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Separation of Semiconducting Single-Walled Carbon Nanotubes by Using a Long-Alkyl-Chain Benzenediazonium Compound

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Abstract: We designed and synthesized 4-dodecyloxybenzenediazonium tetrafluoroborate (**1**), which preferentially reacts with metallic single-walled carbon nanotubes (SWNTs) by kinetic control. We first determined the suitable experimental conditions for the preferential reaction of **1** with individually dissolved SWNTs by monitoring the decrease in absorbance for the metallic SWNT in the range of 400–650 nm in the absorption spectrum of the SWNTs. The reacted SWNTs were thoroughly rinsed with THF to obtain THF-insoluble SWNTs. The Raman spectrum of the THF-insoluble SWNTs showed a strong peak near 180 cm^{-1}, which corresponds to a semiconducting breathing band. The metallic breathing bands ($\approx$220 cm^{-1}) and Breit–Wigner–Fano (BWF) modes (1520 cm^{-1}) corresponding to the metallic SWNTs were much weaker than those of the pristine SWNTs. We also confirmed that metallic peaks in the range of 400–650 nm in the absorption spectrum of THF-insoluble SWNTs that were individually dissolved in an aqueous micelle of sodium cholate were almost nondetectable. All the results indicate that the THF-insoluble SWNTs are semiconducting.

Keywords: chemical separation · chirality · micelles · nanotubes · semiconductors

Introduction

Single-walled carbon nanotubes (SWNTs) have received much attention in nanoscience and nanotechnology because of their unique physical and chemical properties.[1] However, synthesized SWNTs contain both metallic and semiconducting SWNTs. Because of this, their applications, especially in the field of nanoelectronics, are limited. The separation of metallic and semiconducting SWNTs is a great challenge in the science and technology of carbon nanotubes. Toward this goal, separation on the basis of their different physical properties, including differential conductivity,[2] dielectrophoresis,[3] and selective physical adsorption onto the SWNTs,[4] and different chemical selectivity[5] have already been reported, although the efficient bulk separation of metallic and semiconducting SWNTs is difficult. Wong and co-workers,[6] Krupke and Hennrich,[7] and we[8] have summarized the recent developments in this field.

A number of excellent review articles describing the functionalization of carbon nanotubes (CNTs) have been published.[9–11] For the separation of metallic and semiconducting SWNTs, individual solubilization[12] and subsequent selective chemical modification of the metallic or semiconducting SWNTs are required. Strano et al.[5a] reported an interesting method for the separation of metallic and semiconducting SWNTs, that is, they found that 4-chlorobenzenediazonium tetrafluoroborate preferentially reacted with metallic SWNTs in an aqueous micelle of sodium dodecylsulfate (SDS). We have now modified their method. Our strategy is the combination of a kinetically controlled reaction of a benzenediazonium salt carrying a long alkyl chain with metallic SWNTs that have been individually dissolved in an aqueous micelle, and subsequent rinsing of the reacted SWNTs with an organic solvent to separate the unreacted semiconducting SWNTs (Figure 1). If chemically functionalized metallic SWNTs are soluble in an organic solvent, the separation of unreacted and reacted SWNTs should be possible, as unreacted SWNTs are not soluble in

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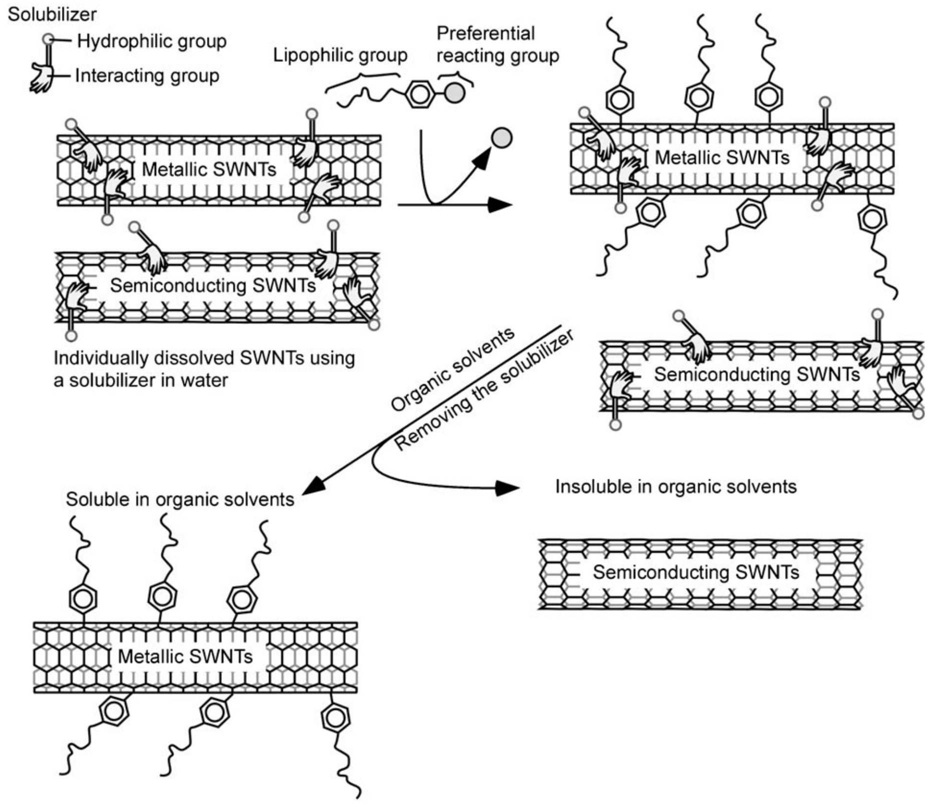

Figure 1. Our strategy of separating semiconducting SWNTs from metallic SWNTs.

any solvent. For this purpose, 4-dodecyloxybenzenediazonium tetrafluoroborate (**1**) was synthesized (Figure 2). It is expected that the **1**-functionalized SWNTs are soluble in organic solvents as **1** has a long alkyl chain. We report herein the separation of semiconducting SWNTs from pristine SWNTs by our described strategy. In this study, sodium cholate (SC) was used to dissolve the SWNTs individually, as steroid surfactants such as SC are better solubilizers[13] for SWNTs than SDS, which is known as a typical surfactant that individually dissolves SWNTs in water.

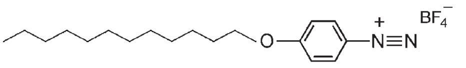

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Figure 2. Chemical structure of compound **1**.

Results and Discussion

SWNTs show characteristic absorption bands in the near-infrared (NIR) region owing to the interband transition between the mirror-image spikes in the density of states (DOS) of the SWNTs.[14] The first semiconducting (S_{11}), the second semiconducting (S_{22}), and the first metallic (M_{11}) transition bands of the SWNTs used in this study appear in the absorption ranges of 800–1350, 600–800, and 400–600 nm, respectively. As described in the Experimental Section, we first dissolved the SWNTs in a solution of SC in deuterium oxide and confirmed that they were individually dissolved[15] in the solution by measuring their Vis/NIR spectrum. A certain amount of compound **1** (0.15–0.75 mM) was then added to the solution, and the change in the Vis/NIR spectra with time was monitored. A typical example is shown in Figure 3, in which the concentration of **1** was 0.30 mM. We see that after the addition of **1**, the metallic SWNT band (400–650 nm) decreased with time and reached a constant value after several hours, whereas the changes in the absorption bands of both the first and the second semiconducting SWNT bands were much smaller than that of the metallic band. When the concentration of **1** was 0.15 mM, the reaction of **1** with the metallic SWNTs was slow; when the concentration of **1** was 0.75 mM, we noticed a decrease in the first and second semiconducting peaks together with a decrease in the metallic bands (data not shown). Thus, we decided that 0.30 mM is a suitable concentration of **1** for its preferred reaction with the metallic SWNTs.

For the 0.30 mM solution of **1**, after the absorbance of the M_{11} bands reached a constant state, we conducted the following treatment, namely, the solution was filtered, and the solid SWNTs obtained were rinsed well with water to remove SC, then dried under vacuum. Here we tested several solvents to investigate whether they solubilize the **1**-functionalized SWNTs by measuring the Vis/NIR spectra of the solubilized SWNTs; THF was found to be a good solvent. Next, the dried solid was rinsed well with THF to dissolve the **1**-functionalized SWNTs. This rinsing procedure was repeated more than five times with 10 mL each of THF until the absorbance of the SWNT bands in the THF solution reached a nondetectable level. We thus obtained the THF-insoluble SWNTs on the filter, which were characterized by Raman and Vis/NIR spectroscopy.

Raman spectroscopy is a powerful tool for probing the separation of metallic and semiconducting SWNTs; namely, Raman peaks in the range of 160–203 and 203–280 cm^{-1} are radial breathing modes (RBMs) originating from the semiconducting and metallic SWNTs, respectively.[16] The Raman spectra of the THF-insoluble and the pristine SWNTs excited at 514.5 nm are shown in Figure 4. From the RBMs

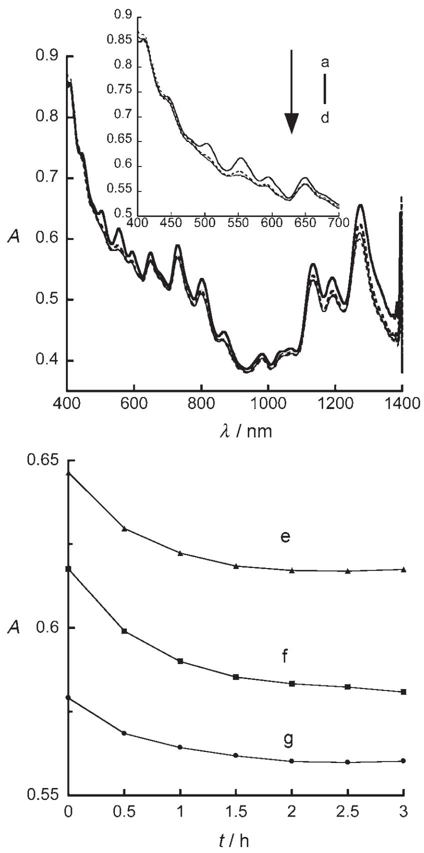

Figure 3. Top: Vis/NIR spectra of the raw SWNTs individually dissolved in a solution of SC (22 mm) in deuterium oxide before (a) and after the addition of **1** (0.30 mm) (b) after 1 h; c) after 2 h; d) after 3 h). Bottom: Time course of the absorbance at 502 nm (e), 554 nm (f), and 594 nm (g).

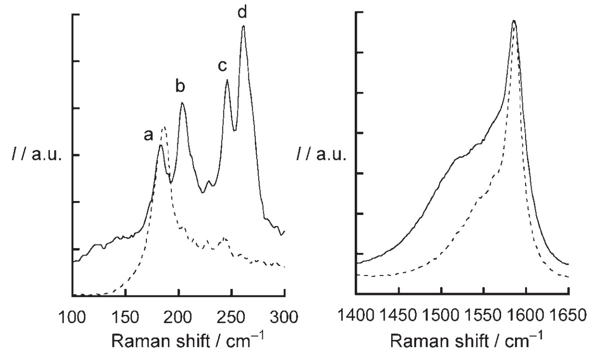

Figure 4. Raman spectra (514.5 nm excitation with an Ar ion laser) of the pristine SWNTs (solid line) and the THF-insoluble SWNTs (dotted line).

(Figure 4, left), we see an S_{33} semiconducting band (a = 184 cm^{-1}) and metallic bands M_{11} (b = 203 cm^{-1}, c = 246 cm^{-1}, and d = 262 cm^{-1}) from the pristine SWNTs, which are typical of the HiPco SWNTs used herein.[5a,j] The diameters of the pristine SWNTs estimated from the peaks of the RBMs by using the relationship $d = 223.5/(\nu - 12.5)$[15a] were 1.30, 1.17, 0.957, and 0.896 nm for the peaks a–d, respectively. By using the revised Kataura plot,[5b] peaks a–d are assigned to the (10,9) or (14,4), (10,7), (12,0), and (8,5) nanotube chirality indices, respectively. It was found that for the THF-insoluble SWNTs, the intensities of the Breit–Wigner–Fano bands (1500–1600 cm^{-1}), which originate from the metallic SWNTs, were much weaker than those of the pristine SWNTs, and the RMB peaks (b, c, and d) were drastically decreased. As a result, after the separation, we see one strong semiconducting peak at 184 cm^{-1}. All these results are strong evidence that the THF-insoluble SWNTs are effectively semiconducting SWNTs.

We also recorded Raman spectra at an excitation wavelength of 785 nm (Figure 5); we observed the S_{22} semiconducting bands a = 206, b = 215, c = 234, and d = 267 cm^{-1}, whose diameters are estimated to be 1.14, 1.10, 1.01, and 0.878 nm, respectively. From the revised Kataura plot, these bands (a–d) are assigned to the (12,4), (9,7), (11,3), and (10,2) indices, respectively. We also observed typical G and D bands (Figure 5, right) for the pristine SWNTs, which are also typical for HiPco SWNTs.[5a,j] The intensity of the semiconducting S_{22} band at 267 cm^{-1} was found to be drastically decreased, suggesting that the semiconducting SWNTs with the smaller diameter reacted with **1**.

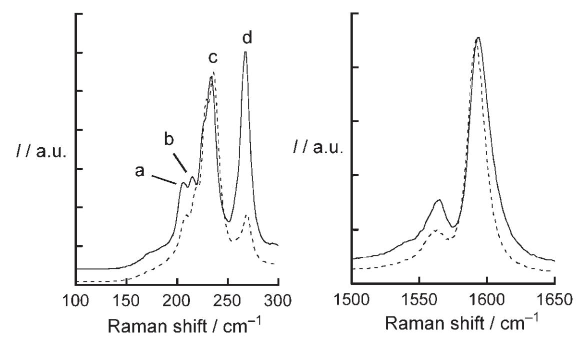

Figure 5. Raman spectra (785 nm excitation with a diode laser) of the pristine SWNTs (solid line) and the THF-insoluble SWNTs (dotted line).

Furthermore, we recorded the Vis/NIR absorption spectrum of the THF-insoluble SWNTs individually dissolved in an aqueous micelle of SC (Figure 6); the metallic-band peaks in the range of 400–600 nm are almost nondetectable,

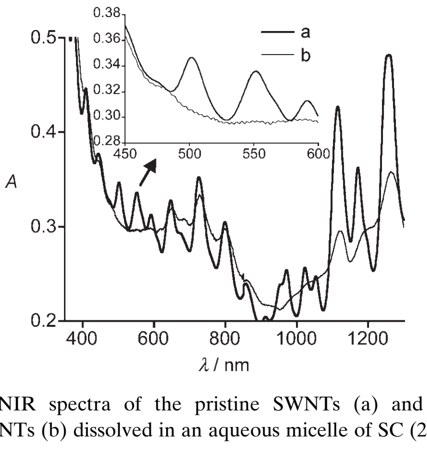

Figure 6. Vis/NIR spectra of the pristine SWNTs (a) and the THF-insoluble SWNTs (b) dissolved in an aqueous micelle of SC (22 mm).

whereas the semiconducting bands S_{11} and S_{22} are evident. This is further strong evidence that the THF-insoluble SWNTs are semiconducting SWNTs.

Finally, we recorded scanning electron microscopy (SEM) images of the SWNTs (Figure 7); the SEM image of the THF-insoluble SWNTs is somewhat different from that of the pristine SWNTs,[17] that is, the THF-insoluble SWNTs form larger bundled structures, which would have been produced in the water-treatment (reaction in water) and drying processes described in the Experimental Section. It is known that as-produced SWNTs have a tendency to form strong bundled structures during purification processes such as the water treatment.[17]

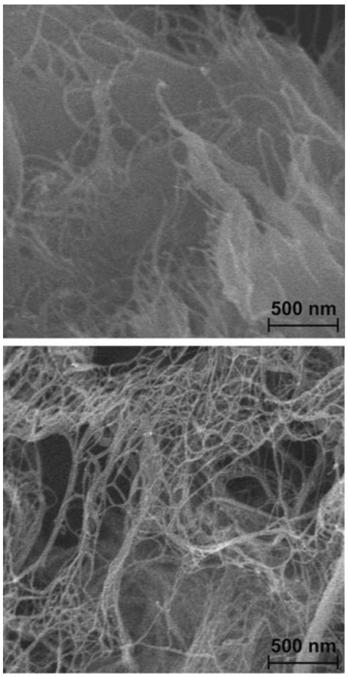

Figure 7. SEM images of the THF-insoluble SWNTs (top) and the pristine SWNTs (bottom).

Conclusions

We have synthesized a long-chain-carrying benzenediazonium salt, which selectively reacts with metallic SWNTs that are individually solubilized in an aqueous micelle of SC. By solvent (THF) extraction of the reacted metallic SWNTs, we separated the unreacted THF-insoluble SWNTs, which were identified as semiconducting SWNTs by Raman and Vis/NIR spectroscopy. The method presented herein is simple and therefore highly useful for supplying high-quality semiconducting SWNTs.

Experimental Section

Materials

SC and as-produced SWNTs (HiPco; the length and diameter of the pristine SWNTs are 1–10 μm and 0.8–1.2 nm, respectively) were purchased from Wako Chemical Industries, Ltd. and Carbon Nanotechnologies Inc., respectively, and were used as received.

Synthesis of 1

The reaction of *p*-acetamidophenol (Wako Pure Chemical Industries, Ltd.) with potassium hydroxide (Nacalai Co.) and 1-bromododecane (TCI) in ethanol produced *N*-(4-dodecyloxyphenyl)acetamide, which was hydrolyzed in acidic ethanol to give 4-dodecyloxyaniline. Under nitrogen atmosphere, nitrosonium tetrafluoroborate was dissolved in CH_3CN/CH_2Cl_2 (1:1 *v*/*v*), and the solution was cooled at −30 °C, then 4-dodecyloxyaniline was added over 30 min. After the addition was complete, the reaction solution was stirred for 1 h at room temperature. The solution was diluted with diethyl ether to generate a precipitate, which was collected and dried to give **1**. Yield: 83 %. IR (KBr): $\tilde{\nu}_{C-H} = 3085$, 3031, 2993, 2915, 2854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 8.5$ (d, $J = 9.7$ Hz, 2H, PhH), 7.2 (d, $J = 9.7$ Hz, 2H, PhH), 4.2 (t, 2H, CH_2), 1.8 (q, 2H, CH_2), 1.4 (q, 2H, CH_2), 1.2 (m, 16H, CH_2), 0.8 ppm (t, 3H, CH_3); elemental analysis: calcd (%) for $C_{18}H_{29}N_2OBF_4 + 0.6H_2O$: C 55.86, H 7.86, N 7.24 %; found C 55.71, H 7.65, N 7.68 %.

Solubilization, Chemical Modification, and Separation of As-Produced SWNTs

The typical SWNT solubilization procedures are as follows.[12] The as-produced SWNTs (≈1.0 mg) were placed in an aqueous solution of SC (22 mM), and the mixture was sonicated with a bath-type sonicator (Branson 5510) for 1 h at room temperature. After sonication, the sample was centrifuged (HITACHI KOKI, CS100GXL) at 118 000 *g* for 4 h. The supernatant was then carefully decanted to obtain individually dissolved SWNTs.

A given amount of **1** was added to the aqueous solution of the individually dissolved SWNTs. After the reaction mixture was stirred for a specific time, it was passed through a filter (Advantec Inc., PTFE; pore size 100 nm), and the residue on the filter was rinsed with copious amounts of water and then dried in a vacuum oven at 50 °C for 1 h. The obtained solid was suspended in THF with sonication (1 min), followed by shaking with a vortex shaker for 3 h; these procedures were repeated until no absorption of the SWNTs in THF appeared in the absorption spectra.

Vis/NIR and Raman Spectroscopy

The Vis/NIR spectra for the SWNTs were recorded with a spectrophotometer (JASCO, V-570). Raman spectra were recorded with a Renishaw Ramanscope (System 1000; $\lambda_{ex} = 514.5$ nm, Ar ion laser) and a Laser Raman Spectrophotometer (JASCO Corporation, NRS-3100; $\lambda_{ex} = 785$ nm, diode laser).

SEM Study

SEM images of the SWNTs were taken with a field-emission scanning electron microscope (Hitachi S-4500).

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