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# *Communications to the Editor*

## Chromatographic Purification of Soluble Single-Walled Carbon Nanotubes (s-SWNTs)

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While the scientific and technological potential of single-walled carbon nanotubes (SWNTs) has attracted considerable attention to this area,[1] progress in the field is currently hampered by the difficulty of preparing sufficient quantities of high-quality materials. Present purification methods rely on filtration, centrifugation, and chromatographic techniques to separate the nanotubes from the residual impurities which usually consist of trace amounts of catalyst, nanoparticles, and amorphous carbon after the as-prepared SWNTs (AP-SWNTs) have been treated with acid or oxidizing reagents.[2−8]

After we discovered a method for the dissolution of short SWNTs (100−300 nm in length[2]), we expected that the dissolved materials would be purified by the dissolution process.[9,10] Although this expectation is partially fulfilled, it is now clear that the dissolution process also takes into solution some of the impurities that are present in the processed SWNTs.

Chromatography is attractive for nanotube purification because of the power of the method and the fact that fullerene purification has relied heavily on this technique. Unlike the fullerenes,[11,12] however, most forms of carbon nanotubes are insoluble in organic solvents. Thus previous chromatographic purifications of nanotubes have relied on size exclusion chromatography of surfactant-stabilized dispersions with water as the mobile phase,[5,6] although there is a report in which poly(phenylacetylene) wrapped MWNTs were passed through a gel permeation chromatography (GPC) column.[7] In the present paper we report the separation of soluble SWNTs from the particulate matter that is solubilized in our nanotube dissolution process.[9,10]

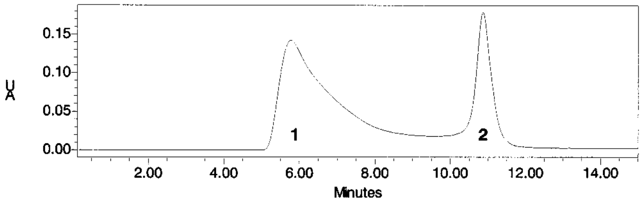

**Figure 1.** The chromatogram obtained with use of a photodiode array detector (PDA, with wavelength detection at 310 nm) on a THF solution of s-SWNTs (Waters 600-996 chromatograph fitted with a Styragel HMW7 column).

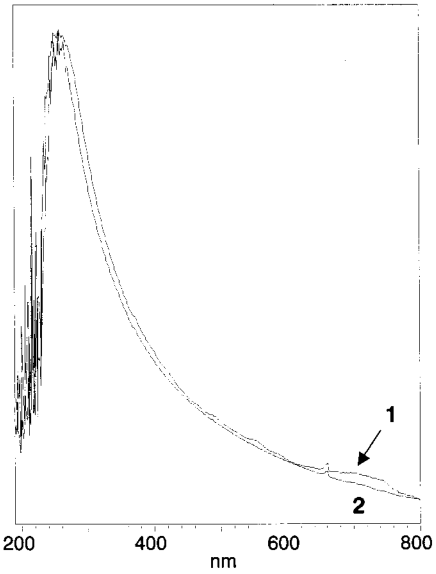

**Figure 2.** UV−visible absorption spectrum obtained from the PDA detector of the eluting components, where 1 and 2 refer to the fraction numbers in Figure 1. The large band at ∼300 nm is common to both fractions, whereas the peak at ∼700 nm is unique to fraction 1.

SWNTs were prepared by a modified electric arc technique; this technique is known to give SWNTs that are about 1.4 nm in diameter (equivalent to the (10,10) SWNT).[13] The initial purification, shortening, and polishing steps followed literature methods.[2,3] The shortened SWNTs were covalently functionalized with octadecylamine to give soluble SWNTs (s-SWNTs), with lengths of about 100−300 nm, and characterized by using previously reported techniques.[9]

Solutions of s-SWNTs were prepared in THF at a concentration of 0.5 mg/mL, and 100 $\mu$L amounts were injected into a Waters 600-996 chromatograph fitted with a Styragel HMW7 column with THF as the mobile phase. The chromatogram (Figure 1, obtained using a photodiode array detector (PDA)) shows the elution of two bands. The first band, which corresponds to the void volume for the column, eluted with a retention time of about 6 min, whereas the second band appeared after 12 min.

As may be seen from the UV−visible spectrum obtained from the PDA of the eluting components (Figure 2), the first fraction

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(1) Yakobson, B. I.; Smalley, R. E. *Am. Sci.* **1997**, *85*, 324−337.

(2) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253−1255.

(3) Rinzler, A. G.; Liu, J.; Dai, H.; Nilolaev, 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.

(4) Dillon, A. C.; Gennett, T.; Jones, K. M.; Alleman, J. L.; Parilla, P. A.; Heben, M. J. *Adv. Mater.* **1999**, *11*, 1354−1358.

(5) Duesberg, G. S.; Blau, W.; Byrne, H. J.; Muster, J.; Burghard, M.; Roth, S. *Synth. Met.* **1999**, *103*, 2484−2485.

(6) Duesberg, G. S.; Muster, J.; Krstic, V.; Burghard, M.; Roth, S. *Appl. Phys. A* **1998**, *67*, 117−119.

(7) Tang, B. Z.; Xu, H. *Macromolecules* **1999**, *32*, 2569−2576.

(8) Holzinger, M.; Hirsch, A.; Bernier, P.; Duesberg, G. S.; Burghard, M. *Appl. Phys. A* **2000**, *70*, 599−602.

(9) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95−98.

(10) Hamon, M. A.; Chen, J.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Adv. Mater.* **1999**, *11*, 834−840.

(11) Kraetschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

(12) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379−3383.

(13) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Lamy de la Chappelle, M.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, *388*, 756−758.

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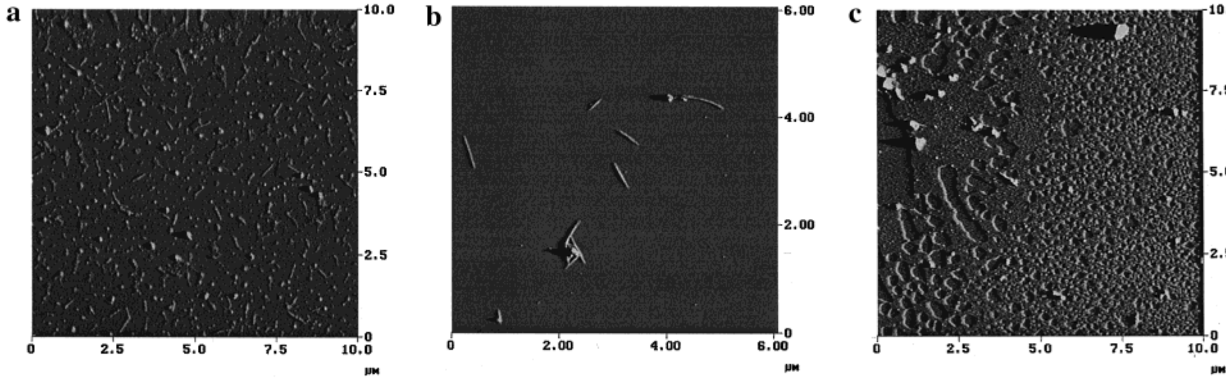

**Figure 3.** AFM images of (a) as-prepared s-SWNT starting material, (b) fraction 1 in Figure 1, and (c) fraction 2 in Figure 1 (Digital Instruments Nanoscope IIIA operating in the tapping mode with samples prepared by evaporation of THF solutions of the components on mica substrates).

(1) contains a broad peak between 600 and 800 nm in addition to the monotonic decrease from the peak at 250 nm[9] seen in both fractions. We assign this peak to the transition between the first pair of singularities in the density of states of the metallic SWNTs with a diameter of about 1.4 nm (~1.7 eV).[14−19] We can also discern features at 550 (2.2 eV) and 490 nm (2.5 eV) in the PDA spectrum of fraction 1, which are seen by other authors in solid and liquid SWNT samples.[17,19]

Further support for this assignment comes from the AFM images shown in Figure 3 which were obtained on a Digital Instruments Nanoscope IIIA operating in the tapping mode with samples prepared by evaporation of THF solutions of the components on mica substrates. Panel a in Figure 3 shows the starting material, whereas panels b and c show the first and second fractions, respectively. Figure 3a is not representative of the whole sample, but has been chosen to show all three components of the sample: (1) SWNTs, (2) nanoparticulate impurities, and (3) finely divided impurities. It is clear from Figure 3b that the first fraction contains the nanotube material, whereas Figure 3c shows that the second fraction contains the nanoparticulate and finely divided impurities.

The near-IR (NIR) of a film cast from a THF solution of the first fraction showed two absorptions centered at 5500 (0.7 eV) and 10000 $cm^{-1}$ (1.3 eV) which are always apparent in our s-SWNTs samples,[9,10] and have been assigned to the transitions between the first and second pairs of singularities in the density of states of the semiconducting SWNTs that are about 1.4 nm in diameter.[14−18] By comparison of the solution absorbances in the NIR, we estimate that about 50% of the s-SWNTs elute from the column in the first fraction. A Raman spectrum of a solution of the first fraction in $CS_2$ showed the characteristic SWNT bands[9,10] at 170 and 1590 $cm^{-1}$ (the NIR and Raman spectra are included in the Supporting Information).

The second fraction does not show the metallic (visible) or semiconducting (NIR) transitions nor does it show the characteristic Raman bands and therefore does not contain SWNTs. The AFM (Figure 3c) shows this sample to contain nanoparticulate and finely divided impurities. Based on these observations and the fact that the TEM is featureless, we tentatively assign the second fraction to amorphous carbon and disordered nanoparticles that have been rendered soluble by our dissolution process.

The present results further establish the usefulness of s-SWNTs,[9,10,19−22] and bring a new level of rigor to SWNT purification. The extension of these techniques offers the promise of SWNTs sorted by length, diameter, and chirality.

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**Supporting Information Available:** Figures showing the NIR and Raman spectra of Fractions 1 and 2 and the as-prepared s-SWNT material (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Wildoer, J. W. G.; Venema, L. C.; Rinzler, A. G.; Smalley, R. E.; Dekker, C. *Nature* **1998**, *391*, 59−61.

(15) Odom, T. W.; Huang, J.-L.; Kim, P.; Lieber, C. M. *Nature* **1998**, *391*, 62−64.

(16) Pichler, T.; Knupfer, M.; Golden, M. S.; Fink, J.; Rinzler, A.; Smalley, R. E. *Phys. Rev. Lett.* **1998**, *80*, 4729−4732.

(17) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synth. Met.* **1999**, *103*, 2555−2558.

(18) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435−445.

(19) Boul, P. J.; Liu, J.; Mickelson, E. T.; Huffman, C. B.; Ericson, L. M.; Chiang, I. W.; Smith, K. A.; Colbert, D. T.; Hauge, R. H.; Margrave, J. L.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *310*, 367−372.

(20) Mickelson, E. T.; Chiang, I. W.; Zimmerman, J. L.; Boul, P. J.; Lozano, J.; Liu, J.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem. B* **1999**, *103*, 4318−4322.

(21) Shi, Z.; Lian, Y.; Zhou, X.; Gu, Z.; Zhang, Y.; Iijima, S.; Gong, Q.; Li, H.; Zhang, S.-L. *Chem. Commun.* **2000**, 461−462.

(22) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879−5880.