1520 *Chem. Mater.* **2006,** *18,* 1520−1524

Highly Exfoliated Water-Soluble Single-Walled Carbon Nanotubes

Feng Liang,[†,‡] Jonathan M. Beach,[†,‡] Pradeep K. Rai,[§,‡] Wenhua Guo,[†,‡] Robert H. Hauge,[†,‡]
Matteo Pasquali,[§,†,‡] Richard E. Smalley,[†,‡,⊥] and W. E. Billups*,[†,‡]

Departments of Chemistry and Chemical & Biomolecular Engineering and
The Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005

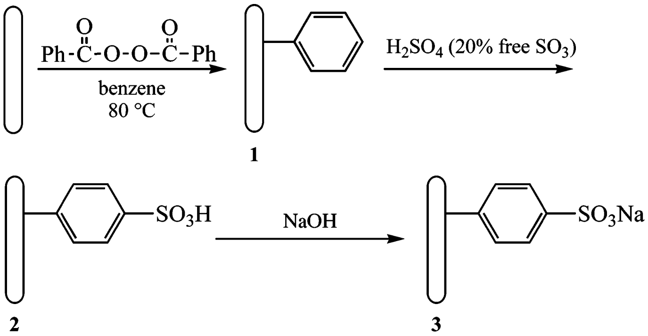
Received December 6, 2005. Revised Manuscript Received January 24, 2006

Single-walled carbon nanotubes functionalized by phenyl groups can be sulfonated in oleum (H_2SO_4, 20% free SO_3) to give materials that exhibit high solubility in water as determined by centrifugation in conjunction with UV−vis−near-infrared measurements. Cryo-transmission electron microscopy images show that extensive debundling occurs during the sulfonation step.

Introduction

Applications of carbon nanotubes in biological nanotechnology[1] will require nanotubes that are soluble in water, a medium essential to studies involving live cells. Surfactant wrapping[2] and DNA-assisted dispersion[3] have been used to achieve water-soluble, individual single-walled carbon nanotubes (SWNTs); however, these methods require harsh sonochemical treatments, and the yields are low. One of the most promising routes to soluble nanotubes involves chemical functionalization, at either the ends or the sidewalls of the nanotubes. One approach involves the reaction of carboxylic acid groups that are formed during purification of the SWNTs with glucosamine,[4] proteins,[5] or oligomeric or polymeric water-soluble molecules.[6] Water-soluble aryl sulfonated SWNTs have also been formed in oleum in a one-step reaction[7] but with a low degree of functionalization. In this manuscript, we describe a convenient and scalable route to achieve highly functionalized SWNTs **2** and **3**, which form thermodynamically stable solutions in water. The reactions are outlined in Scheme 1.

Scheme 1



Experimental Section

Materials. Studies were carried out using both crude and purified[8] SWNTs (∼6 wt % iron) that were prepared by the HiPco process.[9] Benzoyl peroxide (reagent grade, 97%), sulfuric acid (fuming, ACS reagent, 20% as free SO_3), and sodium hydroxide (ACS reagent, >97.0%, pellets) were purchased from Aldrich.

Synthesis of Phenylated SWNTs 1. SWNTs functionalized by phenyl groups were prepared using benzoyl peroxide[10] as the source of phenyl radicals. In a typical experiment, SWNTs (40 mg, 3.33 mmol of carbon) and benzene (50 mL) were added to a 100 mL three-necked round-bottom flask equipped with a homogenizer.[11] The contents were homogenized for 10 min, and the benzoyl

---

[*] Corresponding author. E-mail: billups@rice.edu.

[†] Department of Chemistry.

[§] Department of Chemical & Biomolecular Engineering.

[‡] The Smalley Institute for Nanoscale Science and Technology.

[⊥] Deceased.

(1) (a) Chen, R. J.; Bangsaruntip, S.; Drouvalakis, K. A.; Kam, N. W. S. K.; Shim, M.; Li, Y.; Kim, W.; Utz, P. J.; Dai, H. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 4984−4989. (b) Kam, N. W. S.; O'Connell, M.; Wisdom, J. A.; Dai, H. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 11600−11605. (c) Bianco, A.; Kostarelos, K.; Partidos, C. D.; Prato, M. *Chem. Commun.* **2005**, *5*, 571−577. (d) Kam, N. W. S.; Jessop, T. C.; Wender, P. A.; Dai, H. *J. Am. Chem. Soc.* **2004**, *126*, 6850−6851. (e) Cherukuri, P.; Bachilo, S. M.; Litovsky, S. H.; Weisman, R. B. *J. Am. Chem. Soc.* **2004**, *126*, 15638−15639.

(2) (a) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. *Science* **2002**, *297*, 593−596. (b) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2003**, *3*, 1379−1382. (c) Islam, M. F.; Rojas, E.; Bergey, D. M.; Johnson, A. T.; Yodh, A. G. *Nano Lett.* **2003**, *3*, 269−273.

(3) (a) Zheng, M.; Jagota, A.; Semke, E. D.; Diner, B. A.; Mclean, R. S.; Lustig, S. R.; Richardson, R. E.; Tassi, N. G. *Nat. Mater.* **2003**, *2*, 338−342. (b) Zheng, M.; Jagota, A.; Strano, M. S.; Santos, A. P.; Barone, P.; Chou, S. G.; Diner, B. A.; Dresselhaus, M. S.; Mclean, R. S.; Onoa, G. B.; Samsonidze, G. G.; Semke, E. D.; Usrey, M. L.; Walls, D. J. *Science* **2003**, *302*, 1545−1548. (c) Strano, M. S.; Zgeng, M.; Jagota, A.; Onoa, G. B.; Heller, D. A.; Barone, P. W.; Usrey, M. L. *Nano Lett.* **2004**, *4*, 543−550.

(4) Pompeo, F.; Resasco, D. E. *Nano Lett.* **2002**, *2*, 369−373.

(5) Huang, W.; Taylor, S.; Fu, K.; Lin, Y.; Zhang, D.; Hanks, T. W.; Rao, A. M.; Sun, Y.-P. *Nano Lett.* **2002**, *2*, 311−314.

(6) (a) Fernando, K. A. S.; Lin, Y.; Sun, Y.-P. *Langmuir* **2004**, *20*, 4777−4778. (b) Huang, W.; Fernando, S.; Allard, L. F.; Sun, Y.-P. *Nano Lett.* **2003**, *3*, 565−568. (c) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879−5880. (d) Lin, Y.; Rao, A. M.; Sadanadan, B.; Kenik, E. A.; Sun, Y.-P. *J. Phys. Chem. B* **2002**, *106*, 1294−1298. (e) Lin, Y.; Hill, D. E.; Bentley, J.; Allard, L. F.; Sun, Y.-P. *J. Phys. Chem. B* **2003**, *107*, 10453−10457. (f) Lin, Y.; Zhou, B.; Fernando, S.; Liu, P.; Allard, L. F.; Sun, Y.-P. *Macromolecules* **2003**, *36*, 7199−7204.

(7) Hudson, J. L.; Casavant, M. J.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 11158−11159.

(8) Xu, Y.; Peng, H.; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2005**, *5*, 163−168.

(9) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *J. Vac. Sci. Technol., A* **2001**, *19*, 1800−1805.

(10) (a) Peng, H.; Reverdy, P.; Khabashesku, V. N.; Margrave, J. L. *Chem. Commun.* **2003**, 362−363. (b) Ying, Y.; Saini, R. K.; Liang, F.; Sadana, A. K. *Org. Lett.* **2003**, *5*, 1471−1473.

10.1021/cm0526967 CCC: $33.50

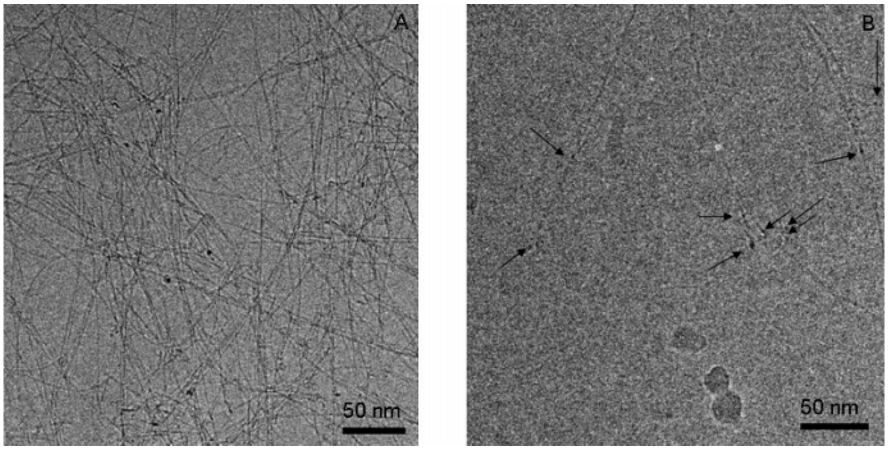


Figure 1. Cryo-TEM images of sulfonated SWNTs **2** (A) prepared from purified materials and (B) from raw materials.

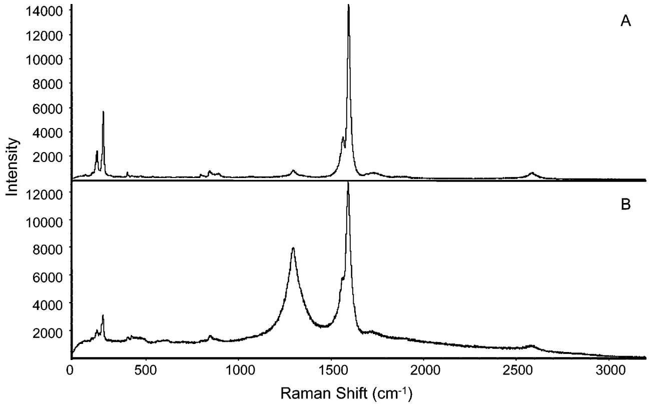


Figure 2. Raman spectra (780 nm excitation) of (A) purified SWNTs and (B) phenylated SWNTs obtained by reaction with benzoyl peroxide.

peroxide (807 mg, 3.33 mmol) was then added. The mixture was then heated under argon at 80 °C for 2 h with homogenizing. After cooling, the contents of the flask were diluted with benzene (100 mL), filtered through a poly(tetrafluoroethylene) membrane (0.2 μm), and washed with chloroform.

Synthesis of Sulfonated SWNT 2. The phenylated SWNTs **1** (20 mg) were dispersed in oleum (20 mL, H_2SO_4, 20% as free SO_3) and heated under argon at 80 °C for 4 h to yield the sulfonated SWNTs **2**. The suspension was then poured carefully into 100 mL of ice water, filtered through a polycarbonate membrane (0.22 μm), and washed with water.

Synthesis of Sulfonated SWNT Salt 3. The phenyl sulfonated SWNTs **2** (20 mg) were treated with a 1 M NaOH (30 mL) solution overnight at 80 °C under argon. The contents were then diluted by water (100 mL), filtered through a polycarbonate membrane (0.22 μm), and washed with water.

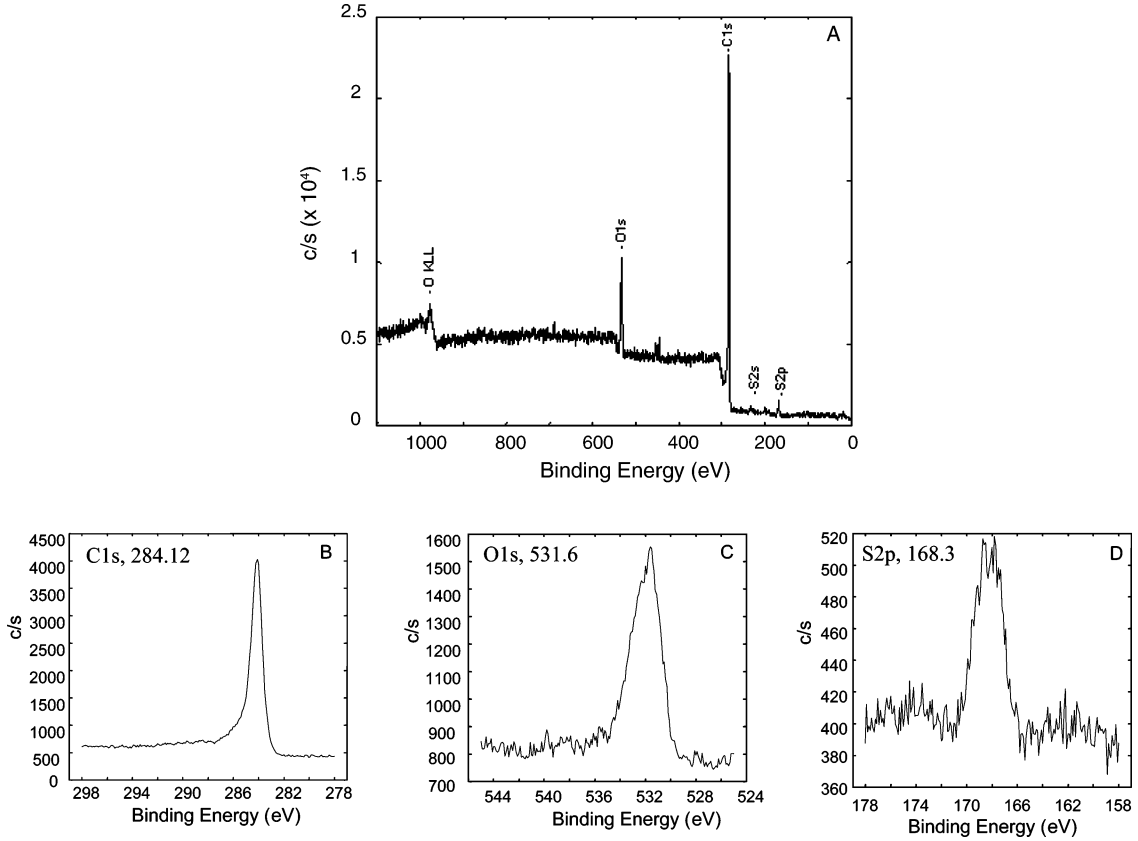


Figure 3. XPS of sulfonated SWNTs **2**. (A) Survey of the spectral region from 0 to 1100 eV, (B) the carbon 1s region, 83.05%, (C) the oxygen 1s region, 14.13%, and (D) the sulfur 2p region, 2.82% (atomic percentage).

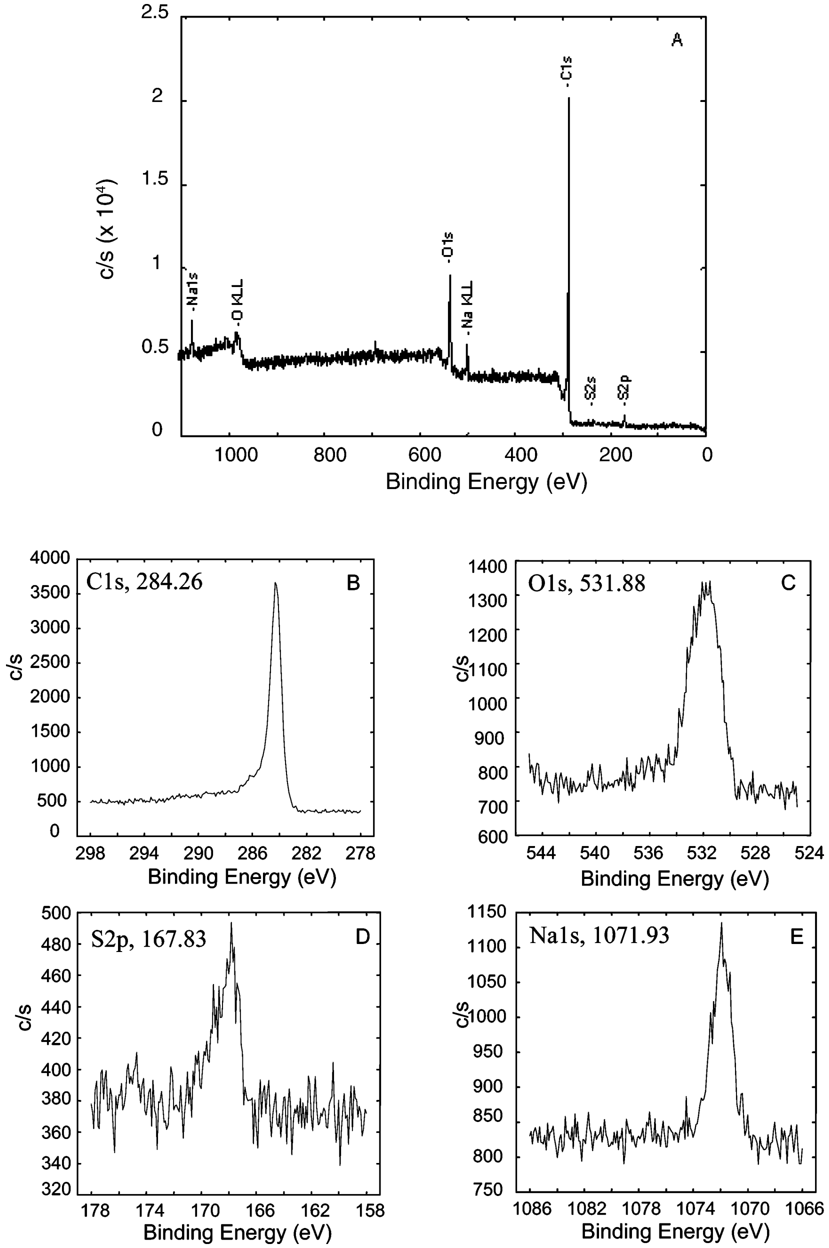


Figure 4. XPS of sulfonated SWNT sodium salts **3**. (A) Survey of the spectral region from 0 to 1100 eV, (B) the carbon 1s region, 84.35%, (C) the oxygen 1s region, 11.78%, (D) the sulfur 2p region, 1.66%, and (E) the sodium 1s region, 2.22% (atomic percentage).

Characterization. The functionalized SWNTs were characterized by Raman spectroscopy, thermogravimetric analysis (TGA), cryo-transmission electron microscopy (cryo-TEM), and X-ray photoelectron spectroscopy (XPS). Raman spectra of solid samples were collected using a Renishaw 1000 microraman system equipped with a 780 nm laser source. The thermal degradation studies were carried out using a SDT 2960 Simultaneous differential scanning calorimeter−thermogravimetric analyzer from TA Instruments. Cryo-TEM images were obtained using a JEOL 2011 instrument operating at 200 kV. A Physical Electronics (PHI QUANTERA) XPS/ESCA system was used to acquire the XPS data. The base pressure of the system was 5×10^{-9} Torr. A monochromatic Al X-ray source at 100 W was used with a pass energy of 26 eV and a 45° takeoff angle. The beam diameter was 100.0 μm.

Solubility measurements were made by centrifugation in conjunction with UV−vis−near-infrared (nIR) absorbance.[12] After mixing, the samples were centrifuged on a Fisher Centrific model 225 Benchtop centrifuge at 5100 rpm. UV−vis−nIR absorbance spectra were measured on a Shimadzu UV-3101PC spectrometer in 1 mm path length Starna cells with Teflon closures. At low concentration in water, light absorbance in the range from 400 to 1400 nm scales linearly with concentration. This Beer's law behavior yields calibration curves for measuring the concentration of the sulfonated SWNTs in water.

Results and Discussion

Cryo-TEM images of **2** prepared from purified SWNTs are presented in Figure 1A. These images demonstrate that extensive debundling occurs during the sulfonation step. Cyro-TEM images recorded using a dilute solution of the sulfonated SWNTs prepared from raw HiPco nanotubes

---

(11) Sadana, A. K.; Liang, F.; Brinson, B.; Arepalli, S.; Farhat, S.; Hauge, R. H.; Smalley, R. E.; Billups, W. E. *J. Phys. Chem. B* **2005**, *109*, 4416−4418.

(12) Rai, P. K.; Pinnick, R. A.; Parra-Vasquez, A. N. G.; Davis, V. A.; Schmidt, H. K.; Hauge, R. H.; Smalley, R. E.; Pasquali, M. *J. Am. Chem. Soc.* **2006**, *128*, 591−595.

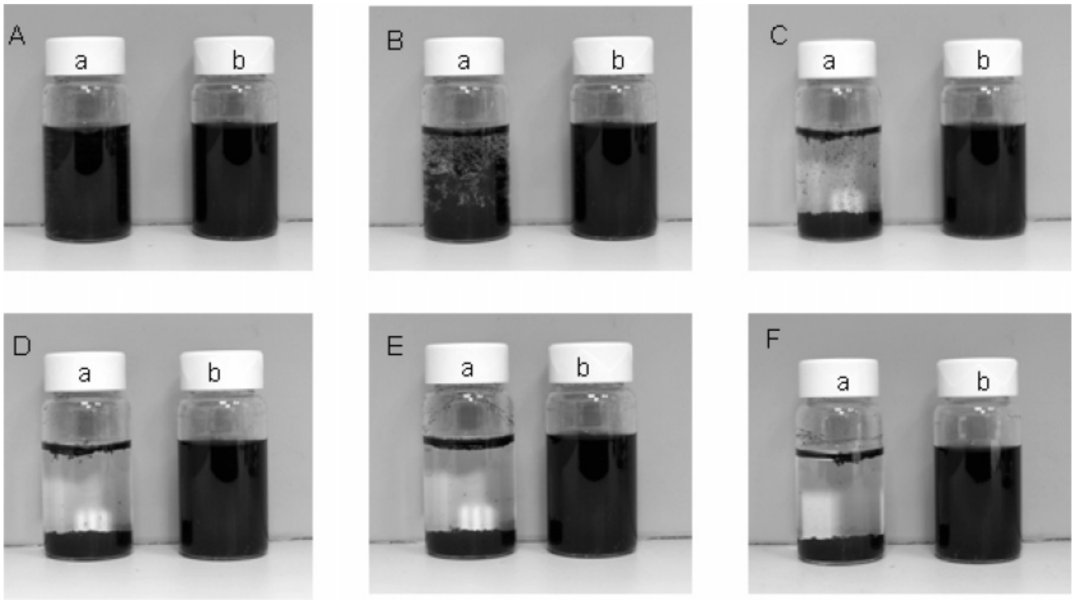


Figure 5. Photographs of (a) pristine SWNTs and (b) sulfonated SWNTs **2** in H_2O. (A) Immediately after sonication; (B) after 1 min; (C) after 5 min; (D) after 24 h; (E) after 10 days; and (F) after 1 month.

exhibit similar behavior (Figure 1B). It is interesting that the material prepared from the unpurified nanotubes has the catalyst (seen as black spots) still attached to the ends of the tubes.

The carbon/phenyl ratio of **2**, as determined by TGA, was found to be 18. This high degree of functionalization can also be inferred by inspection of the Raman spectrum (Figure 2). Whereas a small disorder mode (D-band) that is related to sp^3-hybridized carbon is observed at 1290 cm^{-1} for the purified SWNTs (Figure 2A), the functionalized SWNTs exhibit a much larger D-band (Figure 2B), confirming the high level of functionalization observed by TGA analysis. The sulfonated SWNTs **3** and the precursor phenylated SWNTs exhibit D- and G-bands of similar intensities.

XPS spectra of **2** and **3** are presented in Figures 3 and 4, respectively. The atomic percentages for **2** were found to be 83.05 for C 1s, 14.13 for O 1s, and 2.82 for S 2p, indicating that a monosulfonation product is formed. For **3** (Figure 4), the atomic percentages are 84.35 for C 1s, 11.78 for O 1s, 2.22 for Na 1s, and 1.66 for S 2p. These results indicate that the sulfur-to-sodium ratio is approximately 1:1.

Thermodynamically stable solutions of **2** are formed after sonication for 2 min. Visual inspection of these solutions (Figure 5) showed no indication of flocculation after several months. In contrast, a solution of the purified SWNTs began to flocculate within 1 min after sonication for 10 min.

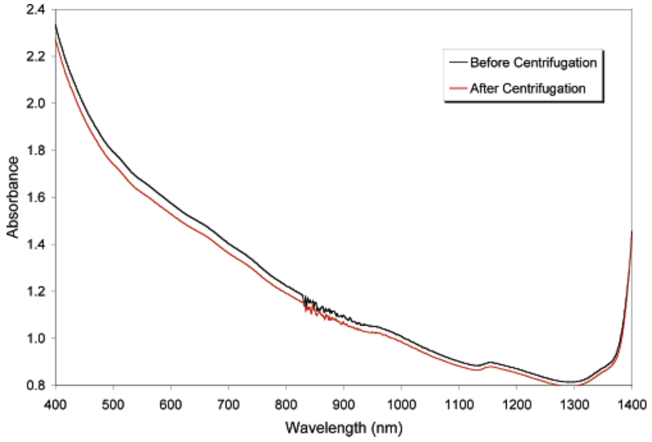


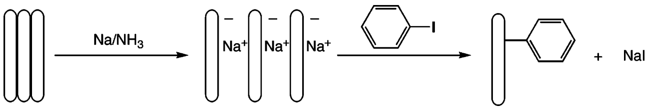
Figure 6. UV−vis−nIR spectra of sulfonated SWNTs **2** in water (500 ppm initial dispersion) before centrifugation and after centrifugation of the top phase.

Solubility measurements of **2** were made by centrifugation in conjunction with UV−vis−nIR absorbance.[12] Centrifugation of concentrated (500 and 1000 ppm) dispersions of sulfonated SWNTs for 12 or more hours (during which equilibrium is reached) resulted in a clear phase separation where the isotropic phase is supernatant. Dilution of the isotropic phase with a known amount of water followed by UV−vis−nIR absorbance measurements provided a quantitative estimation of solubility, that is, the maximum concentration that can exist in the isotropic phase. Figure 6 shows the UV−vis−nIR spectra of the sulfonated SWNTs in water (500 ppm initial dispersion) before and after centrifugation of the top phase. The UV−vis−nIR spectra of the 1000 ppm initial dispersion before and after centrifugation in the top phase can be found in Supporting Information (Figure S1). The UV−vis−nIR spectra of functionalized SWNTs do not exhibit absorption peaks for specific chirality vectors that are dominant in pristine SWNTs. The first van Hove features arising from transitions involving the $\nu_1 \rightarrow c_1$ of the pristine SWNTs are sensitive to adsorption of any species on the surface of the nanotubes.[13] Because ν_1 valence electrons become largely depleted in the functionalization process, they do not contribute to UV−vis−nIR absorption peaks for specific chirality vectors of SWNTs. The isotropic phase at the top is optically uniform and structureless. The concentration of sulfonated SWNTs of the top phase is calculated to be ∼492 ppm on the basis of UV−vis−nIR absorption data at 500 nm. This is one of the highest values achieved for functionalized SWNTs.

---

(13) Ramesh, S.; Ericson, L. M.; Davis, V. A.; Saini, R. K.; Kittrell, C.; Pasquali, M.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2004**, *108*, 8794−8798.

Scheme 2



SWNTs functionalized by phenyl groups were also prepared by treating nanotube salts with iodobenzene (Scheme 2).[14,15] These results can be found in Supporting Information. Sulfonation of the phenylated SWNTs in oleum (H_2SO_4, 20% free SO_3) was carried out as described earlier.

The solubility of the sulfonated SWNTs prepared by Birch phenylation was determined to be ~258 ppm (Figure S2 in Supporting Information). Although the Raman spectrum presented in Figure 7 suggests a high level of functionalization, the carbon/phenyl ratio determined by TGA is 26. The lower degree of functionalization observed for this product probably accounts for the disparity in the solubility of the two materials.

Conclusion

In summary, sulfonation of SWNTs that have been functionalized by phenyl groups provides a convenient and scalable way to achieve highly exfoliated water-soluble SWNTs. The solutions are stable for several months. Studies of these materials in biological systems are underway.

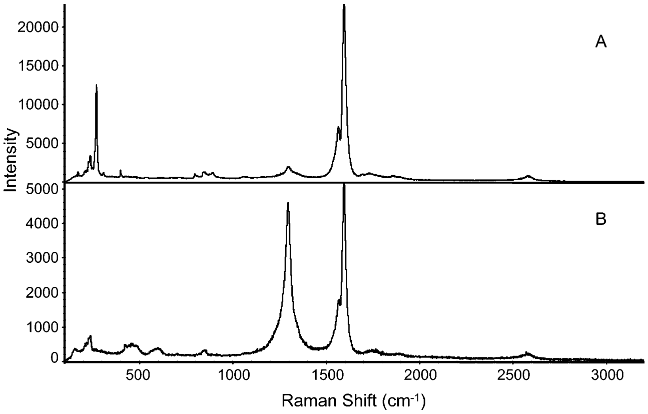


Figure 7. Raman spectra (780 nm excitation) of (A) purified SWNTs and (B) phenylated SWNTs obtained by Birch phenylation.

Acknowledgment. We thank the Robert A. Welch Foundation (C-0490), Texas Advanced Technology Program (003604-0113-2003), DARPA (ONR-20041018), and the National Science Foundation (CHE-0450085) for support of this work.

Supporting Information Available: UV−vis−nIR spectra of sulfonated SWNTs **2** obtained by reaction with benzoyl peroxide (1000 ppm initial dispersion in water) and obtained by Birch phenylation (500 ppm initial dispersion) before centrifugation and after centrifugation of the top phase. Experimental details for the synthesis of phenylated SWNTs obtained by Birch arylation is also provided (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0526967

---

[14] Liang, F.; Alemany, L. B.; Beach, J. M.; Billups, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 13941−13948.

[15] Chattopadhyay, J.; Sadana, A. K.; Liang, F.; Beach, J. M.; Xiao, Y.; Hauge, R. H.; Billups, W. E. *Org. Lett.* **2005**, *7*, 4067−4069.