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Superacid-Surfactant Exchange: Enabling Nondestructive Dispersion of Full-Length Carbon Nanotubes in Water

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Abstract

Attaining aqueous solutions of individual, long single-walled carbon nanotubes is a critical first step for harnessing the extraordinary properties of these materials. However, the widely used ultrasonication–ultracentrifugation approach and its variants inadvertently cut the nanotubes into short pieces. The process is also time-consuming and difficult to scale. Here we present an unexpectedly simple solution to this decade-old challenge by directly neutralizing a nanotube-chlorosulfonic acid solution in the presence of sodium deoxycholate. This straightforward superacid-surfactant exchange eliminates the need for both ultrasonication and ultra-centrifugation altogether, allowing aqueous solutions of individual nanotubes to be prepared within minutes and preserving the full length of the nanotubes. We found that the average length of the processed nanotubes is more than 350% longer than sonicated controls, with a significant fraction approaching $\sim 9 \mu\text{m}$, a length that is limited by only the raw material. The nondestructive nature is manifested by an extremely low density of defects, bright and homogeneous photoluminescence in the near-infrared, and ultrahigh electrical conductivity in transparent thin films ($130 \Omega/\text{sq}$ at 83% transmittance), which well exceeds that of indium tin oxide. Furthermore, we demonstrate that our method is fully compatible with established techniques for sorting nanotubes by their electronic structures and can also be readily applied to graphene. This surprisingly simple method thus enables nondestructive aqueous solution processing of high-quality carbon nanomaterials at large-scale and low-cost with the potential for a wide range of fundamental studies and applications,

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b04429. Cryo-TEM, TGA, AFM, Raman, XPS, UV–vis-NIR absorption, PL characterizations of S2E-SWCNTs. Stability test of HiPco S2E-SWCNTs, SWCNT concentration optimization for S2E, SWCNT extraction in the DOC-CTAB-SWCNT system. S2E-graphene. Transmittance curves, sheet resistance *versus* transmittance, and stability of electrical conductivity for S2E-TCFs. (6,5)-SWCNT sorting from S2E- and sonic- SWCNTs. Hyperspectral PL image of S2E-SWCNTs. Detailed information on various sources of carbon materials (PDF)

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Notes

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including, for example, transparent conductors, near-infrared imaging, and high-performance electronics.

Graphical abstract

Keywords

carbon nanomaterials; solution processing; defects; transparent thin films; photoluminescence; nanometrology; nanomanufacturing

The remarkable optical, electrical, and mechanical properties of single-walled carbon nanotubes (SWCNTs) come with an important caveat: They only occur in long, low-defect, and individually dispersed nanotubes. However, SWCNTs have an inherent tendency to bundle together due to cumulatively strong van der Waals interactions (~ 0.5 eV/nm for 1.4 nm diameter nanotubes),¹ with the resulting, less exceptional material properties being more representative of the agglomerated bundle than of the individual tubes. To overcome this limitation, in 2002, O'Connell *et al.*² introduced a method of dispersing surfactant-stabilized individual SWCNTs in aqueous solutions *via* ultrasonication followed by ultracentrifugation. This technique and its variants are foundational to many fundamental and applied studies as they allow SWCNTs to be analyzed at the single nanotube level^{3–5} and even further isolated into pure single chirality SWCNT structures.^{6–10}

However, ultrasonication damages SWCNTs, creating defects and cutting them into short pieces,^{11–13} which dramatically degrade the electrical conductivity, weaken the mechanical strength, and in the case of semiconducting SWCNTs, quench the photoluminescence (PL).^{3,14–16} Furthermore, both ultrasonication and ultracentrifugation require costly equipment, and the methods are time-consuming and energy intensive, all of which present significant challenges to large-scale production. As such, many current studies that make use of individually dispersed SWCNTs are largely limited to the short version (typically 300–500 nm) of this extraordinary material.

To overcome these issues, alternative methods have been actively pursued. For instance, it has been shown by Wenseleers *et al.*¹⁷ and later confirmed by Subbaiyan *et al.*¹⁸ that gentle stirring of SWCNTs in aqueous surfactant solutions can scratch off loose nanotubes from the

surface without causing measurable damage to their carbon bonding structure. However, the procedure takes several weeks, and the yield is extremely low, limiting it to microscopic sample preparation. Graf *et al.*¹⁹ recently demonstrated high-speed shear mixing as a way to successfully disperse SWCNTs in toluene, but the method also is energy intensive and time-consuming (96 h of high-speed shear mixing is required). Moreover, toluene is incompatible with common SWCNT sorting processes that are aqueous based^{6–10} and is a less environmentally friendly solvent compared to water. Covalent surface modifications can render SWCNTs soluble in water after heavy functionalization,²⁰ but these reactions would cause the loss of both the optical and electrical properties that make SWCNTs attractive materials in the first place.

Although SWCNTs are generally difficult to disperse in aqueous solutions, Penicaud *et al.* showed that Li/Na-reduced SWCNT salts can dissolve in some organic solvents.²¹ Notably, Pasquali and co-workers found that SWCNTs will spontaneously dissolve in chlorosulfonic acid.²² The discovery of this true solvent for SWCNTs has led to the fabrication of high-quality CNT fibers and thin films.²³ Unfortunately, both Li/Na and superacids are extremely reactive and corrosive, making them incompatible with established SWCNT sorting methods and many other applications.^{6,8–10}

Here we introduce an unexpectedly simple method, which we call superacid-surfactant exchange (S2E), to achieve aqueous solutions of full-length individually dispersed SWCNTs, without causing structural damage. Using just two solution-mixing steps, S2E involves the direct neutralization of a SWCNT-superacid solution in the presence of a surfactant. Unlike ultrasonication, our method yields individual nanotubes within minutes without causing structural defects or cutting the nanotubes into short pieces. The processed SWCNTs feature an extremely low density of defects, bright and homogeneous PL in the near-infrared, and more than an order of magnitude improvement over sonicated controls in the electrical conductivity of transparent thin-films. We further demonstrated that using established sorting techniques, long SWCNTs of pure single chirality can be separated, highlighting the ability of S2E to produce full-length, chirality-sorted SWCNTs *via* scalable aqueous solution processing for a wide range of potential applications.

RESULTS AND DISCUSSION

Aqueous Dispersion of Individual SWCNTs Obtained by Superacid-Surfactant Exchange

We found that the addition of HiPco SWCNTs dissolved in chlorosulfonic acid to a basic aqueous solution of sodium deoxycholate (DOC) resulted in a homogeneous, black aqueous solution of SWCNTs (Figure 1a–d). This process takes just minutes to complete. UV–vis–NIR absorption spectra and PL excitation–emission maps (Figure 1e,f) of the supernatant unambiguously confirm sharp absorption peaks and bright fluorescence that are characteristic of individually suspended semiconducting SWCNTs.² Cryo-transmission electron microscopy (cryo-TEM) imaging of the rapidly frozen solution further confirmed that the nanotubes were individualized rather than bundled together (Figure S1).

Unlike ultrasonication and other previous SWCNT dispersion methods, our S2E technique is driven by two acid–base reactions that are chemically reversible:

Crystalline SWCNTs can spontaneously dissolve in chlorosulfonic acid, as established by Pasquali and co-workers.²² The superacid protonates the weakly basic nanotubes, exfoliating the bundled material into individual structures due to the Coulombic repulsion between the positively charged nanotubes (eq 1a). Our experiments suggest that as hydroxide anions neutralize the protonated SWCNTs in the second step, the “naked” nanotubes are then immediately encapsulated by the surrounding DOC molecules and thus stay as individual particles in the aqueous solution (eq 1b). This superacid-surfactant exchange process is sensitive to the solution pH. At pH ~ 11, the solution was stable for more than 6 months (Figure S2). Further addition of the SWCNT-superacid solution can cause the pH to drop below ~7, at which point the nanotubes coagulated and precipitated (Figure S2). We attribute this pH dependence to the fact that DOC has a pK_a of ~6.7, therefore at low pH it loses its solubility and hence efficacy as a surfactant.

We also found that S2E was more effective in a certain concentration window of SWCNTs (Figure S3). This phenomenon can be understood in light of the diffusion kinetics requiring DOC to encapsulate the “naked” SWCNTs in a timely manner; rebundling occurs otherwise since the acid–base reactions are instantaneous. Lower concentrations are translated into larger average distances between the “naked” SWCNTs, which gives the surfactant molecules enough time to stabilize the tubes as individual particles in an aqueous suspension. Interestingly, by adding cetrimonium bromide (CTAB) to the neutralized solution, the suspension can be concentrated easily to a high final concentration of ~80 mg/L with salts simultaneously removed. The addition of this second surfactant caused the solution to phase separate, which might have occurred due to the specific molecular packing arrangement of CTAB and DOC on the SWCNT surfaces induced by Coulombic attractions, causing the materials to become more hydrophobic and collect in the surfactant-rich bottom phase (Figures S4 and S5, see Supporting Information for more details).

We note that adding surfactants directly into the superacid-SWCNT solution does not work to suspend the nanotubes individually because the surfactant molecules are chemically unstable in the superacid. Among the various surfactants that are commonly used for dispersing SWCNTs, we found that DOC was most effective for S2E (Figure S6). DOC features rigid but slightly bent steroid rings that can easily accommodate the curved nanotube surface,²⁴ thus presumably enabling the high dispersion stability of the individual SWCNTs. Although HiPco materials, the most studied source of SWCNTs, were used here for demonstration purposes, other sources of SWCNTs, including CoMoCAT SG65i, CoMoCAT SG76, and MEIJO eDIPS EC1.0 (Table S1), were similarly successful at

individual dispersal (Figure S7). Our experiments further suggest that S2E is an effective and general method for dispersing other carbon nanomaterials, including graphene in water (Figure S8).

The Nondestructive Nature of S2E Enables Retention of the SWCNTs' Full Length

The S2E-SWCNTs were significantly longer than controls prepared using ultrasonication (sonic-SWCNTs). After only 2 h of sonication, HiPco sonic-SWCNTs were cut into short pieces with an average length (L_{avg}) of just 0.35 μm . In contrast, the L_{avg} of the S2E-SWCNTs was 1.18 μm , which was 237% longer than the sonic-SWCNT control (Figure 2a–c). The average length of the sonic-SWCNTs continued to decrease with increasing sonication time (Figure 2d). Similar trends were observed for the three other sources of SWCNTs studied, including CoMoCAT SG65i, CoMoCAT SG76, and MEIJO eDIPS EC1.0 (Figure S9). L_{avg} for the corresponding S2E-SWCNTs was 1.64, 1.75, and 2.96 μm , respectively, which was more than 460% as large as the sonicated controls.

We further confirmed the nondestructive nature of S2E by monitoring the presence of nanotube defects using Raman spectroscopy. The D peak of carbon materials, occurring at $\sim 1350\text{ cm}^{-1}$, arises from structural defects (*e.g.*, atomic vacancies or sp^3 hybridized bonds). Meanwhile, the G peak ($\sim 1590\text{ cm}^{-1}$) corresponds to sp^2 bond stretching. The ratio of the integrated areas of the D peak to G peak ($I_{\text{D}}/I_{\text{G}}$) is directly correlated with the density of defects within the carbon lattice. We found that S2E-SWCNTs had the lowest $I_{\text{D}}/I_{\text{G}}$ ratio at ~ 0.02 for HiPco materials (Figure 2e and Figure S10). In contrast, the $I_{\text{D}}/I_{\text{G}}$ for HiPco sonic-SWCNTs increased, ranging from ~ 0.05 to ~ 0.08 with increasing sonication time. Interestingly, $I_{\text{D}}/I_{\text{G}}$ is roughly proportional to $1/L_{\text{avg}}$, suggesting that the defects introduced by sonication are mainly located at the nanotube ends (*i.e.*, end defects) which define the length of the tube. $I_{\text{D}}/I_{\text{G}}$ of the S2E-SWCNTs was even lower than the starting raw HiPco material (black star in Figure 2e), possibly due to the purification effect of the superacid.²⁵ Only nanotubes with a highly crystallized structure can be fully protonated by the superacid, while amorphous carbon and highly defective tubes cannot dissolve well, causing these materials to remain as solids that precipitate out of solution, thus lowering the total defects in the S2E-processed samples.

Enhanced Electrical Conductivity in Transparent Conducting Films of S2E-SWCNTs

Transparent conducting films (TCFs) are an emerging application of carbon nano-tubes.²⁶ The sheet resistance (R_{S}) of a nanotube TCF is dominated by the junction resistance.¹⁴ The longer the nanotubes, the fewer the junctions that are encountered by the current traversing the film, and as a result, the conductivity of a nanotube film scales with nanotube length by a power law.¹⁴ Based on four-point probe measurements, we found that TCFs made from S2E-SWCNTs showed an R_{S} as small as 66 Ω/sq at 75% optical transmittance at 550 nm, which was 11.5-times more conductive than the sonic-SWCNT control TCF (760 Ω/sq ; Figure 3a,b). Notably, the SWCNT-TCFs exhibited high transmittance in both the visible and NIR wavelengths (Figure S11).

We further evaluated the performance of these TCFs using the ratio of the optical (σ_{op}) and current (σ_{dc}) conductivity, which is correlated to the sheet resistance (R_s) and the optical transmittance (T), according to the following equation:²⁷

$$\frac{\sigma_{\text{op}}}{\sigma_{\text{dc}}} = \left(\frac{1}{\sqrt{T}} - 1 \right) \times \frac{R_s}{188} \quad (2)$$

A lower $\frac{\sigma_{\text{op}}}{\sigma_{\text{dc}}}$ value indicates better optoelectronic performance of the TCF (*i.e.*, higher conductivity at higher optical transparency). Figure 3c shows the sheet resistance–transmittance curves of TCFs fabricated from HiPco S2E-SWCNTs in comparison with the sonic-SWCNT control and other HiPco TCFs reported in the literature. At 550 nm, the HiPco S2E-SWCNT TCFs had a $\frac{\sigma_{\text{op}}}{\sigma_{\text{dc}}}$ of 0.26, which was 3.4-times more conductive than the sonicated controls. The conductivity of these HiPco thin films is comparable with the best reported in the literature.²⁸

In the case of MEIJO eDIPS EC1.0 SWCNTs, the enhancement was even more pronounced, with a $\frac{\sigma_{\text{op}}}{\sigma_{\text{dc}}}$ value of 0.06 for S2E-SWCNTs and 0.54 for the sonication control, which is an 8-fold improvement in the conductivity (Figure 3c and Figure S12). The conductivity of the MEIJO eDIPS EC1.0 S2E-SWCNTs (130 Ω/sq at 83% transmittance) was also significantly better than that of indium tin oxide (ITO), the most widely used transparent conducting film (blue star in Figure 3c). Notably, this high conductivity was achieved without having to chemically dope the nanotubes, as is commonly practiced for conductive thin films.²⁷ X-ray photoelectron spectroscopy (XPS) and Raman scattering confirm that our S2E-SWCNTs are not doped, which is consistent with the observed high stability of the film conductance (see Figures S13–S15 and Supporting Information for more details). This result suggests S2E nanotube TCFs would be ideal in applications such as flexible electronics, since doped films are not stable and tend to lose conductivity over time.²⁷

Long, Chirality-Pure, Individual S2E-SWCNTs Show Significantly Brighter Photoluminescence in the near-Infrared

Separating SWCNTs by chirality is important for taking full advantage of the remarkable optical and electrical properties of these low-dimensional materials as well as to enable important fundamental studies.^{7,29} Nearly all established separation techniques are based on aqueous solution processing methods.⁷ However, the cutting effects of ultrasonication and the limited scalability of ultracentrifugation have created major obstacles to obtaining long, chirality-pure SWCNTs at reasonably large quantities.

To demonstrate that our S2E dispersion method is compatible with established sorting techniques, we applied aqueous two phase (ATP) separation, a highly scalable solution-based sorting technique,^{9,10} to S2E processed nano-tubes. In ATP, SWCNTs spontaneously partition into two immiscible aqueous phases depending on their structures, resulting in the

isolation of single chirality SWCNTs.^{9,10} Although ATP has been successfully used to purify single chiralities from a SWCNT mixture, the sorted nanotubes are typically short (<500 nm) due to the need for sonication in order to prepare the starting aqueous solution of individually dispersed nanotubes.¹⁸ Applying ATP separation to S2E dispersed nanotubes is straightforward since the aqueous S2E-SWCNT solution can be directly used as a starting material for the separation method.

Figure 4a shows the UV-vis-NIR absorption spectra of (6,5)-SWCNT sorted from S2E-SWCNT solutions of HiPco materials that initially contained an assortment of different chiralities. The successful separation is clearly evident by the sharp absorption peaks characteristic of the (6,5) chirality, including its first (E_{11} at 987 nm) and second (E_{22} at 571 nm) optical transitions. Consistently, the PL map (Figure 4b) also presents a single excitation-emission feature of (6,5)-SWCNT, in stark contrast with the map for the starting mixture (Figure 1f), thus unambiguously confirming the separation of a single chirality from the heterogeneous starting material. We also demonstrated this aqueous processing compatibility for other SWCNT sources (Figure S16).

Notably, we observed that the NIR PL of the S2E-SWCNTs was significantly brighter than the sonication control. Using PL imaging, we could quantitatively analyze the fluorescence at the individual particle level.³⁰ In Figure 4c,d we compared the NIR PL images of S2E (6,5)-SWCNTs to the sonic (6,5)-SWCNT control, which was also sorted to pure single chirality *via* ATP. Although the absorption spectra for the sorted S2E-SWCNTs and the sonicated control are nearly identical (Figure S17), the individually resolved fluorescent nanotubes exhibit significant differences in both length distribution and PL intensity. More than 50% of the fluorescent nanotubes from the sonication control were shorter than the spatial resolution of our microscope (0.56 μm) and therefore displayed as “dots” in the image. In contrast, 80% of the S2E-SWCNTs can be spatially resolved to reveal their lengths, which ranged from 0.6 to 7.44 μm in consistence with AFM measurements (Figure 4e). Over a large spectral range (900–1600 nm), 93.5% of the fluorescent S2E-nanotubes (out of 200 counts) emitted at 988 nm, which is the E_{11} emission of (6,5)-SWCNT (Figure S18). Their PL intensities were also brighter than the sonicated control (Figure 4f).

The PL down the length of these S2E-SWCNTs was homogeneous, both in terms of emission wavelength and intensity, which excludes the existence of quenching sites. Since the exciton diffusion length at room temperature is significantly lower than 500 nm in defect-free nanotubes,³ the PL intensity is not expected to vary significantly along the length of SWCNTs that are longer than the diffraction limit. However, we observed a correlation between the PL intensity per unit length and the length in the S2E (6,5)-SWCNTs (Figure 4g). For longer SWCNTs (>1.2 μm), the average PL intensity per unit length was 96% brighter than that of the sonicated control. Even for those nanotubes within the same length range (0.6–1.2 μm), S2E nanotubes were still 45% brighter than the sonication control. This intensity difference suggests that besides cutting, ultrasonication also introduces quenching defects, which causes excitons to decay nonradiatively. Eliminating the need for sonication, as made possible through S2E, avoids cutting nanotubes and the introduction of structural defects, opening the possibility of scaled solution processing of long, chirality pure, individual SWCNTs that are largely free of defects.

CONCLUSIONS

We have demonstrated a nondestructive method to address the long-standing challenge of dispersing full-length SWCNTs in water by directly neutralizing SWCNT-superacid solutions in the presence of a surfactant. Our method is unexpectedly simple, producing aqueous solutions of individually dispersed nanotubes in minutes and completely eliminating the need for ultrasonication and ultracentrifugation. It is also fully compatible with established chirality sorting techniques, allowing long, individual semiconducting nanotubes to be separated at large scale. The processed nanotubes retain their full lengths and are nearly defect-free, demonstrating significantly improved optical and electrical properties compared to sonicated controls. Because of its nondestructive nature, S2E can reveal the true distributions of diameter, chirality, and length of a sample and hence may be adapted as a powerful metrology method to provide valuable feedbacks to guide nanotube synthesis and processing. This nondestructive processing method can be readily applied to other carbon nanomaterials, including graphene, thus paving the way for scalable aqueous solution processing of high-quality carbon nanomaterials for many fundamental studies and practical applications^{7,29} where high-quality, long, and defect-free carbon nanomaterials are actively sought after.

METHODS

Superacid-Surfactant Exchange (S2E)

Raw HiPco SWCNT materials (Rice University, lot no. 194.3) were dissolved in chlorosulfonic acid (Sigma-Aldrich, 99.9%) at a concentration of ~0.5 mg/mL (the concentration varied from ~0.1 to ~0.5 mg/mL for different SWCNT sources). This SWCNT-superacid mixture was added drop-by-drop to an aqueous solution of 0.5 M NaOH and 1 wt/v% DOC (Sigma-Aldrich, 97%) until the solution pH increased to and stayed stable at ~11. (Safety Note: All S2E experiments should be performed in a fume hood with protection. Goggles, acid protection gloves, and lab coats are required. Particularly, in the neutralization step, the addition of super acid-SWCNT mixture to basic aqueous solution may trigger violent acid–base reactions that can generate much heat and smoke.) Undissolved particulates were removed using a low-speed benchtop centrifuge at 6000 *g* for 30 min. All dispersion and characterization experiments were performed at room temperature. This S2E procedure was applied to various carbon materials from major commercial sources. Table S1 provides an overview of the sources and batch numbers of graphene and the four types of SWCNTs studied. Note that for graphene, sodium cholate (Sigma-Aldrich, 99%) was used in place of DOC as it appeared more effective.

As controls, sonic-SWCNTs were prepared by the ultrasonication plus ultracentrifugation approach from 1 mg/mL solutions of raw SWCNT material in deuterium oxide (D₂O, Cambridge Isotope Laboratories, Inc. 99.8%), following an established protocol,¹⁰ using DOC as the surfactant (tip sonication at 15 W, Qsonica S-4000) at increasing sonication times.

Phase Separation of Individual SWCNTs

After the superacid-surfactant exchange, an aqueous solution of 1.5 wt/v% CTAB was added to the S2E-SWCNT solution, such that the final concentrations of CTAB and DOC were 0.5 wt/v% and 0.67 wt/v%, respectively. The addition of CTAB solution spontaneously generated a phase separation, which can be accelerated by centrifuging at 2000 *g* for 2 min (Eppendorf centrifuge 5810R). The surfactant-rich bottom phase was collected and then diluted to the desired S2E-SWCNT concentration for further electrical and optical measurements.

ATP-Sorting of S2E-SWCNTs

The ATP separation method was used to isolate (6,5)-SWCNTs from the S2E- and sonic-SWCNT samples, following a procedure established by Subbaiyan *et al.*¹⁰ Three major sources of SWCNTs, including HiPco, CoMoCAT SG76, and CoMoCAT SG65i, were used in this experiment to demonstrate the general compatibility of S2E. Since ATP separation is sensitive to the surfactant type and pH of the solution, we performed an extra step to remove the CTAB by centrifugal ultrafiltration (Amicon Ultra-15, PLHK Ultracel-PL membrane, 100 kDa) and adjusting the pH to ~8.

SWCNT Length Characterization

The individually dispersed SWCNTs were deposited on (3-aminopropyl) triethoxysilane functionalized SiO₂/Si substrates, following a previously published method.¹⁵ In order to totally remove the surfactants and other possible organic solvents, the coated wafers were annealed in air at 300 °C for 1 h. All AFM images were recorded in tapping mode on a Veeco Multimode AFM with conical AFM probes backside-coated with gold (Tap300GD-G, with a force constant of 40 N/m, Ted Pella).

Fabrication and Characterization of TCFs

Dispersed S2E-SWCNTs and sonic-SWCNTs were filtered through a 0.025 μ m nitrocellulose membrane (Merck Millipore Ltd.). The membranes were placed in a vacuum oven at room temperature for 12 h. After drying in a vacuum oven at room temperature, the nitrocellulose membrane with the attached SWCNT film was cut into 3 cm $\times$ 1 cm strips and transferred onto a glass slide according to a method established by Wu *et al.*²⁶ Prior to transferring, the glass slides were cleaned in piranha solution at 90 °C for 45 min, followed by rinsing in Nanopure water and blow-drying with argon. Then in order to fully remove the remaining surfactants and residues from the nitrocellulose membrane, the thin films were immersed in 40% nitric acid solution for 0.5 h as described by Geng *et al.*³¹ and then immersed in Nanopure water for 2 h. The amount of residue surfactant is below the sensitivity limit of XPS, since no sodium or bromide peaks were observed in the XPS spectra of the TCF films fabricated from S2E-SWCNTs (Figure S13). We used a four-point probe method to measure the electrical conductivities of the films. The electrodes were deposited on SWCNT strips at equal spacing by thermally evaporating silver (80 nm thickness) using a Metra Thermal Evaporator. *I*–*V* curves were measured on a Cascade probe station using a Keithley S4200 semiconductor parameter analyzer. Each data point was the average of at least three measurements.

Spectroscopic Characterization

The PL of the SWCNT solutions was characterized with a Horiba Jobin Yvon NanoLog spectrofluorometer using a liquid-N₂ cooled InGaAs array. Note that for PL spectroscopy measurements, D₂O was used in place of Nanopure water as the solvent. UV–vis–NIR absorption spectra were measured with a spectrophotometer equipped with a broadband InGaAs detector (Lambda 1050, PerkinElmer). For TCFs, an integrating sphere (Labsphere Model No. 150MM RSA ASSY) equipped with a broadband InGaAs detector attached to the UV–vis–NIR spectrophotometer was also used. Raman scattering was measured from thin-film samples using a LabRAM ARAMIS Raman microscope (Horiba Jobin Yvon) in duo scan mode, which averaged spectra from a 30 × 30 μm² area. Each sample was measured from at least 10 different regions and averaged to ensure the data were statistically meaningful.

NIR PL Microscopy

Small aliquots of S2E-SWCNT and 2h sonic-SWCNT solutions in 1 wt/v% DOC-D₂O were physisorbed on poly D-lysine coated glass slides (part no. P35GC-0-10-C, MatTek Corporation). Single tube PL imaging was performed by hyperspectral imaging³⁰ on an inverted fluorescent microscope custom-built by Photon Etc, Inc. (Montreal, Canada). Our microscope integrates a Nikon Eclipse Ti–U equipped with an oil immersion objective (UAPON 150XOTIRF, NA = 1.45, Olympus) and a liquid-N₂ cooled two-dimensional InGaAs detector (Cougar 640, Xenics, Inc.) to improve the collection efficiency in the NIR. SWCNTs were excited with a collimated, 730 nm diode laser (Shanghai Dream Lasers Technology) at a power density of 1 kW/cm². The PL emission was collected in Integrate Then Read mode of the detector. To achieve low dark current levels, broadband PL images were also obtained using Read While Integrate modes. The integration time was 4 s.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Supercid-surfactant exchange. (a) Schematic illustration of the neutralization of a SWCNT-superacid suspension with NaOH aqueous solution in the presence of the surfactant DOC. Photographs of (b) raw SWCNT powder, (c) SWCNT-superacid solution, and (d) aqueous solution of SWCNTs stabilized by 1 wt % DOC. (e) UV-vis-NIR absorption spectrum and (f) excitation-emission PL map of 1 wt % DOC stabilized SWCNTs in D₂O, showing the optical fingerprints characteristic of individually dispersed SWCNTs.

Figure 2. Nondestructive nature of superacid-surfactant exchange. Representative AFM topography images of (a) S2E-SWCNTs and (b) sonic-SWCNTs on a Si substrate. Scale bars: 1 μm . (c) Length distributions of S2E-SWCNTs (red) and sonic-SWCNTs (black). The length distributions are fitted by log-normal functions (red and black lines). (d) The average SWCNT length (L_{avg}) and (e) Raman I_D/I_G ratio as a function of sonication time. The red stars and black squares represent S2E-SWCNTs and sonic-SWCNTs, respectively. The black star in (e) represents the raw HiPco SWCNT material.

Figure 3.

Electrical and optical properties of S2E-SWCNT TCFs benchmarked against sonic-SWCNT controls and ITO. (a) Photograph of a TCF fabricated from S2E-SWCNTs on top of a logo of the Wang Laboratory (logo credit: Lucy J. Wang, Anna Y. Wang, Y.H.W.). (b) I - V curves of TCFs made from S2E-SWCNTs (red) and sonic-SWCNTs (black) at 75% transmittance at a wavelength of 550 nm. (c) Sheet resistance *versus* optical transmittance for TCFs made from S2E-SWCNTs (red circles) and sonic-SWCNTs (black circles). The sources of SWCNTs used were MEIJO eDIPS EC1.0 (open red circles) and HiPco (closed red circles). The blue star indicates the typical sheet resistance of an ITO film at ~80% transmittance. Other data points (gray) shown are literature values of HiPco TCFs as cited in the text.

Figure 4.

Bright NIR PL from long, single chirality-pure (6,5)-SWCNTs sorted from S2E-SWCNTs and sonic-SWCNTs. (a) UV-vis-NIR absorption spectra of HiPco S2E-SWCNT starting material (black) and (6,5)-SWCNTs sorted from S2E-SWCNTs *via* ATP (red). The absorption spectra are offset for clarity. (b) Excitation-emission PL map of the sorted S2E (6,5)-SWCNTs in 1 wt/v% DOC-D₂O. Broadband (900–1600 nm) PL images of (c) the sorted S2E (6,5)-SWCNTs and (d) the sonicated (6,5)-SWCNT control. Scale bars are 10 μm. (e) The length distributions of the S2E (6,5)-SWCNTs (red) and sonicated (6,5)-SWCNT control (black). (f) Histogram of the PL intensity of each pixel. Intensity counts lower than 100 were attributed to background noise and rejected from the statistics. (g) Correlation between PL intensity per unit length and the SWCNT length for S2E (6,5)-SWCNTs (red) and the sonicated (6,5)-SWCNT control (black).