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A Simple Method of Separating Metallic and Semiconducting Single-Walled Carbon Nanotubes Based on Molecular Charge Transfer

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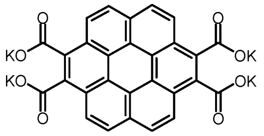
Single-walled carbon nanotubes (SWNTs) exhibit fascinating electronic, thermal, and mechanical properties with several possible applications.[1,2] They can be semiconducting, semimetallic, or metallic depending on the geometrical structure. Metallic SWNTs can function as conductive additives and as leads in nanoscale circuits, while the semiconducting ones can be used to design field effect transistors. As-grown SWNTs are typically mixtures of metallic and semiconducting nanotubes, which limit their applicability. There have been several attempts to separate semiconducting and metallic nanotubes. Physical methods such as dielectrophoresis[3] and density gradient centrifugation[4] as well as chemical methods including covalent and noncovalent functionalization[2] such as adsorption of bromine[5] and diazotization[6] have been employed to separate metallic and semiconducting SWNTs. Recently, fluorous chemistry has been used for effecting the separation.[7] These approaches do not always allow bulk scale separation with high selectivity and require cumbersome ultracentrifugation. It is, therefore, highly desirable to find a simple and scalable separation strategy which also avoids high speed centrifugation. We have investigated whether molecular charge transfer between SWNTs and an appropriate π-system can be exploited for the effective separation of metallic and semiconducting nanotubes, since $\pi-\pi$ interaction with aromatic molecules enables the solubilization of SWNTs[2] and there appears to be selectivity in the interaction of electron donor and acceptor molecules with SWNTs and graphene.[8] With this purpose, we have made use of the potassium salt of coronene tetracarboxylic acid, **I**, which has a large π skeleton attached to four electron-withdrawing groups and exhibits charge-transfer interaction with graphene causing solubilization in an aqueous medium.[9,10]



I

We have investigated the interaction of SWNTs with **I** by varying the concentration of the latter and the time of interaction. For this purpose, we have taken pure SWNTs[11] in a 5 mM or 10 mM solution of **I** in water and sonicated the mixture at 50 °C for 3 h, followed by heating at 70 °C for 12 h. The resulting mixture was set aside for 24 h when a precipitate appeared at the bottom of the container.[12] The precipitate as well as the solid extracted from the solution were examined by electronic absorption spectroscopy and Raman spectroscopy.[13]

Pristine SWNTs show bands at around 750 nm (M_{11}) corresponding to the metallic nanotubes and around 1040 nm (S_{22}) and 1880 nm (S_{11}) due to the semiconducting species due to Van Hove singularities in the optical absorption spectra (Figures 1 and S1).

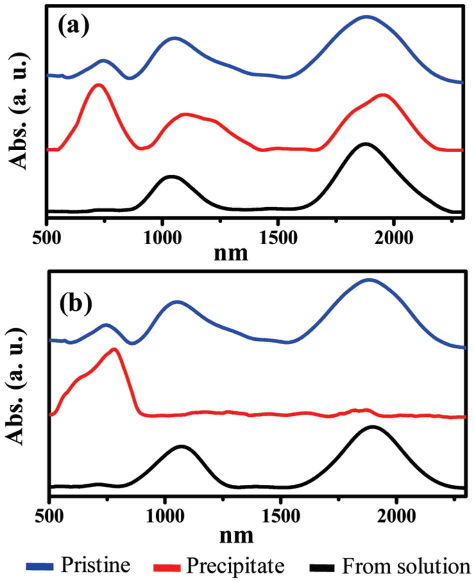


Figure 1. Optical absorption spectra of pristine SWNTs (blue), precipitate (red), and SWNTs from solution (black) obtained with (a) 5 mM and (b) 10 mM of **I** (spectra obtained after background subtraction; refer to Figure S1 for optical absorption spectra without background subtraction).

SWNTs extracted from the solution exhibit only the S_{11} and S_{22} bands due to the semiconducting species as can be seen from Figure 1. SWNTs in the precipitate, however, exhibit bands due to both the metallic and semiconducting species when a 5 mM solution of **I** was used but only the band due to the metallic species when a 10 mM solution of **I** was used (compare Figure 1a and b). Thus, optical absorption spectra clearly demonstrate the separation of metallic and semiconducting SWNTs on interaction with **I**.

These results are supported by Raman spectra.[14] SWNTs prepared by arc discharge show Raman bands due to the radial breathing mode (RBM) in the Raman spectra in the 100−200 cm^{-1} region and the G-band in the 1500−1600 cm^{-1} (G-band) region. The G-band of the semiconducting tubes consists of two features around 1570 cm^{-1} (radial) and 1590 cm^{-1} (longitudinal). The G-band of the metallic tubes shows bands around 1585 cm^{-1} (radial) and 1540 cm^{-1} (longitudinal), the latter broadened into a Breit−Wigner Fano (BWF) line shape due to strong coupling in the density of states.[1,15] The 1540 cm^{-1} feature is generally used as a signature of metallic SWNTs. SWNTs extracted from the 10 mM solution of **I** exhibit features of the G-band corresponding to the semiconducting species, whereas the precipitate shows features of pure metallic species with the prominent feature around 1540 cm^{-1} (Figure 2a). Pristine SWNTs show two RBM bands due to semiconducting and metallic species (Figure 2b). SWNTs from the

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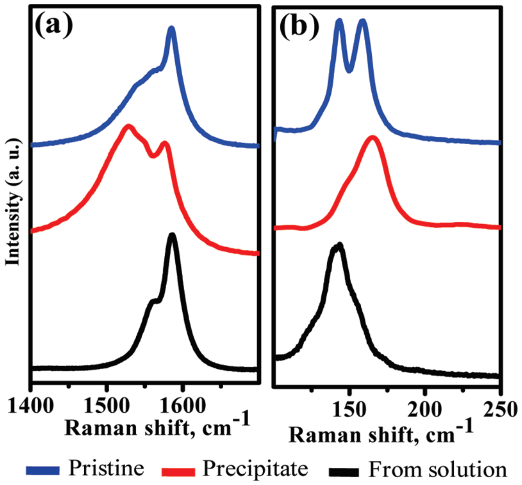

Figure 2. Raman (a) G-band and (b) radial breathing mode (RBM) of pristine SWNTs (blue), precipitate (red), and SWNTs from solution (black) obtained with 10 mM of **I**.

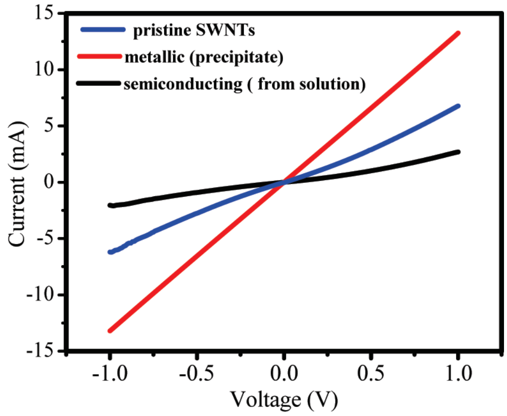

Figure 3. *I*−*V* measurements of pristine SWNTs (blue) as well as prue metallic (red) and semiconducting (balck) nanotubes obtained by separation.

solution show only the band due to the semiconducting ones, and SWNTs in the precipitate correspond to the metallic species.

We have compared the *I*−*V* characteristics of SWNTs (measured by the two-point probe method between two gold electrodes) from the solution and precipitate with those of the pristine nanotubes. Pristine SWNTs show a nonlinear *I*−*V* curve while the metallic nanotubes show linear behavior with conductivities of 92.5 and 1538.5 mS/cm respectively at 300 K. The latter value is comparable to that in the literature.[16] Semiconducting nanotubes exhibit a low conudctivity of 53.5 mS/cm and a nonlinear *I*−*V* curve (Figure 3). These results are in accord with the spectroscopic data.

Having obtained pure semiconducting and metallic SWNTs, we have examined their interaction with electron donor and acceptor molecules.[8] On interaction with an electron acceptor molecule, tetracyanoethylene (TCNE), the 1540 cm^{-1} feature in Raman spectra due to metallic species disappears (Figure S5). This is due to a change in the Fermi level of the nanotubes. Electron-donating molecules such as tetrathiafulvalene (TTF) have no effect on the Raman spectrum of metallic SWNTs. Upon interaction of an electron-donating molecule, TTF, with semiconducting carbon nanotubes, the 1540 cm^{-1} feature appears and increases significantly with an increase in the concentration of TTF (Figure S6). This remarkable change on the electronic structure of SWNTs is reversible.

In conclusion, we have been able to separate semiconducting and metallic SWNTs from the mixture in the as-prepared sample by employing interaction with **I**. The method depends on the concentration of **I** and the time of interaction. The separation occurs due to molecular charge transfer between **I** and SWNTs and is accompanied by the debundling of the SWNTs as evidenced by electron microscope images (Figure S2). We believe that this method can be readily employed as a routine laboratory procedure.

Supporting Information Available: Physical characterization and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) **I** was prepared starting from perylene by oxidative benzogenic Diels−Alder reaction with *N*-ethyl maleimide, followed by hydrolysis of the resulting diimide with KOH in methanol. **I** which is soluble in water shows a charge-transfer band with graphene around 460 nm and around 510 nm with SWNTs.
(11) SWNTs were prepared by the arc-discharge method and purified by interaction with hydrogen and acid treatment(Vivekchand, S. R. C.; et al. *Small* **2005**, *1*, 920). In a typical experiment, 1 mg of SWNTs was mixed with 5 mL of the aqueous solution of **I**.
(12) Keeping the reaction mixture for longer periods (48 h) results in the precipitation of some semiconducting nanotubes.
(13) Adsorbed **I** could be removed from the nanotubes by extensive washing with water or by heating the nanotubes at 400 °C (Figure S3).
(14) We have used a 632 nm laser for Raman studies. 632 nm excitation resonates roughly equal populations of both metallic and semiconducting tubes for the diameter range of the tubes used in this study (∼1.2 to 1.8 nm), whereas the 514 nm laser excites semiconducting nanotubes exclusively. (Kataura, H.; et al. *Synth. Met.* **1999**, *203*, 2555. Zheng, M.; et al. *Science* **2003**, *302*, 1545)
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