Selective Functionalization and Free Solution Electrophoresis of Single-Walled Carbon Nanotubes: Separate Enrichment of Metallic and Semiconducting SWNT

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Received August 7, 2006. Revised Manuscript Received December 19, 2006

p-Hydroxybenzene diazonium salt was utilized to selectively functionalize metallic single-walled carbon nanotubes (SWNT) at 45 °C with high selectivity. Deprotonation in alkaline solution induces a negative charge on the functionalized SWNT for electrophoretic separation. We applied this concept to enrich metallic and semiconducting fractions separately using the induced differences in electrophoretic mobilities. Free solution electrophoresis was utilized to separate selectively reacted samples into nonmobile and negative electrophoretic mobility fractions. Raman spectroscopy and UV−vis−nIR absorption spectroscopy confirm both the separation of reacted and unreacted SWNT, and after annealing, the enrichment of metallic and semiconducting SWNT respectively in two distinct fractions.

Introduction

Single-walled carbon nanotubes (SWNT) are cylindrical molecules of graphene[1,2] and have been highlighted as novel sources for future nanoelectronics.[3,4] They are either metallic or semiconducting depending on their chiralities.[5] Both metallic and semiconducting SWNT have potential for widespread applications, ranging from ultra-low-resistance materials with metallic SWNT[6] to field-effect transistors with semiconducting SWNT.[4,7] However, SWNT are invariably produced by synthetic protocols as mixtures of all electronic types.[5,8] Since 2003, there have been several proposed methods to separate and sort SWNT according to their electronic properties using dielectrophoresis,[9−11] selective flocculation,[12] selective adsorption[13] of Br and other species,[14,15] density gradient induced centrifugation,[16] and other methods.[17]

Early efforts to fractionate carbon nanotubes by electronic type using selective flocculation with amines[12] and dielectrophoresis[10] reported promising enrichment relying predominately on low-wavenumber radial breathing modes[18] (RBM) evident in Raman spectroscopy that can be assigned to distinct metallic or semiconducting nanotubes.[19,20] The Raman tangential mode corresponding to the C−C phonon splits into circumferential and longitudinal components. The former can couple to the continuum of states in metallic nanotubes, creating a distinctive Breit-Wigner-Fano line shape[21] that is also used to indicate enrichment. Morphology[22] (i.e., bundling and aggregation) invariably shifts the interband transitions of SWNT, moving various nanotubes into and out of resonance with the Raman excitation energy as to obscure an analysis of separation.[8] Dyke et al.[17] proposed a chromatographic method to separate functionalized SWNT, but noted that aggregation is easily confused for an apparent but marginal enrichment. Chen et al.[13] utilized a selective Br adsorption method followed by centrifugation quantified by photoabsorption spectroscopy and thus side-stepped

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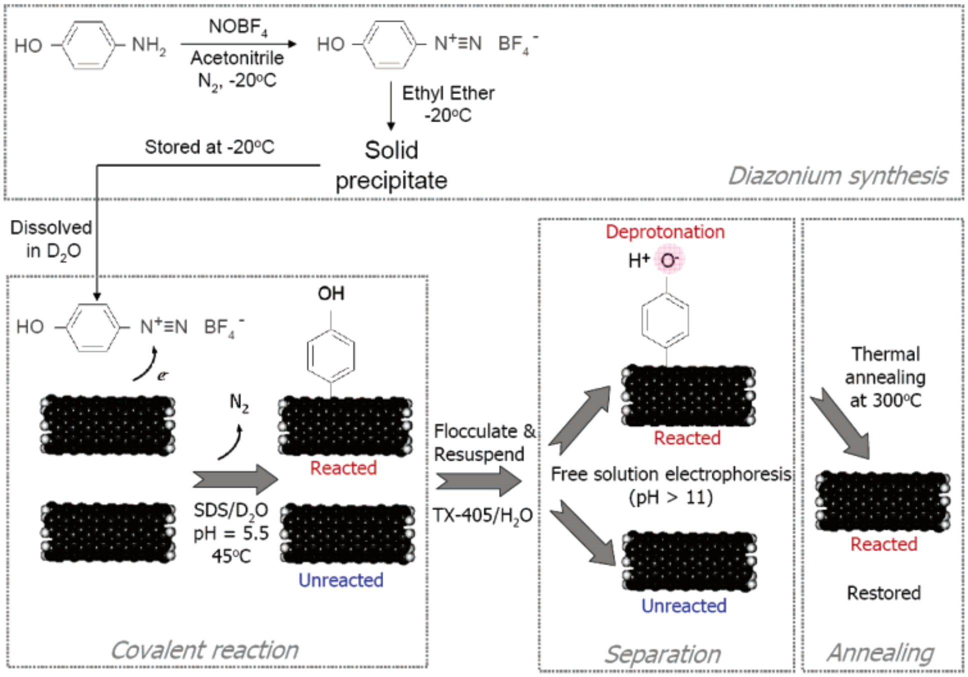
Scheme 1



complications with Raman, but the method yields limited enrichment. It is noteworthy that several groups report alternate dielectrophoresis conditions[9,23] that yield a more compelling case for metal/semiconductor separation. However, the separated fractions are typically collected on the electrode itself, potentially limiting scalability. In contrast, several techniques have been identified to separate nanotubes by diameter with great success, including ion exchange of DNA-SWNT,[24] gel electrophoresis/column chromatography,[25] and centrifugation of DNA-SWNT with a density gradient.[26] Recently, Arnold et al.[16] used this centrifugation method to separate single electronic type SWNT from mixtures of laser-ablation-grown SWNT, utilizing the density gradient induced by competing mixtures of surfactants, resulting in a very compelling metal/semiconducting separation. Ultracentrifugation is necessarily an energy-intensive processing step, and there remains a need for a method with potentially higher throughput, better selectivity and yield, and more favorable scalability.

In this work, we present a unique scheme for separating and sorting carbon nanotubes by electronic structure based on our previous work on selective functionalization of metallic and semiconducting types. We have shown that electron-withdrawing reagents such as diazonium salts can selectively react metallic SWNT over semiconducting SWNT under certain conditions.[27] Others have utilized our results for on-chip diminishment of metallic pathways in SWNT-FET devices.[28,29] In the present scheme, we selectively attach *p*-hydroxybenzene groups to metallic nanotubes, and then use free solution electrophoresis at high pH to separate the reacted metals from unreacted semiconductors. The alkaline solution deprotonates the moiety on the nanotube, creating a selective negative charge (Scheme 1). We demonstrate separation of a starting sample into two distinct fractions that are enriched in metallic and semiconducting nanotubes, respectively. The approach is not limited by electrode deposition and is scalable to large volumes. Photoabsorption and Raman spectroscopy are used to benchmark the separation; however, we are careful to analyze collected fractions and control samples in identical aggregation states[22,25] (i.e., solution, annealed solid, etc.). As a result, we demonstrate the fractionation of a starting SWNT sample into metallic and semiconducting samples such that Raman spectra from the latter two sum to approximately yield the initial. As an aside, we also note that, in spite of the vast literature on SWNT covalent functionalization, this is the first work to demonstrate the separation of reacted and unreacted SWNT, as evidenced by a Raman D-peak enrichment. Future efforts will focus on scale-up and improving the separation.

Experimental Section

Reactants. HiPco SWNT were suspended in D_2O with 1 wt % sodium dodecyl sulfate (SDS) and ultrasonicated, followed by ultracentrifugation to disperse individually suspended SWNT as described previously.[30] The 4-hydroxybenzene diazonium salt was

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prepared by the reaction of nitrosonium tetrafluoroborate ($NOBF_4$) and 4-aminophenol ($HO-C_6H_4-NH_2$), as described in Scheme 1. The diazonium salt is stored at −20 °C and metered out into D_2O immediately before reaction.

Selective Functionalization. The reaction of SWNT with 4-hydroxybenzene diazonium salt was performed at 45 °C and pH 5.5 by injecting the diazonium salt solution into a reactor vessel containing SWNT, using a syringe pump (Cole-Parmer). The total volume of 500 μL of the diazonium solution, with concentrations described below, was added at an injection rate of 20.83 μL/h into the total volume of 5 mL of SWNT solutions. The reactor was well-stirred throughout the reaction time of 24 h. The conversion of functionalized metallic SWNT was controlled by varying the concentration of diazonium salt as discussed below. Selectivity for metallic SWNT was observed to the near exclusion of semiconducting SWNT when the concentration of diazonium salt was 0.245 mM. Some of the semiconducting SWNT as well as all the metallic SWNT were reacted when the concentration was 0.344 mM. These two reacted samples and a control were prepared and used for the free solution electrophoresis.

Free Solution Electrophoresis. The SDS surfactant possesses an interfering negative charge, but is favorable for the selective reaction of SWNT. We resuspended the reacted SWNT in Triton-X-405 (TX-405) for the diazonium functional group to dominate the electrophoretic mobilities during the free solution electrophoresis. The reacted SWNT suspended in SDS/D_2O were flocked from the solution by adding an equal volume of acetone and then resuspended in 2 wt % aqueous TX-405 solution prior to electrophoresis. Electrophoresis was performed using a custom-made Pyrex glass cell, which has two reservoirs connected with a glass tube (o.d. = 6 mm, length = 120 mm). The injection port was positioned at the center of this glass tube and plugged with a rubber septum. Platinum wire (Fisher Co., 28 gauge) was used for the electrodes and 10 mM aqueous sodium phosphate solution containing 3 wt % TX-100 was used as the buffer. The pH of the buffer solution was adjusted to be 11.5 by adding NaOH for the hydroxyl group attached to the functionalized SWNT to be deprotonated. The functionalized SWNT were slowly injected (500 μL for 1 h) to minimize diffusion and convection by the injection pressure. The voltage was held constant at 100 V (~4 mA current) using a Thermo Electron Corporation power supply for 2 h. Two fractions were collected following electrophoresis: One at the center of the glass tube, where the original SWNT were injected (center fraction), and the other at the cathode reservoir, where the positive electrode was immersed ((+) fraction).

Characterization. The separated fractions, both from the center and the cathode reservoir, were characterized by Raman and UV−vis−nIR absorption spectroscopy to investigate the extent of enrichment of specific electronic types. The Raman spectra at two excitation laser wavelengths of 632.8 nm (HeNe laser) and 785 nm (diode laser) were obtained with a Kaiser Raman RXN1 analyzer, and UV−vis−nIR spectra were observed using a Shimadzu UV-310PC absorption spectrometer. Raman features at low wavenumber RBM were also investigated on SWNT, where functional groups had been removed via annealing. Each separated fraction was drop-dried on a Si wafer, rinsed with water for 5 s, and annealed at 300 °C under UHP N_2 atmosphere for 1 h prior to the Raman observation.

Results and Discussion

Scheme 1 shows the separation protocol comprising three steps. First, the SWNT suspended in SDS/D_2O were covalently reacted with 4-hydroxybenzene diazonium salt. The extent of reaction, and thus selectivity, was controlled by the concentration of a diazonium solution added to the SWNT. After the reaction, the reacted SWNT suspended in SDS/D_2O was flocked from solution and resuspended in 2 wt % nonionic surfactant (TX-405) prior to electrophoresis. Resuspension in a nonionic surfactant allows the negatively charged functional group to dominate the electrophoretic mobility. To investigate the possible flocculation of SWNT due to the use of TX-405/H_2O instead of SDS/D_2O, which would lower the separation efficiency, Raman spectra of SWNT suspended in SDS/D_2O and TX-405/H_2O was compared and presented in the Supporting Information (Figure S1). The fluorescence peaks of SWNT suspended in TX-405/H_2O show similar intensity compared to those of SWNT suspended in SDS/D_2O, and are red-shifted, indicating that SWNT are well-suspened in TX-405/H_2O and free from flocculation. The separation of SWNT by free solution electrophoresis was performed at high pH (>11.0, a 3.9 M NaOH solution was added), causing the hydroxyl group to be deprotonated. Finally, the functionalized SWNT separated by free solution electrophoresis were restored to their pristine state by thermal annealing at 300 °C for 1 h.

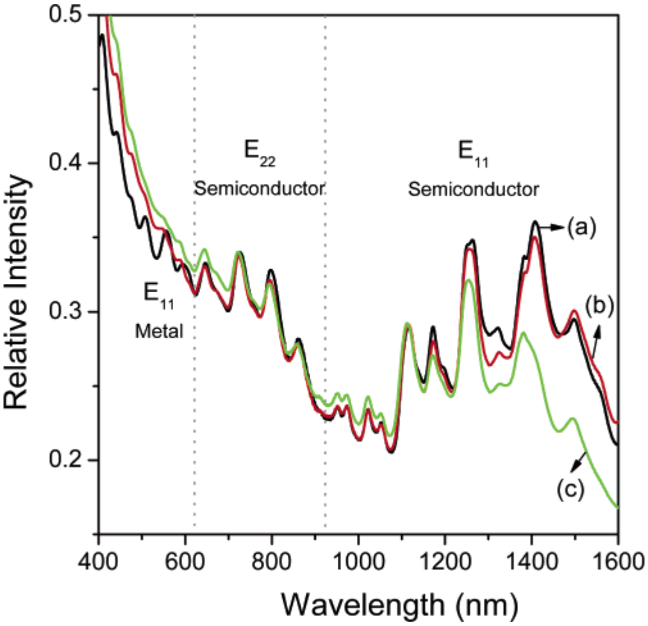

Figure 1. UV−vis−nIR absorption spectra of samples with different selectivities and reaction extents for metallic SWNT used in free solution electrophoresis: (a) control, (b) reaction 1, and (c) reaction 2.

Selective Functionalization. Figure 1 shows the UV−vis−nIR absorption spectra of two samples reacted with different concentrations of 4-hydroxybenzene diazonium solution together with unreacted SWNT (control) as a reference. All samples are suspended in 1 wt % SDS/D_2O. When 0.245 mM diazonium solution is injected (Figure 1b), the peak intensities representing the first Van Hove transition of metallic species ($E_{11,m}$) in the 440−645 nm region abruptly decrease when compared to those of unreacted SWNT (control, Figure 1a), while the peak intensities representing the second ($E_{22,sc}$) and first ($E_{11,sc}$) Van Hove transition of the semiconducting species show little change. This result indicates that only metallic SWNT are covalently functionalized over semiconducting SWNT at a diazonium concentration of 0.245 mM (reaction 1, Figure 1b). When excess

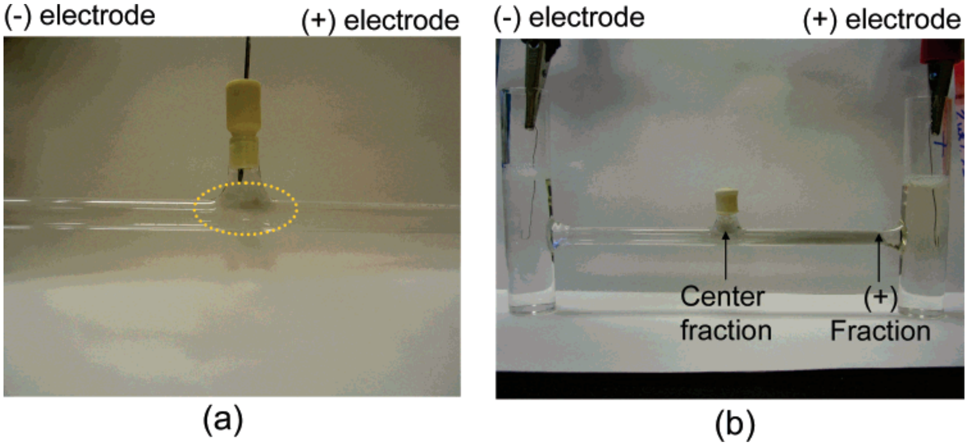

Figure 2. Images of SWNT migration following free solution electrophoresis: (a) control and (b) reaction 1.

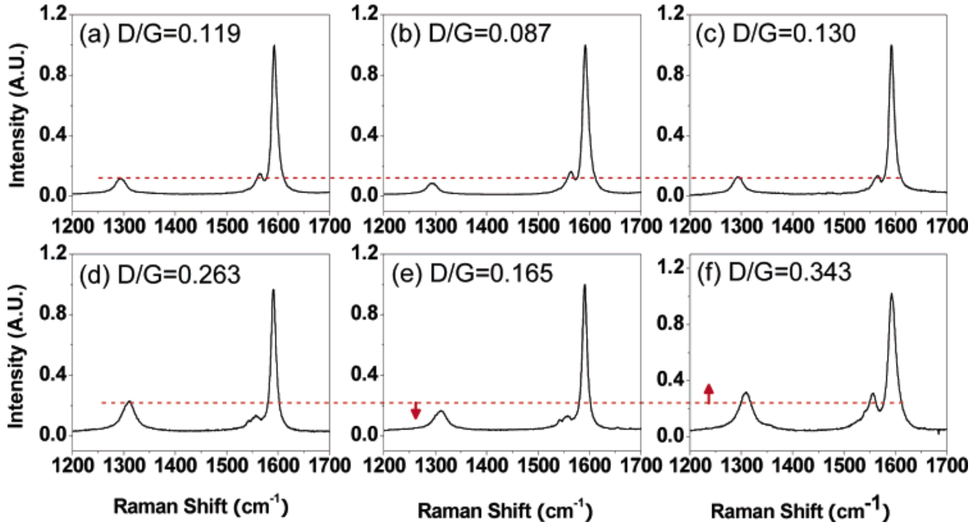

Figure 3. Raman features of separated fractions after free solution electrophoresis of reaction 1. 785 nm laser excitation: (a) original sample, (b) center fraction, and (c) (+) fraction. 632.8 nm laser excitation: (d) original sample, (e) center fraction, and (f) (+) fraction.

diazonium is injected, as in Figure 1c where 0.344 mM diazonium is added, semiconducting SWNT with large diameter, i.e., small band gap, are also partially reacted with diazonium reagents along with the metallic SWNT (reaction 2). These results confirm that the electronic-structure selective chemistry can be performed with the 4-hydroxybenezene diazonium. The selectivity can be controlled by adjusting the concentration of the diazonium salt added to the starting sample.

Free Solution Electrophoresis. Free solution electrophoresis was performed on both the reacted sample (reaction 1) and the unreacted sample (control) to investigate the possibility of separation according to varying electrophoretic mobility determined by the reaction extent. Figure 2 shows images of the control and reaction 1 after free solution electrophoresis at 100 V for 2 h. Each sample was slowly injected at the center of the glass tube to minimize diffusion by injection. As can be seen in Figure 2a, most of the control stays at the center, where the sample is injected, while reaction 1 is separated into two fractions (Figure 2b), with one staying at the center where the sample was injected (center fraction) and the other moving to the cathode ((+) fraction). Migration toward the cathode, which can be observed only in reaction 1, might originate from the negatively charged functional groups attached to the SWNT by selective functionalization with 4-hydroxybenzene diazonium reagents.

To confirm that the functionalized SWNT, rather than nonfunctionalized SWNT, actually move to the cathode, Raman spectra were collected at two excitation laser wavelengths (785 and 632.8 nm) on the separated fractions of reaction 1. Figure 3 shows the disorder mode (D peak, 1295 cm^{-1}) and tangential mode (G peak, 1592 cm^{-1}) at 785 nm excitation (Figures 3a−3c) and 632.8 nm (Figures 3d−3f) for the original sample, center fraction, and (+) fraction of reaction 1, in order. The intensity ratio of the D peak to the G peak (D/G) is related to the extent of functionalization.[31] The D/G ratio for the center fraction (Figure 3b) has decreased when compared to that of the original sample (Figure 3a), indicating enrichment of unreacted SWNT, while the ratio is increased for (+) fraction (Figure 3c), indicating enrichment of reacted SWNT, in 785 nm Raman spectra. These trends become more pronounced at 632.8 nm laser excitation, where more metallic SWNT are in resonance.[19] The above results confirm the trend of functionalized SWNT migrating to the cathode, while nonfunctionalized SWNT remain in the center. Since only

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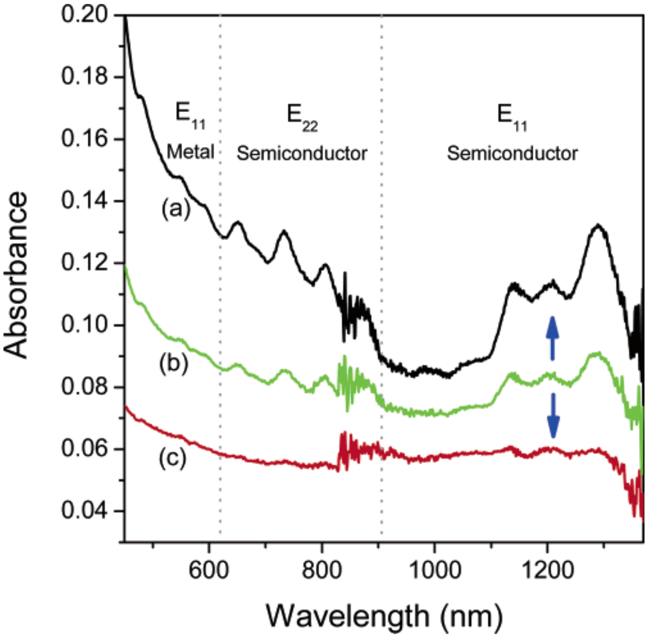

Figure 4. UV−vis−nIR absorption spectra of separated fractions in reaction 1: (a) center fraction, (b) original sample, and (c) (+) fraction.

the metallic SWNT in the original sample of reaction 1 are almost completely reacted with 4-hydroxybenzene diazonium salt, leaving the semiconducting SWNT unreacted, we anticipate enrichment of semiconducting SWNT at the center fraction and metallic SWNT at the (+) fraction.

To investigate that the functionalized SWNT collected at the cathode are actually enriched in metallic species, and the nonfunctionalized SWNT collected at the center are enriched in semiconducting species, the separated fractions from reaction 1 were analyzed by UV−vis−nIR absorption and Raman spectroscopy. Figure 4 shows the UV−vis−nIR absorption spectra of center fraction (Figure 4a), the original sample (Figure 4b), and the (+) fraction (Figure 4c) of reaction 1 suspended in 2 wt % TX-405/H_2O. When compared to the original sample (Figure 4b), two notable changes in the absorption spectra are observed in the separated fractions. The peak intensities representing the v1 → c1 transitions of semiconducting SWNT ($E_{11,sc}$) in the control (Figure 4b) are abruptly decreased in the (+) fraction (Figure 4c), while the intensities are insignificantly changed in the center fraction (Figure 4a). The above results indicate that the center fraction is enriched in unreacted semiconducting SWNT and the (+) fraction is enriched in reacted metallic SWNT, inferred by the decreased intensity of semiconducting SWNT in this fraction. Considering that the metallic SWNT were selectively reacted with diazonium to the near exclusion of semiconducting SWNT (Figure 1b), the above results are in accordance with the changes of D/G ratio in Figure 3.

To further investigate the enrichment of one electronic-type SWNT after the free solution electrophoresis, we observed the radial breathing modes (RBM) of the separated fractions using 633 nm Raman laser excitation, at which both metallic and semiconducting SWNT are in resonance. The separated samples were drop-dried on a Si wafer and rinsed with water to remove the surfactants. Then, the samples were annealed at 300 °C under UHP N_2 flow for 1 h to remove the functional groups, which had been attached to the SWNT by the selective reaction. The RBM features of five different samples are compared in Figure 5. Both metallic and semiconducting SWNT are observed. The chiral vectors for metallic species are shown in blue and those for semiconducting species in red.[32,33] When the SWNT are covalently reacted with diazonium salts, peaks in the RBM should be decayed. As can be seen in Figure 5a, when the SWNT are reacted with diazonium salts, in which metallic SWNT are mostly reacted as shown in Figure 1b, most of the peaks representing metallic SWNT in the RBM region decay (Figure 5(a-3)). However, when the reacted SWNT are annealed at 300 °C, most of the peaks, which decayed due to the covalent reaction, are recovered (Figure 5(a-2)) to the level of the control (Figure 5(a-1)). These results indicate that annealing at 300 °C in N_2 flow is apparently sufficient to remove most of the diazonium functional groups from the SWNT surface and that the Raman features presented in Figures 5b and 5c are largely free from the phenoxide functionalities. In a comparison of the RBM features of the (+) fraction and center fraction, notable changes are observed; peaks representing metallic SWNT become dominant compared to those for semiconducting SWNT in the (+) fraction (Figure 5b), and the exact opposite trend was observed with the center fraction (Figure 5c). The area ratio of metallic over semiconducting RBM is calculated and represented in Figure 5. This ratio for the (+) fraction is increased 97% above the original sample, indicating the enrichment of metallic species. The ratio for the center

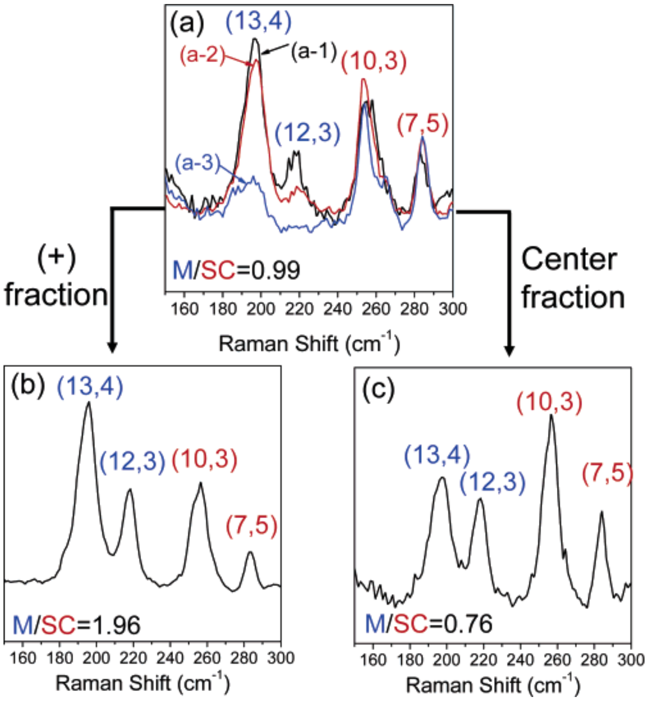

Figure 5. 632.8 nm Raman features in the RBM of separated fractions from reaction 1 after annealing: (a-1) control; (a-2) original, reaction 1 after annealing; (a-3) original, reaction 1 before annealing; (b) (+) fraction, reaction 1 after annealing; (c) center fraction, reaction 1 after annealing. Samples were annealed at 300 °C for 1 h with UHP N_2 flow.

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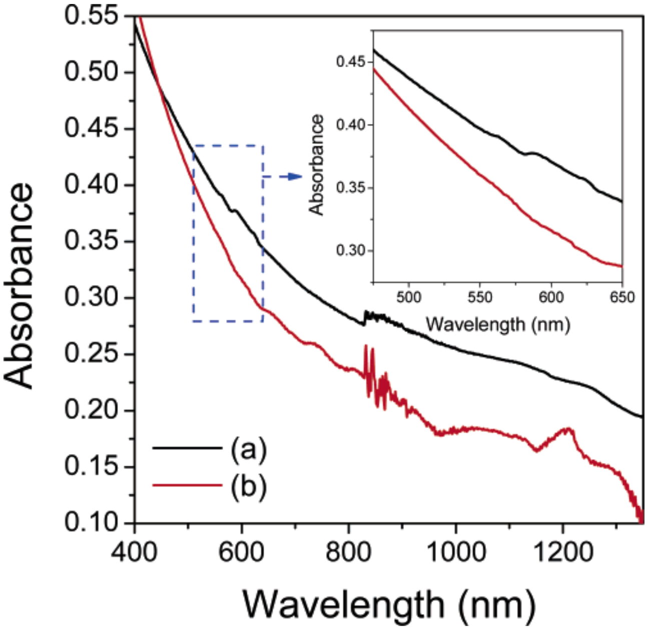

Figure 6. UV−vis−nIR absorption spectra of separated fraction after annealing at 300 °C: (a) (+) fraction; (b) center fraction. Both samples are resuspended in 2 wt % TX-405/H_2O after annealing.

fraction is decreased 23% below the original sample, indicating the enrichment of semiconducting species. It should be noted that the RBM, which are usually used to benchmark the enrichment of one electronic type of SWNT, can be influenced by several spectroscopic artifacts, mainly aggregation as we have reported previously[8,11,22] and others have since confirmed,[6] that misinform an apparent enrichment. That is, as the interband transitions of SWNT are red-shifted in energy as bundles are formed, the species, which were not in resonance in their pristine states, are brought into resonance, resulting in the increase in the overall intensity. The opposite phenomenon is also possible, leading to the decrease in the overall intensity of specific species.[22] These effects are not operative in the interpretation of our spectra for three reasons: The first is that our annealed samples are processed identically, yielding materials in the same aggregation state and direct comparison of RBM intensities is appropriate. Second, we observe a systematic increase of metallic modes and a corresponding and quantitative decrease in metallic modes in the remaining sample compared to the aggregated control. Because the interband shifting is unidirectional in energy with aggregation, the spectral differences cannot be aggregation.

The annealed sample of each fraction was resuspended in 2 wt % TX-405/H_2O and the UV−vis−nIR absorption spectra of both fractions were observed, as presented in Figure 6. Even though the absorption intensities of both samples (center fraction and (+) fraction) are weak, the two samples showed different trends. The center fraction (Figure 6b) shows peaks representing the first Van Hove transition of semiconducting species ($E_{11,sc}$) in the 900−1350 nm region and the second Van Hove transition of the same species ($E_{22,sc}$) in the 550−900 nm region; however, it does not show any peak representing the first Van Hove transition of metallic species ($E_{11,m}$) in the 440−645 nm region. In contrast, (+) fraction (Figure 6a) shows peaks representing metallic species ($E_{11,m}$), together with peaks representing semiconducting species. However, the peak intensities of these semiconducting species in the (+) fraction are insignificant compared to those of the center fraction. The above results confirm the Raman results (Figure 5) that the center fraction is enriched in semiconducting SWNT while the (+) fraction is enriched in metallic SWNT. As for the reason why the resuspended SWNT after annealing shows reduced absorption intensities, compared to those of the initial SWNT, we suspect the difficulty in separating the bundles of SWNT after annealing, since it is possible that radicals end up recombining across SWNT to prevent their dispersion again in solution. Based on the findings of this research, future efforts will focus on scale-up and improving the separation.

Conclusion

We showed the enrichment of one electronic-type SWNT is possible by combining two schemes: the selective functionalization of SWNT using 4-hydroxybenzene diazonium salt followed by free solution electrophoresis. The scheme introduced in this study is focused on the separation of functionalized from nonfunctionalized SWNT by their differences in electrophoretic mobilities. Using this method, we were able to separate metal-enriched SWNT from semiconductor-enriched SWNT, since only the metallic SWNT are selectively functionalized over the semiconducting SWNT in the SWNT mixtures used for the separation. Since the selectivity for specific type of SWNT can be controlled by the diazonium chemistry, this separation scheme may be used to further separate the SWNT with different chiralities. Moreover, since the selective functionalization utilized in this study is valid not only for HiPco SWNT but also for SWNT prepared by other synthetic methods, this separation scheme can be applied to other SWNT.

Acknowledgment. We acknowledge a Class A grant from the Intel Corporation. M.S.S. appreciates an NSF-Career Award for the support of this research and a grant from the ACS-PRF. W-J.K. is grateful for support by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-214-D00260).

Supporting Information Available: Raman spectra of SWNT suspended in H_2O using different surfactants. This material is available free of charge via the Internet at http://pubs.acs.org.

CM061862N