Chem. Mater. **2007,** *19,* 5765−5772

Effect of Mild Nitric Acid Oxidation on Dispersability, Size, and Structure of Single-Walled Carbon Nanotubes

Maxim N. Tchoul,[†] Warren T. Ford,*[,†] Giulio Lolli,[‡] Daniel E. Resasco,[‡] and Sivaram Arepalli[§]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, School of Chemical, Biological and Materials Engineering, University of Oklahoma, 100 East Boyd Street, Norman, Oklahoma 73019, E.R.C. Inc./NASA-Johnson Space Center, Mail Code ES4, 2101 NASA Parkway, Houston, Texas 77058

Received July 3, 2007. Revised Manuscript Received August 29, 2007

Oxidation of single-walled carbon nanotubes (SWNTs) with nitric acid increases their dispersability in water, methanol, and *N*,*N*-dimethylformamide. Two oxidation protocols, sonication in 8 M HNO_3 at 40 °C and reflux in 2.6 M HNO_3, have been examined using SWNTs produced by the CoMoCat, HiPco, and pulsed laser vaporization (PLV) methods. The dispersability of all types of nanotubes increased substantially after 1 h of sonication and after 2−4 h of reflux. Longer treatments resulted in little further improvement in dispersability and at reflux degraded the SWNTs. Stable dispersions of CoMoCat SWNTs in DMF at concentrations as high as 0.4 g/L were achieved without the use of surfactants or polymers. Raman spectroscopy showed greater covalent functionalization of the SWNTs by the reflux procedure than by the sonication procedure. Concurrent with improved dispersability, oxidation resulted in smaller diameters and shorter lengths as determined from AFM images, which show mostly bundles rather than individual tubes. The lengths of SWNTs after oxidation decreased in the order PLV > HiPco > CoMoCat. Recommendations for the method of conditioning of the various types of SWNTs depend on their intended use.

Introduction

Oxidation of carbon nanotubes is a basic technique for their chemical modification. Carboxylic acid groups created on the CNT surface by oxidation[1−4] provide opportunity to synthesize many different functional groups on SWNTs[5−8] as well as polymers grafted to SWNTs.[6,9−11] Chemically modified carbon nanotubes are more soluble than pristine nanotubes[5,12−14] and are more easily incorporated into a polymer matrix.[7,15,16] At the same time, oxidation damages nanotubes, resulting in structural defects,[4] shortening of tubes,[17] accumulation of carbonaceous impurities,[18] disappearance of small diameter nanotubes,[19−21] and overall loss of material.[18,22] To oxidize nanotubes efficiently for further chemical functionalization and not lose valuable material, one should choose the oxidation conditions carefully.

Nitric acid has been the most frequently utilized agent for oxidation of carbon nanotubes. The HNO_3 methods can be divided into two categories: (1) Treatment with boiling diluted (2−3 M) nitric acid for 16−48 h.[2,4,17,23] (2) Treatment with a mixture of concentrated sulfuric and nitric acids (usually 3:1 by volume) in an ultrasonic bath for 3−5

---

[*] To whom correspondence should be addressed. E-mail: warren.ford@okstate.edu.

[†] Oklahoma State University.

[‡] University of Oklahoma.

[§] NASA-Johnson Space Center.

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

(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.

(3) Martinez, M. T.; Callejas, M. A.; Benito, A. M.; Cochet, M.; Seeger, T.; Anson, A.; Schreibert, J.; Gordon, C.; Marhic, C.; Chauvet, O.; Fierro, J. L. G.; Maser, W. K. *Carbon* **2003**, *41*, 2247.

(4) Zhang, J.; Zou, H.; Qing, Q.; Yang, Y.; Li, Q.; Liu, Z.; Guo, X.; Du, Z. *J. Phys. Chem. B* **2003**, *107*, 3712.

(5) Hamon, M. A.; Chen, J.; Hu, H.; Chen, Y.; Itkis, M. E.; Rao, A. M.; Elkund, P. C.; Haddon, R. C. *Adv. Mater.* **1999**, *11*, 834.

(6) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.

(7) Zhu, J.; Kim, J.; Peng, H.; Margrave, J. L.; Khabashesku, V. N.; Barrera, E. V. *Nano Lett.* **2003**, *3*, 1107.

(8) Zhao, B.; Hu, H.; Haddon, R. C. *Adv. Funct. Mater.* **2004**, *14*, 71.

(9) Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 170.

(10) Hong, C.-Y.; You, Y.-Z.; Pan, C-Y. *Chem. Mater.* **2005**, *17*, 2247.

(11) Lin, Y.; Meziani, M. J.; Sun, Y.-P. *J. Mater. Chem.* **2007**, *17*, 1143.

(12) Peng, H.; Alemany, L. B.; Margrave, J. L.; Khabashesku, V. N.; Barrera, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 15174.

(13) Dyke, C. A.; Tour, J. M. *Chem. Eur. J.* **2004**, *10*, 812.

(14) Liu, Y.; Yao, Y.; Adronov, A. *Macromolecules* **2005**, *38*, 1172.

(15) Mitchell, C. A.; Bahr, J. L.; Arepalli, S.; Tour, J. M.; Krishnamoorti, R. *Macromolecules* **2002**, *35*, 8825.

(16) Sen, R.; Zhao, B.; Perea, D.; Itkis, M. E.; Hu, H.; Love, J.; Bekyarova, E.; Haddon, R. C. *Nano Lett.* **2004**, *4*, 459.

(17) 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.; Elkund, P. C.; Smalley, R. E. *Appl. Phys. A* **1998**, *67*, 29.

(18) Hu, H.; Zhao, B.; Itkis, M. E.; Haddon, R. C. *J. Phys. Chem. B* **2003**, *107*, 13838.

(19) Yang, Y.; Zou, H.; Wu, B.; Li, Q.; Zhang, J.; Liu, Z.; Guo, X.; Du, Z. *J. Phys. Chem. B* **2002**, *106*, 7160.

(20) Yang, C.; Park, J. S.; an, K. H.; Lim, S. C.; Seo, K.; Kim, B.; Park, K. A.; Han, S.; Park, C. Y.; Lee, Y. H. *J. Phys. Chem. B* **2005**, *109*, 19242.

(21) Miyata, Y.; Maniwa, Y.; Kataura, H. *J. Phys. Chem. B* **2006**, *110*, 25.

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

(23) Zhang, X.; Sreekumar, T. V.; Liu, T.; Kumar, S. *J. Phys. Chem. B* **2004**, *108*, 16435.

10.1021/cm071758l CCC: $37.00 © 2007 American Chemical Society
Published on Web 10/12/2007

h.[2,4,7,8,24] Procedures employing piranha solution (a mixture of 96% H_2SO_4 and 30% H_2O_2),[25] ozone,[26] H_2O_2,[21] and $KMnO_4$[4] have been reported less frequently than nitric acid procedures.

Treatment of SWNTs with diluted nitric acid was introduced by Rinzler et al.[17] to purify material produced by laser vaporization. Refluxing in 2.6 M HNO_3 for 45 h reduced metal content and improved separation of SWNTs from amorphous carbon during the next step of cross-flow filtration. This procedure was adopted by many other researchers with some modifications in temperature and time[1,18,27,28] because it is less destructive than concentrated nitric acid.

Treatment with a mixture of concentrated sulfuric and nitric acids and treatment with piranha solution were introduced by Liu et al.[2] as methods for shortening of nanotubes. The shortening rate was estimated to be 130 nm/h for H_2SO_4/HNO_3 and 200 nm/h for piranha during a bath sonication. Both of these solutions as well as concentrated H_2SO_4, HNO_3, or H_2O_2 alone were found to selectively eliminate smaller diameter nanotubes from the material.[19−21] Concentrated H_2SO_4 and HNO_3 selectivity destroyed small metallic tubes,[20] whereas hydrogen peroxide selectively destroyed small semiconducting nanotubes.[21]

IR spectra have shown that nitric acid treatment produces carboxylic acid groups on SWNTs.[1,4,11] Owing to carboxylic acid groups, oxidation makes SWNTs more dispersable in polar solvents. Although several methods have been reported for determination of the "solubility" of carbon nanotubes,[29−32] neither the term solubility nor a standard method for its determination has been established. Most "solutions" of SWNTs are in fact dispersions. In this paper we use "soluble" to mean a SWNT dispersion that is sufficiently stable for its further use, which in our case will be the preparation of polymer composites. Although partial solubility of SWNTs in water after oxidation has been reported,[24,27,33] to our knowledge the effect of oxidation on solubility has not been studied in detail. Here we report the increase in solubility of nanotubes in *N*,*N*-dimethylformamide (DMF), water, and methanol after a short time of oxidation by diluted nitric acid. The treatments allow dissolving nanotubes without dispersing agents such as surfactants, which can simplify the preparation of nanotube-based composites and coatings and simplify further chemical modification of the nanotubes via the carboxylic acid groups. Because carboxylation of the nanotube surface is always accompanied by cutting and etching of the nanotubes, the experimental results are highly useful for finding a balance between increasing the solubility and destroying the nanotubes.

Experimental Section

Materials. SWNTs produced by the CoMoCat,[34] HiPco,[35] and pulsed laser vaporization (PLV)[36] processes were used in this work. CoMoCat SWNTs in the form of a 2% aqueous gel, grade S-P94-02gel, batch # OSU-A-007, purified by the basic (alkali) protocol,[32] were obtained from Southwest Nanotechnologies, Inc., Norman, OK. As-produced HiPco SWNTs in the form of a puffy fibrous powder, lot # R0488, were obtained from Carbon Nanotechnologies, Inc., Houston, TX. Laser oven SWNTs in the form of a black powder, batches JSC-334, -335, and -338, purified by the soft-baking protocol,[37] were obtained from NASA-Johnson Space Center, Houston, TX. All solvents were obtained from Pharmco and Spectrum and dried over anhydrous potassium carbonate. All other chemicals were obtained from Sigma and Aldrich and used without further purification. Water was purified by ion exchange and active carbon treatment with a Barnstead E-pure system.

Instruments and Measurements. Ultrasonication was performed using a Fisher FS-30 160W 3QT ultrasonic cleaner or a Microson XL-2000 22 kHz ultrasonic cell disruptor. Dispersions were filtered using a vacuum glass filtration cell and 0.45 μm porous PTFE membranes. Centrifugation was performed on an IEC EXD centrifuge (IEC, Needham, MA). UV−vis absorption in the range of 400−1100 nm was analyzed using a HP8453 spectrophotometer and glass cells. Atomic force micrographs were obtained using a Multimode Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) operating in the tapping mode. The samples were prepared by applying a drop of a DMF dispersion on a mica chip for 10 min followed by drawing away excess liquid with filter paper and drying the chip in flowing nitrogen. To determine the size distribution, the length and height of images of about 100 objects from two or three different spots of the substrate were measured. Raman spectra were obtained using a Coherent He−Ne laser at an excitation wavelength of 633 nm. The laser power varied from 0.89 to 3.0 mW for different samples; the duration of a scan was 60 s. The solid samples were prepared by filtering the DMF dispersions using 0.2 μm PTFE membranes. The backscattered light was analyzed using a Jobin Yvon LabRam 600 single-grating spectrometer with a CCD detector. Thermogravimetric analyses were performed using a Shimadzu TGA50/50H instrument in the range of 20−800 °C in air at a scan rate of 5 °C/min.

Oxidation of Carbon Nanotubes by 8 M Nitric Acid with Sonication. The SWNTs were dispersed in DMF at a concentration of 0.5 g/L by bath sonication for 40 min at 40−50 °C. In a typical procedure, 20 mL of this dispersion was filtered and washed on the filter with 10 mL of methanol and 10 mL of water. The solid was transferred into 20 mL of 8 M HNO_3 in a glass vial, and the mixture was sonicated in a bath at 40−50 °C for a time ranging from 30 min to 5 h. The mixture was diluted 1:2 with deionized

---

(24) Zhao, W.; Song, C.; Pehrsson, P. E. *J. Am. Chem. Soc.* **2002**, *124*, 12418.

(25) Ziegler, K. J.; Gu, Z.; Peng, H.; Flor, E. L.; Hauge, R. H.; Smalley, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 1541.

(26) Cai, L.; Bahr, J. L.; Yao, Y.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 4235.

(27) Mamedov, A. A.; Kotov, N. A.; Prato, M.; Guldi, D. M.; Wicksted, J. P.; Hirsch, A. *Nat. Mater.* **2002**, *1*, 190.

(28) Martinez, M. T.; Callejas, M. A.; Benito, A. M.; Cochet, M.; Seeger, T.; Anson, A.; Schreibert, J.; Gordon, C.; Marhic, C.; Chauvet, O.; Fierro, J. L. G.; Maser, W. K. *Nanotechnology* **2003**, *14*, 691.

(29) Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. *Chem. Commun.* **2001**, *2*, 193.

(30) Rouse, J. H. *Langmuir* **2005**, *21*, 1055.

(31) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E.; Schmidt, J.; Talmon, Y. *Nano Lett.* **2003**, *3*, 1379.

(32) Matarredona, O.; Rhoads, H.; Li, Z.; Harwell, J. H.; Balzano, L.; Resasco, D. E. *J. Phys. Chem. B* **2003**, *107*, 13357.

(33) Hu, H.; Yu, A.; Kim, E.; Zhao, B.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C. *J. Phys. Chem. B* **2005**, *109*, 11520.

(34) Kityanan, B.; Alvarez, W. E.; Harwell, J. H.; Resasco, D. E. *Chem. Phys. Lett.* **2000**, *317*, 497.

(35) Dai, H.; Rinzler, A. G.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1996**, *260*, 471.

(36) Arepalli, S.; Nikolaev, P.; Holmes, W.; Files, B. S. *Appl. Phys. Lett.* **2001**, *78*, 1610.

(37) Gorelik, O. P.; Nikolaev, P.; Arepalli, S. Nasa Contractor Report, Nasa/Cr-2000-208926, December 2000, http://mmptdpublic.jsc.nasa.gov/jscnano/pubs/CR-200-208926.pdf, accessed 07-02-2007.

water and filtered using a 0.45 μm PTFE filter. The solid was washed on the filter with water until the filtrate was neutral, washed with 10 mL of methanol, washed with 10 mL of DMF, and redispersed in 20 mL of DMF by bath sonication for 60 min. The filtrates from CoMoCat and HiPco nanotubes were colorless, but the filtrate from PLV nanotubes was light gray. AFM analysis of the PLV filtrate indicated the presence of nanotubes.

Oxidation of Carbon Nanotubes by 2.6 M Nitric Acid at Reflux. For this experiment all SWNT materials were used as received. In a typical procedure, 20 mg of the material was transferred into a round-bottom flask filled with 40 mL of 2.6 M HNO_3 and equipped with a magnetic stirring bar and a reflux condenser. The flask was immersed in an oil bath at 120 °C. For each material, mixtures were refluxed for times ranging from 1 to 12 h, cooled to room temperature, and filtered. The solid was washed on the filter with water until the filtrate was neutral, washed with 10 mL of methanol, washed with 10 mL of DMF, and redispersed in 40 mL of DMF by bath sonication for 60 min. All of the filtrates were colorless.

Material Balance. To measure the loss of nanotubes during oxidation, a 50 mg sample of each type of nanotubes was treated with nitric acid for the optimum time using either of the protocols described above. The solids were filtered and dried at 100 °C to constant mass. The contents of metal oxide in both the pristine SWNTs and the recovered solid was measured by TGA in air. According to the manufacturers, the nanotube materials contained carbon and metallic residues of Mo in CoMoCat, Fe in HiPco, and Co, Ni, and Y in the weight ratio of 1:1:5 in PLV materials. For the calculations it was assumed that the initial SWNT sample contained carbon and metal and that upon heating to 800 °C in the TGA experiment all carbon was converted into gases and the metal was converted to ash containing MoO_3 from CoMoCat, Fe_2O_3 from HiPco, and $Co_3O_4 + NiO + Y_2O_3$ from PLV materials. The oxidized SWNT sample was assumed to contain carbon and metal oxides. Details of the material balances are in Table 4 of the Supporting Information.

Dispersability of Oxidized SWNT. To evaluate the "solubility," a dispersion of oxidized nanotubes was diluted with a solvent in 10 mL glass vials to yield a series of concentrations from 0.01 to 0.4 mg/L. Each vial was sonicated by the tip sonicator at 10 W for 15 min at room temperature. After standing for 2 h, the dispersions were examined for the presence of visible particles. Because the dispersions with concentration of ≥ 0.1 g/L appeared black, they were placed into a 2 mm glass cell for better observation. The highest concentration of SWNTs with no visible particles is reported as the solubility value for a certain solvent. These values of the solubility are good for comparison among our samples but may vary from the values determined by other methods. In our samples at the solubility limit a black solid was visible on the bottom of the vial beginning about 3−4 h after preparation, while the supernatant liquid remained homogeneous. After 6 days typically 75−80% of the SWNTs remained in the supernatant as measured by NIR absorption at 850 nm.

Results

Here we define the solubility as the highest weight percent of nanotubes that can be dispersed in a solvent with no particles visible for at least 2 h. Figure 1 reports the solubilities of three different types of SWNTs in DMF, methanol, and water after oxidation. The solubility increased rapidly for 1 h by the nitric acid sonication protocol and for 2−4 h by the reflux protocol. Treatments for longer times gave smaller increases of solubility. The solubility of all samples was greater in DMF than in water or methanol.

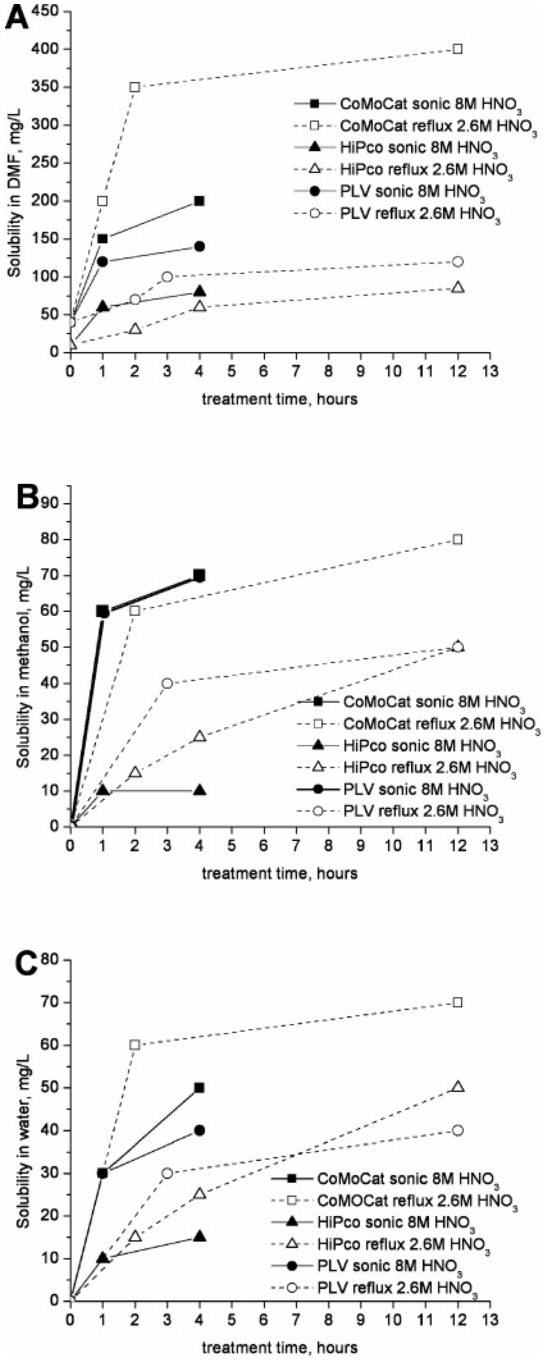

Figure 1. Solubility of oxidized nanotubes: (A) DMF; (B) methanol; (C) water.

Figure 2 shows resonance Raman spectra of the samples reported in Figure 1. The degree of functionalization can be estimated by the intensity of the D-band (I_D) at ~1300 cm^{-1} (due to defects in the structure of the nanotube sidewall) relative to the intensity of the G-band (I_G) at ~1590 cm^{-1} (due to the longitudinal stretching vibrations of the sp^2 carbons of semiconducting SWNTs).[38] The intensity ratio I_D/I_G increased with time of oxidation. The refluxing nitric acid treatment gave larger I_D/I_G than the sonication method with every type of SWNT. Increased I_D/I_G correlates qualitatively but not quantitatively with increased solubility. In the Supporting Information Raman spectra plotted as

---

(38) Thomsen, C.; Reich, S. *Phys. Rev. Lett.* **2000**, *85*, 5214.

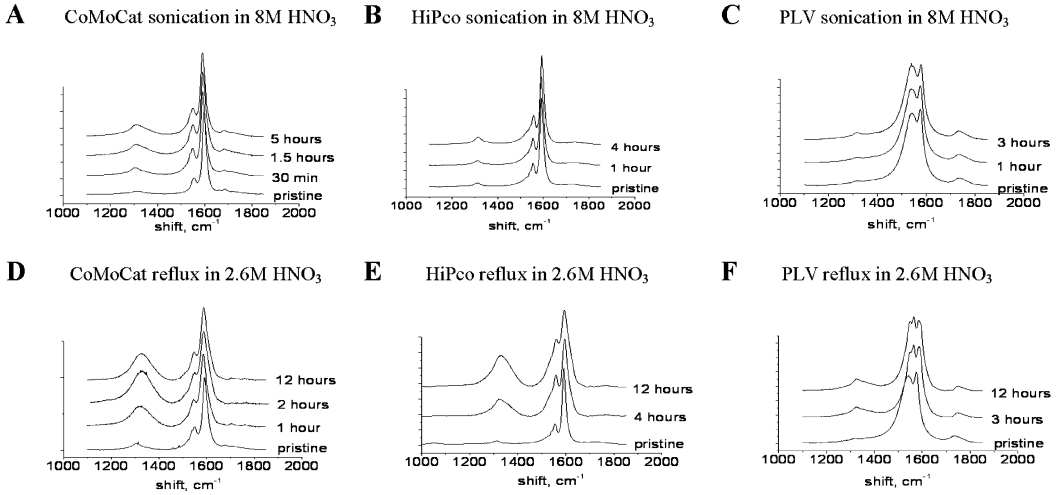

Figure 2. Raman spectra of the oxidized SWNTs. The spectra have been normalized to the intensity of the G-band at ~1590 cm^{-1}.

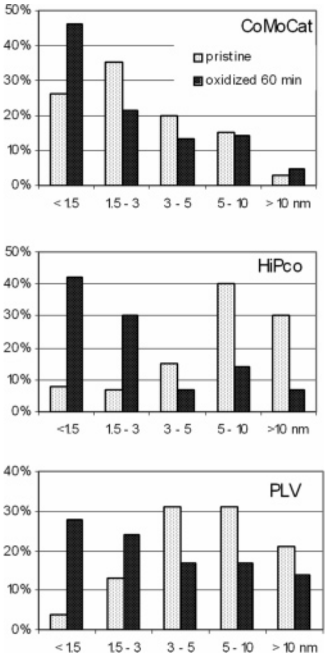

Figure 3. Diameter distribution for all three types of nanotubes before and after sonication in 8 M HNO$_3$ for 60 min.

absolute peak intensities show that the increases of the I_D/I_G ratios were due more to a decrease of I_G than to an increase of I_D.

Increasing degree of functionalization of SWNTs or formation of amorphous carbon or both can be observed by decreasing intensities of bands due to specific types of nanotubes in electronic absorption spectra in the near-infrared region for semiconducting and in the visible region for metallic SWNTs. However, there was no significant decrease in NIR intensity of any of the sonicated samples, and there was a small increase in intensity of the D band in the Raman spectra after 1 h of oxidation. Therefore, during that first hour functionalization, not formation of amorphous carbon, was the cause of the increase of solubility. Only a little functionalization causes a marked increase of solubility. Longer oxidation times may have produced amorphous carbon. NIR absorption spectra of solutions of the SWNTs in the Supporting Information show greater decreases in the peak heights for CoMoCat tubes than for HiPco tubes over longer times of nitric acid treatment and more rapid decrease of peak heights by the reflux method than by the sonication method. The electronic spectra of the PLV tubes were virtually unchanged by either nitric acid treatment. If much of the PLV tubes had been converted to amorphous carbon, the broad peak at 975–1100 nm in the NIR spectrum would have been reduced in intensity.

Figure 3 reports AFM measurements of the distributions of diameters of bundles of the three types of pristine SWNTs and the samples from oxidation with sonication for 1 h. In all cases the fractions of individual SWNTs and small bundles of SWNTs increased and the average diameters decreased with nitric acid treatment. Examples of the AFM images are in the Supporting Information. Because the deposition of the SWNT bundles on mica may be kinetically controlled, all AFM samples were prepared from dispersions of about the same concentration on mica for the same length of time before removal of excess liquid dispersion. Consequently, the relative diameters and lengths of the SWNT bundles are considered reliable even if the absolute sizes reported may have systematic errors.

Figure 4 reports AFM measurements of the distributions of lengths of the three types of pristine SWNTs, samples from the sonication method after 1 and 3 h, and samples from the reflux method after 2–4 and 12 h. The average length of bundles and individual SWNTs of all three types decreased after nitric acid oxidation. SWNTs from the reflux method had smaller average lengths than SWNTs from the sonication method.

Figure 5 reports gravimetric measurements of the amounts of SWNTs remaining after 1 and 3–4 h by the sonication method and after 2–4 and 12 h by the reflux method. The metal and carbon contents were determined thermogravimetrically. There was little or no loss of carbon from any sample by the sonication method and significant loss of carbon by the reflux procedure. More of the metal catalyst residues were removed by the reflux procedure.

Figure 6 shows the radial breathing mode (RBM) region of the Raman spectra of CoMoCat nanotubes recovered from both oxidation methods. The peaks of some of the smallest diameter [6,4], [6,5], and [7,5] tubes are identified in the

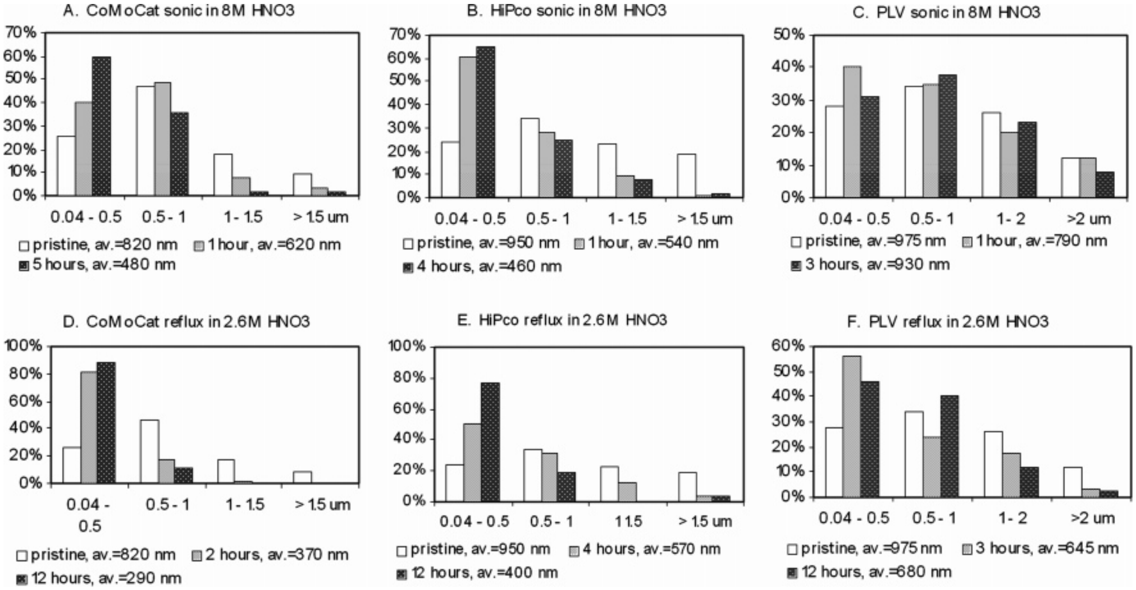

Figure 4. Length distributions of SWNTs after oxidation.

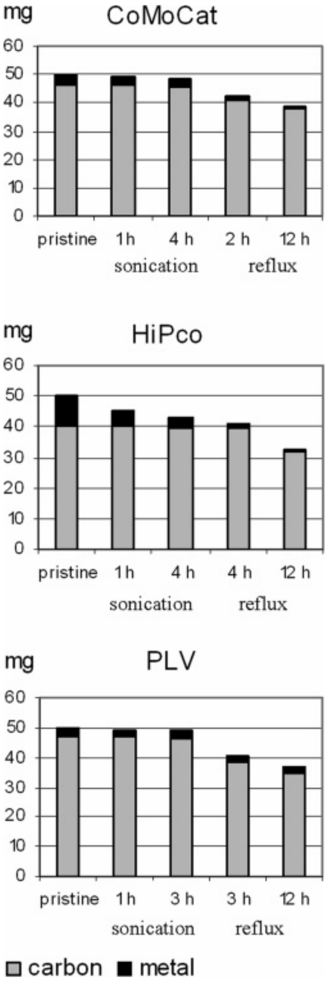

Figure 5. Amounts of carbon and metal left after nitric acid oxidation of SWNTs.

spectra of the pristine tubes.[39] The intensities of the peaks do not correlate with amounts of the tube types in a sample because of wide variations in efficiency of resonant energy transfer. Although [6,5] and [7,5] nanotubes comprise 60%

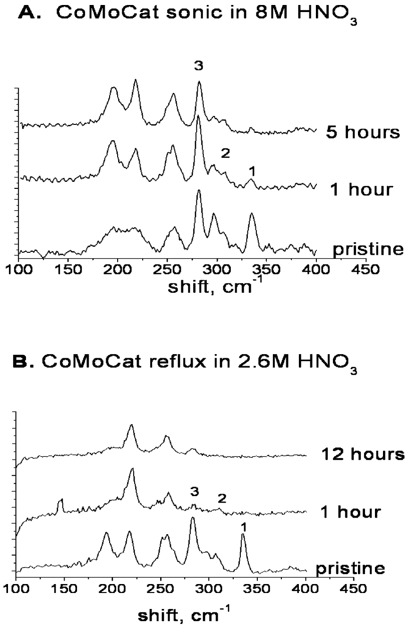

Figure 6. RBM region of Raman spectra of oxidized CoMoCat SWNTs. The labeled peaks correspond to the nanotubes: (1) [6,4]; (2) [6,5]; (3) [7,5].

of the semiconducting tubes from the CoMoCat process,[39] and the [6,5] tubes are most abundant, the [6,5] RBM peak is small due to weak resonance with the 633 nm laser. The small diameter CoMoCat tubes disappeared after the refluxing nitric acid treatment, and the amounts of small diameter tubes were reduced markedly after the sonication in nitric acid. The RBM regions of Raman spectra of the HiPco and PLV nanotubes (see Supporting Information) show small shifts of the peak frequencies and much less loss of peak intensities than that from the CoMoCat nanotubes.

---

(39) Jorio, A.; Santos, A. P.; Ribeiro, H. B.; Fantini, C.; Souza, M.; Vieira, J. P. M.; Furtadq, C. A.; Jiang, J.; Saito, R.; Balzano, L.; Resasco, D. E.; Pimenta, M. A. *Phys. Rev. B* **2005**, *72*, 07520711.

Discussion

Mechanism of Oxidation of SWNT. As discussed by others,[2,4,40,41] *an oxidizing agent such as nitric acid first attacks the ends and structural defects in the sidewalls of SWNTs*. The capped ends of SWNTs are more strained due to curvature and are attacked more readily than the less strained sidewalls. Oxidation of open ends etches away carbon atoms. Oxidation at defects in sidewalls may cut the tubes into pieces. These processes shorten the tubes. The AFM length data in Figure 4 show that all of the tubes were shortened by both oxidation methods.

More severe oxidation introduces more functional groups on the sidewalls of the nanotubes and shortens the tubes still more. The AFM length data show shorter tubes from the reflux method than from the lower temperature sonication method. The Raman spectra show larger increases of the I_D/I_G ratio by the reflux method than by the sonication method. Moreover, the reflux method caused loss of carbon material (Figure 5), but little carbon was lost by the sonication method. Therefore, in general, the lower temperature sonication method mainly oxidized tube ends and cut tubes at sidewall defects with minimal loss of carbon atoms. The reflux method destroyed minor fractions of the SWNTs and left the remaining SWNTs more highly functionalized than did the sonication method.

Smaller diameter, more strained SWNTs are oxidized more readily than larger diameter SWNTs.[19,20,42,43] The average diameters of the mixtures of SWNTs are approximately CoMoCat 0.8 nm,[44] HiPco 1.0 nm,[42] and PLV 1.3 nm.[45] The RBM regions of the Raman spectra in Figure 6 and in the Supporting Information show complete disappearance of some components of the CoMoCat material during nitric acid treatment and reductions of peak intensities of the HiPco and PLV materials. Thus, the CoMoCat SWNTs are more reactive than the HiPco and PLV tubes. Similarly, the ratio I_D/I_G, which is indicative of sidewall functionalization, increases most for CoMoCat and least for PLV SWNTs by the sonication method and more for CoMoCat than for PLV by the reflux method. A glance at Figure 2 suggests that I_D/I_G increases more for HiPco than for CoMoCat by the reflux method, but a careful examination reveals that the 2 h reflux of CoMoCat gave a larger I_D/I_G than the 4 h reflux of HiPco. The decrease of I_D/I_G for CoMoCat from 2 to 12 h at reflux (Figure 2B) is probably due to destruction after 12 h of the part of the sample that was most highly functionalized after 4 h.

Oxidizing agents such as nitric acid penetrate between tubes in bundles and via reaction with sidewalls break bundles into smaller bundles and individual tubes. The decreases in diameters of all three types of SWNTs with increasing time of oxidation support this mechanism.

Relation of Solubility to Length, Diameter, and Functionalization of SWNTs. The distributions of diameters of the pristine and the oxidized SWNTs shown in Figure 3 indicate that only minor fractions of the samples were individual tubes of <1.5 nm diameter for CoMoCat and HiPco (and <2 nm diameter for PLV), and most of the tubes are in bundles. The data are presented on a number fraction basis by which a bundle of tubes is counted the same as an individual tube. The weight fraction of individual tubes is much less than the number fraction. Similarly, the length of a bundle of tubes (Figure 4) should usually be greater than the lengths of the individual tubes that comprise the bundle because tubes may pack end-to-end as well as side-by-side. The tube lengths also are reported on a number basis, not a weight basis. Increasing size and molecular weight of a polymer decreases solubility. Similarly, smaller bundles of SWNTs should be more soluble. In the three polar solvents studied, solubilities decreased in the order CoMoCat > HiPco > PLV, which is the order of increasing tube diameter and length.

Solubility also increases with increasing numbers of polar functional groups on the nanotubes. From nitric acid oxidation many of the functional groups are carboxylic acids.[1,4,11,46] The number of sidewall functional groups increases with time in refluxing nitric acid, as shown by the I_D/I_G ratios in Raman spectra. In most cases Figure 1 shows increasing solubility with increasing reflux time for the first 2−4 h, but often no increase in solubility after longer reflux times, even though I_D/I_G increased. For all three types of SWNTs the solubilities were higher in DMF than in methanol and water. Solubility requires attractive forces between the solvent and the nanotubes. All three solvents strongly hydrogen bond to carboxylic acid groups. However, DMF has by far the highest polarizability. We attribute the higher solubilities in DMF to van der Waals attraction between the sidewalls and DMF, which is lacking with methanol and water. DMF has been reported second only to *N*-methylpyrrolidinone in its ability to disperse SWNT.[47]

A few anomalies in the data are not explained by the above generalizations. One anomaly is that the solubility of the HiPco tubes in DMF from the sonication method was higher than that from the reflux method, even though refluxing led to higher solubilities in methanol and water and a higher degree of functionalization as judged by I_D/I_G in the Raman spectra. Another anomaly is that the solubilities of the PLV tubes in all three solvents were no higher from the reflux method than from the sonication method. Moreover, the solubility of PLV tubes in DMF and in water did not increase, and the lengths of the PLV tubes did not decrease, from 3 to 12 h of reflux or from 1 to 4 h of sonication.

Despite a much higher degree of functionalization of the refluxed HiPco SWNTs, as judged by Raman spectra, there

---

[40] Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T.; Liu, J.; Smalley, R. E. *Chem. Phys. Lett.* **2000**, *324*, 213.

[41] Mazzoni, M. S. C.; Chacham, H.; Ordejon, P.; Sanchez-Portal, D.; Soler, J. M.; Artacho, E. *Phys. Rev. B* **1999**, *60*, R2208.

[42] Zhou, W.; Ooi, Y. H.; Russo, R.; Papanek, P.; Luzzi, D. E.; Fischer, J. E.; Bronikowski, M. J.; Willis, P. A.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *350*, 6.

[43] Zhang, M.; Yudasaka, M.; Iijima, S. *J. Phys. Chem. B* **2004**, *108*, 149.

[44] Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 11186.

[45] Yudasaka, M.; Sensui, N.; Takizawa, M.; Bandow, S.; Ichihashi, T.; Iijima, S. *Chem. Phys. Lett.* **1999**, *312*, 155.

[46] Jung, A.; Graupner, R.; Ley, L.; Hirsch, A. *Phys. Status Solidi B* **2006**, *243*, 3217.

[47] Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S.; Korobov, M. *J. Phys. Chem. B* **2000**, *104*, 8911.

was not a corresponding improvement of solubility in water for the refluxed samples compared to the sonicated samples. In fact, the HiPco tubes were less soluble than the CoMoCat and PLV tubes in all solvents by both oxidation methods, with the sole exception of solubility in water after 12 h of reflux. We speculate that either the mechanism by which the bundles form during synthesis or the manufacturer's method of processing the raw SWNTs into customer products resulted in stronger van der Waals attractions between tubes in the HiPco bundles compared with the production and purification of CoMoCat and PLV SWNTs.

We found a major difference in dispersion between different batches of CoMoCat tubes depending on the process used by the manufacturer to remove the silica catalyst support. CoMoCat tubes processed with HF to dissolve the silica and the metal catalyst were much less soluble than the CoMoCat tubes reported here, which were processed with aqueous sodium hydroxide to remove the silica and with hydrochloric acid to remove catalyst residue. We have no explanation for this big difference in solubility depending on the CoMoCat processing method.

Previous Nitric Acid Oxidations. The main differences between our results and previous reports are our milder conditions of sonication at 40 °C in 8 M nitric acid and shorter time of refluxing 2.6 M nitric acid. Jung et al.[43] also reported that most changes of XPS and Raman specta of HiPco SWNTs in refluxing 3 M nitric acid took place within 3 h. Zhang et al.[4] found that oxidation of SWNTs using 3:1 concentrated H_2SO_4 (98 wt %)/HNO_3 (16 M) mixtures, 2.6 M HNO_3, or $KMnO_4$ predominately created carboxylic acid functionalities on nanotubes. Hu et al.[33] estimated the amount of carboxylic groups in SWNT materials refluxed in 3 and 7 M HNO_3 by titration to be from 6 to 11 mol % of carbon atoms, depending on the concentration of acid and time of treatment. The carboxylic acid groups may be on carbonaceous impurities as well as on SWNTs. We have not measured the carboxylic acid content, but the lower temperature sonication method should produce many fewer carboxylic acid groups than any previous oxidation method, as the small increases of I_D/I_G in the Raman spectra suggest. Even though the low-temperature 8 M nitric acid sonication method gave many fewer functional groups, the solubility of the SWNTs approached that of SWNTs from more severe nitric acid treatments.

Hu et al.[18] reported that reflux in 3 and 7 M nitric acid for 12−48 h leads to accumulation of carbonaceous impurities and to loss of material increasing with time of treatment, concentration of acid, or temperature.[18,22,28] For as-prepared arc-discharged SWNTs, reflux in 3 M HNO_3 for 12 h resulted in a loss of 31% of the material, 7% of which was carbon.[18] In our experiments, reflux in 2.6 M HNO_3 for 12 h resulted in 35% loss of as-prepared HiPco SWNTs, 16% of which was carbon (see Figure 5 and the detailed material balance results in the Supporting Information). As shown in Figure 5, the sonication method was less destructive to nanotubes and resulted primarily in dissolution of metal residue and insignificant loss of carbon. For HiPco SWNTs the effect of 4 h of either sonication or reflux was nearly identical. The next 8 h of reflux resulted in a loss of 20% of carbon while the solubility in DMF increased only by 30%. AFM analysis has shown the 30% decrease in average length of individual nanotubes and bundles for this period of time. For the CoMoCat SWNTs, higher solubility in DMF and higher degree of functionalization are accompanied by greater shortening and loss of individual nanotubes and bundles. Therefore, when one chooses the oxidation conditions, duration of treatment as well as nitric acid concentration and temperature have to be considered. To obtain dispersions with no destruction of SWNTs, the sonication method is preferable for all types of nanotubes.

Conclusions

The solubility of single-walled carbon nanotubes in polar solvents can be enhanced markedly without added surfactant or polymer by oxidation with nitric acid under much milder conditions than reported before. Sonication in 8 M nitric acid for 1 h at 40 °C greatly increases solubility in DMF, methanol, and water by introduction of a small number of polar functional groups, splitting of bundles of SWNTs into some individual tubes and mostly smaller diameter bundles, and some shortening of the lengths of bundles. The larger diameter PLV SWNTs are shortened less than HiPco and CoMoCat SWNTs. Treatment times longer than 1 h effect only small increases in solubility. Nanotubes of all three types can be recovered from this treatment with no loss of carbon material and partial removal of residual metallic catalysts. The results are consistent with a mechanism by which the tube ends and sidewall defects are functionalized, and tubes are cut at sidewall defects without extensive functionalization of the remaining sidewalls. The solubility depends on the type of SWNTs, generally decreasing in the order CoMoCat > PLV > HiPco, even though the order of increasing diameters of individual nanotubes is CoMoCat < HiPco < PLV. Compared with the 40 °C sonication method, refluxing the SWNTs in 2.6 M nitric acid for 2−4 h effects somewhat higher solubility, introduces many more sidewall functional groups, and produces smaller diameter bundles. The reflux method also destroys some SWNTs, particularly with CoMoCat materials. Mild nitric acid treatment should be the method of choice to condition SWNTs for many of the larger scale applications of SWNTs such as polymer composites.

Based on Raman spectroscopy and AFM, the recommended procedures for oxidation of nanotubes are as follows:

(a) CoMoCat SWNTs: Sonicate in 8 M HNO_3 for 1.5 h. The reflux procedure is especially harmful for this material.

(b) HiPco SWNTs: Reflux in 2.6 M HNO_3 for 4 h. Reflux allows a higher degree of functionalization. However, the duration should not exceed this time to minimize shortening and material loss.

(c) PLV SWNTs: Sonicate in 8 M HNO_3 for 1−4 h. The sonication method produces longer, more soluble SWNTs without loss of carbon material.

Since every commercial SWNT material is a unique mixture of various types of nanotubes, the stepwise oxidation with monitoring of the size and structure by AFM and Raman spectroscopy are recommended for finding the right conditions for the intended use of the material.

Acknowledgment. We thank the Oklahoma State Regents for Higher Education and the National Science Foundation for Grant EPS-0447262 for financial support.

Supporting Information Available: Raman spectra; AFM micrographs; diameter distribution of nanotubes oxidized by the reflux protocol; UV−vis spectra and material balance results. This information is available free of charge via the Internet at http://pubs.acs.org.

CM071758L