

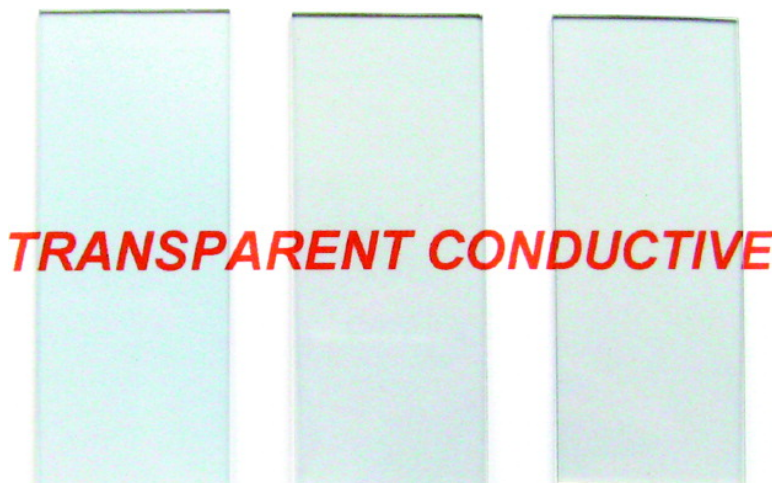
Article

Metallic Single-Walled Carbon Nanotubes for Conductive Nanocomposites

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Metallic Single-Walled Carbon Nanotubes for Conductive Nanocomposites

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Abstract: This article reports an unambiguous demonstration that bulk-separated metallic single-walled carbon nanotubes offer superior performance (consistently and substantially better than the as-produced nanotube sample) in conductive composites with poly(3-hexylthiophene) and also in transparent conductive coatings based on PEDOT:PSS. The results serve as a validation on the widely held view that the carbon nanotubes are competitive in various technologies currently dominated by conductive inorganic materials (such as indium tin oxide).

Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs), there has been much excitement about their superior and in many cases unique properties,^{1,2} including their being ballistic conductors.³ In reality, the high electrical conductivity is associated only with metallic SWNTs, but all of the available production methods for SWNTs yield mixtures of metallic and semiconducting nanotubes. Moreover, metallic SWNTs generally represent the minority fraction in the mixtures (statistically 1:2 for metallic/semiconducting).^{1,2} Thus, post-production separation of metallic and semiconducting SWNTs has been pursued by a number of research groups,^{4–6} with various strategies based on physical and chemical means.^{7–12} We reported earlier a separation method that is uniquely suited for SWNTs produced from the arc-discharge and laser ablation techniques.¹¹ The

separation is based on the observation that semiconducting SWNTs are selectively solubilized via noncovalent interactions with planar aromatic molecules, such as derivatized free-base porphyrin (Scheme 1) or pyrene with long alkyl chains (to facilitate the solubilization of the noncovalently attached nanotubes in common organic solvents).¹¹ Thus, the metallic and semiconducting fractions are obtained from the residue and supernatant, respectively, in the solubilization-based separation process. While there has been much discussion on great potentials and promises of bulk-separated metallic or semiconducting SWNTs,^{4–6} experimental demonstration of such has been scarce.^{13–15} Here, we report the use of the bulk-separated metallic fraction from arc-discharge SWNTs in conductive polymeric nanocomposites to demonstrate unambiguously the superior performance of metallic SWNTs.

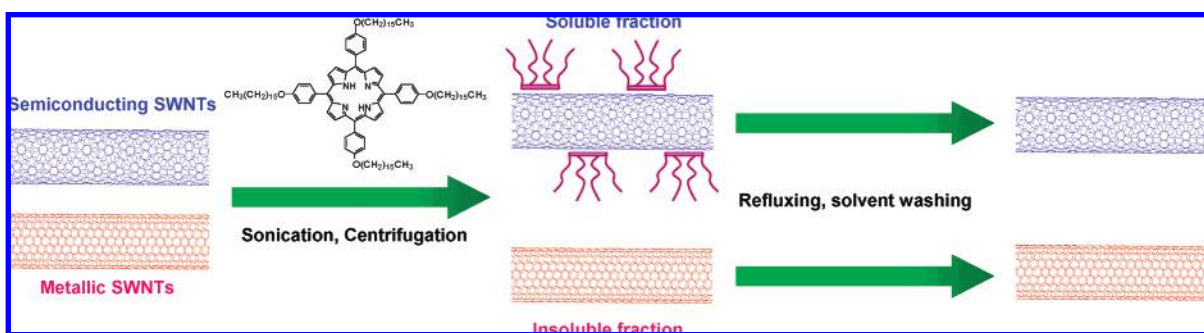
Results and Discussion

The nanotube sample produced from the arc-discharge method was purified by using oxidative acid treatment in procedures that are well-established in the literature.^{16,17} The separation

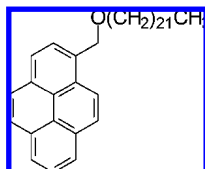
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Scheme 1



Scheme 2. Molecular Structure of DomP



experiment for the purified SWNTs was carried out under conditions similar to those reported previously,¹¹ except for the use of 1-docosyloxymethyl pyrene (DomP, Scheme 2) as the planar aromatic agent.¹⁸ The separated metallic fraction was recovered by thoroughly removing any residual separation agent. Results from electronic microscopy analyses revealed no significant difference in the separated metallic fraction from the preseparation purified SWNTs (Figure 1).

The resonance Raman spectrum (632-nm excitation) of the separated metallic fraction exhibits a Breit–Wigner–Fano (BWF) feature in the G-band region much more pronounced than that of the preseparation purified sample (Figure 2),¹⁹ suggesting substantial enrichment of metallic SWNTs in the separated fraction. More quantitatively, the optical absorption spectral features (Figure 2) due to the electronic transitions between the van Hove singularity pairs of semiconducting SWNTs were carefully measured, which allowed an estimate of the content of metallic SWNTs in the separated fraction:⁴ about 2.5 times that in the preseparation purified sample or about 82% if the content in the latter is at the statistical limit of 1/3.

The separated metallic fraction was dispersed in regioregular poly(3-hexylthiophene) (P3HT) for P3HT/SWNT nanocomposite films of improved electrical conductivity. In the film fabrication experiment, nanotubes were added to a solution of P3HT in chlorobenzene, and the resulting mixture in dark green color appeared homogeneous and stable (without precipitation).²⁰ For the comparison between the separated metallic fraction and the preseparation purified SWNTs, two mixtures of P3HT with 10% (wt/wt) respective nanotube samples were cast into a pair of thin films in a glovebox (under nitrogen to prevent any

oxidation or chemical doping). The absorption spectral features of the nanocomposite films in the visible exhibited no meaningful difference from those of the blank P3HT film, suggesting no ground-state complex formation between the polymers and SWNTs. The results from scanning electron microscopy (SEM) analyses were also similar between the films, both with no nanotubes visible on the film surface. However, when the films were stretched to failure, SWNTs at the torn edges could be observed in the SEM imaging of both films.

As compared in Figure 3 for the two films of the same 10% (wt/wt) nanotube content, the one with the separated metallic fraction is obviously more conductive than the other with preseparation purified SWNTs. The electrical conductivity calculated from the current–voltage (*I*–*V*) curves of the

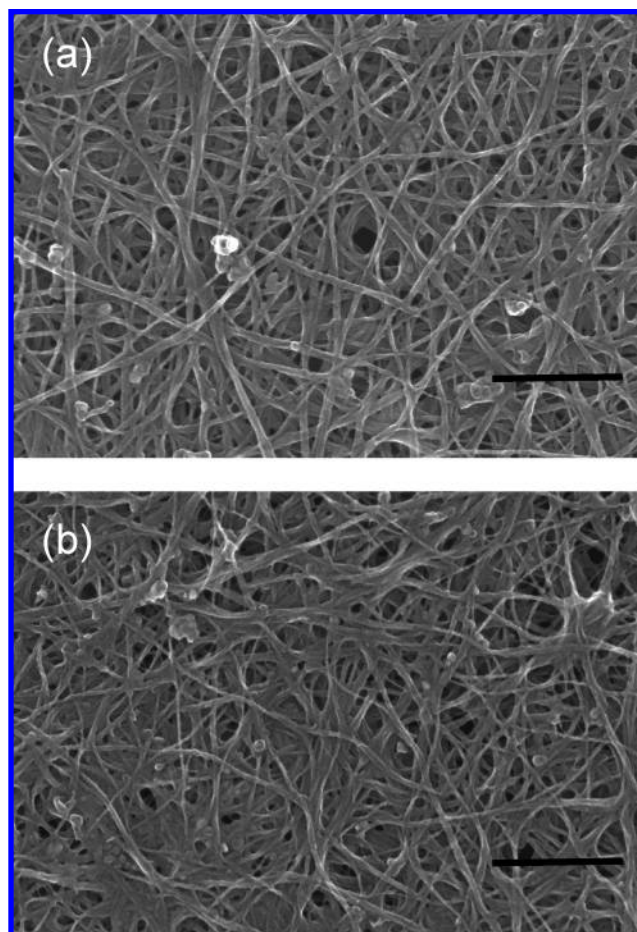


Figure 1. SEM images of (a) the preseparation sample and (b) separated metallic SWNTs (scale bar = 300 nm).

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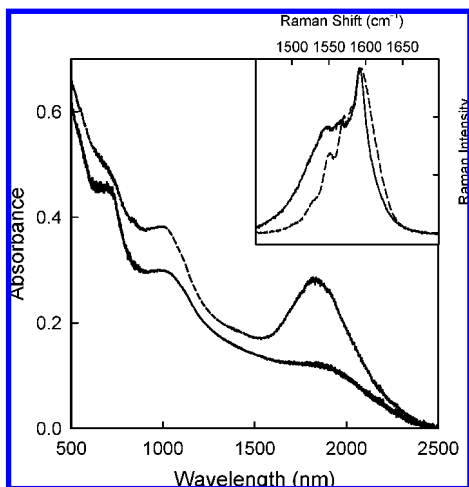


Figure 2. Optical absorption spectra of the prepreparation sample (---) and separated metallic SWNTs (—), and their corresponding Raman G-bands (632-nm excitation) in the inset.

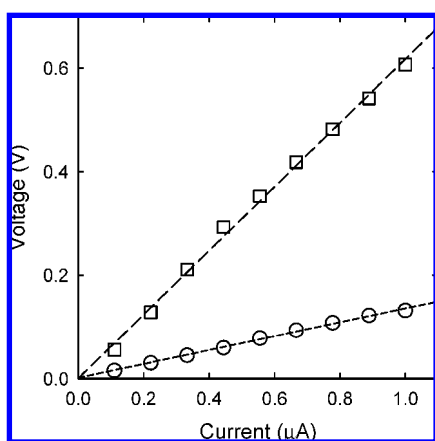


Figure 3. I - V curves for the P3HT/SWNT composite films (10 wt % nanotubes for both) with prepreparation purified SWNTs (\square) and separated metallic SWNTs (\circ). Dashed lines represent the best fits from linear regression.

composite films is 10^{-2} S/cm for the former and 2.3×10^{-3} S/cm for the latter, compared with the conductivity of 10^{-6} to 10^{-7} S/cm for blank P3HT films.²¹

P3HT/SWNT composite films with various loadings (up to 20% by weight) of separated metallic fraction and prepreparation purified nanotube sample were fabricated and evaluated for their electrical conductivity results. The comparison in Figure 4a shows clearly that the films with the enriched metallic SWNTs are consistently more conductive than those with the prepreparation mixture at the same nanotube sample loadings. In fact, the increase in conductivity is more than an order of magnitude with the use of separated metallic fraction at 20% (wt/wt) nanotube sample loading in the films (Figure 4a). It seems that the film conductivity is dictated by available conductive channels, namely the amount of metallic SWNTs. Thus, the actual contents of metallic SWNTs in the nanocomposite films are calculated from the known compositions in both the separated metallic fraction and the prepreparation purified nanotube sample. As shown in Figure 4b, the relationship between the actual contents of metallic SWNTs in the films

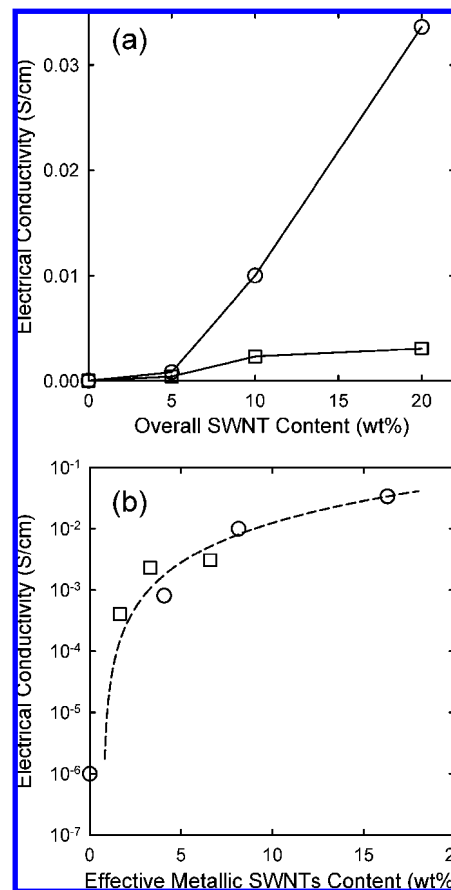


Figure 4. Electrical conductivity results of P3HT/SWNT composite films depending on (a) different amounts of prepreparation (\square) and separated metallic (\circ) nanotube samples, and (b) their corresponding effective metallic SWNT contents in the films (dashed line: the best fit in terms of the percolation theory equation).

and the film electrical conductivity values follows the percolation theory:^{22,23}

$$\delta = |x - x_c|^\alpha \quad (1)$$

where δ is the electrical conductivity, x the content of metallic SWNTs, x_c the percolation threshold where the transition takes place, and α the critical exponent for the conductivity (an index for system dimensionality, theoretically 1.3 and 1.94 for ideal 2D and 3D systems, respectively).²² The best fit in Figure 4b corresponds to x_c of 0.74% (wt/wt) and α of 1.92. It makes sense that these films behave like 3D systems because the film thickness (about 1 μ m) is considerably greater than the average diameters of the dispersed SWNTs or their bundles.²⁴

P3HT is highly colored, so that the films with and without embedded nanotubes are of poor optical transparency in the visible region. To prepare optically transparent conductive thin films, poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was used as matrix. The films were made ultrathin, essentially thin coatings on glass substrate (Figure 5 inset), to facilitate the optical transparency. The film (coating) thickness was controlled in terms of the optical transmittance at 550 nm.

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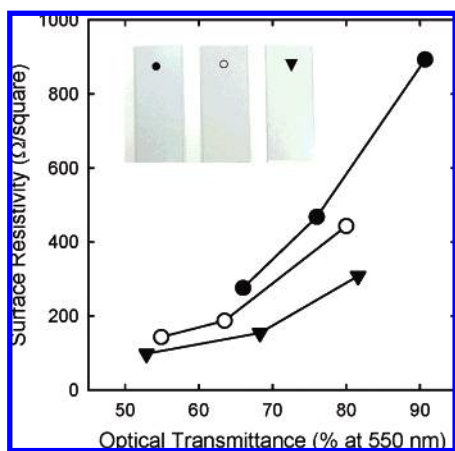


Figure 5. Surface resistivity results of PEDOT:PSS/SWNT films on glass substrate with the same 10 wt % nanotube content (○: pre-separation purified sample and ▼: separated metallic SWNTs; and for comparison, ●: blank PEDOT:PSS without nanotubes) but different film thickness and optical transmittance at 550 nm. Shown in the inset are representative films photographed with tiger paw print as background.

The same approach of solution-phase dispersion and then wet-casting was applied to the fabrication of PEDOT:PSS/SWNT nanocomposite coatings on glass substrate. As well-established, PEDOT:PSS was processed as an aqueous dispersion.²⁵ For solvent compatibility, DMSO was used to disperse nanotubes. The suspension of the nanotubes in DMSO was mixed with the aqueous PEDOT:PSS solution, and the mixture was used for fabricating the transparent conductive coating via spraying. Two PEDOT:PSS/SWNT mixtures with one containing 10% (wt/wt) of the separated metallic fraction and the other 10% (wt/wt) of the pre-separation purified nanotube sample were prepared and so was an aqueous solution of neat PEDOT:PSS (also containing the same amount of DMSO) as reference. Depending on the amount of solution or mixture sprayed, the coating thickness varies, as reflected by the variation in optical transmittance at 550 nm. These coatings were measured carefully for their surface resistivity values. The results compared in Figure 5 demonstrate clearly the enhanced electrical conductivity with the separated metallic SWNTs in the transparent conductive films.

In the development for alternatives to the currently dominating indium tin oxide (ITO) technology,²⁶ PEDOT:PSS transparent conductive films have been demonstrated for some successful uses in organic optoelectronic devices.^{27,28} For example, the organic photovoltaic cell with PEDOT:PSS electrode was found to be only 15% less in efficiency when compared to the same cell with a classic ITO electrode.²⁸ A strategy already discussed in the literature on further improving the performance of transparent PEDOT:PSS electrode is the incorporation of SWNTs.^{29–31} The results presented above suggest that the use of bulk-separated metallic SWNTs might offer the necessary

conductivity enhancement without sacrificing the optical transparency to make the resulting PEDOT:PSS/SWNT composite films competitive to ITO coatings for transparent electrodes and other applications.

We deliberately used conductive polymers in this study to have different nanotube samples (the pre-separation purified nanotubes and the separated metallic and semiconducting fractions) similarly dispersed to allow their comparative performance evaluation on a morphologically equivalent basis. For transparent conductive thin films composed solely of SWNTs, their properties and performance are quite sensitive to the selection of fabrication techniques and many other experimental parameters (including especially the morphological characteristics of the nanotube samples). It remains a significant technical challenge to take full advantage of the separated metallic SWNTs for transparent conductive films of performance much beyond the state of the art.

In summary, semiconducting SWNTs could be extracted from the purified nanotube sample through their preferential interactions with planar aromatic species, yielding substantially enriched metallic SWNTs. When dispersed in conductive polymer thin films, the metallic SWNTs enhance the electrical conductivity of the resulting nanocomposites significantly more than the starting purified nanotube sample. The results not only validate the post-production separation approach, but also demonstrate unambiguously the great potentials of metallic SWNTs in conductive nanocomposites and other relevant applications.

Experimental Section

Materials. Regioregular P3HT ($M_w = 50\,000$, polydispersity index = 1.3–1.6) was purchased from Rieke Metal, Inc., and PEDOT:PSS (Baytron PH500, ~1 wt % solid content) was purchased from H. C. Stark. Solvents THF, DMSO, and DMF were obtained from Mallinckrodt and distilled before use, and chlorobenzene was from Acros.

DomP was synthesized and characterized according to the procedures and methods reported previously.¹⁸

The SWNT sample from the arc-discharge production method was supplied by Carbon Solutions, Inc. The as-received sample was purified by a combination of thermal oxidation and oxidative acid treatments as reported previously.¹⁷ Briefly, the sample (1 g) was heated in a furnace to 300 °C in air for 30 min and then refluxed in diluted nitric acid (2.6 M, 500 mL) for 24 h. The solid was collected via centrifugation, washed repeatedly with deionized water until neutral pH, and then dried in vacuum oven to obtain the purified sample (330 mg).

Measurements. Optical absorption spectra were recorded on Shimadzu UV3100 and UV3600 spectrophotometers. Raman spectra were measured on a Renishaw Raman spectrometer (50 mW diode laser for 785-nm excitation) and Jobin Yvon T64000 Raman spectrometer (Melles-Griot 35 mW He–Ne laser for 632.8-nm excitation). The latter was also equipped with triple monochromator and Olympus BX-41 microscope. SEM images were obtained on a Hitachi S4700 field emission system.

I – V relationships for the nanocomposite thin films were determined by using the traditional four-probe method with Keithley 2400 multimeter controlled by Lab Tracer 2.0 software (Keithley Instruments, Inc.) and a probe station (multiheight probe, Jandel). Electrical conductivity values were calculated according to $\sigma = [(\pi/\ln 2) \cdot (I/V)]/t$, where t is the specimen thickness. Surface resistivity values were calculated according to $R_s = (\ln 2/\pi) \cdot (V/I)$.

Separation. In a typical experiment, a purified SWNT sample (150 mg) was added to a solution of DomP in dry THF (10 mg/mL, 30

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mL). The mixture was homogenized (Fisher Scientific Power Gen 125) for 1 h and then sonicated (VWR model 250D) for 24 h. The mixture was centrifuged at 1380g for 1–2 min to remove the supernatant. The residue containing enriched metallic SWNTs was refluxed in THF for 24 h and then washed repeatedly with THF until the solution from the washing exhibited no pyrene absorption.

Nanocomposite Films. In typical fabrication of P3HT/SWNT films, the purified or separated metallic SWNT sample (2.5 mg) was suspended in chlorobenzene (5 mL) and homogenized for 10 min. It was mixed with a solution of P3HT (47.5 mg) in chlorobenzene, and the mixture was homogenized for 20 min and then sonicated for 24 h. The drop-casting of the P3HT/SWNT composite thin films on clean glass slides was performed in a glovebox under nitrogen atmosphere. The films were dried in vacuum before conductivity measurements.

For PEDOT:PSS/SWNT films, the selected SWNT sample (5 mg) was suspended in DMSO (45 mL) with homogenization for 10 min and then sonication for 1 h. The suspension was mixed with aqueous

PEDOT:PSS solution (5 mL). The mixture was sonicated for 1 h, followed by centrifuging at 2256g for 10 min to remove any solid residues. The supernatant was used for spray-coating onto glass substrates that were maintained at 150 °C. The resulting films were dried in vacuum before optical transmittance and surface resistivity measurements.

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