also promotes a change in the energy values at which the conductance is fully suppressed. The results suggest that the nanoring may be used as a dispositive in which the conductance patterns provide a simple way of measuring the strain strength when compared to the unstrained situation.

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Ultrafast charge photogeneration and dynamics in semiconducting carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) are excellent model systems for the study of photoexcitation dynamics in one-dimensional (1D) quantum confined systems. Theory predicts that Wannier-Mott excitons are the elementary photoexcitations in SWNTs, due to the strong Coulomb interaction caused by the weak screening. Such excitons have peculiar 1D characteristics, such as extraordinary large binding energies, large size and 1D transport. Experimental observations, such as the measured binding energy, typically 0.1-1 eV, and the electron-hole correlation length, in the 1-10 nm domain confirm theoretical predictions. The exciton model alone, however, fails to capture the whole dynamics following photoexcitation, and many other photoexcited species have crowded the complex scenario of SWNTs' optical response, ranging from triplets to bi-excitons and trions. Experiments based on photocurrent, transient absorption and THz spectroscopy also point out a non-negligible photogeneration of free charge-carriers. This is in contrast with the excitonic model and the reduced Sommerfeld factor that predicts that excitons should be the only species generated upon photoexcitation. Attempts to solve this discrepancy proposed non-linear processes, such as exciton-exciton annihilation, as a mechanism of charge-carrier photogeneration. However, there is solid experimental evidence that charge-carrier photogeneration is linear with the pump fluence.

Here we apply broadband ultrafast transient absorption spectroscopy to the semiconducting (6,5) SWNT and show that charge-carriers can be identified by their effect on excitonic resonances, in particular the large Stark shift that they induce on high-energy, easily polarizable excitons (S_{22} and S_{33}). Having identified the Stark shift as a good spectroscopic fingerprint for charge-carriers, we are able to study their dynamics in a nearly ideal 1D system. We find that a fraction of the absorbed photons generates geminate charge-carrier pairs within our temporal resolution (≈ 50 fs), which then recombine on the picosecond timescale following the characteristic kinetic law of random walk in 1D. Our analysis starts from the observation that the first derivative of the ground state absorption spectrum, i.e. a photoinduced red shift of the excitonic transition, can reproduce many of the features observed in the differential transmission ($\Delta T/T$) spectra of semiconducting SWNTs. This effect can be ascribed to different physical mechanisms, such as

bi-excitons or trions formation, thermal effects or Stark effect. Here we unambiguously demonstrate that this derivative shape is indeed due to strong local electric field induced by photogenerated charge-carriers, which shifts the electronic transitions by Stark effect. In particular, we show that the energy shift is stronger for excitons with lower binding energy, as for S_{33} with respect to S_{11} , as expected for the Stark effect. This suggests that the higher energy S_{33} exciton is ideally suited for directly probing charge-carriers in SWNTs and can be exploited to further analyze the charge photogeneration process and to study charge-carrier dynamics in one dimension. Our data show that the free charge-carriers are generated within 50 fs. The temporal evolution of the S_{33} pump-probe dynamics is very accurately reproduced by a power law $\sim t^{-0.5}$. A monomolecular power law decay is the predicted dynamics for geminate recombination of free particles after random walk in an infinite one-dimensional chain. A more detailed modelling of the geminate recombination process indicates that the initial distance between the geminate e-h pair is of the same order of magnitude of the exciton correlation length, thus suggesting that charge-carriers arise from instantaneous linear exciton dissociation.

Our results shed new light onto the charge photogeneration mechanism in SWNTs, suggesting that the nascent exciton dissociates spontaneously, perhaps in presence of extrinsic screening of the Coulomb attraction, possibly due to water or other ambient contamination.

In-situ Observation on Wetting Behavior of Ionic Liquid on a Carbon Nanotube

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Wettability of materials is generally determined by the balance of interface tensions acting at air-liquid, liquid-solid, solid-air boundaries, but it is also well known that nanometer-scale morphologies of solid surface often affects to the wetting. It is therefore interesting question how a carbon nanotube (CNT) wet by liquid, since it has extremely high curvature surface due to their cylindrical shapes with nanometer scale diameters. In this study, we report unique wetting behavior on a single CNT investigated by in-situ electron microscopy. Ionic liquid was employed as a liquid in the present experiment, since it is rather stable in vacuo due to extremely small evaporation pressure. A single CNT was operated to fix to the tip of cantilever probe by using a manipulator in scanning electron microscope (SEM) or transmission electron microscope (TEM). Tip of the CNT is then approached to the surface of ionic liquid, and we recorded the series of TEM or SEM images as movies when the CNT tip is touched to the liquid surface. As the result, meniscus formed at the contact region, besides a thin film with 3nm thickness simultaneously formed to cover entire the CNT. The contact angle measured at the meniscus was almost zero. These results indicate that CNT shows autophobic wetting, although macroscale droplet on a plane graphite surface shows about 25° contact angle. In addition, attractive wetting force was measured on the basis of Wilhelmy method for individual CNTs with 5~15 nm diameters. We found that the measured values tended to be greater than calculated ones using Wilhelmy equation representing the correlation of the force, tube diameter and surface tension. Instead, fitted curve to the experimental data showed an increment in an effective diameter of cylindrical sample. The corrected value was 2.84 nm, which is consistent to the thickness of liquid film formed on CNT. Accordingly, the wetting behavior observed in the present study can be explained by considering that the liquid film acts as a part of a solid cylinder, which suggests a possibility that liquid molecules are rather strongly constrained on the CNT surface.

Photoconductivity spectroscopy of individual suspended carbon nanotubes

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To investigate photoconductivity of chirality-identified carbon nanotubes, we have fabricated field-effect transistors with individual air-suspended nanotubes.^[1] Trenches are etched into SiO₂/Si substrates, and Pt/Ti are deposited on both sides of the trenches. By ethanol chemical vapor deposition, carbon nanotubes are grown over the trenches. We have also constructed a system which can simultaneously measure photocurrent and photoluminescence excitation spectra.^[2] Nanotubes are excited with a wavelength-tunable continuous wave Ti:sapphire laser, and photoluminescence is detected by an InGaAs photodiode array attached to a spectrometer. Photoluminescence imaging and excitation spectroscopy allows us to locate the nanotubes and identify their chirality. For photocurrent microscopy, excitation laser is modulated by an optical chopper and a lock-in amplifier is used for detection.

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In-plane Conduction of Dense Carbon Nanotube Forest formed on Silicon Carbide

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Dense Carbon nanotube forest formed by silicon carbide surface decomposition method (CNTs on SiC) consists of nearly ideally close-packed CNTs.^[1] Generally, CNT conducts in its on-axis direction, yet such highly dense CNT forest may cause high in-plane direction conductivity. In addition, CNTs on SiC do not have entangled or wavy part, it is useful to investigate in-plane conductivity of dense CNT forest. Here we report on the in-plane conductivity evaluation of CNT forest formed on SiC.

On-axis C-face (000-1) of semi-insulating SiC substrates ($< 10^{-8}$ S/cm) were annealed at 1500~1600 °C in vacuum ($\sim 10^{-3}$ Pa). The in-plane conductivity was measured by van der Pauw method in room temperature in air. There are four parts which may contribute to CNTs on SiC in-plane conductivity, CNT caps, CNT bulk, CNT/SiC interface, and SiC bulk. To determine which part(s) is/are dominant in conduction, CNT lengths were varied by controlling decomposition time, which changes CNT bulk conductivity. To confirm which of the other parts conduct, we conducted two approaches, CNT forest removing by acid mixture, CNT cap removing by H₂O₂ mild oxidation.^[2]

As a result, in-plane CNT bulk (cylindrical part) conductivity was estimated to be ~50 S/cm. The SiC bulk conduction is negligible, since the conductance of initial SiC substrate is extremely low as $\sim 10^{-9}$ S. The CNT/SiC interface conductivity was also sufficiently small. The sheet conductivity of CNT caps as $\sim 7 \times 10^{-4}$ S/sq.

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Testing the pseudospin conjecture in carbon nanotubes: transport measurement to determine the scattering strength of charged impurity as a function of chirality

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Metallic carbon nanotubes are predicted to be resilient to scattering by charged impurities while semiconducting carbon nanotubes are susceptible to the same impurities as a result of the pseudospin degree of freedom. However, such pseudospin conjecture has never been tested directly. We have measured the resistivity of nanotubes as a function of the density of charged impurities and determined their scattering cross section as a function of chirality to test this conjecture. We find that the charged impurities affect transport properties of both metallic and semiconducting nanotubes. We will discuss the implication of our results on the pseudospin conjecture.

Nucleation of Graphene and its Conversion to Single Walled Carbon Nanotube revealed

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During catalytic chemical vapor deposition, the chirality of single wall carbon nanotubes is determined when the growing graphene nucleus wraps around the catalyst and converts into a tubular structure. Elucidating this critical process is required to develop deterministic bottom-up strategies aiming at better chiral distribution control. Direct observations of carbon nanotube growth, and theoretical modeling and simulations of the nucleation have been published but experimental atomic-resolution evidence of single-walled carbon nanotube nucleation has, until now, eluded us.

The main challenge is that nucleation involves a few atoms only and a short time scale, thus requiring a combination of high spatial and temporal resolution for direct observation. Here, we overcome the temporal resolution constraint by reducing the growth rate in order to match the temporal resolution of our recording medium. We employ an environmental scanning transmission electron (E-STEM), equipped with an image corrector and a digital video recording system, to follow SWCNT growth using Co-Mo/MgO catalyst and acetylene (C_2H_2) as a carbon source (see Methods). We present atomic-resolution movies that reveal the nucleation of graphene on cobalt carbide nanoparticles followed by its transformation to a single-walled carbon nanotube. We find that the surface termination of the faceted catalyst nanoparticles regulates the nucleation of the graphene sheet and its conversion into a nanotube. Additional density functional theory calculations show that the disparity in adhesion energies for graphene to different catalyst surfaces is critical for nanotube formation: strong work of adhesion provides anchoring planes for the tube rim to attach, while weak work of adhesion promotes the lift-off of the nanotube cap.

Chirality dependence of the absorption cross-section of carbon nanotubes

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On one hand, the synthesis methods of carbon nanotubes produce heterogeneous samples with broad distribution of (n, m) species. On the other hand, absorption spectroscopy is a common and easy tool used to determine concentrations thanks to the molar extinction coefficient. This method is however very difficult to implement for the nanotubes case. In fact it relies on the knowledge of the variation of the nanotube absorption cross-section as a function of the chiral indices. Some theoretical studies pointed a possibly strong variation of this absorption cross-section with diameter, the chiral angle and the family type $(n-m \bmod 3)$.^[1] On the experimental point of view, some measurements of the absolute absorption cross-section through single nanotube spectroscopy was reported for the $(6, 5)$ and $(18, 5)$ species,^[2, 3] and very recently on few chiral species through short-wave IR fluorescence microscopy.^[4]

Here, we report on a new experimental method to scale the (n, m) -dependence of the absorption cross section of single wall carbon nanotubes.^[5] Porphyrin molecules stacked on the wall of the nanotubes provide an original way to achieve efficient and uniform photo-excitation of the whole set of chiral species present in the sample,^[6] which allows to reveal intrinsic properties of the nanotubes. We show that the absorption varies by up to a factor of 3 for zigzag nanotubes of opposite family type. Finally, we propose a phenomenological formula to evaluate quantitatively the absorption cross section of small diameter carbon nanotubes as a function of their chiral indices.^[5]

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Electron temperature dependence of the strength of the electron-phonon coupling in double wall carbon nanotubes

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We applied Time-Resolved Two-Photon Photoemission spectroscopy to probe the electron-phonon (e-ph) coupling strength in double-wall carbon nanotubes. The e-ph energy transfer rate $G(T_e, T_l)$ from the electronic system to the lattice depends linearly on the electron (T_e) and lattice (T_l) temperatures for $T_e > \Theta_{\text{Debye}}$. Moreover, we numerically solved the Two-Temperature Model. We found: (i) a T_e decay with a 3.5 ps time constant and no significant change in T_l ; (ii) an e-ph coupling factor of $2 \times 10^{16} \text{ W/cm}^{-3}$; (iii) a mass-enhancement parameter, λ , of $(5.4 \pm 0.9) \times 10^{-4}$; and (iv) a decay time of the electron energy density to the lattice of 1.34 ± 0.85 ps.

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Identifying dopants and catalytically active sites in nitrogen-doped carbon nanotubes

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Doping carbon nanotubes and graphene with atoms such as nitrogen (N) has long been pursued as means to controlling their electronic and chemical properties. Exciting recent applications such as electrocatalysis have spurred increasing interest in doped carbon materials. However, the local atomic structure of the dopant sites, and which of those are catalytically active, remains a crucial unsolved problem. We have been synthesizing nitrogen-doped single-walled carbon nanotubes (N-SWCNTs) using a floating catalyst chemical vapor deposition method,^[1] which allows the material to be directly deposited on various substrates and characterized by a variety of microscopic and spectroscopic means.

Previously, we investigated the electron beam stability of doped nanocarbons by atomic resolution imaging and first principles molecular dynamics.^[2] More recently, we have studied the atomic and electronic structure of N-SWCNTs by scanning tunneling microscopy and spectroscopy supported by electronic structure calculations.^[3] Spectroscopic measurements on semiconducting nanotubes revealed that these local structures can induce either extended shallow levels or more localized deep levels. In a metallic tube, a single doping site associated with a gap donor state was observed at an energy close to that of the first Van Hove singularity. Our theoretical analysis shows that this feature correspond to a substitutional nitrogen atom, identified for the first time in carbon nanotubes.

We also studied the adsorption and dissociation of oxygen on three nitrogen-doped nanocarbon systems: graphene, single-walled and double-walled carbon nanotubes using density functional theory calculations.^[4] The adsorption and dissociation energies were determined for both pristine and N-SWCNTs of different diameters with various N configurations in order to elucidate the effect of diameter and dopant type. We observed that higher nitrogen concentrations greatly reduce the energy barrier for graphitic nitrogen. Our results contribute towards a better understanding of the catalytic reaction mechanism for nitrogen-doped carbon nanomaterials.

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Observation of Upconversion Photoluminescence from Carbon Nanotubes

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Photoluminescence (PL) properties of single-walled carbon nanotubes (SWNTs) have been intensively studied over the past decade because of their potential applications in optoelectronics and bioimaging, as well as for exploring fundamental exciton physics in one-dimensional electronic systems.^[1,2] Here, we report a novel optical phenomenon in SWNTs: PL emission by excitation with lower energy photons than those of the emission, which is known as upconversion PL (UCPL). UCPL has been attracting much interest related to optical manipulation of phonons in solid, high efficiency solar cells, and bioimaging. Our findings will thus provide a new dimension for optical applications of SWNTs.

The SWNTs were dispersed with 0.2 wt% SDBS in D₂O. PL spectra of SWNTs around (6,5) E₁₁ exciton peak were observed under excitation with higher (2.18 eV, normal PL) and lower (1.13 eV, UCPL) energy photons than (6, 5) E₁₁ exciton energy (1.26 eV). We observed distinct peaks at the photon energy close to (6, 5) E₁₁ in the both PL spectra. The UCPL intensity exhibited weak sublinear dependence on the excitation density; this result rules out the possibility that the observed UCPL originates from a two photon excitation process that should show a quadratic dependence. On the basis of the observations of temperature and excitation photon energy dependence, the UCPL is attributed to the excitation processes mediated by large energy optical phonons in SWNTs. We will discuss the detailed mechanism of the UCPL, and the further enhancement of the UCPL intensity by introducing lower energy local states^[2] in SWNTs.

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Tensile Strength of CNT Fibres: Characteristic Length, Stress Transfer and other Impact Factors

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The initial strength hype over carbon nanotubes arose from predictions of the strength of individual graphene layers, encouraged by measurements of individual MWCNTs and SWCNT bundles in AFM.^[1,2] However, while the scientists were professionally explicit as to what they had measured, the publicity assumed that these figures could also be readily realized in materials made from these components. It's against a background of this overselling that we examine the gradual improvement in strength of macroscopically useful materials. Yarn-like fibres composed of carbon nanotubes made by the direct spinning process^[2] have been used as the subject of this study. There have been occasional observations of strengths greater than 5 N/tex,^[3] which have served to maintain the enthusiasm for on-going developments. Here, we will re-examine those high strength reports in the context of the response of nanotubes aggregates to applied tensile stress.

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Experimentally Determined Electronic States of Oxygen-doped Single-walled Carbon Nanotubes

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Oxygen-doped SWNTs provide new photoluminescence (PL) bands with extraordinary exciton brightening. However, the detailed electronic structure of the oxygen-derived local states has not yet been revealed. We have reported that the electronic potentials of the SWNTs can be determined using an in-situ PL spectroelectrochemical method.^[1-3] Here, we applied this method to determine the precise electronic potentials of the oxygen-doped SWNTs and found that the doping caused change in the oxidation and reduction potentials of the oxygen-doped SWNTs.

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Imaging ultrafast carrier transport in carbon nanotube and nanowire transistors using femtosecond photocurrent microscopy

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We visualize ultrafast carrier dynamics in one-dimensional nanoscale devices such as carbon nanotube and silicon nanowire transistors by using combined, scanning photocurrent microscopy^[1] and time-resolved pump-probe techniques. Spatio-temporal image is particularly useful for investigating the transit times of carriers (which range 1–100 ps) that are photo-generated near one of metallic electrode and subsequently transported toward the opposite electrode through drift and diffusion processes. The carrier dynamics have been studied for various working conditions such as source-drain and gate bias voltages. In particular, the average carrier velocities extracted from the transit times increase for larger gate-bias, which is in accordance with the increased field strength at the Schottky barrier located near metal contacts. Our work will post an important step forward understating ultrafast dynamics in various low-dimensional nanoscale devices and developing future high-speed electronic devices.

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Determining the Progression of CNT Sheet Deformation with Wide Angle X-Ray Diffraction

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Individual carbon nanotubes have extraordinary strength and stiffness; however, after two decades of intensive research we are still unable to effectively use those properties in macroscopic structures. Various methods have been tried to alleviate defects that lead to diminished performance with the goal of producing high strength sheets, yarns or ribbons that can be applied to common polymer matrix composites. The inability to translate the properties of nanotubes demonstrates a lack of understanding about the deformation mechanics of carbon nanotube assemblies. In this work, we investigate the mechanics of carbon nanotube assemblies by evaluating the structural rearrangement that occurs during tensile deformation. Two-dimensional wide angle x-ray diffraction (2D-WAXRD) is used to characterize CNT alignment and a methodology is developed to interpret the diffraction data, thereby making it simpler to quantify alignment. Additionally, field emission SEM imaging is used to qualitatively monitor the alignment of CNTs for structural features that directly affect deformation. Orientation of the sheet specimens is found to play a role in the strength, modulus, and elongation to failure. This effect is examined by 2D-WAXRD to establish a relationship between structural rearrangement and mechanical properties. With a better understanding of the deformation mechanisms within CNT assemblies, it is possible to design processes to achieve fully aligned CNT assemblies that finally utilize the exceptional strength and modulus of individual carbon nanotubes.

Exciton diffusion and related decay processes in individual air-suspended carbon nanotubes

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We investigate exciton diffusion, end quenching, and exciton-exciton annihilation processes in individual air-suspended carbon nanotubes by photoluminescence microscopy.^[1] We have performed excitation spectroscopy on thousands of nanotubes to identify their chiralities and filter out bundles. In such a large dataset, we observe slightly redshifted satellite peaks which suggest the existence of single chirality bundles. Intrinsic exciton diffusion lengths for six different chiralities are obtained by analyzing the length dependence of emission intensity with a random walk theory.^[2,3] We also estimate absorption cross sections by comparing the power dependence with Monte Carlo simulations, and inspired by the agreement, we have obtained an analytical expression that reflects the one-dimensional nature of exciton diffusion.

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Spontaneous Exciton Dissociation and Stark Effect in Carbon Nanotubes

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Under an application of longitudinal electric fields, we have performed simultaneous photoluminescence and photocurrent measurements on individual single-walled carbon nanotubes. We observe nonzero photoconductivity at small fields, indicating that the injected excitons are spontaneously dissociating into free electron-hole pairs.^[1] By modeling the excitation power and voltage dependences of emission intensity and photocurrent, we find that a significant fraction of excitons are dissociating before recombination. We are also able to estimate the absorption cross section and the oscillator strength from the same model. The field-induced redshifts do not depend on excitation power or energy, ruling out effects from heating or relaxation pathways. As the shifts scale quadratically with electric fields, we attribute them to Stark effect.^[2] These results show the potential for controlling excitons in individual nanotubes using external electric fields.

Work supported by KAKENHI, SCOPE, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The samples are fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

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Spontaneous Exciton Dissociation and Stark Effect in Carbon Nanotubes

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Under an application of longitudinal electric fields, we have performed simultaneous photoluminescence and photocurrent measurements on individual single-walled carbon nanotubes. We observe nonzero photoconductivity at small fields, indicating that the injected excitons are spontaneously dissociating into free electron-hole pairs.^[1] By modeling the excitation power and voltage dependences of emission intensity and photocurrent, we find that a significant fraction of excitons are dissociating before recombination. We are also able to estimate the absorption cross section and the oscillator strength from the same model. The field-induced redshifts do not depend on excitation power or energy, ruling out effects from heating or relaxation pathways. As the shifts scale quadratically with electric fields, we attribute them to Stark effect.^[2] These results show the potential for controlling excitons in individual nanotubes using external electric fields.

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Optoelectronics with Metallic Carbon Nanotube pn-Devices

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Conventional optical photodetectors are based on semiconductors with relatively large band gaps. However, recent measurements of quasi-metallic nanotubes have shown band gaps on the order of 10-100meV, where optoelectronic devices are still severely lacking. For nanoscale devices with ballistic transport, not much is known about the depletion fields and their associated separation of photo-induced carriers, which is central to optoelectronic device operation. Here, we introduce the electronic and optoelectronic properties of quasi-metallic nanotube pn-devices, which have smaller band gaps than most known bulk semiconductors. These carbon nanotube-based devices deviate from conventional bulk semiconductor device behavior due to their low dimensional nature. We observe rectifying behavior based on band-to-band tunneling of ballistic carriers instead of ideal diode behavior, as limited by the diffusive transport of carriers. We observe substantial photocurrents at room temperature, suggesting that these quasi-metallic pn-devices may have a broader impact in optoelectronic devices operating at room temperature. A new technique based on photocurrent spectroscopy is presented to identify the unique chirality of nanotubes in a functional device. This chirality information is crucial in obtaining a theoretical understanding of the underlying device physics that depends sensitively on nanotube chirality, as is the case for quasi-metallic nanotube devices. A detailed model is developed to fit the observed I-V characteristics, which enables us to verify the band gap from these measurements as well as the dimensions of the insulating tunneling barrier region.^[1]

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Double-resonance Raman scattering of iTO and LA phonons in carbon nanotubes

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We present resonance Raman measurements of single-wall carbon nanotubes in the spectral region of 1950 cm^{-1} and 2450 cm^{-1} . We analysed a HiPCO sample using laser excitation energies between 1.58 eV and 2.73 eV, focussing on the combinational modes of iTO (in-plane transverse optical) and LA(longitudinal acoustic) derived phonon bands. Both peaks can be explained by double-resonance Raman scattering. The Raman band around 2450 cm^{-1} is an intervalley scattering process between two inequivalent \mathbf{K} points, whereas the other Raman band originates from an intravalley process around a single \mathbf{K} point.

We find a multipeak structure for the intravalley iTOLA mode that can be explained by the large variety of different carbon nanotubes probed. Using a geometric model, we calculate the resonant wave vector for the intervalley iTOLA of the four lowest optical transitions for all carbon nanotubes with diameters between 0.5 nm and 2.5 nm. Hence we can derive the appropriate energies of the combinational Raman bands as well as explain our experimental findings.

Single-wall carbon nanotube films filled with acceptor molecules for transparent electrodes

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In this work we propose a new approach for modification of optical and electronic properties of thin (thinner than 100 nm) films of single-wall carbon nanotubes (SWNTs) via their gas phase filling with different acceptor molecules (iodine^[1], CuCl^[2]). The modified films can serve as efficient transparent electrodes with parameters comparable with those of indium tin oxide (ITO) films. We have realized a gas phase filling of aerosol-grown SWNT films with two types of acceptors – iodine and CuCl. HRTEM measurements have revealed well-ordered one-dimensional crystals inside nanotubes. With both fillers the optical transparency of SWNT films remained higher than 90%. The optical absorption bands, corresponding to E₁₁ transition (for iodine) and both E₁₁ and E₂₂ transitions (for CuCl) have been suppressed. This happened due to a Fermi level shift into the valence band. The filled SWNT films have demonstrated a drop of electrical resistance of one order of magnitude (down to 70 Ohm/square).

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Electron Tomography for Quantitative 3-Dimensional Characterization of Carbon Nanotube Composites

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A variety of carbon nano-additives are being integrated into industrial composites, yielding bulk materials with enhanced structural and electrical properties. This enhancement is determined by the meso and nanoscale arrangement of the incorporated filler species. A quantitative understanding of the spatial arrangement of these fillers is, therefore, required to establish structure property relationships for materials design and optimization. Here we demonstrate the use of advanced electron microscopic techniques (energy-filtered transmission electron microscopy, tomography) in extracting high-resolution 3-dimensional microstructural information from high volume fraction aligned carbon nanotube (CNT)-polymer composites.^[1-3]

High-quality, electron-transparent samples were prepared from these composite materials using a focused ion beam. A tilt series of energy-filtered images (optimized for contrast) was collected. An image stack of the 3D volume was reconstructed from the tilt series using the Simultaneous Iterative Reconstruction Technique (SIRT). The stack was then segmented using a novel image-processing algorithm, developed in-house. This algorithm results in time savings on the order of a few hours as compared to traditional manual segmentation, thereby enabling high-throughput tomography of low contrast CNT-Polymer composites. The segmented images were further converted to high resolution (z-depth Resolution: 1.5 nm, 10% of average NT diameter and inter-NT spacing) 3D visualizations of the nanotube morphology within the matrix. The visualizations thus obtained were imported into MATLAB as voxel volumes to obtain NT packing fractions. These volumes can additionally be used to extract other dispersion metrics or be employed in finite element models to quantitatively understand the role of the microstructure on continuum scale composite properties.

The details of the image acquisition, processing, reconstruction and microstructural quantification methodologies will be presented in conjunction with tomography results from varied NT loading systems.

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SWNT vs MWNT. Comparative study of electrical properties in composites and transparent films

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For novel applications of carbon nanotubes, their quality and properties are crucial. In our study, we have compared the influence of SWNT and MWNT added in small amounts into some epoxy compounds on the electrical conductivity, with the commercially available SWNT produced by OCSiAl (“Tuball” ®) being used. SWNT were used as produced without further purification. The “as-produced” material contained less than 10% of inorganic impurities and more than 75% of SWNT. Concentration of SWNT as low as 0.0001% was enough to obtain the conductivity well above percolation threshold (10^{-6} S/cm). The same conductivity could be obtained by the use of MWNT at much higher concentrations, above 0.01%.

It is well known that CNT can be used to produce conductive coating on the surface of polymer film. The properties of such conductive films depend on the quality of CNT used. We have prepared conductive films on the PET surface by the use of spray coating. The film made of SWNT had the resistance about 110 Om/sq., while transmittance was above 90% at 550 nm. We compared it to the film made of commercially available MWNTs. Its resistance was from 10 to 100 times higher at about the same transmittance. The superior characteristics of the conductive films made of SWNT “Tuball” make them useful for such applications as touch screens, solar cells and smart windows.

Slip inhibition between graphenes by de-fluorination of fluorinated multi-walled carbon nanotubes

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Carbon nanotubes (CNTs) are the strongest and stiffest materials in terms of tensile strength and elastic modulus. However, the mechanical properties of macroscale CNT materials still fail to match the mechanical properties of their constituent CNTs. Especially, a significant mechanical weakness of macroscale multi-walled carbon nanotube (MWCNT) materials is an interfacial slip between graphenes within a MWCNT or between adjacent MWCNTs. The graphene of MWCNTs consists of sp^2 -hybridized carbon atoms bound by covalent bonds. In contrast, adjacent graphenes interact through van der Waals forces in the case of the contact point between neighboring MWCNTs and the interlayer of MWCNTs. Therefore, the interfacial slips between adjacent nanotubes^[1] and between graphenes of MWCNTs^[2] reduce the mechanical properties of the macroscale materials. In order to form covalent bonds between the contacting or overlapping graphenes, the generation of sp^3 -hybridized carbon atoms at the points is needed.

Fluorination of carbon atoms in carbon materials with sp^2 -hybridized orbitals changes the hybridization of carbon atoms to sp^3 -hybridized orbitals.^[3] In this study, we performed de-fluorination of fluorinated MWCNT fibers to form connections between the overlapping graphenes through dangling bonds from sp^3 -hybridized carbon atoms. Scanning electron microscopy and transmission electron microscopy observations of the tip of the fractured de-fluorinated MWCNT fibers after tensile tests revealed that all layers in each MWCNT were broken and the interfacial slip of graphenes was inhibited by de-fluorination. However, the tensile strength of de-fluorinated MWCNT fibers was lower than that of as-prepared MWCNT fibers before fluorination. We conclude that the poor tensile strength of de-fluorinated MWCNT fibers resulted because fluorination and de-fluorination destroyed the graphenes of their constituent MWCNTs.

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Microsecond-Resolution Single-Molecule Dynamic Sensing

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Single-molecule chemistry can be monitored using optical fluorescence, mechanical forces, or electronic conduction. Of these three, electronic solid state devices offer a straightforward solution to the fundamental bandwidth limitations of the optical and mechanical techniques. Furthermore, single-walled carbon nanotube (SWNT) field effect transistors (FETs) offer ideal properties for this application since they combine high bandwidth and excellent sensitivity with a nanoscale active area that is ideal for single-molecule biofunctionalization. Recent work has shown that it is straightforward to label a SWNT-FET with a single molecule and then study that molecule's dynamic interactions with surrounding analytes ^[1].

Here, we extend this principle of single-molecule sensing to a temporal resolution of 2 μ s, exceeding the bandwidth of fluorescence- and force-based transduction by nearly one-hundred fold. At the microsecond scale, SWNT-FETs report protein transitions and motions that have remained hidden to other techniques. For example, applying the technique to the enzymatic activity of T4 lysozyme has resolved a broad distribution of motions in the range of 1 to 200 μ s – too fast to be observed by FRET but too slow for NMR or molecular dynamics modeling. Statistical analysis of thousands of events reveals the characteristic timescales and energy landscape of these motions and the biochemistry that drives them. The technique is easily generalized to other proteins to generate similar “fingerprints” of biochemical activity.

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Highly thermal conductive CNT/carbon fiber/polymer Composite for thermal interface material

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In 2004, we developed the super-growth chemical vapor deposition technique to synthesis high-purity, long and exclusively single walled CNTs. The growth efficiency of this technique is superior to other SWNT enabling industrial mass production (in ton-scale), an aspect which will soon become reality. Furthermore, the single wall carbon nanotubes synthesized using this technique (SG-SWNT) exhibits several unique properties such as high aspect ratio, high surface area, high purity and good dispersibility, making them one of the best available conductive fillers for the development of composites. These properties were utilized for the development of a highly conductive rubber-like composite by mixing long single wall-nanotubes (SWNTs), an ionic liquid, and a fluoridated co-polymer.

We investigate the various factors critical for achieving SG-SWNT/polymer with superior electrical and mechanical properties, such as dispersion method, evaluation of CNT in solution (for process control), compounding. These investigations have culminated in the development of SG-SWNT/polymer composite with excellent electrical and thermal conductivity, high durability and environmental resistance. I would be introducing some of our recent results and achievements in this area, during the course of my presentation. Recently, efficient thermal transfer from devices is important issue for high many fields, such as supercomputer, automobile and space craft. In general, high thermal materials are hard and high density. However, to decrease the thermal resistance, soft and high thermal conductive materials are required.

In this presentation, we propose the high thermal conductive CNT/carbon fiber/polymer composite. Thermal conductivity of our composite is about 100 W/mK, this value is almost same as that of iron or brass. This high thermal conductivity is achieved by increasing of thermal transfer efficiency between carbon fiber with CNTs.

Photocurrent microscopy reveals chiral index fingerprint and thermoelectric power of CNT FETs

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We have performed scanning photocurrent microscopy and spectrally-resolved photoconductivity measurements of field-effect transistors (FETs) made from individual suspended carbon nanotubes (CNTs). Photoconductivity peaks associated with individual CNTs are referenced against existing Rayleigh scattering measurements to uniquely identify chiral indices. There is a close agreement between our assigned exciton resonances and the previously published exciton resonances. We further investigate the spatial-dependence, polarization-dependence, and gate-dependence of photocurrent and photovoltage in these devices. While previous studies of surface-bound CNT FET devices have identified the photovoltaic effect as the primary mechanism of photocurrent generation, our measurements show that photothermoelectric phenomena play a critical role in the optoelectronic properties of suspended CNT FETs. We have quantified the photothermoelectric mechanisms and identified regimes where they overwhelm the photovoltaic mechanism.

Electronic Dissipation in Single-Walled Carbon Nanotubes Imaged by Kelvin Probe Force Microscopy

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Electronic dissipation in single-walled carbon nanotubes (SWNTs) has been studied extensively due to their outstanding electrical properties. However, the precise role of defects, disorder and chirality in electronic scattering remain largely unknown due to the lack of experimental methods that effectively distinguish these effects. Here, we demonstrate Kelvin Probe Force Microscopy (KPFM) as a quantitative tool for studying electronic scattering in active SWNT field effect transistors. KPFM has a unique advantage of directly imaging dissipative electrostatic gradients along a SWNT. The electrostatic potential profile of a device can be used, for example, to distinguish between pristine SWNTs and those containing a single point defect.

For pristine SWNTs, we observe a uniform potential gradient that directly determines the inelastic mean free path λ as a function of bias and can distinguish contact resistance from homogeneous inelastic scattering. At 185 K, we observe λ decreasing from nearly 1 μm at low bias to 100 nm at high bias. Fitting λ to established models determines the roles of surface plasmon-polariton scattering in one limit and optical phonon emission at the other. We find the optical phonon mean free path for spontaneous emission to be 62 ± 20 nm at 300 K, nearly 50 nm longer than observed in previous experimental studies.

In contrast to the pristine case, SWNTs with point defects exhibit a sharp potential step at a defect site. The resistance of a defect is then directly determined by the magnitude of the potential step. The shape of the potential step reveals the defect's scattering potential and propensity for trapping charges. The combination of KPFM and two-terminal transport data are well fit to a one-dimensional Frenkel-Poole model of conduction.

Distinguishing individual and ensemble carbon nanotubes by Raman spectroscopy

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Raman spectroscopy on single-walled carbon nanotubes (SWCNTs) is one of the most powerful methods to analyse their structural, optical, and electronic properties. While Raman studies are usually performed on mixed SWCNT ensembles, it is essential to investigate the inherently distinct Raman signal of the underlying individual tubes.

Using isopropanol as a precursor, our samples were grown from patterned iron catalyst particles by CVD in a tube furnace system. Using ST-cut quartz as a substrate, we obtain perfectly aligned, mostly individual tubes, as confirmed by Raman spectroscopy, AFM and SEM imaging.

We present Raman spectra acquired under different excitation wavelengths from many individual SWCNTs and compare them to those of SWCNTs in areas with higher density that interact with each other. We assess the inherent variation of the acquired Raman signal along individual tubes statistically and discuss whether the Raman spectra from nanotube ensembles can be modelled by a superposition of individual SWCNT spectra. We show the importance of our findings when e.g. using the Raman intensities of D and G modes for the determination of defect concentration or their position and lineshape for deducing the metallic / semiconducting content of the sample.

Using Image force microscopy to visualize optical absorption in individual single walled carbon nanotubes

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Image Force Microscopy detects near-field resonant optical scattering by measuring the dipole-dipole force interaction through the use of an SPM tip.^[1] This technique provides exceptional spatial resolution, circumventing the traditional difficulties with far-field optical detection, where the weak scattered light collection efficiencies and background signal levels affect measurements from small target volumes. To demonstrate the image force technique, samples of HiPco single-walled carbon nanotubes was used. The nanotubes were dispersed in sodium deoxycholate using standard sonication and ultracentrifugation techniques, resulting in a concentrated suspension with sharp absorption and strong photoluminescence features.^[2,3] Single nanotubes were imaged by wide-field micro-photoluminescence in dilute conditions in solution and spin coated on mica substrates. Spectra of single nanotubes were obtained to verify sample quality and tube individualization. These samples were then studied using simultaneous image force, topography, and confocal/tip-enhanced photoluminescence in our near-field scanning probe system.

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