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Fabrication of Free-standing, Conductive, and Transparent Carbon Nanotube Films**

By Hongwei Gu and Timothy M. Swager*

Single-walled carbon nanotubes (SWCNTs) have attracted considerable attention as a result of their remarkable strengths,^[1–3] elasticities,^[4,5] superb electrical properties,^[6] and high thermal conductivities.^[7,8] A major application identified for SWCNTs is to function as a coating agent to form transparent electrical conductors,^[9–18] which is a crucial component of many optoelectronic devices such as flat-panel displays^[19–21] and solar cells.^[22] When compared with commercially available flexible transparent conductors, carbon nanotube films have several advantages: (i) They have high environmental stability and flexibility. SWCNTs are generally inert to bases, humidity, and high temperatures. (ii) Bending nanotube films shows only small changes in resistance.^[23] (iii) SWCNTs have high transmittance in the visible region and the neutral color is an advantage over indium tin oxide (ITO) in display applications.^[23] (iv) SWCNT films can be fabricated at low cost by solution coating and printing as opposed to ITO, for which vacuum sputtering is typically required.

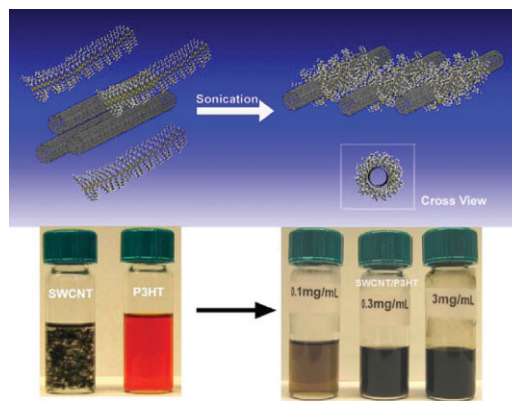
These features have prompted considerable efforts and innovations directed at creating transparent SWCNT films, including vacuum filtering,^[16] drop-casting,^[15,24,25] and Langmuir–Blodgett deposition.^[26–28] However, it remains a challenge to fabricate high-quality free-standing, conductive, and transparent SWCNT films. To accomplish this goal, we report herein our efforts to create homogenous nanotube dispersions that are stable to slow solvent evaporation and to develop a method that allows films to be released from substrates, purified, and transferred to new substrates.

A critical element of our procedure is the formation of homogenous SWCNT dispersions that are highly stable (months to years). Most commercial SWCNTs are “bundled”^[29–31] into van der Waals-induced aggregates. These aggregates can be dispersed to different degrees by ultrasonic treatment, and additives are used to create dispersions in aqueous or organic solutions.^[32–37] However, these suspensions usually have relatively low SWCNT concentrations and some methods require covalent bonds to the nanotube surface.^[38–41] In the latter case, the added defects generally lower the conductance of SWCNTs.

To create highly stable dispersions, we have made use of high molecular weight (MW) regiorandom poly(3-hexylthiophene) (P3HT)^[42] to disperse the isolated nanotubes via noncovalent interactions. Conjugated polymers such as P3HT,^[43] poly(phenylene vinylenes) (PPV),^[37,44] and poly(phenylene ethynylenes) (PPE)^[33] have previously demonstrated utility in dispersing SWCNTs. We find that high MW P3HT forms qualitatively more stable dispersions and that the conducting polymer properties of P3HT also have advantages in producing more conductive SWCNT/polymer composite films.

SWCNTs were purified by HCl treatment to remove residue metal catalysts before using and Scheme 1 depicts the formation of stable carbon nanotube suspensions. Purified bundled nanotubes were subjected to sonication in a P3HT/chloroform solution. P3HT binds to the surface of SWCNTs via π – π interactions and the higher MW allows for enhanced polymer binding due to the incremental additive nature of the attractive interactions. The careful purification of the SWCNTs to remove residual iron catalyst results in SWCNT/P3HT dispersions that are stable for more than 1 year. The high MW regiorandom P3HT can produce stable dispersions as high as 3 mg of SWCNTs per mL, which is higher than reported in previous studies using noncovalent functionalization approaches.^[32–37,43,44]

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) reveal that purified SWCNTs form large bundles (Fig. 1a and d) of ~ 100 nm. After ultrasonic agitation with P3HT, the SWCNTs are dispersed and samples prepared



Scheme 1. Procedure for the formation of homogenous SWCNT dispersions.

[*] Prof. T. M. Swager, Dr. H. Gu
Department of Chemistry and Institute for Soldier Nanotechnologies
Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139 (USA)
E-mail: tswager@mit.edu

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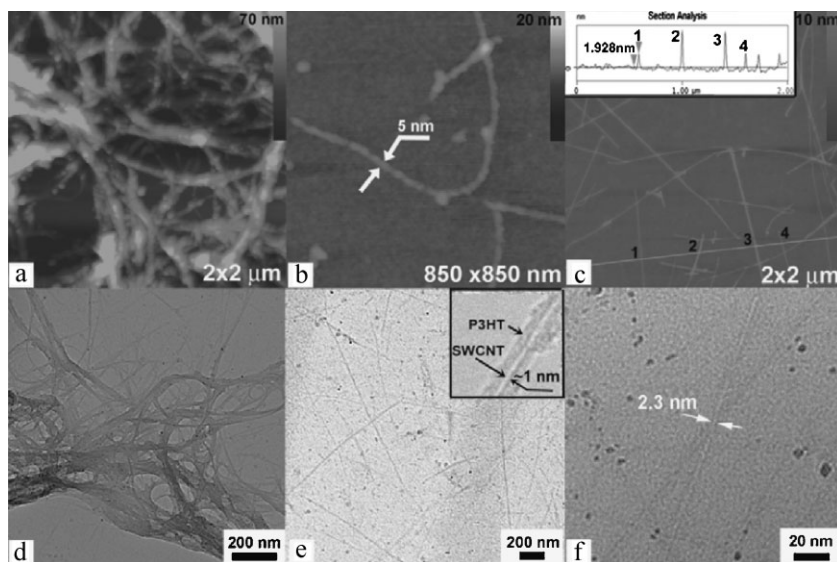


Figure 1. AFM (a) and TEM (d) images of purified SWCNT bundles, respectively. Crude SWCNT/P3HT conjugates before washing away the excess P3HT (b and e), and after removing excess polymer (c and f).

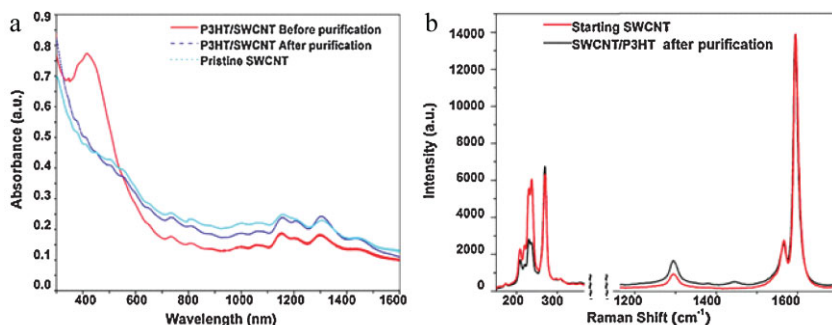


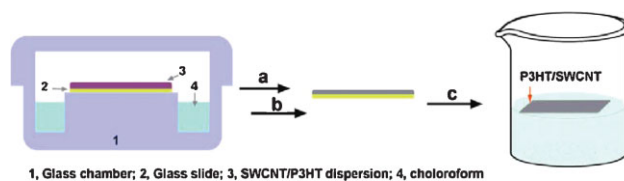
Figure 2. a) UV-vis-NIR spectra of crude and purified dispersions of SWCNT/P3HT. b) Micro-Raman thin film spectra of purified SWCNT bundles and purified SWCNT/P3HT (785 nm excitation, 0.3 mW).

from the evaporation of diluted solutions revealed that the polymer/carbon nanotube complex is ~ 5 nm wide (Fig. 1b and e). High-resolution TEM (HRTEM) (Fig. 1e, inset) reveals a “cable-like” structure wherein individual carbon nanotubes (~ 1 nm) are surrounded by multilayers of P3HT. The excess P3HT can be removed from the dispersed tubes by first precipitating the P3HT/SWCNTs by the addition of 10 mL chloroform and 3 mL methanol. The excess P3HT stays in solution and can be removed by centrifugation and decantation. The SWCNT/P3HT complexes are then redispersed by ultrasonic treatment in chloroform, and this process can be monitored by using UV-vis-NIR spectroscopy to monitor absorption bands (~ 420 nm) associated with excess P3HT (Fig. 2a). The purified SWCNT/P3HT materials do not exhibit the π - π^* transitions associated with the P3HT. However, based on the weight of the final products (see Experimental Section) the mixture is roughly 1:1 SWCNT/P3HT by weight. We find that the diameter of the purified SWCNT/P3HT is in

the range of 1.9–2.5 nm (Fig. 1c and f), which is consistent with previous scanning tunneling microscopy observations of SWCNT/P3HT complexes.^[45]

Figure 2b shows micro-Raman spectra of acid-purified SWCNT bundles and the purified SWCNT/P3HT (excess P3HT removed). Excitation at 785 nm clearly reveals the characteristic peaks from G-mode, D-mode, and radial breathing mode (RBM) peaks. After normalizing the intensities of the two spectra at G-band (1594.8 cm^{-1}), the peak intensity of D-band (1350 cm^{-1}) is slightly increased in the SWCNT/P3HT sample, which may reflect some damage of the nanotube surface after ultrasonic treatment. The RBM peak at $\sim 269\text{ cm}^{-1}$ can be used to estimate the diameter (d) of P3HT-free nanotubes at about 0.91 nm ($\omega_{\text{RBM}} = 223.5\text{ cm}^{-1} (\text{nm}/d) + 12.5\text{ cm}^{-1}$).^[46] The SWCNT/P3HT materials display lower intensity for the lower frequency (200 – 250 cm^{-1}) RBM peaks and slightly higher intensity for the 269 cm^{-1} peak relative to the bundled SWCNTs. These results, along with the observation that some of the CNTs resist dispersion and are removed in the preparation of the suspensions (see Experimental Section), indicate that P3HT selectively disperses the small-diameter nanotubes. This is expected as the smaller nanotubes have weaker inter-nanotube interactions and higher electron affinities, which should make for more favorable interactions with the electron donating P3HT.

Scheme 2 details how we prepared free-standing SWCNT films. The initial film is prepared on a glass slide from the SWCNT dispersion (excess P3HT) by slow evaporation in a closed container having a reservoir of chloroform. The slow evaporation provides a high-quality uniform film. Once evaporated, the excess P3HT is removed by rinsing with chloroform and then chloroform/hydrazine. The hydrazine treatment reduces any oxidized P3HT and thereby improves its solubility.



Scheme 2. Illustration of the major steps for formation of a free-standing SWCNT thin film. a) Chloroform washing to remove excess P3HT. b) NH_2NH_2 /Chloroform washing. c) Dipping into deionized water to release from the substrate.

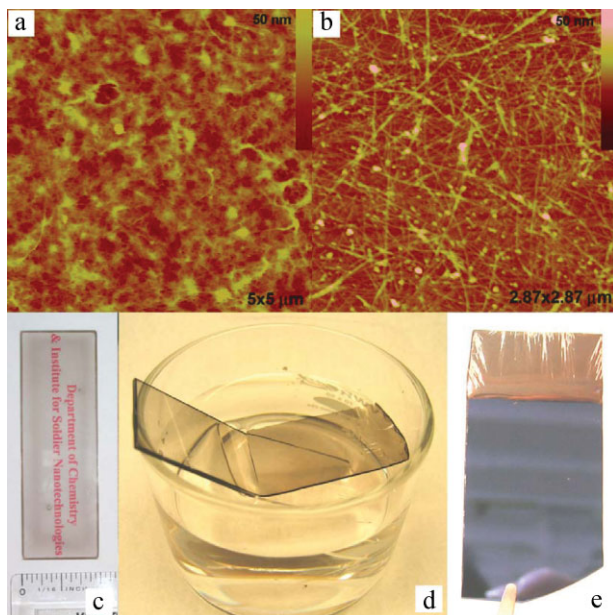


Figure 3. AFM images of an as-prepared (a) and purified (b) SWCNT/P3HT thin film. c) Optical image of a purified SWCNT/P3HT film deposited on glass slides. d) Optical image of a free-standing SWCNT/P3HT film floating on a water surface. e) A SWCNT/P3HT film transferred onto a SiO₂ substrate.

Figure 3a shows the AFM image of SWCNT/P3HT films formed on glass slides after the initial slow evaporation. Individual SWCNTs are homogeneously embedded in the P3HT matrix. After removing excess P3HT, the thin films remain intact and have an optically uniform nanoporous carbon nanotube network. Figure 3c shows a photograph of a 250 nm thick SWCNT/P3HT film after a chloroform/hydrazine rinse. AFM of this latter film shows it to be uniform and composed of individual SWCNT/P3HT complexes (Fig. 3b). A free-standing, light pink-colored SWCNT/P3HT film is readily released from the glass slide substrate when it is dipped into deionized water. This free-standing film floats on the water surface (Fig. 3d), and can be easily transferred to other substrates such as a SiO₂ wafer (Fig. 3e) or plastic sheets. Different film thicknesses can be prepared simply by changing the concentration of the SWCNT/P3HT dispersion. This process is readily scalable and we have obtained free-standing films 6 in. in diameter by evaporating on silicon wafer substrates.

The average transmittance of 250, 150, and 50 nm-thick SWCNT/P3HT films over the visible region (380–780 nm) is 65, 75, and 90%, respectively (Fig. 4a). The sheet resistance ranged from about 2700 to

950 Ω sq⁻¹ and is significantly reduced after I₂ vapor doping, with the lowest resistivity being around less than 200 Ω sq⁻¹ (Fig. 4b). The doping with I₂ likely enhances the P3HT conductance that facilitates conduction between SWCNTs, and doping can also inject additional holes into the SWCNTs. The nanotube films are relatively stable, and the resistance measurements over 6 months of exposure to ambient atmosphere resulted in only 5% (SWCNT/P3HT) and 35% (doped SWCNT/P3HT) increases in resistance. The free-standing nanotube film can be applied to a plastic substrate and two-point resistant measurements of films display no detectable resistance changes when bent at an angle of 150° over a 2 cm long sample. These materials compare favorably to commercial flexible conductors such as ITO/poly(ethylene terephthalate) (PET) (Kintec Company, Hong Kong), which displays a 100 Ω sq⁻¹ sheet resistance at 80% transmittance and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS, from H. C. Starck) coated PET has a 350 Ω sq⁻¹ sheet resistance at 80% transmittance. To further demonstrate the utility of these materials we have used a 150 nm thick SWCNT/P3HT film as an electrode for the electropolymerization of 3-hexylthiophene to give an additional layer of P3HT (Fig. 4c). After 20 cycles, a 2 μm thick P3HT layer is produced (Fig. 4c, inset), which is nearly three times thicker than P3HT deposited on clean ITO glass electrodes that were subjected to the same conditions. After hydrazine reduction, the electropolymerized overlayers display a P3HT absorption peak at 420 nm (Fig. 4d).

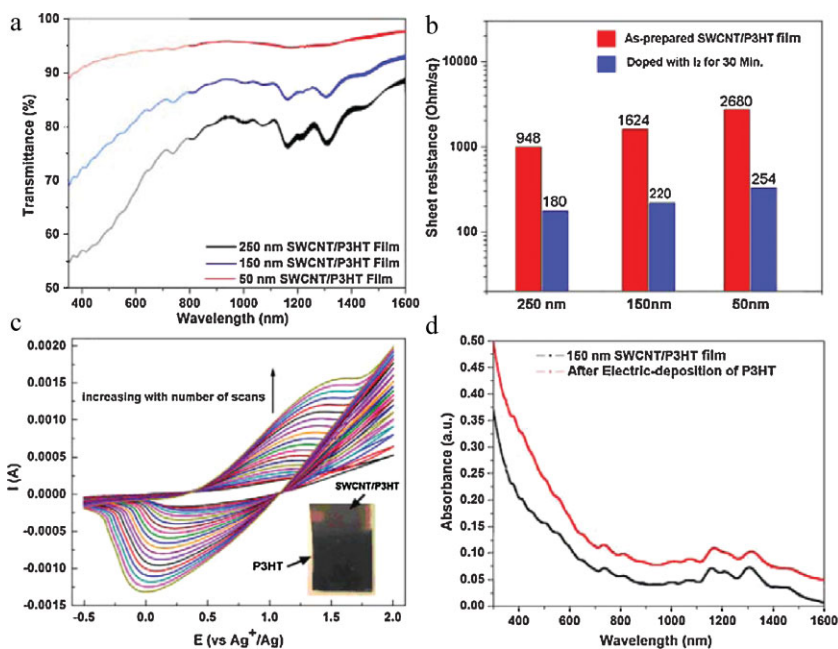


Figure 4. a) Transmittance spectra of SWCNT/P3HT films with different thicknesses. b) Sheet resistance of SWCNT/P3HT films before and after I₂ doping. c) Cyclic voltammogram of P3HT coated on a 150 nm SWCNT/P3HT film (0.1 M TBAPF₆, 0.1 M hexylthiophene, scan speed: 100 mV s⁻¹) (inset: Optical image showing the increased optical density of 2 μm P3HT coated on a 150 nm SWCNT/P3HT film). d) UV-vis-NIR spectra of 150 nm SWCNT/P3HT film and SWCNT/P3HT + P3HT film.

In summary, we have described a new and convenient method to fabricate free-standing, transparent, and conductive SWCNT films. SWCNT films combined with the conducting polymer P3HT display electrical and optical performance that is comparable to commercial ITO and PEDOT/PSS systems. We anticipate that continuing advances in the design and development of flexible conductors can give rise to additional improvements in the performance of optoelectronic devices.

Experimental

P3HT Synthesis: P3HT was synthesized by the adaptation of the procedure reported by Sugimoto et al. [42] with some modifications. A solution of 3-hexylthiophene (Aldrich) (0.77 g, 4.6 mmol) in 10 mL dry chloroform is added dropwise to a stirred solution of anhydrous ferric chloride (2.46 g, 15.2 mmol) in 10 mL chloroform over 10 min at room temperature. The mixture is activated by ultrasonication for 2 h, followed by the addition of ammonium hydroxide (10 mL, 30%) to quench the reaction. The chloroform layer is collected after centrifugation and washed twice with 10 mL ammonium hydroxide. Purified P3HT ($M_n = 52.8$ kDa, PDI = 1.97) was formed by washing with 2% hydrazine aqueous solution, and then precipitated by adding 20 mL methanol.

SWCNT Dispersion Preparation: Raw (HiPCO) SWCNTs, received from Carbon Nanotechnologies Inc. (now part of Unidym CNI lot# R0204), are purified by HCl treatment. Purified SWCNTs (10 mg) and P3HT (25 mg) are mixed in 10 mL chloroform and ultrasonically agitated for 2 h. After high-speed centrifugation (4500 rpm, 60 min), a black precipitate (~1 mg, mostly SWCNT bundles) is removed. The remaining clear SWCNT/P3HT dispersion is then treated with 5 mL of methanol and 27 mg of a dark brown precipitate is obtained after centrifugation. This precipitate is SWCNTs covered by P3HT multilayers, and the orange-colored supernatant is excess P3HT. Redispersing the above precipitate in 10 mL chloroform followed by 10 min of ultrasonication furnishes a uniform stable SWCNT dispersion. Repeated precipitation by the addition of 10 mL of chloroform and 3 mL of methanol and centrifugation gives 18 mg solid. Based upon the initial starting masses and the fact that small amounts of SWCNTs were removed from the initial dispersion by centrifugation, the mass ratio of purified SWCNT/P3HT is roughly 1:1. Dispersing the purified SWCNT/P3HT complex into 3 mL chloroform can produce suspensions that are stable for more than a year with concentrations up to 3 mg mL⁻¹ of SWCNT. With the addition of an additional 5 mg of P3HT, these SWCNT suspensions have demonstrated stabilities exceeding 1.5 years.

SWCNT/P3HT Film Fabrication: In a sealed chamber and under the saturated vapor of chloroform, 3 mL of an SWCNT/P3HT dispersion (0.1 mg mL⁻¹) is dropped on a clean glass slide (2.5 × 1 in.²). An SWCNT/P3HT film is formed after 3 h. Excess P3HT is removed by successively dipping the glass slide into chloroform and a hydrazine/chloroform solution for 30 min. By quickly transferring the slide to deionized water, a free-standing film is released from the glass slide. This nanotube film (250 nm thick as measured by AFM cross-section analysis) is floating on the water surface and ready for further manipulations. The concentration of the SWCNT/P3HT dispersion determines the thickness. On a glass slide (2.5 × 1 in.²), evaporation of a 3 mL dispersion (0.05 mg mL⁻¹) produces a 100 nm thick film and 3 mL of a more dilute dispersion (0.03 mg mL⁻¹) provides a 50 nm thick film. When using 3 mg mL⁻¹ dispersions, we can make SWCNT films with over 10 μm thick.

Electrochemical Deposition of P3HT on SWCNT/P3HT Films: The electrochemical experiment was performed in CH₂Cl₂, which was purified and dried prior to use. Tetra-*n*-butylammoniumhexafluorophosphate (TBAPF₆) (0.1 M) was used as a supporting electrolyte. The concentration of the solutions of 3-hexylthiophene was 0.1 M. Cyclic voltammetric (CV) experiments were performed with an Autolab

PGSTAT 20 potentiostat (Eco Chemie). A SWCNT/P3HT film (150 nm thick) was used as a working electrode, a platinum wire as a counter, and a Ag/AgCl wire as a reference electrode. Electropolymerization was accomplished by repeatedly cycling an electrode potential between the limits -0.5 and 2 V at a potential scan rate 100 mV s⁻¹. The increase in current after each potential scan shows that P3HT is being deposited onto the SWCNT/P3HT working electrode.

Characterization: TEM and HRTEM spectra are obtained on JEOL 2011 electron microscopes operated at 200 kV. ARM spectra are obtained on Nanoscope IV D3100. Micro-Raman and UV-vis-NIR Spectra are obtained on a Kaiser Hololab 5000R Raman Spectrometer and a Cary 6000i UV-vis-NIR spectrophotometer, respectively.

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