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Article

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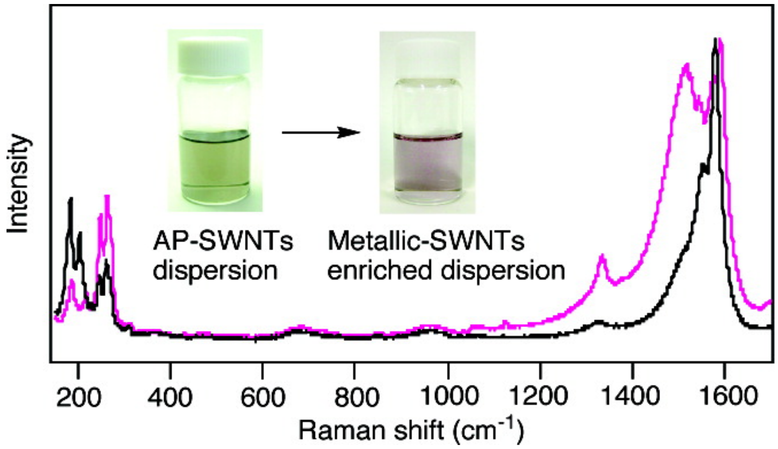

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Large-Scale Separation of Metallic and Semiconducting Single-Walled Carbon Nanotubes

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Abstract: In the applications of single-walled carbon nanotubes (SWNTs), it is extremely important to separate semiconducting and metallic SWNTs. Although several methods have been reported for the separation, only low yields have been achieved at great expense. We show a separation method involving a dispersion−centrifugation process in a tetrahydrofuran solution of amine, which makes metallic SWNTs highly concentrated to 87% in a simple way.

Introduction

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have led to the proposal of many potential applications.[1,2] However, SWNTs are typically grown as the bundles of metallic and semiconducting tubes, thus hindering widespread applications. Therefore, it is technologically critical to separate metallic and semiconducting SWNTs in high yields. Starting from carboxy-functionalized SWNTs with assistance of octadecylamine[3] or porphyrins,[4] semiconducting SWNTs have been separated from their metallic counterparts. On the other hand, metallic SWNTs have been separated from semiconducting counterparts by using complexation with bromine[5] or alternating current dielectrophoresis,[6] but the amount of the separated metallic SWNTs is quite small in this technique. Metallic and semiconducting SWNTs wrapped by DNA have been separated by anion exchange chromatography.[7] The main problem of anion exchange chromatography separation is its expense and removal of the wrapping DNA from SWNTs. Starting from as-prepared SWNTs rather than carboxy-functionalized SWNTs, we have developed a convenient amine-assisted method that makes metallic SWNTs remarkably enriched in a simple way.

Experimental Section

The first step toward the separation is to disperse SWNT bundles. A typical dispersion procedure is as follows: 1 mg of SWNTs (HiPcoTM, Carbon Nanotechnologies)[8] was added to 10 mL of a 1.0 M solution of 1-octylamine in tetrahydrofuran (THF) and then sonicated for 2 h at room temperature (AP-SWNTs) followed by centrifugation (45620*g*, 12 h) of the suspension to remove nondispersible SWNTs. The resulting supernatant solution and deposit of SWNTs are designated as SWNTs-OS1 and SWNTs-OD1, respectively. SWNTs-PS1 is the first supernatant solution of SWNTs treated by a dispersion−centrifugation process in a 5.0 M THF solution with propylamine, and SWNTs-PS2 is the second supernatant solution of SWNTs when the process is repeated. SWNTs-PH is a supernatant solution of SWNTs treated in a

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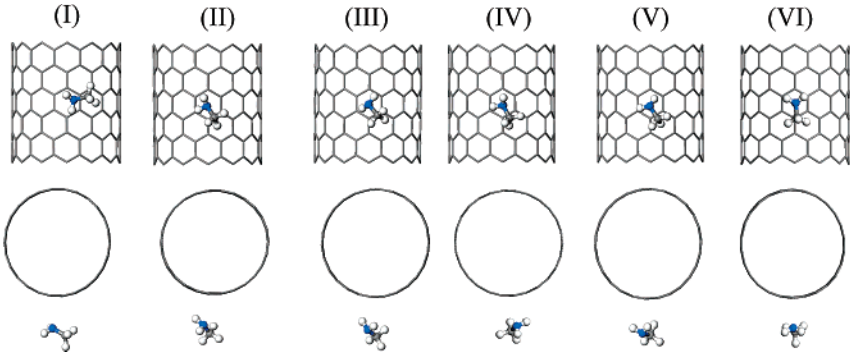

Figure 1. Optimized structures for the adsorption of NH_2CH_3 on a (13,0) SWNT under different interaction ways. Blue ball: N. Gray ball: C. White ball: H.

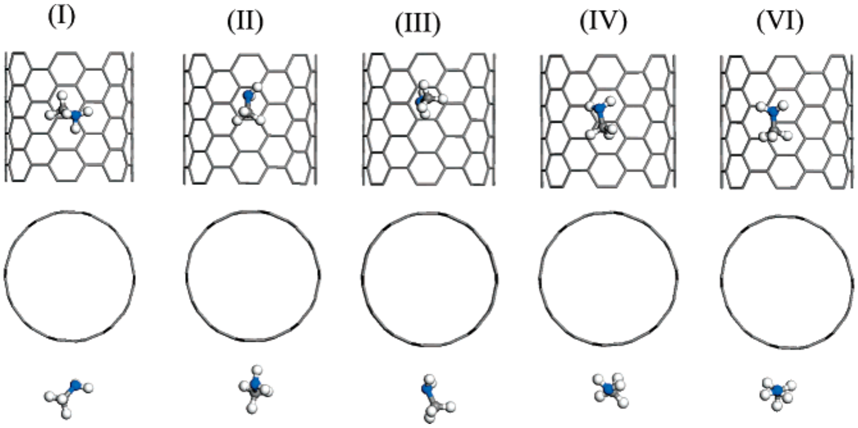

Figure 2. Optimized adsorption configurations of NH_2CH_3 on a (7,7) SWNT under different interaction ways.

3.0 M solution of isopropylamine in THF and hexane (4:1). Scanning electron microscope (SEM) observation was carried out with a JEOL JSM-6700FT field emission electron microscope (accelerating voltage: 5.0 kV; beam current: 10 μA). The specimen was fixed to the sample holder via a piece of adhesive carbon tape (DTM 9101, JEOL Datum). Atomic force microscopy (AFM) observation was carried out on a Digital Instruments Nanoscope III in the tapping mode of operation. Well-dispersed SWNTs in THF were dropped and dried on a freshly cleaved mica surface. Raman spectra were measured with a Jasco NRS-2100 spectrophotometer using laser excitation at 514.5 nm. The solution-phase optical absorption data were recorded with a Shimadzu UV-3150 spectrophotometer using a Pyrex cell with a path length of 10 mm.

The IV characteristics of SWNTs bucky paper on the membrane filter were recorded using four-probe configuration using an Agilent 4156 device parameters analyzer. The sheet resistance (R_s) was estimated in the low current−low bias linear regime, and the resistivity (ρ) was calculated using the relation $\rho = t \cdot R_s$. The thickness (t) of the SWNT bucky paper was estimated using a Tencor Apha-Step surface profiler.

Results and Discussion

In the amine-assisted method, it is important that metallic SWNTs are more strongly adsorbed by amines than semiconducting SWNTs[9] and the adsorbed amines are removable after separation. We have studied the adsorption of methylamine (NH_2CH_3) on metallic and semiconducting SWNTs by using the local density functional theory and ultrasoft pseudopotential plane-wave methods.[10] Since the reactivity of SWNTs depends on their diameters (SWNTs of smaller diameters have higher reactivity),[11] the (13,0) and (7,7) tubes having similar diameters of 1.018 and 0.952 nm were chosen as the typical examples of semiconducting and metallic SWNTs, respectively. Six possible adsorption modes were considered: interaction via (I) the N lone pair, (II) one H atom of NH_2 group (labeled by H_N), (III) two H_N atoms, (IV) one H_N atom and one H atom of CH_3 group (labeled by H_C), (V) two H_N atoms and one H_C atom, and (VI) two H_C atoms and the N lone pair (Figures 1 and 2). Full optimization was performed for both atomic positions and lattice lengths with a cutoff energy of 240 eV and two k points. The convergence tolerance of force on each atom was 0.01 eV/Å. Static total energies of the relaxed structures were calculated with a larger 310 eV cutoff energy.

The adsorption energies per NH_2CH_3, defined as

$$E_a = E(\text{SWNT}) + E(\text{NH}_2\text{CH}_3) - E(\text{SWNT} + \text{NH}_2\text{CH}_3)$$

are given in Table 1, together with the optimized distances between NH_2CH_3 and SWNT. NH_2CH_3 has a tendency to adsorb SWNT through the interaction of the H atoms (rather than the N lone pair). The most noticeable in Table 1 is that the metallic (7,7) SWNT is more strongly adsorbed by NH_2CH_3 than the semiconducting (13,0) SWNT, regardless of the adsorption modes. It is also interesting that the adsorption energies between NH_2CH_3 and (7,7) are relatively small (0.11−0.18 eV), suggesting that NH_2CH_3 is not only easily removable but also has

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Table 1. Adsorption Energy (E_a) and Equilibrium Molecule−Tube Distance (d) of NH_2CH_3 on the (13,0) and (7,7) Nanotubes[a]

	E_a (eV)		d (Å)	
mode	(13,0)	(7,7)	(13,0)	(7,7)
(I)	−0.04	−0.11	3.23^b	3.23^b
(II)	−0.11	−0.18	2.73^c	2.30^c
(III)	−0.07	−0.17	2.58^c, 2.97^c	2.52^c, 2.81^c
(IV)	−0.07	−0.17	2.80^c, 2.64^d	2.51^c, 2.60^d
(V)	−0.08	$-^e$	2.85^c, 2.96^c, 2.70^d	
(VI)	−0.08	−0.18	3.16^b, 2.89^d, 2.90^d	3.16^b, 2.70^d, 2.89^d

[a] The distance criterion of the hydrogen-bond-like link between NH_2CH_3 and the nanotube is set to 3.0 Å. [b] Shortest N−C distance. [c] Shortest H_N−C distance. [d] Shortest H_C−C distance. [e] No energy minimum can be located.

no significant effect on the electronic structure of (7,7). This contrasts with the fact that the electronic structures of SWNTs are significantly changed by covalent functionalization.[12−14] It has been found experimentally that amines tend to interact with carboxy-functionalized semiconducting SWNTs.[3] Theoretical calculations, however, indicate that amines interact more preferably with as-prepared metallic SWNTs. In this context, the complex of amine and as-prepared metallic SWNTs may have a higher solubility in organic solvents than the case of semiconducting SWNTs, suggesting a possible separation of metallic from semiconducting SWNTs.

Figure 3a shows the visible−near-infrared (vis-NIR) absorption spectra of AP-SWNTs (dispersed in a THF-octylamine solution), SWNTs-OD1 and SWNTs-OS1. Three regions are identified in Figure 3a: first interband transitions for metals, M_{11} (400−650 nm), and first and second interband transitions for semiconductors, S_{11} (900−1600 nm) and S_{22} (550−900 nm).[15−17] Remarkably, SWNTs-OS1 has stronger absorption peaks in the metallic M_{11} band and weaker absorption peaks in the semiconducting S_{11} and S_{22} bands than those of SWNTs-OD1, indicative of the enrichment of metallic SWNTs in the supernatant and semiconducting SWNTs in the deposit, respectively. The selective decay of semiconducting absorption bands and the enhancement of metallic absorption bands in SWNTs-OS1 demonstrate that the dispersion−centrifugal separation process is effective for the separation of SWNTs according to their electronic properties. To enrich further the metallic SWNTs, SWNTs-OS1 was filtrated and subject to the dispersion−centrifugal separation process repeatedly. The absorption in the metallic M_{11} band increases gradually in the supernatant fraction after each dispersion−centrifugation process. The final supernatant after five dispersion−centrifugation processes is labeled by SWNTs-OS5. The absorption spectrum of SWNTs-OS5 shows stronger metallic and weaker semiconducting transitions (see Figure 3a). Meanwhile, SWNTs-OD1 was treated eight times by repeating the dispersion−centrifugal separation process. The vis−NIR spectrum of the deposit (SWNTs-OD8) showed the further enrichment of semiconducting tubes.

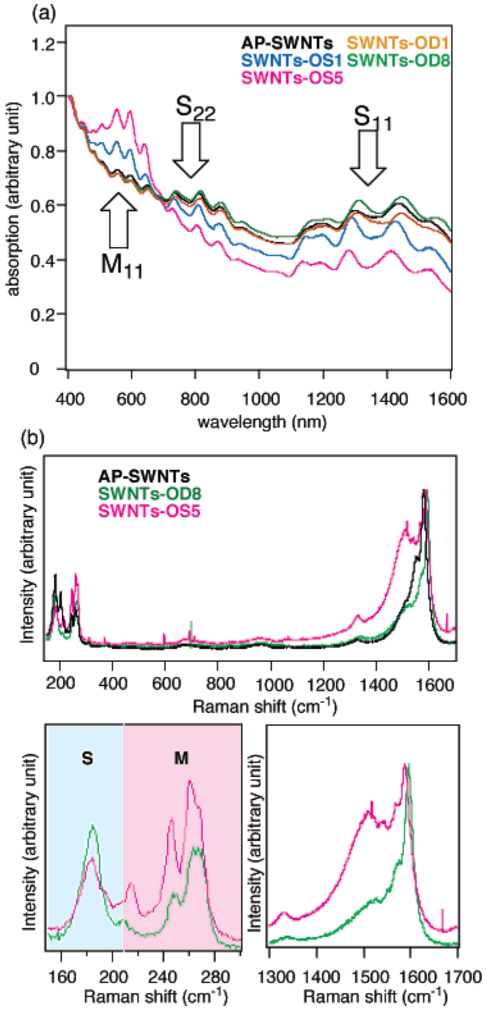

Figure 3. Structural characterization of SWNTs treated by an octylamine-THF solution. (a) Vis−NIR spectra of AP-SWNTs, SWNTs-OS1, SWNTs-OS5, SWNTs-OD1, and SWNTs-OD8. (b) Raman spectra of SWNTs-OD8 and SWNTs-OS5.

Raman spectroscopy is a powerful tool for the characterization of SWNTs, from which their diameter and electronic properties can be estimated.[18] Raman spectra of AP-SWNTs (film), SWNTs-OS5 (film), and SWNTs-OD8 (film) were measured with an excitation frequency of 514.5 nm, as shown in Figure 3b. The diameters of SWNTs are estimated to be typically 0.9−1.3 nm from the radial breathing modes (RBM). A detailed comparison with the plot of Kataura et al.[16] allows us to conclude that the Raman peaks around 160−200 and 200−280 cm^{-1} are due to semiconducting and metallic SWNTs, respectively. The significantly stronger peaks around 200−280 cm^{-1} in SWNTs-OS5 and 160−200 cm^{-1} in SWNTs-OD8 provide additional evidence for the enrichment of the metallic SWNTs. This is further supported by the much broader G band of SWNTs-OS5 (Figure 3b), which is characteristic of metallic SWNTs.[19,20] The concentration of metallic tubes is estimated to increase from ca. 41% in AP-SWNTs to ca. 72% in SWNTs-

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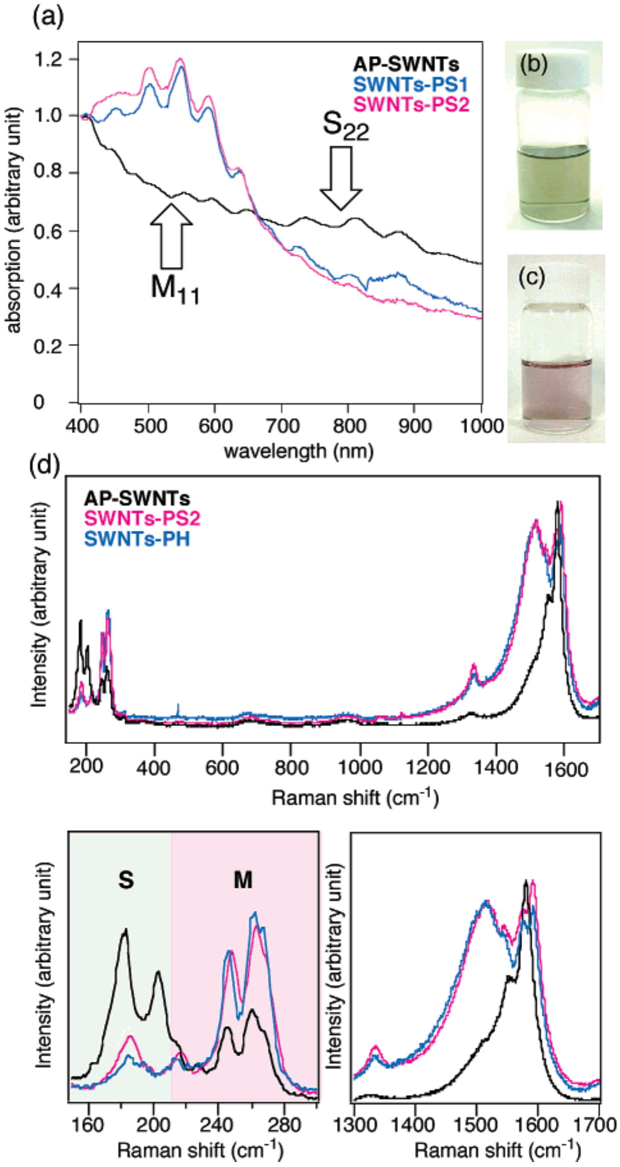

Figure 4. Structural characterization of SWNTs-PS, SWNTs-PS2, and SWNTs-PH. (a) Vis-NIR spectra of AP-SWNTs, SWNTs-PS1, and SWNTs-PS2. Photographs of (b) SWNTs-AP and (c) SWNTs-PS2. (d) Raman spectra of AP-SWNTs, SWNTs-PS2, and SWNTs-PH.

OS5. On the other hand, the concentration of semiconducting tubes is estimated to increase from ca. 59% in AP-SWNTs to ca. 64% in SWNTs-OS5.

Many other amines also have satisfactory dispersion efficiency to SWNT bundle.[21] In the case of 5.0 M solution of propylamine in THF, more effective separation was achieved. Figure 4a displays the vis−NIR spectra of AP-SWNTs, a supernatant solution of SWNTs treated with propylamine (labeled by SWNTs-PS1), and a supernatant solution of SWNTs treated twice by the dispersion−centrifugation process with propylamine (labeled by SWNTs-PS2). Compared with SWNTs-OS1 and SWNTs-OS5, much stronger absorption peaks were observed in the metallic M_{11} band for SWNTs-PS1 and SWNTs-PS2. Meanwhile, the characteristic absorption peaks of the semiconducting S_{11} band even disappear in SWNTs-PS2. These results indicate that the metallic SWNTs are more effectively separated from semiconducting SWNTs by using propylamine. Interestingly, SWNTs-PS2 shows different color (purple) from AP-SWNTs (see Figure 4b,c). By observing Raman spectra, the concentration of metallic tubes is estimated to increase from ca. 41% in AP-SWNTs to ca. 82% in SWNTs-PS2. (Figure 4d). We also carried out the dispersion−centrifugation process in a 3.0 M solution of isopropylamine in THF and hexane (4:1). As shown in Figure 4d, treatment of SWNTs in a mixed solvent (SWNTs-PH) provides a higher separation; the concentration of metallic tubes is now as high as ca. 87%.

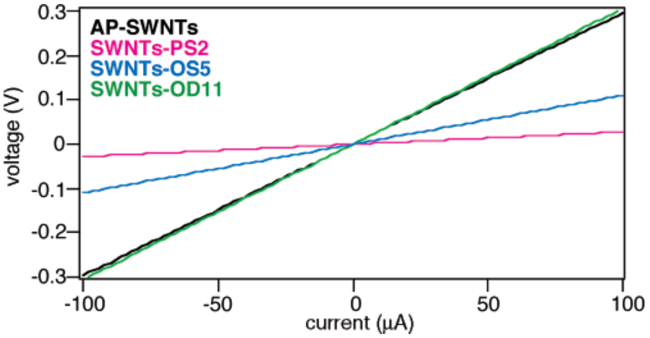

Figure 5. Current versus voltage characteristic of SWNT thin films.

The resistivities of thin films of AP-SWNTs, SWNTs-OS5, SWNTs-OD11, and SWNTs-PS2 were measured by using four-point probe techniques. The resistivities of the bucky papers made from the enriched metallic SWNTs-OS5 and SWNTs-PS2 are about 2.4 and 0.44 Ω·cm, which are 1.8 and 9.5 times more conductive than that of AP-SWNTs. In contrast, the resistivity of the enriched semiconducting SWNTs-OD11 sample is 8.5 Ω·cm, which is twice as large as that of AP-SWNTs. These results are in qualitative agreement with the NIR and Raman data (Figure 5).

Conclusions

In summary, by taking advantage of amines adsorbing metallic SWNTs more strongly, we have developed a separation method that makes metallic SWNTs highly enriched. The weakly adsorbed amines are easily removable after separation. This separation method is simple and convenient, suggesting a potential industrial utilization for widespread applications of SWNTs.

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Supporting Information Available: SEM images of AP-SWNTs and SWNTs-OS1. AFM image and cross-sectional profile of SWNTs-OS1. This material is available free of charge via the Internet at http://pubs.acs.org.

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