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Bulk Separative Enrichment in Metallic or Semiconducting Single-Walled Carbon Nanotubes

Zhihong Chen, Xu Du, Mao-Hua Du, C. Daniel Rancken, Hai-Ping Cheng, and Andrew G. Rinzler*

Department of Physics, University of Florida, Gainesville, Florida 32611-8440

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ABSTRACT

A postsynthesis method of separating metallic from semiconducting single-walled carbon nanotubes and a method based on absorption spectroscopy for assay of the separation efficiency are described. The separation method relies on chemical discrimination in the charge-transfer complex formation between bromine and the metallic versus semiconducting nanotubes and takes advantage of the resulting density difference to effect a centrifugation-based separation. Calculations support the proposed separation mechanism.

The existence and availability of both metallic and semiconducting single-walled carbon nanotubes testify to the rich diversity of nature. The lack of availability of nanotube samples that are either *purely* metallic or *purely* semiconducting attests to another well-known facet of nature: “There is no free lunch.” Visions of future nanotube-based nanoelectronics, of necessity involving a kind of orchestrated self-assembly for the integration of millions of nanotubes into functional circuits, will almost certainly require nanotubes of known electronic classification (metallic or semiconducting). Optical applications are also hindered by this lack of pure samples. As only recently explained, the absence of fluorescence from photoexcited bulk samples (despite the known direct band gap of the semiconducting fraction) is due to Foerster luminescence quenching induced by the metallic nanotubes in the mix.¹ The parasitic effects of the undesired metallic or semiconducting portion likewise frustrate other potential applications (e.g., chemical sensors).

Yet all known methods of nanotube synthesis (carbon arc, laser vaporization, chemical vapor deposition) produce them in a range of diameters and chiral angles resulting in a mixture of both metallic and semiconducting types. Because the nanotube diameter is constrained by the size of the catalyst particle from which it grows,^{2,3} it is tempting to imagine obtaining sufficient control over the particle size to yield identical nanotubes of one type or the other. (In polymer synthesis, for example, metallocene-based catalysts yield unprecedented control over polyolefin stereoregularity and molecular weight.) The futility of such an approach is made evident by recognizing that the diameter difference between a (10, 10) metallic and a (9, 11) semiconducting nanotube

is a mere 0.03 Å. Worse still, at the high temperatures required for nanotube synthesis (polymer synthesis proceeds at much lower temperatures), thermal vibrations make it likely that even identically sized catalyst particles will nevertheless allow sufficient variation in the nanotube diameters to let them span both metallic and semiconducting types. Such considerations make clear the need for a postsynthesis method of separating metallic from semiconducting nanotubes.

We describe here a method that yields a separative enrichment of samples in metallic or semiconducting nanotubes and a characterization technique that quantifies our measure of success. Our method owes much to a recent enabling discovery from a group at Rice University. They found that an aqueous suspension of surfactant-stabilized, *individual* nanotubes acquire a specific gravity near 1 and that such individual nanotubes remain in suspension during high-speed centrifugation.¹ This finding led us to ponder the questions of whether (1) complex formation in the nanotubes, known to occur with a wide range of atomic and molecular species (essentially those found to form graphite intercalation complexes), would show discrimination between the metallic and semiconducting nanotubes (i.e., show some measure of preference for binding with one over the other type) and (2) there existed a chemical species for which such specific complex formation could proceed in the surfactant-stabilized aqueous suspension. If so, then the more highly complexed fraction, having acquired a greater specific gravity, could be separated out by an additional centrifugation step. A schematic of the idea is shown in Figure 1.

The alkali metals are perhaps the best-studied charge transfer dopants of the nanotubes;^{4–9} however, the violent

* Corresponding author. E-mail: rinzler@phys.ufl.edu.

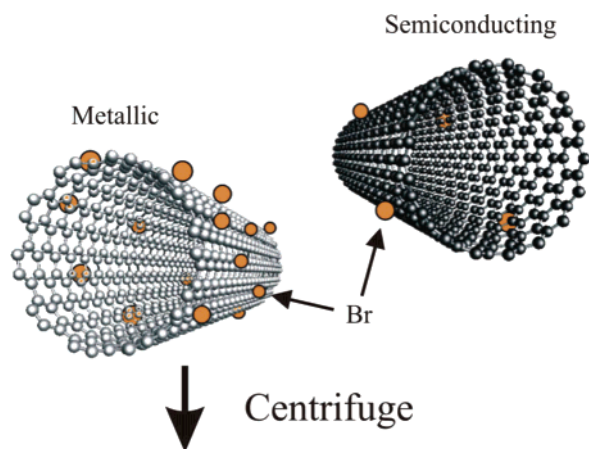


Figure 1. Preferential charge-transfer complex formation for density-based metallic/semiconducting nanotube separation.

reaction of the alkali metals with water excluded them as candidates. Halogens such as bromine and iodine, however, have been shown to complex readily with nanotubes;^{4,8,10} moreover, they have appreciable solubility in water. We consequently undertook separation experiments using bromine and iodine. To explore computationally the relative binding strength of the halogens with the metallic versus the semiconducting nanotubes, we simultaneously undertook density functional theory (DFT) calculations with a local density approximation (LDA) as well as the usually more accurate generalized gradient approximation (GGA).

To characterize the metallic versus semiconducting nanotubes in our samples, we rely on optical absorption spectra of thin films formed from the collected fractions. Absorption spectra of laser vaporization-grown nanotubes, with nanotube diameters ranging from ~ 1.1 to ~ 1.6 nm, typically exhibit three broad absorption bands of relevance.¹¹ These correspond to transitions between mirror image van Hove singularities of the nanotubes with absorbance peaks centered at ~ 1700 and ~ 950 nm corresponding to v_1-c_1 and v_2-c_2 singularity transitions, respectively, for the semiconducting nanotubes and another peak centered at ~ 650 nm corresponding to the v_1-c_1 singularity transitions for the metallic nanotubes in the sample. The metallic band sits on the rising edge of a broad π plasmon, centered in the near-UV. The breadth of these bands arises from the (inverse) dependence of the transition energies on the nanotube diameters and the variation of those diameters in the sample. A comparison of the integrated intensities of one of the semiconducting bands with the metallic band provides a measure of the fraction of semiconducting to metallic nanotubes present. Differences in the absorption (and scattering) cross sections between the semiconducting and metallic nanotubes do not permit this ratio of integrated intensities to yield their fractional concentration directly. However, the ratio of such ratios, for distinct samples, can provide a measure of the excess of one subfraction (e.g., the semiconducting nanotubes) in one sample relative to that in the other, each normalized to its respective metallic fraction.¹²

Charge-transfer doping of the nanotubes modifies the electronic populations of the van Hove singularities involved

in these electronic transitions, dramatically affecting their absorbance spectra.¹³ Before such spectra can yield quantitative information about their relative metallic/semiconducting content, the nanotubes, which have been exposed to a charge-transfer reagent, must first be de-doped. Such de-doping was effected by a 600°C bake in flowing argon gas.¹² Our novel method for producing highly uniform, ultrathin, optically transparent films composed of pure nanotubes proved useful in generating near-ideal samples for the spectroscopic measurements.¹²

Nanotubes produced by high-yield methods typically self-assemble into bundles containing tens to hundreds of hexagonally close-packed nanotubes.¹⁴ Although the van der Waals force binding these nanotubes is weak on a per atom basis (compared with that of chemical bonds), the involvement of many atoms results in a substantial net binding strength. Debundling these so-called “ropes” to yield individual nanotubes is consequently nontrivial. To disrupt these bonds, for a given energy input (e.g., via ultrasonication or shear mixing), it is useful first to reduce the number of atoms involved by shortening the bundle lengths. We consequently began with purified, pulsed laser vaporization-grown nanotubes, shortened by ultrasonication in strongly oxidizing acid¹⁵ to a mean length determined by atomic force microscopy (AFM) to be ~ 800 nm.

The dropwise addition of diluted bromine or iodine to nanotubes in a surfactant-stabilized aqueous suspension while monitoring the nanotube absorbance bands showed that the charge-transfer reactions indeed occurred in the aqueous environment. Details of these experiments and the details for a typical separation are provided in the Supporting Information. Here we outline the steps. Cut nanotubes suspended in 3 wt % Triton X-100/DI water were centrifuged twice, retaining only the supernatant nanotube suspension to yield a sample consisting of individual nanotubes and small bundles. Immediately following the second supernatant decant, a diluted quantity of bromine was vigorously stirred into the decanted suspension followed by 12 h of centrifugation at $24\,000g$. (Iodine did not yield evidence of separation in an early experiment, so efforts were concentrated on bromine.) The supernatant and sediment from this centrifugation were collected separately, deposited as thin films on quartz substrates, and de-doped by the 600°C bake in preparation for the spectral analysis.

Parts A and B of Figure 2 show the spectra for a supernatant and its corresponding sediment sample, respectively. SC1 and SC2 label the semiconducting bands, and M, the metallic band. To facilitate quantitative extraction of the integrated intensities for comparison, the features in the spectra were least-squares fitted with Lorentzians. Figure 2C directly compares the Lorentzians normalized to the same metallic band *areas*. Parts D–F of Figure 2 show the corresponding curves for a control sample to which no Br was added during the final centrifugation but otherwise treated identically to the other samples (including the 600°C bake). Figure 2C exhibits the key result, showing that the semiconducting nanotube content has been substantially

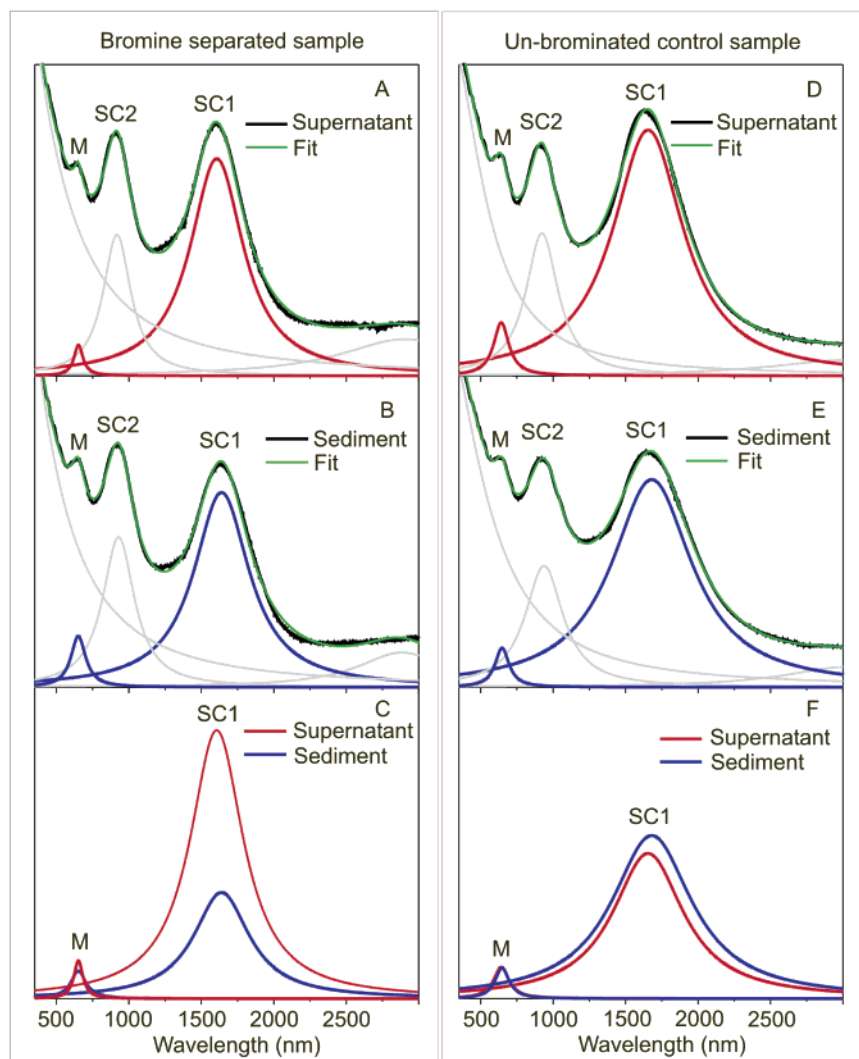


Figure 2. (A) Absorption spectrum for a Br-separated supernatant sample overlaid fit to five Lorentzians. The two Lorentzians corresponding to the metallic (M) and semiconducting (SC1) bands are highlighted. (B) The same for the corresponding sediment sample. (C) Comparison of the Lorentzians from A and B normalized to the same underlying metallic band areas. (E, F) Corresponding spectra, fits, and comparison for a control sample (no Br during the final centrifugation). For the separated samples, we consistently obtain Lorentzian line widths that are somewhat narrower for the supernatant than the sediment samples. This may be a consequence of the smaller fraction of bundles in the supernatant over the sediment and line broadening due to tube–tube band structure perturbations. This may make the separation quality appear slightly better in the plot than it actually is. Note however that the separation ratios given in Table 1 normalize out any such effect in the division by the larger-bandwidth sediment peak integrated intensities.

enhanced in the supernatant sample at the expense of that in the sediment.

Evident in Figure 2F, which directly compares the Lorentzian fits from Figure 2D and E, is the somewhat surprising observation of a small, oppositely directed separation, consistently observed in the control samples. That is, Triton X-100-suspended nanotubes treated as above but not subjected to bromine and centrifuged again for a final cycle (equivalent to the Br-treated sample) yielded an excess of semiconducting nanotubes in the sediment. A consideration of this (oppositely directed) separation suggests that the Triton X-100 surfactant exhibits enhanced stabilization for the metallic nanotubes. That is, the semiconducting nanotubes come out of the metastable suspension at a higher rate than the metallic ones to then sediment out during the 12-h centrifugation. In retrospect, it should perhaps not be surprising that differences in the nanotube band structure

should also be manifest in more subtle differences in their chemical interactions with other species. This result also suggests an alternate and/or contributing mechanism for the separation observed in the Br-exposed samples, i.e., the additional Br associated with the metallic nanotubes interferes with their surfactant stabilization such that, besides acquiring an increased density, these nanotubes also come out of suspension during the long centrifugation.

The experiment has been repeated a number of times with variation in the amount of Br added to the centrifuged sample and with nanotubes from distinct production batches, ultrasonicated using a cup horn (more violent) or bath (less violent) sonicator for varying times to disrupt nanotube bundles. Table 1 summarizes these results. The ratio of the integrated intensity of the first semiconducting (SC1) fitted Lorentzian band to that of the metallic (M) Lorentzian band, labeled $R_z = I(\text{SC1})/I(\text{M})$, yields a relative measure of the

Table 1. Integrated Intensities for the SC1, SC2, and M Fitted Lorentzian Bands and Ratios Formed from These for the Sediment and Supernatant Samples^a

sample	Br conc (mg/mL)	z = sup, sed	I(SC1)	I(SC2)	I(M)	$R_{z2} =$ $I(SC2)/I(M)$	$R_{z1} =$ $I(SC1)/I(M)$	SC2 R_{sup}/R_{sed}	SC1 R_{sup}/R_{sed}
batch 1; B11h	0 (control)	sup sed	412.04 285.95	114.76 83.53	20.57 10.34	5.58 8.08	20.03 27.66	0.69	0.72
batch 1; B12h	0 (control)	sup sed	75.75 73.58	27.70 25.77	5.17 4.01	5.36 6.43	14.67 18.36	0.83	0.80
batch 1; B14h	8.0	sup sed	304.50 312.39	99.02 96.61	9.71 15.73	10.20 6.14	31.37 19.86	1.66	1.58
batch 1; B12h	5.3	sup sed	94.98 96.57	32.66 36.83	3.28 7.13	9.96 5.17	28.96 13.54	1.93	2.14
batch 1; C2h, B6h	5.2	sup sed	71.69 73.97	26.80 25.38	3.42 4.07	7.85 6.24	20.99 18.18	1.26	1.15
batch 1; C2h, B6h	8.0	sup sed	105.54 104.74	34.67 35.09	3.98 5.56	8.71 6.32	26.50 18.85	1.38	1.41
batch 1; C2h, B6h	10.9	sup sed	115.27 70.37	37.16 20.54	4.94 3.16	7.53 6.50	23.34 22.25	1.16	1.05
batch 2; B18h	8.0	sup sed	35.14 49.04	12.26 22.09	0.90 3.56	13.68 6.21	39.20 13.79	2.20	2.84
batch 2; B11h, C5m	1.6	sup sed	117.03 90.71	37.66 35.25	3.26 4.78	11.55 7.37	35.89 18.97	1.57	1.89
batch 2; B6h, C10m	1.3	sup sed	109.07 114.78	35.99 37.61	4.10 5.64	8.78 6.67	26.61 20.34	1.32	1.31

^a Distinct starting batches are indicated in the first column where B or C specifies the use of the bath or cup horn sonicator, respectively, followed by the times for which they were used in hours (h) and minutes (m). At the highest Br concentration (10.9 mg/mL, denoted by *), the suspension became cloudy, indicating that the surfactant's ionic concentration tolerance had been exceeded. Data in the first and eighth rows correspond to the spectra shown in Figure 2. Values of the integrated intensities vary widely because the film thicknesses varied.

semiconducting to metallic nanotube ratio in the sediment or supernatant sample (as specified by the subscript *z*). The ratio of these ratios, R_{sup}/R_{sed} , then yields the excess of semiconducting nanotubes in the supernatant versus the sediment sample normalized to the metallic content in each. A ratio of 1 indicates no separation, and a ratio greater than (less than) 1 indicates an increased concentration of semiconducting (metallic) nanotubes in the supernatant relative to that in the sediment. A check on this procedure is provided by forming the corresponding ratios using SC2 rather than SC1. Given the complexities ignored by our simple fitting procedure, the lack of perfect numerical agreement between the use of SC1 or SC2 is not surprising. The agreement is adequate, however, to support our conclusions regarding the separation.

DFT calculations were carried out on three representative nanotubes: the (10, 0) semiconducting, (9, 0) metallic, and (6, 6) metallic nanotubes. The LDA calculations gave nanotube–Br binding energies of –0.96, –1.23, and –1.17 eV, respectively, and the GGA calculations yielded nanotube–Br binding energies of –0.70, –0.90, and –0.88 eV, respectively. A significantly enhanced interaction of Br with the metallic nanotubes is clearly predicted within both approximations. This manifests itself as a significantly increased time-averaged Br associated with the metallic nanotubes compared with that for the semiconducting nanotubes in their respective dynamic equilibria.

Consistent with these calculations are the experimental results, which show a repeated enhancement in the semi-

conducting nanotube concentration (relative to the metallic concentration) in the Br-exposed supernatant with respect to the sediment. We do not observe a clear trend in the separation efficiency with bromine concentration for the small variations made. The major factor in the separation efficiency appears to be the degree to which the nanotubes are dispersed as individuals. The cup horn sonicator concentrates far more energy on the sample than the bath sonicator, so its nanotube dispersion was expected to be better. However, AFM images of the cup horn sonicated material showed its dispersion to be poorer. We ascribe the worse separation evident in Table 1 for the cup horn sonicated material to this poorer nanotube dispersion. Subsequent experiments have indicated that the problem with cup horn sonication in Triton X-100 is a degradation of this surfactant's effectiveness at elevated temperatures (its cloud point is only 66 °C) and solution heating in the cup sonicator, despite the use of a cold (flowing) water jacket. In an experiment to determine if the process could be repeated, a separated supernatant sample was vacuum filtered, washed with Triton X-100 solution, and redispersed by ultrasonication to again be processed in a second Br-exposed centrifugation. This further separation yielded an enrichment ratio (using SC1) of $R_{sup}/R_{sed} = 1.3$.

For an independent confirmation of the semiconducting nanotube enrichment in the Br-treated supernatant versus the corresponding sediment, four probe resistance measurements were performed as a function of temperature on films of the supernatant and their corresponding sediment for both a

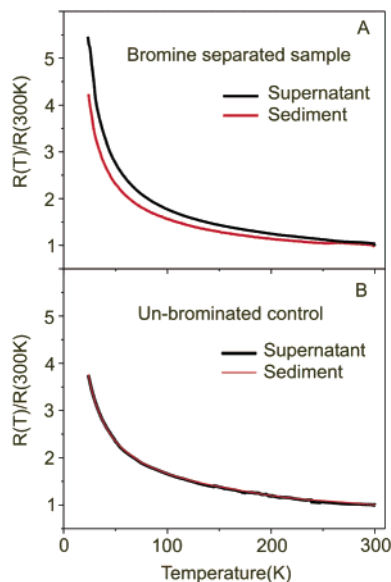


Figure 3. (A) Four-probe temperature-dependent resistance measurements on films formed from a bromine-separated supernatant and sediment. (B) Corresponding measurements for an un-brominated control sample. (Films de-dope as above prior to measurement.)

bromine-separated sample and an un-brominated control sample. The resistance for such films typically exhibits variable-range hopping-like increasing resistance with decreasing temperature ascribed to thermally dependent phonon-assisted hopping at the tube–tube contacts.¹⁶ Such behavior is especially pronounced for cut nanotubes where the tube–tube overlap is smaller than for longer nanotubes. Parts A and B of Figure 3 show the temperature-dependent resistance (normalized to the 300 K resistance) of the separated and control films, respectively. Consistent with our expectations, the semiconducting nanotube-enriched sample shows an overall greater resistance and stronger temperature dependence compared to the metallic nanotube-enriched sample.

Three other methods of metallic/semiconducting nanotube separation have recently been reported.^{17–19} Further work is needed to assess the relative merits of these distinct methods as well as the various techniques used for the assay of the separation quality. Given this progress, along with recently reported methods for length-sorting nanotubes,^{15,20,21} we look forward to the rapidly approaching day when nanotube-based supramolecular assembly experiments *begin* by ordering from a catalog nanotubes of the desired transport classification (metallic or semiconducting) of the desired length, as required for the particular experiment or device function.

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Supporting Information Available: Experimental details, method for the production of uniform transparent

nanotube films, doping–de-doping data, and justification for the analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added in Proof: Further experiments using sodium duodecyl sulfate as the surfactant have not resulted in metallic/semiconducting nanotube separation and moreover provide further evidence (as is suggested above) that the separation mechanism involves the bromine induced destabilization of the Triton X-100 surfactant shell, with greater specificity for the metallic nanotubes.

Note Added after ASAP Posting: The second author's name in reference 19 has been corrected. This paper was originally posted ASAP on 8/20/03. The corrected version was posted on 9/02/03.

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