

Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments

Xiaoyou Xu,[†] Robert Ray,[†] Yunlong Gu,[†] Harry J. Ploehn,[†] Latha Gearheart,[‡] Kyle Raker,[†] and Walter A. Scrivens^{*†}

Department of Chemistry & Biochemistry, Department of Chemical Engineering and USC Nanocenter, University of South Carolina, 631 Sumter Street, South Carolina 29208, and Department of Chemistry, Presbyterian College, 503 South Broad Street, Clinton, South Carolina 29325

Received March 18, 2004; Revised Manuscript Received August 10, 2004; E-mail: scrivens@mail.chem.sc.edu

This report describes a preparative electrophoretic method for the purification of single-walled carbon nanotubes (SWNTs) derived from arc-discharge soot. During the course of this investigation, two new classes of nanomaterials were isolated from the crude soot. One of these components is short, tubular carbon, and the other component is a mixture of fluorescent nanoparticles derived from the SWNTs.

Crude nanotube soot contains a variety of impurities that vary by the method of synthesis. Compared with the soot from chemical vapor deposition^{1,2} or laser ablation,³ arc-discharge SWNTs are very impure.^{4,5} The unique existence of graphitic sheets in arc-discharged soot makes the purification of this material particularly problematic because the approach of purifying SWNTs through oxidative processes⁶ is ineffective because of the greater oxidative stability of graphitic sheets compared to nanotubes. Microfiltration also becomes inapplicable because particles in the arc soot rapidly block the pores of filtration membranes.⁷

There have been reports on the migration of SWNTs to electrodes^{8,9} and the separation of SDS-coated nanotubes through capillary electrophoresis,¹⁰ but currently no preparative electrophoretic methods for purifying SWNTs exist.¹¹ We now report on the separation of SWNTs from other species in arc soot with preparative electrophoresis in agarose gel and glass bead matrices.

To electrophoretically purify nanotubes, stable aqueous suspensions of charged tubes must be made. Arc-discharged soot, either produced in our lab^{12,13} or purchased from MER,¹⁴ was oxidized with 3.3 N HNO₃ and then extracted with basic water (NaOH, pH 8.4).¹⁵ Almost all SWNTs, as well as other soluble impurities, are extracted into the suspension (30 wt % of soot), which we called crude SWNTs suspension. It should be noted that these suspensions are stable for months at 0.2 wt % without the need for surfactants or sonication; such stable, surfactant-free suspension has been recently discussed in the literature.¹⁶ The sediment that remains after these water washes was analyzed by TEM and consists mainly of graphitic sheets and larger carbonaceous aggregates (8 wt % of soot).

For comparison, nanotube soot produced by two other methods was also processed and analyzed. Laser soot gives more crude SWNTs suspension (40 wt % of soot) and also more sediment (18 wt % of soot). HiPco soot gives much less crude SWNT suspension (10 wt % of soot) and much larger amount of sediment (25 wt % of soot). However, TEM verifies that the majority of the sediment from both laser and HiPco soot is SWNTs, implying that these tubes are more difficult to suspend than tubes produced by the arc-discharge method.

Initially, traditional gel electrophoresis of the suspension was done through a small 1% agarose gel slab.¹⁵ To our surprise, the

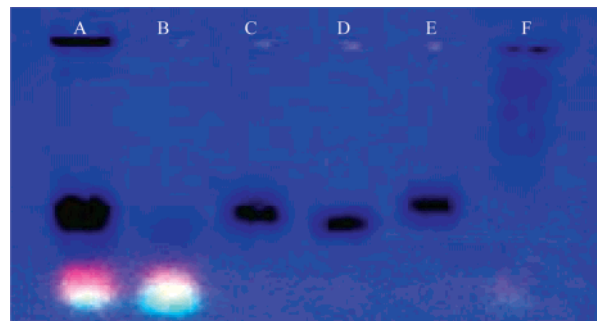


Figure 1. Electrophoretic profile in 1% agarose gel under 365-nm UV light. (A) crude SWNTs suspension. (B) Fluorescent carbon. (C) Short tubular carbon. (D) and (E) Further separation of (C). (F) Cut SWNTs.

suspension separated into three classes of materials: long nanotubes that did not penetrate the gel matrix, a slow moving dark band, which was later determined to be short, irregular, tubular material, and a fast moving band of highly fluorescent material (Figure 1, well A). Ultimately, to obtain multi-milligram quantities of these materials for analysis, agarose gel and glass bead electrophoresis columns were used.¹⁵

The fluorescent material (Figure 1, well B) separated into a number of components that fluoresced different colors under 365-nm UV light (Figure 2A). The tubular material (Figure 1, well C) was further fractionated into materials with different electrophoretic mobilities (Figure 1, wells D and E), indicating that this fraction was also a mixture.

The origin and nature of these two bands was then probed. Purified tubes, free from fluorescent or tubule material, were subjected to the same mild acid workup conditions used to purify the crude soot; no fluorescent or tubular materials were formed. The tubes were then subjected to harsh oxidative chopping conditions using known procedures¹⁷ for cutting nanotubes (Figure 2D), and the resulting material was run on the gel (Figure 1, well F). The chopped tubes could now penetrate the gel, and a small amount of fluorescent material was produced in the process. Interestingly, no dark tubular material was produced during the chopping process.

Quantitatively, all of the fluorescent components make up only 10% of the mass of the SWNT suspension. These materials fluoresced green-blue, yellow, and orange, in order of elution (Figure 2A). The relative sizes of these materials were roughly estimated by partitioning them with Centricon filtration devices and were found to be 3000–10 000, 10 000–30 000, and 30 000–50 000 nominal molecular weight limit (NMWL), respectively. The quantum yield of the yellow fluorescent material was measured at 366 nm excitation and found to be 0.016. Each of the three fluorescent bands was purified by dialysis to afford salt-free material. Initial characterization of these fluorescent materials by

[†] University of South Carolina.

[‡] Presbyterian College.

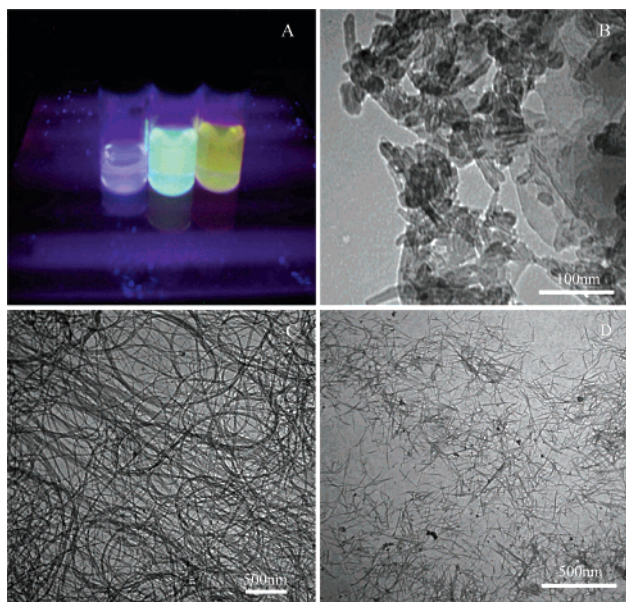


Figure 2. Picture of different fractions of fluorescent carbon under 365 nm (A) and TEM images of short tubule carbon (B), purified SWNTs (C), and chopped SWNTs (D).

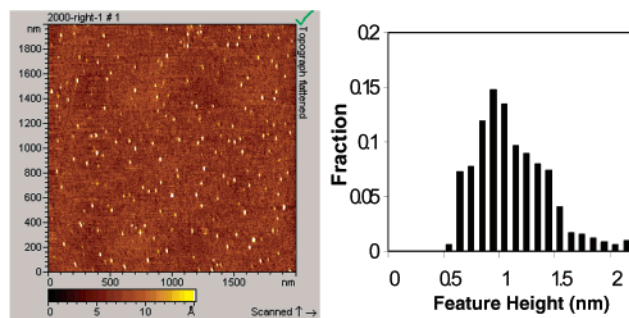


Figure 3. A typical AFM topography image (left) for the orange fluorescent fraction (200-fold dilution of dialyzed aqueous solution) deposited onto mica. Feature height distribution (right) for this sample based on data from three images and 521 distinct features.

^1H NMR and ES-MS was inconclusive; FT-IR indicated the presence of carboxyl functionality, and EDAX analysis showed that the fluorescent materials contain no metal residue from the catalysts used in the nanotube synthesis. Elemental analysis showed C, 53.93%; H, 2.56%; N, 1.20%; and O, 40.33%.

AFM was used to quantify the size of any nanoparticles found in the orange subfraction of the fluorescent material.¹⁵ A typical AFM topography image (Figure 3) clearly shows a uniform distribution of similar features. The observed lateral feature diameter, 18.0 ± 0.4 nm (95% confidence interval), is consistent with the estimated probe tip radius of curvature. This observation indicates that the orange subfraction contains nanoparticles with maximal lateral dimensions less than 18 nm. From the feature height distribution (Figure 3, right), the mean and median feature heights are 1.02 ± 0.03 and 0.96 nm, respectively, with a standard deviation of 0.30 nm. About 89% of the features have maximal heights between 0.6 and 1.4 nm. These statistics show that the nanoparticles have a narrow distribution of vertical sizes centered at about 1 nm. This size range is the same as that expected for the diameter of

SWNTs, but is considerably greater than that expected for nontubular, polyaromatic carbon fragments.

The tubular material made up 37 wt % of the mass of SWNT suspension. FT-IR and EDAX showed that the material is carboxylated carbonaceous material containing no metals. TEM analysis of this material shows short tubular structures with capped tips that have a layer of material around the hollow center (Figure 2B). Despite the structural differences, this material gives Raman spectra similar to carbon nanohorns.^{15,18}

Finally, the highly purified tubes, free from fluorescent and tubule material, made up only 53% of the SWNT suspension.

We have demonstrated the purification of long and cut SWNTs through preparative electrophoresis. We anticipate these methods will be useful for the analysis and purification of other water-stable nanoparticles, and the isolated fluorescent carbon and short tubular carbon species promise to be interesting nanomaterials in their own right.

Acknowledgment. We are grateful to Steve Kistler and Jim Sodez at USC for helping us with the electrophoresis. We are also grateful to Jim Tour and Chris Dyke at Rice University for providing samples of HiPco and laser soot as well as doing the Raman spectroscopy of the nanotube materials. This work was supported by Grant NCC5-174 and NAG-1-03017 (NASA) and CTS-0103135 (NSF).

Supporting Information Available: Diagram of the electrophoresis apparatus, procedures, and spectra reported herein (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Hafner, J. F.; Bronikowski, M. J.; Azami, B. R.; Nikolaev, P.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, *296*, 195–202.
- Kong, J.; Soh, H.; Cassell, A.; Quate, C. F.; Dai, H. *Nature* **1998**, *395*, 878–881.
- Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C. B.; Rodriguez-Macias, F. J.; Boul, P. J.; Lu, A. H.; Heymann, D.; Colbert, D. T.; Lee, R. S.; Fischer, J. E.; Rao, A. M.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A* **1998**, *67*, 29–37.
- Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603–605.
- Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Delachapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, *388*, 756–758.
- Dillon, A. C.; Gennett, T.; Jones, K. M.; Alleman, J. L.; Parilla, P. A.; Heben, M. J. *Adv. Mater.* **1999**, *11*, 1354–1358.
- Shelimov, K. B.; Esenaliev, R. O.; Rinzler, A. G.; Huffman, C. B.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, *282*, 429–434.
- Gao, B.; Yue, G. Z.; Qiu, Q.; Cheng, Y.; Shimoda, H.; Fleming, L.; Zhou, O. *Adv. Mater.* **2001**, *23*, 1770–1773.
- Yamamoto, K.; Akita, S.; Nakayama, Y. *J. Phys. D.: Appl. Phys.* **1998**, *31*, 34–36.
- Doorn, S. K.; Fields, R. E., III; Hu, H.; Hamon, M. A.; Haddon, R. C.; Selegue, J. P.; Majidi, V. *J. Am. Chem. Soc.* **2002**, *124*, 3169–3174.
- O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265–271.
- Scrivens, W. A.; Tour, J. M. *J. Org. Chem.* **1992**, *57*, 6932–6936.
- Cassell, A. M.; Scrivens, W. A.; Tour, J. M. *Chem. Mater.* **1996**, *8*, 1545–1549.
- Materials and Electrochemical Research Corporation Home Page. <http://www.mercorp.com>, accessed August 2004.
- Details found in Supporting Information
- Huang, H.; Kajiura, H.; Yamada, A.; Ata, M. *Chem. Phys. Lett.* **2002**, *356*, 567–572.
- Liu, J.; Rinzler, A.; Dai, H.; Hafner, J.; Bradley, R.; Boul, P.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C.; Rodriguez-Macias, F.; Shon, Y.; Lee, T.; Colbert, D.; Smalley, R. *Science* **1998**, *280*, 1253–1256.
- Iijima, S.; Yudasaka, M.; Yamada, R.; Bandow, S.; Suenaga, K.; Kokai, F.; Takahashi, K. *Chem. Phys. Lett.* **1999**, *309*, 165–170.

JA040082H