Dielectrophoresis Field Flow Fractionation of Single-Walled Carbon Nanotubes

Haiqing Peng, Noe T. Alvarez, Carter Kittrell, Robert H. Hauge, and Howard K. Schmidt*

Carbon Nanotechnology Laboratory, Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, 6100 South Main Street, Houston, Texas 77005

Received April 7, 2006; E-mail: hks@rice.edu

Separation of Single-Wall Carbon Nanotubes (SWNTs) by size, type, and length has become an active field of research; SWNTs with specific and uniform properties are not only of fundamental interest but also needed for applications in electronics, biomedicine, and other areas. As-produced SWNTs from the HiPco process in the Carbon Nanotechnology Laboratory (CNL) at Rice University contain more than 50 individual (n, m) types.[1] Nominally, two-thirds of the SWNTs are direct band gap semiconductors, and one-third are metallic. Using band gap fluorescence, Weisman and co-workers determined that the diameters of semiconductive HiPco SWNTs range from 0.7 to 1.3 nm.[1] HiPco SWNTs, used in this study, have a mean diameter ranging from 1.01 to 1.15 nm and an average length ranging from 0.85 to 1.25 μm.[2]

Length separation has recently been demonstrated by using Size Exclusion Chromatography (SEC) and a two-phase liquid–liquid extraction process.[3,4] A variety of approaches have been employed for type separation or enrichment, including dielectrophoresis,[5–9] selective elimination,[10] covalent functionalization,[11,12] selective adsorption,[13–15] and ion exchange chromatography.[16] Electrophoretic means have also been developed to purify or separate SWNTs.[17,18] In an electrophoresis length separation study, Strano and co-workers found longer SWNTs had smaller average diameters compared with the diameters of shorter nanotubes.[18] Krupke and co-workers first reported type separation of SWNTs with dielectrophoresis in 2003[5] and subsequently anticipated type and length separation using dielectrophoresis.[6]

In this communication, we report type separation and diameter enrichment of semiconducting SWNTs with Dielectrophoresis Field Flow Fractionation (DEP–FFF).[19] The fractions could be collected for further analysis or application. All experiments were performed with a DFF-30 system manufactured by Adeptas, Inc. (Houston, Texas). The length, width, and height of the dielectrophoresis chamber are 28, 2.5, and 0.025 cm, respectively. The bottom of the chamber is fitted with an interdigitated array of gold electrodes (28 cm × 2.8 cm) on a polyimide substrate that are alternately grounded or driven with an AC signal. Each element is 50 μm wide and 2 μm thick; the interelectrode spacing is 50 μm. For the present work, we slightly modified the DFF-30 by adding a continuous planar electrode to the top of the separation chamber and providing thereon a small voltage ($\sim$ −0.5 V) with respect to the grounded element of the interdigitated DEP electrodes on the bottom of the chamber. This drives the SWNT with a slight electrophoretic drift, mimicking gravity sedimentation for the neutrally buoyant surfactant-coated SWNT.

A typical experiment is described in the following: a syringe pump (Harvard PHD 2000) constantly pumps the mobile phase, 1% SDBS solution, into the chamber. The DEP frequency and voltage were set to 1 MHz and 10 V peak-to-peak, respectively; 150 μL of SWNT in 1% SDBS was injected into the mobile phase through a septum near the entrance of the chamber. The sample
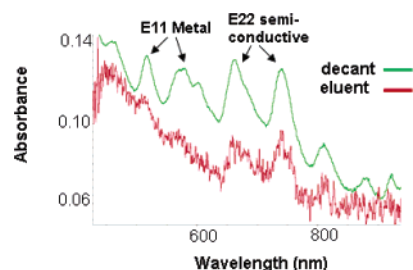
Figure 1. Visible absorption spectra collected from starting SWNTs' supernatant solution and the eluent (the scale of the spectrum from SWNTs' decant was minimized by a factor of 3 for comparison).
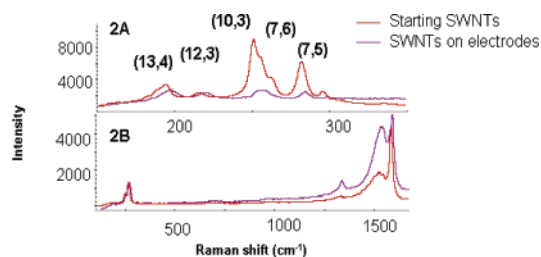

Figure 2. Raman spectra collected with a 633 nm (A) and a 514 nm (B) laser excitation.

decant solution preparation procedure was described previously elsewhere,[20] and the SWNT concentration of the decant is 10 mg/L. The flow rate of the mobile phase was set to 0.02 cm³/min. The eluent from the DEP–FFF system was directed into a Nano-Spectralyzer (Applied NanoFluorescence, LLC, Houston, Texas) fitted with a flow-cell for continuous collection of simultaneous fluorescence and visible absorption spectra.

In this study, we collected the visible absorption spectrum of the eluent online to study the relative intensity between the first van Hove transition of metallic SWNTs, from 440 to 645 nm wavelengths, and the second van Hove transition of semiconductive SWNTs, from 640 to 800 nm wavelengths.[11] Figure 1 shows a visible absorption spectrum collected in an experiment when the fluorescence emission intensity peaked and a spectrum collected from the starting decant solution. By integrating the peak areas assigned to metallic and semiconductive SWNTs, we found that, in the eluent, the metallic tubes were approximately 70% depleted compared to the starting SWNT solution. The noise level rose due to the dilution effect from the mobile phase.

We have also collected Raman spectra (Renishaw 1000 micro-Raman) from the SWNT deposited on the electrodes after the experiment was finished to compare to the Raman spectrum collected from the starting material, which was made by air-drying the SWNT in 1% SDBS solution. Figure 2A shows the Radial Breathing Mode (RBM) region (150–350 cm⁻¹) of the Raman spectra collected from the dried SWNT from the starting material
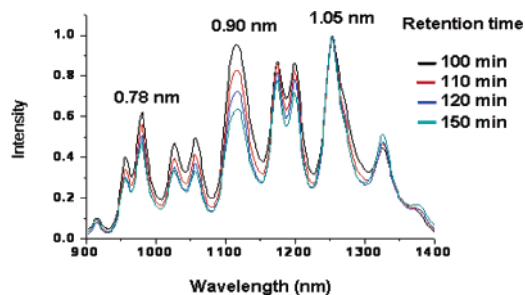
Figure 3. Fluorescence spectra collected from eluent at different retention times with a 785 nm laser excitation. The labels on the top of the peaks are the diameters of the SWNTs.

and the SWNT deposited on the electrodes using a 633 nm laser excitation. The (n, m) assignments labeled in Figure 2A are from refs 8 and 11. While quantifying metallic enrichment from Raman analysis of solid SWNT samples is problematic,[12,21] Figure 2A clearly shows qualitatively that the content of semiconductive SWNTs on the electrodes is much less than that of the starting SWNT, consistent with prior work.[5,8] Figure 2B shows Raman spectra collected from starting material and SWNTs deposited on the electrodes, respectively, using a 514 nm laser for excitation. There is a significant enhancement of the G^- band centered at 1532 cm^{-1} relative to the G^+ band centered at 1592 cm^{-1} in the spectrum collected from SWNTs deposited on the electrodes. The enhanced G^- band, known as a broad Breit−Wigner−Fano line,[22] is strong evidence that, in the SWNT deposited on the electrodes, metallic species are dominating. However, we cannot rule out that, besides being deposited on the electrodes, some metallic SWNTs remained in solution, retarded and diluted into the tail of the eluent exiting in the DEP chamber.

In Krupke's previous work,[6] metallic and semiconducting SWNTs were separated due to different sign of the DEP force above the "crossover" frequency of approximately 3 MHz. We believe the effects observed under our experimental conditions arise from differences in the magnitude of the DEP force experienced by the various SWNT types. We utilized in-solution band gap fluorescence to study the correlation between the band gap of semiconducting SWNTs and retention time in the DEP system. Figure 3 shows a series of fluorescence spectra obtained at various retention times during the experiment.

Typically, we observed semiconducting SWNTs eluting after 90−160 min retention time. The fluorescence emission was obtained with a 785 nm laser as the excitation; the spectra were normalized to the peak centered at 1252 nm. The fluorescence emission peaks (E_{11}) at lower wavelength are assigned to emission from larger band gap SWNTs.[1] The band gap of semiconducting SWNTs, which is inversely proportional to diameter,[23] determines its dielectric constant. From Figure 3, we observed the enrichment trend: the signal from smaller tubes became weaker with increasing retention time, which indicates that they are selectively depleted or retained during the early stage of the dielectrophoresis experiment. Variation in dielectric constant will lead to differences in dielectrophoretic force and, therefore, control the vertical height of semiconducting SWNTs in the flow. In the laminar flow in this system, the velocity of particles is position dependent vertically, that is, the middle of

the stream flows faster than the top and bottom layers next to the electrodes. We believe that, under our experiment conditions, the velocity difference of semiconducting SWNTs with different diameters originates from their band gap difference and results in the diameter enrichment shown in Figure 3.

Using Dielectrophoresis Field Flow Fractionation, we not only separated metallic and semiconducting SWNTs but also observed the enrichment of semiconducting SWNTs with various diameters and band gaps.

Supporting Information Available: Complete information for the design of the dielectrophoresis chamber and complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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