

Enrichment of Single Chirality Carbon Nanotubes

Ming Zheng* and Ellen D. Semke

DuPont Central Research and Development, Wilmington, Delaware 19880

Received March 6, 2007; E-mail: ming.zheng@usa.dupont.com

Single-walled carbon nanotubes (SWNTs) are a family of one-dimensional tubular molecular structures with unique physical and chemical properties. Conceptually, they are hollow cylinders formed by rolling up a graphene sheet made up of hexagonally bonded sp^2 carbon atoms. The direction and magnitude of a roll-up vector prescribe the chirality and diameter, respectively, of the resulting tube. These geometric parameters in turn determine the tube's electronic band structure.¹ Powerful spectroscopy techniques have been developed to measure geometric and electronic band structures of SWNTs.^{2,3} Tremendous progress has also been made in SWNT synthesis. However, making SWNTs of defined structures still remains to be a major challenge in the fundamental studies and applications of SWNTs. Physically separating different SWNT structures is thus a fascinating scientific problem with technological importance. The separation problem has drawn considerable attention over the past few years. Many separation mechanisms have been devised and various degrees of separation demonstrated,^{4–10} yet there is still a long way to the ultimate goal of total fractionation of a given nanotube mixture into its single chirality components.

We have been developing a separation approach based on DNA-wrapped carbon nanotubes.^{4,5,11,12} Helical wrapping by any single-stranded DNA sequences effectively disperses SWNTs into aqueous phase.⁴ A particular sequence, polyGT, self-assembles onto SWNT to form a regular structure, allowing structural-based sorting of SWNTs by conventional ion-exchange chromatography (IEX).⁵ A major factor that limits separation resolution in our approach, and probably also in many other physical separation approaches, is the broad tube length distribution. Ultrasonically dispersed CNTs are randomly cut during the process, resulting in tubes ranging from 50 to 1000 nm in length. To the first order of approximation, the electronic structure of a SWNT is not dependent on its length. However, length becomes a relevant factor when tubes undergo differential movement driven by an external field or flow pressure during a separation process. A broad length distribution inevitably reduces separation resolution. To address this issue, we have developed a very effective length sorting method based on size-exclusion chromatography (SEC).¹² Here, we report a much improved IEX separation of small diameter SWNTs achieved by conducting SEC separation first to narrow length distribution. This combination allows us to obtain a few single chirality enriched SWNTs and to reveal some new spectroscopic features associated with these tubes.

The SWNT dispersion and separation in this work followed previous published procedure,^{4,5} with some changes outlined below. For dispersion, 5 mg CoMoCAT tubes (Southwest Nanotechnologies, Norman, OK) was ultrasonically dispersed with 5 mg of (GT)₃₀ in 1 mL of buffer solution of 2x SSC (0.3 M NaCl, 0.03 M sodium citrate)/0.5 mM EDTA/pH 7. The same buffer was also used for elution in both SEC and IEX separations. After centrifugation to remove bundled and nonsoluble materials, the entire dispersion solution was fractionated by two SEC columns in series (21.2 mm

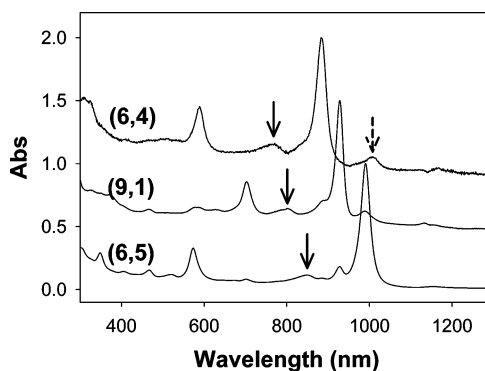


Figure 1. Optical absorption spectra of three single chirality enriched SWNT species. For sample preparation, three fractions from an IEX run were exchanged into D_2O and concentrated by 5-fold for the (6,4) and (9,1) fractions. Spectra from the three samples were taken, rescaled and off-set vertically for easy comparison.

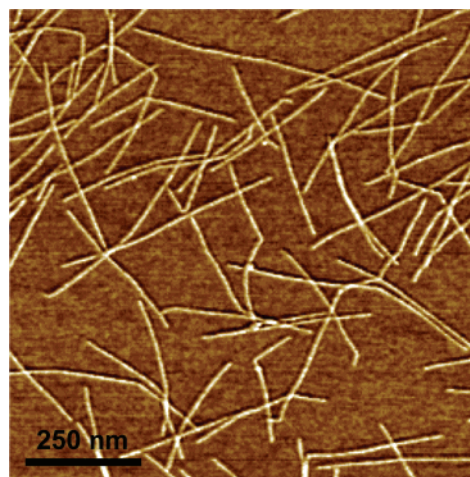
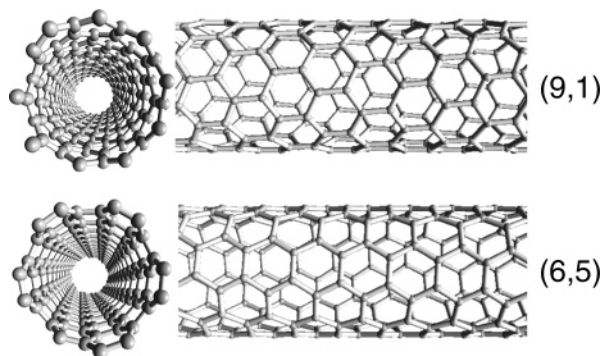


Figure 2. AFM phase image of a (6,5) fraction on mica. AFM sample preparation is described in ref 4.

$\times 250$ nm, 2000 and 1000 Å pore size, Sepax, Newark, DE). A 5 mL SEC fraction was then fractionated through an IEX column (Biochrom, Terre Haute, IN) with a 0–1 M sodium benzoate salt gradient.

The elution of semiconducting tubes in IEX follows the order of (6,4), (9,1), (6,5), (8,3), and (7,5) as the elution salt concentration increases. Figure 1 shows optical absorption spectra of fractions that are enriched in (6,4), (9,1), and (6,5), respectively. Figure 2 illustrates the purity and length distribution of a representative fraction. Spectral assignment is based on Bachilo et al.² The (6,5) tubes represent the most abundant species in the CoMoCAT material. We have previously reported the purification of (6,5) tubes.¹¹ This material has been studied extensively and has yielded valuable information about exciton–phonon interaction¹³ and optical activities relating to the handedness of SWNTs.¹⁴ The current (6,5) spectrum not only shows E_{11} (991 nm) and E_{22} (574 nm) transitions,

Scheme 1. Structure Comparison of (9,1) and (6,5) Semiconducting Tubes with Same Diameter but Different Chirality



but also unveils for the first time E_{33} transition at 348 nm. The (9,1) tubes are identical to (6,5) in diameter (0.757 nm) but have different chirality (Scheme 1). Their E_{11} and E_{22} are at 928 and 703 nm, respectively, slightly red-shifted from the values (912 nm, 691 nm) obtained by fluorescence measurement for SDS-suspended (9,1) tubes.² The (6,4) fraction has two prominent peaks at 883 and 589 nm, corresponding to the E_{11} and E_{22} transitions, respectively. These are again red-shifted from the reported values (873 and 578 nm) for SDS-suspended (6,4) tubes.²

Figure 1 also reveals some other interesting spectral features. There is a clear asymmetry in the E_{11} peak line shape in each spectrum, with longer tail extending on the shorter wavelength side. The (9,1) E_{11} peak line width (full width at half-maximum) (17.7 meV) is 24% narrower than that of (6,5) and (6,4) (23.4 meV for both type of tubes). In each spectrum, there is a broad feature (indicated by a solid arrow) accompanying the E_{11} , at a position 0.20–0.21 eV higher in energy than the E_{11} . This feature is most clear for the smaller diameter (6,4) species, which also exhibits a lower energy feature (0.175 eV below the E_{11} , indicated by a dashed arrow). We speculate that these features are manifestation of the phonon–exciton interactions.

The resolution improvement as the result of the length control is further highlighted by the large difference in abundance of the three tubes in the starting CoMoCAT material. Spectroscopic measurements of relative tube abundance in CoMoCAT have been reported.^{15,16} Assuming equal optical extinction coefficient, we estimate that (6,4) and (9,1) are less than (6,5) by 100 and 20 times, respectively. Our estimate for (6,4) might be lower than its real abundance in the starting material, for we have observed that prolonged sonication reduces its separation yield. We have also noticed that SEC fractions with shorter tubes contain more (6,4) tubes. Both observations suggest structural instability of smaller diameter tubes under sonication. The much lower abundance of (9,1) than its same-diameter counterpart (6,5) is also observed in

SWNTs made with HIPCO² and alcohol CVD¹⁷ processes, implying a role for chirality in tube formation.

In summary, we have shown resolution enhancement by length control in our DNA-base SWNT separation process. Chiral separation is clearly demonstrated by the purification of (9,1) from the same diameter but different chirality and much more abundant (6,5) species. Such exquisite separation must be the result of chirality-dependent interactions between DNA-wrapped SWNTs and the IEX resin. These interactions could be electrostatic in nature, arising from chirality-dependent DNA-wrapping, and/or electrodynamic in nature, originating from chirality-dependent van der Waals forces. Indeed, the requirement of chaotropic salts for the IEX elution suggests that van der Waals interactions play a role.¹⁸ Our future research aims at quantitative understanding of all these interactions and rational design of IEX resins in order to further improve both resolution and recovery of the DNA-based separation process.

Acknowledgment. We would like to thank Mr. Robert S. Mclean for the AFM measurement.

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JA071577K