Chromatographic Purification and Properties of Soluble Single-Walled Carbon Nanotubes

Bin Zhao, Hui Hu, Sandip Niyogi, Mikhail E. Itkis, Mark A. Hamon, Paragranjita Bhowmik, Mark S. Meier, and Robert C. Haddon*

Contribution from the Departments of Chemistry and Chemical and Environmental Engineering, University of California, Riverside, California 92521-0403, and Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received February 22, 2001

Abstract: We report an improved chromatographic purification of soluble single-walled carbon nanotubes (s-SWNTs) using gel permeation chromatography. Three fractions are separated by gel permeation chromatography, and the first fraction contains 74% of the s-SWNTs as detected by atomic force microscopy and UV and near-infrared spectroscopy.

Introduction

Since the discovery of carbon nanotubes in the early 1990s,[1] research has focused on their extraordinary mechanical, thermal, and electronic properties. The purification of this material still presents a significant challenge. There are many reports on the purification of single-walled carbon nanotubes (SWNTs), and most of them involve filtration, centrifugation, or chromatography.[2−8] Recently, we have reported the purification of soluble-SWNTs (s-SWNTs) by high-performance liquid chromatography (HPLC) with a Styragel HMW7 column, which yielded two fractions; the yield of s-SWNTs in this purification is about 50%.[9] In this paper, we report an improved purification of s-SWNTs by HPLC with a PLgel MIXED-A column. In addition, we provide the first information on the electronic properties of our purified s-SWNTs.

A comparison of the characteristics of the Styragel HMW7 and PLgel MIXED-A columns is shown in Table 1. Three fractions are obtained with the new column in which the first fraction contains the s-SWNTs that are recovered with improved purity and yield as compared with our previously published work.[9]

Table 1. Comparison of the Styragel HMW7 Column and PLgel MIXED-A Column

	styragel HMW7	PLgel MIXED-A
stationary phase	polystyrene divinyl benzene resin	polystyrene divinyl benzene resin
column dimens (mm)	300 × 7.8	300 × 7.5
effective MW range	500 000−(1 × 10^8)	2000−(4 × 10^7)
particle size (μm)	20	15−20
flow rates (mL/min)	1.0	0.5
fraction 1 compn	s-SWNTs	s-SWNTs
retention time (min)	6	8
fraction 2 compn	nanoparticulates and amorphous carbon with trace amount of s-SWNTs	nanoparticulates with trace amount of s-SWNTs
retention time (min)	12	9
fraction 3 compn		amorphous carbon
retention time (min)		19

Results and Discussion

The chromatogram of the s-SWNTs in tetrahydrofuran (THF) (Figure 1) shows the elution of three bands. The first band eluted with a retention time of about 8 min, and the second band followed immediately. The third band appeared around 19 min. The atomic force microscopy (AFM) image of the starting material (Figure 2a) shows s-SWNTs together with impurities. Fraction 1 (Figure 2b) contains s-SWNTs of high purity.

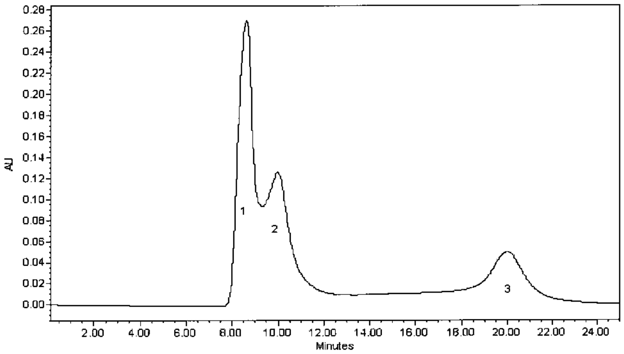

Figure 1. Chromatogram obtained by use of a PDA (with wavelength detection at 350 nm) on a THF solution of s-SWNTs (Waters 600-996 chromatograph fitted with a PLgel MIXED-A column).

---

(1) Iijima, S. *Nature* (*London*) **1991**, *354*, 56−58.

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

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

(4) 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.

(5) 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.

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

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

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

(9) Niyogi, S.; Hu, H.; Hamon, M. A.; Bhowmik, P.; Zhao, B.; Rozenzhak, S. M.; Chen, J.; Itkis, M. E.; Meier, M. S.; Haddon, R. C. *J. Am. Chem. Soc.* **2001**, *123*, 733−734.

10.1021/ja010488j CCC: $20.00

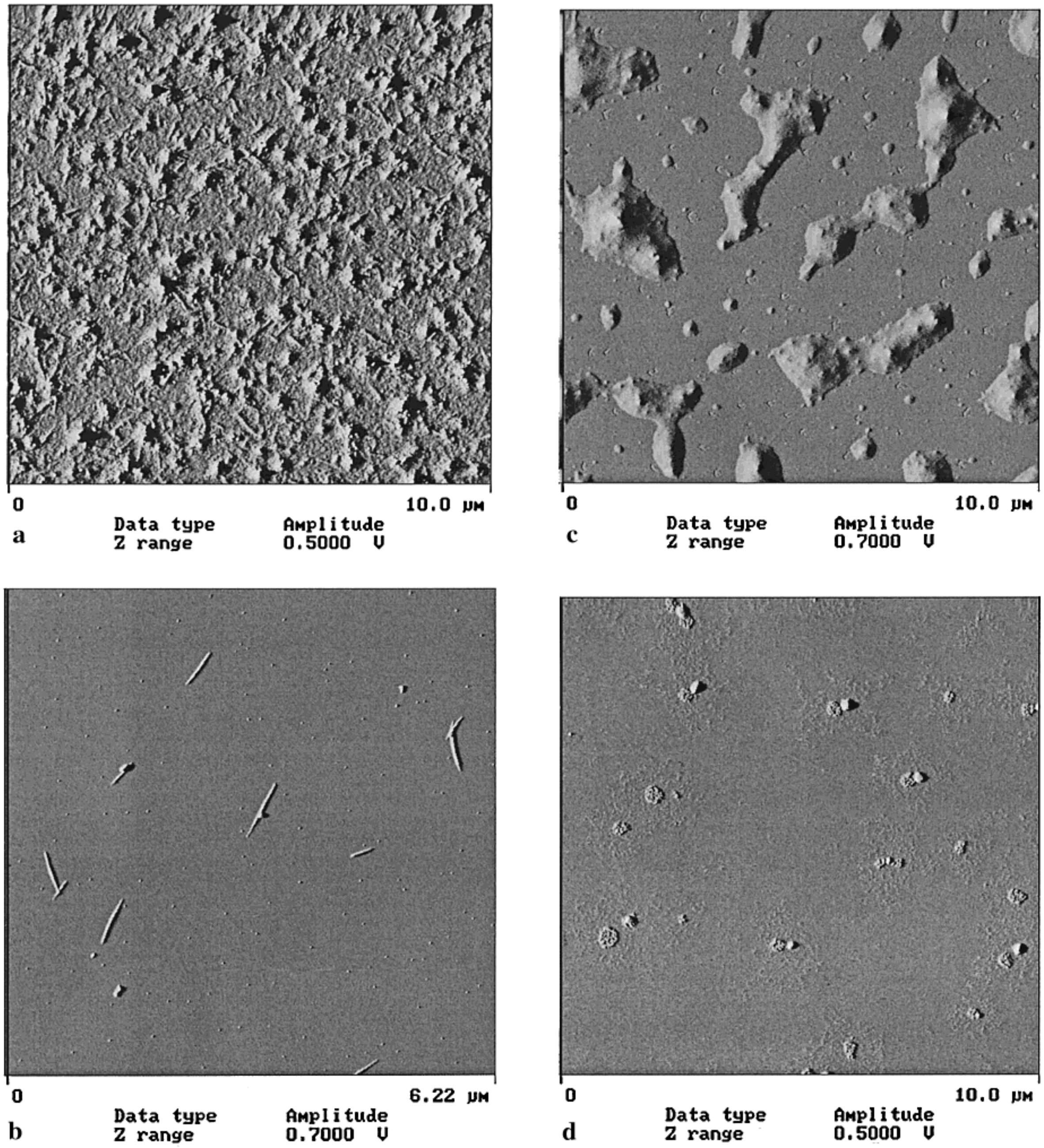

Figure 2. (a) s-SWNT starting material, (b) fraction 1, (c) fraction 2, and (d) fraction 3 imaged by AFM (Digital Instruments nanoscope IIIA, using tapping mode) on the fractions separated by a PLgel MIXED-A column.

Fraction 2 (Figure 2c) shows large globular impurities that are tentatively assigned to functionalized nanoparticulates, while the impurities in fraction 3 (Figure 2d) seem to consist of functionalized amorphous carbon.

The UV−visible spectra (Figure 3) for all three fractions have also been obtained from the photodiode array detector (PDA) attached to the Waters 600-996 chromatograph. The spectrum of fraction 1 shows a broad peak between 600 and 800 nm, which is characteristic of the transition between the first pair of singularities in the density of states (DOS) of the metallic SWNTs with a diameter of about 1.4 nm (~1.7 eV). Other features at 550 (2.2 eV) and 490 nm (2.5 eV), which are discernible in the PDA spectrum of fraction 1, are usually observed in SWNT samples.[10−12]

The IR spectrum of s-SWNT-CONH$(CH_2)_{17}CH_3$ starting material is shown in Figure 4a. The absorptions at 2922 and 2850 cm^{-1} are due to the long chain ν(C−H) stretch. In the near-infrared (NIR) spectrum of fraction 1 (Figure 4b), two absorptions centered at 5400 (0.67 eV) and 10 000 cm^{-1} (1.3 eV) have been assigned to the transitions between the first and the second pairs of singularities in the DOS of the semiconducting SWNTs that are about 1.4 nm in diameter (Figure 4a).[10,11] From Beer's Law the yield of s-SWNTs is estimated to be 74% by comparison of the NIR spectra of the starting material and fraction 1. This recovery of s-SWNTs is higher than the yield of 50% that we reported in our previous work.[9] The mid-

---

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

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

(12) 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.

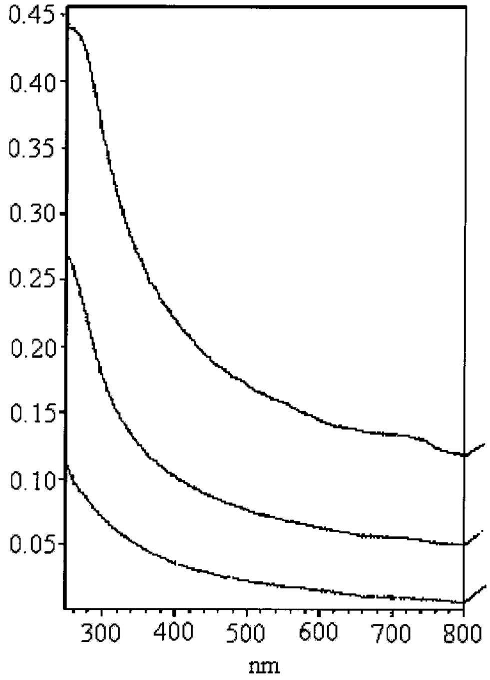

Figure 3. UV−visible absorption spectrum obtained from PDA detector of the eluting fractions, where 1, 2, and 3 refer to the fraction numbers in Figure 1 (separated by a PLgel MIXED-A column). The peak between 700 and 800 nm is unique to fraction 1.

IR of fraction 2 (Figure 4c) shows absorbance at 3356, 2922, and 2850 cm^{-1}, which is the characteristic ν(N−H) and ν(C−H) stretch from octadecylamine.

Liquid state Raman spectra of the starting material and all fractions that are separated by the Styragel HMW7 and PLgel MIXED-A columns are shown in Figure 5a,b. Fraction 1 from both columns shows the Raman radial ($\omega_r = 170$ cm^{-1}) and tangential modes ($\omega_t = 1589$ cm^{-1}), at frequencies that are similar to those of the SWNT raw soot and shortened SWNTs reported previously.[13,14] The second fraction that is separated in both columns shows trace amounts of s-SWNTs. Fraction 3 from the PLgel MIXED-A column does not contain s-SWNTs.

Fractions 2 and 3 from the PLgel MIXED-A column do not show the absorptions at 5400 and 10 000 cm^{-1} in the NIR or the 600−800 nm broad peaks in the UV−visible spectra that relate to SWNTs. The Raman SWNT resonances at 170 and 1589 cm^{-1} are also absent from fractions 2 and 3. This indicates that fractions 2 and 3 do not contain SWNTs at the observable level for these spectroscopic techniques.

The availability of SWNTs that are free of contaminants at the spectroscopic level allows us to study the intrinsic electronic properties of this material. We measured the emission spectrum of chromatographically purified s-SWNT-CONH(CH$_2$)$_{17}$CH$_3$ obtained from the Styragel HMW7 column[9] in a THF solution that had an absorbance of 0.09 at a wavelength of 300 nm. The unrefined s-SWNT starting material shows strong broadband photoluminescence centered at 580 nm when excited at 520 nm (curve b, Figure 6); similar strong luminescence of solubilized polymer-bound SWNTs was recently reported.[15] Fraction 2 also shows strong photoluminescence (curve c, Figure 6) with a spectrum similar to that observed for the starting material. This fraction contains no s-SWNTs according to AFM, NIR, and Raman analyses. In contrast, fraction 1 shows extremely weak luminescence with a quantum yield 2 orders of magnitude lower than fraction 2. According to AFM, NIR, and Raman analyses, this fraction contains high-purity s-SWNTs. It may be noted that luminescence of our starting s-SWNT material is dominated by the presence of fraction 2, which masks the weak emission from pure s-SWNTs. Exclusion of this highly luminescent fraction provides an opportunity to study the intrinsic luminescent properties of SWNTs. Weak features between 650 and 750 nm (1.9−1.65 eV) (curve a, Figure 6) may be associated with the first emission band of metallic SWNTs. These results also explain the origin of the broadband luminescent background observed in the Raman spectra of the starting material and fraction 2 (Figure 5). The electron paramagnetic resonance (EPR) resonance previously reported for solutions of s-SWNTs[16]

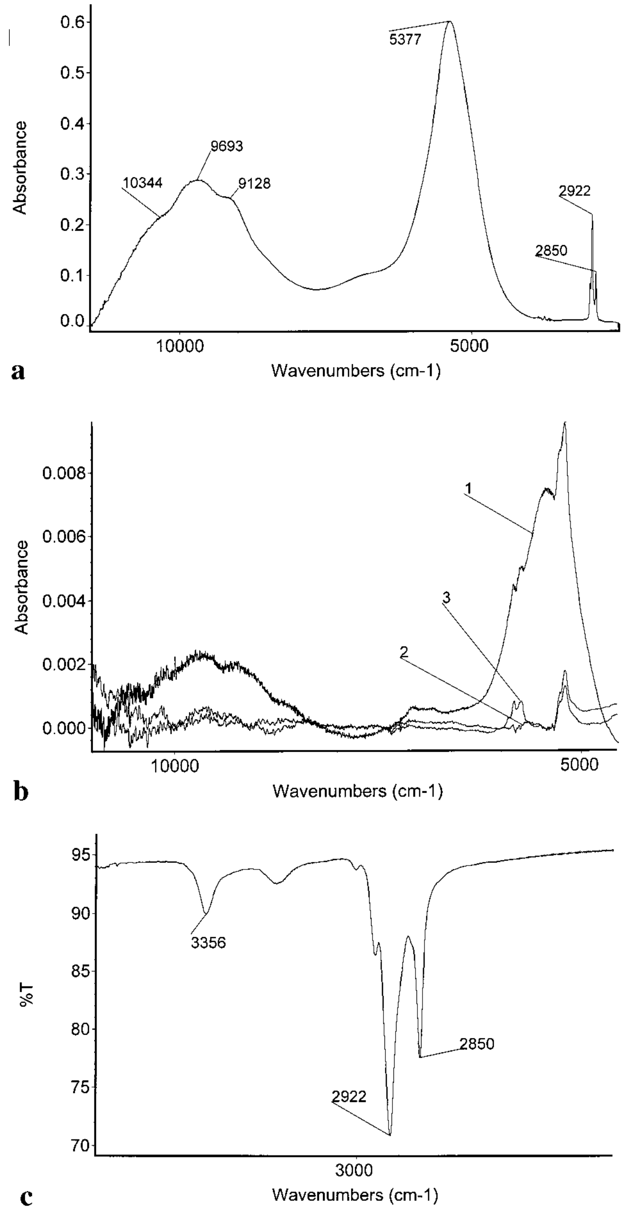

Figure 4. (a) NIR spectrum of starting material in CS$_2$ solution and (b) NIR spectra of the eluting fractions in THF solutions (1, 2, and 3 refer to fraction numbers 1, 2, and 3; quartz cell, light path 10 mm, Nicolet Magna-IR 560 E.S.P. spectrometer). (c) NIR spectrum (on a sapphire substrate, Nicolet Magna-IR 560 E.S.P. spectrometer) of fraction 2 (separated by a PLgel MIXED-A column).

---

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

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

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

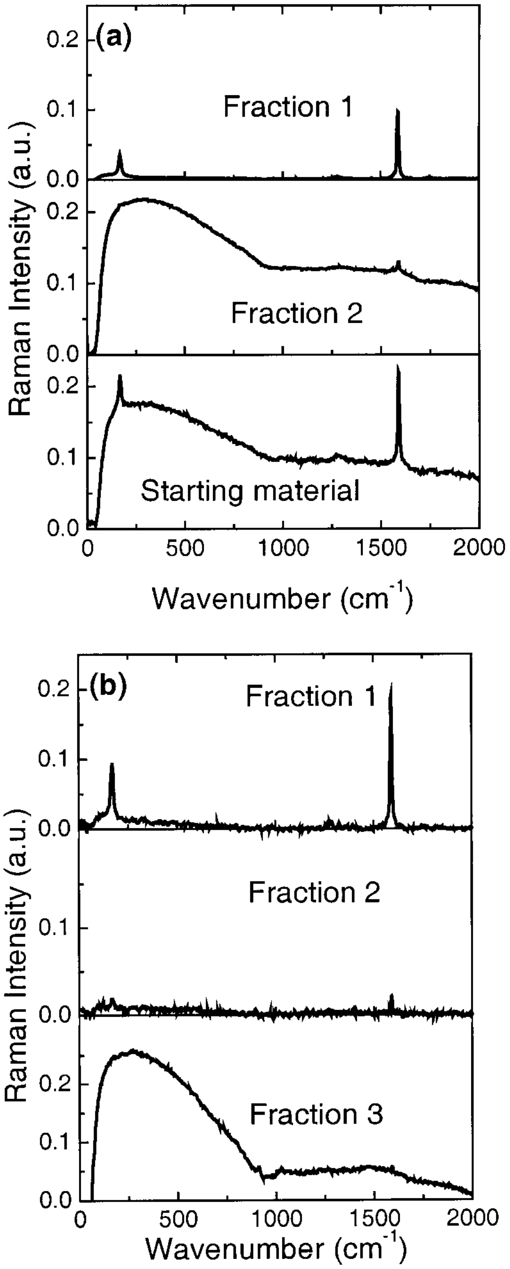

Figure 5. (a) Raman spectra of fractions of s-SWNTs (in THF solution) separated by a Styragel HMW7 column and the starting material.[9] (b) Raman spectra of fractions of s-SWNTs (in THF solution) separated by a PLgel MIXED-A column.

is also found to be associated with fraction 2 and not with the purified SWNTs obtained in fraction 1.

As suggested by a reviewer, it is possible that the absence of photoluminescence in the purified s-SWNTs is associated with the change in bundling or with doping that accompanies the processing of as-prepared SWNTs into soluble material; these chemical treatments are known to produce an upshift in the Raman radial mode frequency of about 10 cm^{-1}.[17] Recent experiments on solutions of SWNT material in aniline have also detected strong fluorescence.[18]

Experimental Section

Preparation of SWNTs. SWNTs were prepared by a modified electric arc technique that gives SWNTs about 1.4 nm in diameter (equivalent to the (10,10) SWNT).[19] The initial purification, shortening, and polishing steps followed literature methods.[4,5] The shortened SWNTs were covalently functionalized with octadecylamine to give s-SWNTs with a length of about 300 nm (s-SWNT-CONH$(CH_2)_{17}CH_3$)[13,14]

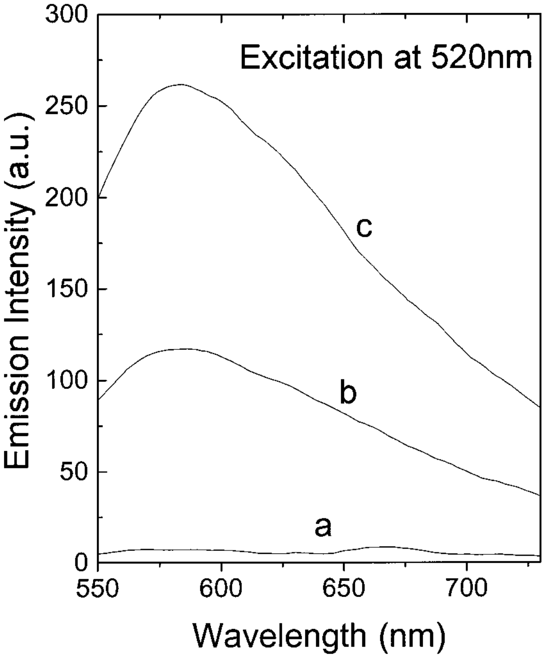

Figure 6. Emission spectra of s-SWNTs (in THF solution, separated by a Styragel HMW7 column),[9] where a, b, and c refer to fraction 1, the starting material, and fraction 2.

Chromatography. The s-SWNT samples were dissolved in THF (Fisher, HPLC grade) to give a solution of s-SWNT starting material at a concentration of 0.5 mg/mL. The solutions were injected into a Waters 600-996 chromatograph fitted with a PLgel 20 μm MIXED-A column (300 mm × 7.5 mm). The amount of each injection was 50 μL, and THF was used as the mobile phase with a flow rate of 0.5 mL min^{-1}. The UV−visible spectra were obtained from the PDA attached to the Waters 600-996 chromatograph.

Atomic Force Microscopy. The AFM images were recorded on a Digital Instruments nanoscope IIIA using the tapping mode. The AFM samples were prepared by dropping the s-SWNTs samples in THF solution on mica substrates.

NIR Spectra. The solution state NIR spectra were recorded with a Nicolet Magna-IR 560 E.S.P. spectrometer in THF using a quartz cell with a path length of 10 mm.

Raman Spectra. Raman spectra were measured with a Bruker RFS100/S FT spectrometer using laser excitation at 1064 nm. This laser energy matches the first transition between the Van Hove singularities in the DOS of the semiconducting SWNTs of the diameters that are produced by the arc method, and thus, our Raman measurements relate primarily to the semiconducting and not the metallic SWNTs in the sample.[20]

Fluorescence Spectra. The fluorescence spectra were measured on an Instruments S. A. Fluorolog 3-22 spectrofluorimeter.

Conclusion

We report a simple HPLC method to purify s-SWNTs in THF. Refinement of these techniques offers the promise of

---

(16) Chen, Y.; Chen, J.; Hu, H.; Hamon, M. A.; Itkis, M. E.; Haddon, R. C. *Chem. Phys. Lett.* **1999**, *299*, 532−535.

(17) Rao, A. M.; Chen, J.; Richter, E.; Eklund, P. C.; Haddon, R. C.; Venkateswaran, U. D.; Kwon, Y.-K.; Tomanek, D. *Phys. Rev. Lett.* **2001**, *86*, 3895−3898.

(18) Sun, Y.; Wilson, S. R.; Schuster, D. I. *J. Am. Chem. Soc.* **2001**, *123*, 5348−5349.

(19) 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.

(20) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. W.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525−2528.

SWNTs separated by length, diameter, and chirality. The availability of SWNTs that are free from contaminants at the spectroscopic level allows us to study the intrinsic electronic properties of this material. We conclude that the intrinsic solution fluorescence and EPR of SWNTs have yet to be definitively observed.

Acknowledgment. This work was supported by the office of Naval Research under Award No. N00014-99-1-0770 and by the MRSEC Program of the National Science Foundation under Award No. DMR-9809686.

JA010488J