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Dispersion and Separation of Small-Diameter Single-Walled Carbon Nanotubes

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Abstract: The dispersion of small-diameter single-walled carbon nanotubes (SWNTs) produced by the CoMoCAT method in tetrahydrofuran (THF) with the use of amine was studied. The absorption, photoluminescence, and Raman spectroscopies showed that the dispersion and centrifugation process leads to an effective separation of metallic SWNTs from semiconducting SWNTs. Since this method is simple and convenient, it is highly applicable to an industrial utilization for widespread applications of SWNTs.

Introduction

Many potential applications of single-walled carbon nanotubes (SWNTs) have been extensively expected because of their excellent mechanical and electrical properties.[1,2] However, SWNTs are typically grown as bundles of metallic and semiconducting tubes, which offer a hindrance to their widespread applications. Dispersion of SWNTs by using dispersants such as sodium dodecyl sulfate (SDS) is useful for their analysis, purification, and modification. Since there is no method for selective preparation of SWNTs having specific electrical properties, it is technologically critical to separate metallic and semiconducting SWNTs. There have been several reports of separation of metallic and semiconducting SWNTs by physical adsorption, electrophoresis, anion exchange chromatography, and chemical reaction.[3−8] For the effective separation of semiconducting and metallic SWNTs, exfoliation of SWNTs bundles is very important. We have already reported an effective exfoliation method of SWNTs produced by a high-pressure catalytic CO decomposition (the HiPco method): dispersion of SWNTs in organic solvents with amine.[9] Recently, we have also developed a convenient amine-assisted separation method, by which metallic SWNTs were remarkably enriched in a simple way.[10]

The diameter and helicity distribution of SWNTs depends not only on preparation methods, such as arc discharge, laser ablation, and chemical vapor deposition, but also on the conditions including the carbon source and catalyst.[1,11,12] It was reported that the diameter and electronic property strongly affect the covalent and noncovalent interactions of SWNTs.[8,10,13] It is of great interest to elucidate whether the interaction between SWNTs and amine depends on their diameter or electronic property. We herein report the dispersion and separation of

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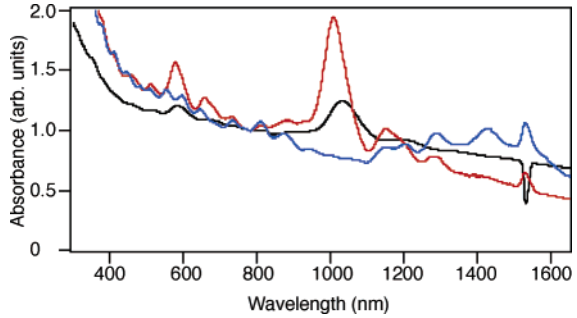

Figure 1. Absorption spectra of AP-CoMoCAT (black), CoMoCAT-O1 (red), and HiPco-O1 (blue) normalized at 780 nm.

CoMoCAT SWNTs, which have a different helicity distribution from that of HiPco SWNTs, by the amine-assisted method.

Experimental Section

CoMoCAT SWNTs[11c] and HiPco SWNTs[11b] were purchased from South West Nanotechnologies and Carbon Nanotechnologies, Inc., respectively. A typical dispersion procedure is as follows: 1 mg of SWNTs was added to 10 mL of a 1 M solution of octylamine in tetrahydrofuran (THF) and then sonicated for 2 h at 5−10 °C (AP-CoMoCAT and AP-HiPco) followed by centrifugation (45 620*g*, 12 h) of the suspension to remove nondispersible materials. No visible particle was observed in a THF solution containing amine kept in a refrigerator after a few weeks. THF is the best solvent for which this dispersion−centrifugation process could be used. Chloroform, acetone, ethanol, dichlorobenzene, and dimethylformamide are not appropriate for this process. 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 fluorescence was measured with a Shimadzu CNT-RF spectrometer. Raman spectra were measured with a Jasco NRS-2100 spectrophotometer using laser excitation at 514.5 and 633 nm. 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). The $I-V$ characteristics of SWNTs bucky paper on the membrane filter were recorded using the four-probes configuration using an Agilent E5270B 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 $\rho = tR_s$. The thickness (t) of the SWNT bucky paper was estimated using a Tencor Alpha-Step surface profiler.

Results and Discussion

Figure 1 shows absorption spectra of the CoMoCAT and the HiPco SWNTs in a THF solution containing octylamine (1 M, labeled by AP-CoMoCAT and AP-HiPco). After centrifugation (labeled by CoMoCAT-O1 and HiPco-O1), absorption peaks became sharper and slightly shifted to a shorter wavelength region. A similar phenomenon has been reported in the dispersion of SWNTs in D_2O with a surfactant and is associated with exfoliation of SWNTs bundles. The CoMoCAT SWNTs have pronounced absorption bands at 576 and 1007 nm, corresponding to the E22 and E11 transitions of the (6,5) nanotube.[14,15] According to the absorption spectra in a THF solution containing amine, the CoMoCAT SWNTs (E11 800−1300 nm) should be thinner than the HiPco SWNTs (E11 1100−1600 nm).[16] Figure 2 shows the contour plots of fluorescence intensities of CoMoCAT-O1 and HiPco-O1, respectively. The positions of the peaks are similar to those reported previously in dispersion of the SWNTs in D_2O.[9,12a,15,17] A small red shift of the fluorescence peak of the SWNTs in THF compared to that in D_2O was observed, and this might be due to the differences of solvent and the interaction between SWNTs and dispersants. CoMoCAT-O1 shows one dominant structure (6,5) along with four possible structures (7,5), (7,6), (8,3), and (8,4). Absorption and fluorescence spectra showed a clear difference in the diameter distribution of SWNTs between CoMoCAT-O1 (0.76−0.92 nm) and HiPco-O1 (0.83−1.2 nm).

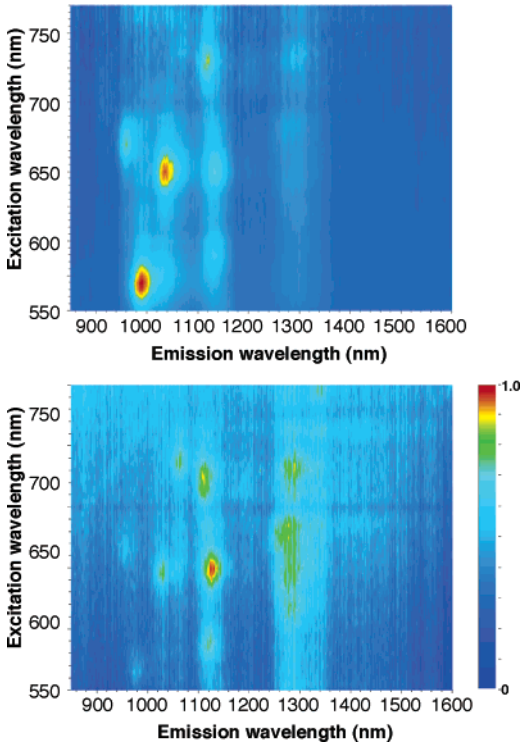

Figure 2. Contour plots of normalized fluorescence intensities for the CoMoCAT-O1 and the HiPco-O1.

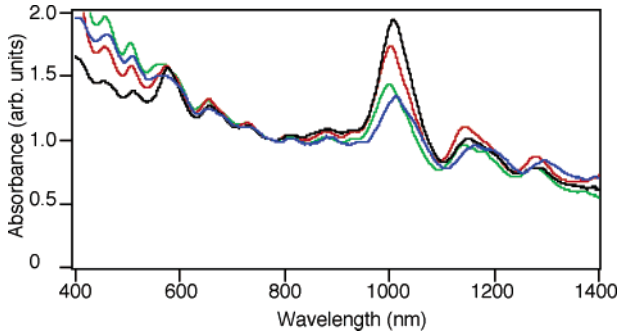

Figure 3. Absorption spectra of CoMoCAT-O1 (black), CoMoCAT-P3 (red), CoMoCAT-P5 (blue), and CoMoCAT-iP3 (green) normalized at 780 nm.

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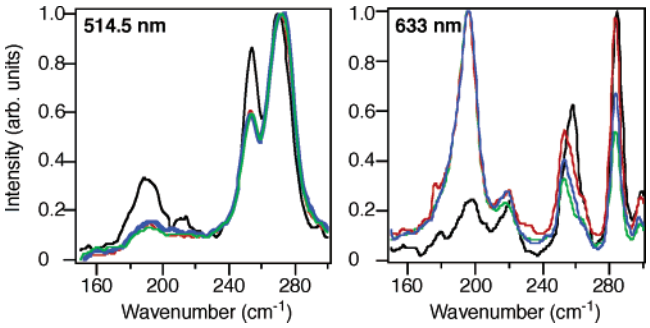

Figure 4. Raman spectra of AP-CoMoCAT (black), CoMoCAT-P3 (red), CoMoCAT-P5 (blue), and CoMoCAT-iP3 (green).

To obtain enriched metallic SWNTs, CoMoCAT SWNTs were dispersed in a THF solution with propylamine (3 and 5 M) and isopropylamine (3 M), and then centrifuged (labeled by CoMoCAT-P3, CoMoCAT-P5, and CoMoCAT-iP3, respectively). After centrifugation, weak supernatant solutions were obtained and concentrated to measure absorption spectra. The absorbance of CoMoCAT-P3 solution at 453 nm concentrated from 40 to 7 mL and the absorbance of CoMoCAT-O1 at 453 nm were 0.21 and 0.21, respectively. The low dispersibility of SWNTs in high-concentration amine solutions might be due to the low density of these solutions.[18] The absorption spectra normalized at 780 nm showed that the characteristic metallic absorption bands increased with an increase of amine concentration, as shown in Figure 3. Decrease of the characteristic band assigned to (6,5) SWNTs having a diameter of 0.76 nm was also observed, and this suggests that the interaction between semiconducting SWNTs having a small diameter and the amine is not strong enough to maintain a stable dispersion under such conditions.[17]

Raman spectroscopy is a powerful tool for the characterization of SWNTs, from which their diameter and electronic properties can be estimated.[19] Raman spectra of AP-CoMoCAT (film), CoMoCAT-P3 (film), CoMoCAT-P5 (film), and CoMoCAT-iP5 (film) were measured with excitation wavelengths of 514.5 and 633 nm, as shown in Figure 4. The diameters of the SWNTs are estimated to be typically 0.76−1.2 nm from the radial breathing modes (RBM).[20,21] A detailed study of the plots by Kataura et al.[22] allows us to assign the Raman peaks. Metallic SWNTs have RBM wavenumbers in the range between 220−300 cm^{-1} with an excitation wavelength of 514.5 nm and 150−230 cm^{-1} with an excitation wavelength of 633 nm. By contrast, semiconducting SWNTs have RBM wavenumbers in the range between 170−220 cm^{-1} with an excitation wavelength of 514.5 nm and 230−300 cm^{-1} with an excitation wavelength of 633 nm. The proportions of the metallic SWNTs areas of CoMoCAT-P5 in the RBM region with an excitation wavelength of 514.5 and 633 nm were 83% and 79%, respectively. (The proportions of the metallic SWNTs areas of AP-CoMoCAT: 514.5 nm, 69%; 633 nm, 32%.) As shown Figure 5, the SEM images of the samples of AP-CoMoCAT and CoMoCAT-P3 show the existence of the SWNTs clearly. These results suggest the amine strongly interacts with metallic SWNTs having larger diameters than semiconducting SWNTs having smaller diameters.

Figure 6 shows the resistivities of thin films of AP-CoMoCAT SWNTs, CoMoCAT-P5 and CoMoCAT-iP3, measured by using

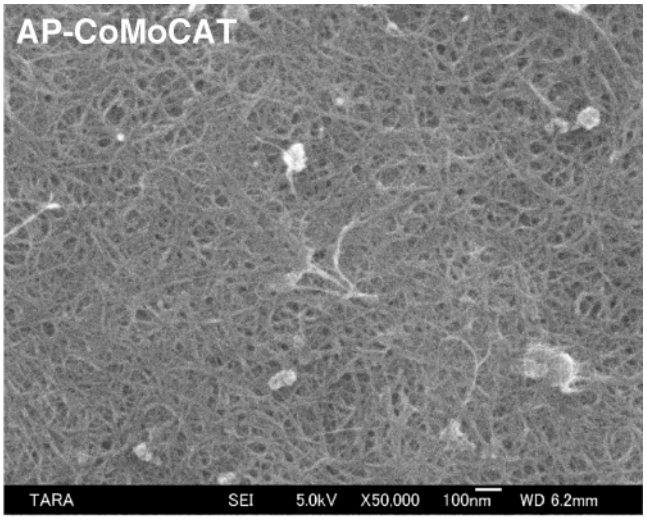

Figure 5. SEM images of AP-CoMoCAT film and CoMoCAT-P3 film.

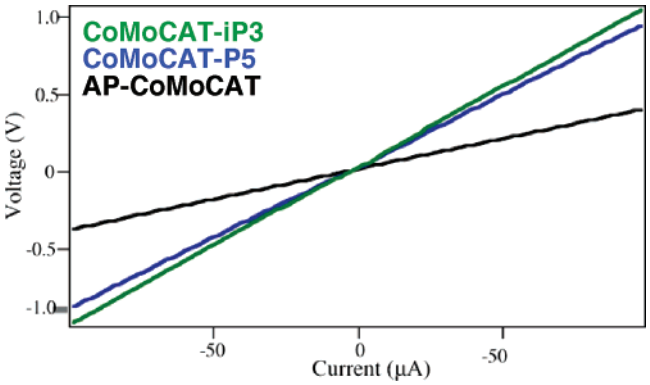

Figure 6. Current vs voltage characteristic of CoMoCAT-SWNTs thin films.

(18) Density of THF, octylamine, propylamine, and isopropylamine at 25 °C: 0.889, 0.782, 0.719, and 0.694, respectively. The dispersibility of HiPco SWNTs using various amines was reported in ref 9.
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the four-point probe techniques. The resistivity of the bucky papers made from the enriched metallic CoMoCAT-iP3 was about 2.45 Ω·cm, which is 5.7 times smaller than that of AP-CoMoCAT SWNTs (13.9 Ω·cm).

Conclusions

In summary, the amine is effective in dispersing CoMoCAT SWNTs in a THF solution. Effective dispersion and exfoliation methods of SWNTs in organic solvents are very important for modification of SWNTs. The dispersion−centrifugation process for the CoMoCAT SWNTs makes metallic SWNTs highly enriched.

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Supporting Information Available: Complete ref 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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