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Sidewall Functionalization of Single-Walled Carbon Nanotubes with Hydroxyl Group-Terminated Moieties

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Single-walled carbon nanotubes functionalized with the OH group-terminated moieties ("hydroxyl nanotubes") have been prepared by fluorine displacement reactions of fluoronanotubes with a series of diols and glycerol in the presence of alkali, LiOH, NaOH, or KOH or with amino alcohols in the presence of Py as a catalyst. The "hydroxyl nanotubes" were characterized by optical spectroscopy (Raman, ATR-FTIR, UV−vis−NIR), electron microscopy (TEM), atomic force microscopy (AFM), and thermal degradation (TGA and VTP-MS) materials characterization methods. The degree of sidewall functionalization in the prepared SWNT derivatives was estimated to be in the range of 1 in 15 to 25 carbons, depending on derivatization method and alcohol reagent used. The hydroxyl nanotubes form stable suspension solutions in polar solvents, such as water, ethanol, and dimethylformamide, which facilitate their improved processing in copolymers and ceramics nanofabrication and provide for compatibility with biomaterials.

Introduction

Chemical manipulation of single-wall carbon nanotubes (SWNT), especially sidewall functionalization, has recently become an area of escalated fundamental and technological interest. Both covalent and noncovalent sidewall chemistry of SWNTs have been reported, including direct fluorination and subsequent derivatization, addition of radicals, carbenes, and nitrenes as well as the 1,3-dipolar and electrophilic additions, and modification through van der Waals interactions with aromatic molecules or polymers.[1−3] The applications of functionalized SWNTs as reinforcers for fabrication of covalently integrated polymer composites[4−6] and as vehicles for targeted drug delivery have recently been demonstrated.[7] These studies have confirmed the need for derivatization of the SWNTs with the organic functional groups which can provide high binding affinity and selectivity through covalent or hydrogen bond formation. They also suggest that, for improving the processing, particularly in biomedical applications, the covalent sidewall functionalization with moieties terminated with hydrophilic substituents, such as hydroxyl groups, should be of primary importance.

Recent experimental studies[2] showed that fluoronanotubes prepared by direct fluorination of SWNTs can be used as versatile precursors for preparation of sidewall-functionalized nanotube derivatives through a nucleophilic substitution of fluorine. On the basis of enhanced reactivity of fluoronanotubes, two one-step chemical methods for preparation of the SWNTs functionalized with the hydroxyl group-terminated moieties have been developed in the present work. Method I (Scheme 1) involves reactions of fluoronanotubes **(1)** with a series of alkane diols and triols pretreated with the alkali bases, such as LiOH, NaOH, or KOH. The series studied herein included ethylene glycol (**2a**), 1,3-propanediol (**2b**), 1,4-butanediol (**2c**), 1,2-propanediol (**2d**), 1,2-butanediol (**2e**), and glycerol (**2f**). In the method II (Scheme 2) the reactions of fluoronanotubes with amino alcohols, such as 2-aminoethanol **(2g)**, 3-aminopropanol (**2h**), and diethanol amine (**2i**), in the presence of pyridine as a catalyst have been utilized. For simplicity, we denote the new SWNT sidewall derivatives prepared by these two methods as "hydroxyl nanotubes". In this paper we provide a full description of the syntheses and characterization data of these derivatives. Some of these data we only briefly presented earlier at the meetings.[8−10]

Experimental Procedures

Materials. In these studies raw SWNTs, prepared at Rice University in the Carbon Nanotechnology Laboratory by the HiPco process, have been thoroughly purified to remove iron and other impurities as described previously.[11] After purifica-

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(1) Khabashesku, V. N.; Margrave, J. L. Chemistry of Carbon Nanotubes. In *Encyclopedia of Nanoscience and Nanotechnology*; Nalwa, S., Ed.; American Scientific Publishers: Steveson Ranch, 2003; and references therein.

(2) Khabashesku, V. N.; Billups, W. E.; Margrave, J. L. *Acc. Chem. Res.* **2002**, *35*, 1087.

(3) Bahr, J. L.; Tour, J. M. *J. Mater. Chem.* **2002**, *12*, 1952.

(4) Barrera, E. V. *JOM* **2000**, *52*, 38.

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

(6) Zhu, J.; Peng, H.; Rodriguez-Macias, F.; Margrave, J. L.; Khabashesku, V. N.; Imam, M. A.; Lozano, K.; Barrera, E. V. *Adv. Funct. Mater.* in press.

(7) Pantarotto, D.; Partidos, C. D.; Graff, R.; Hoebeke, J.; Briand, J.-P.; Prato, M.; Bianco, A. *J. Am. Chem. Soc.* **2003**, *125*, 6160.

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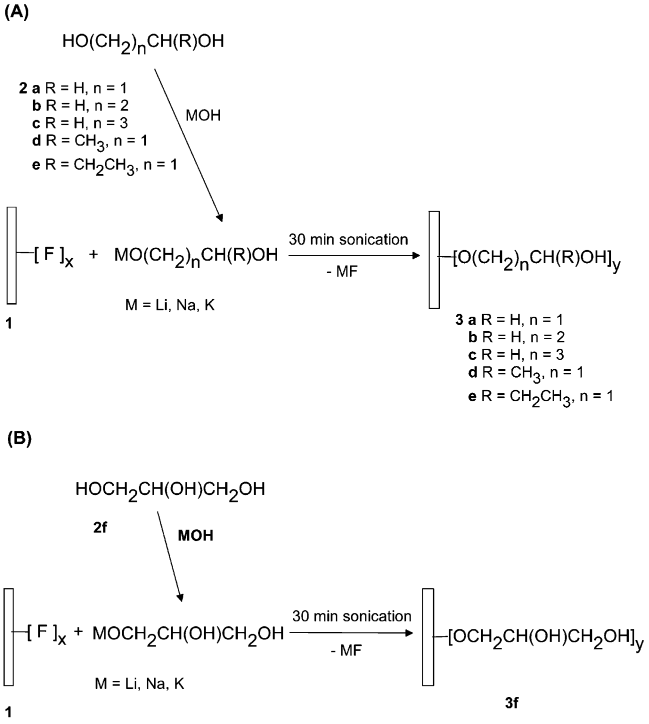
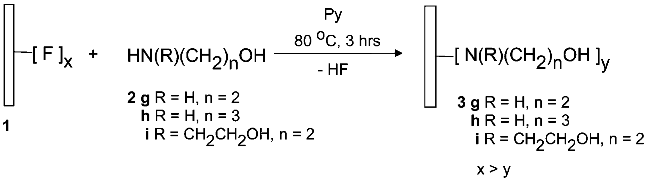
Scheme 1. Chemical Routes for Preparation of "Hydroxyl-nanotubes" by Method 1



Scheme 2. Chemical Routes for Preparation of "Hydroxyl-nanotubes" by Method 2



tion the iron content in the SWNTs did not exceed 1 wt %. The purified SWNTs, supplied by Carbon Nanotechnologies Inc., Houston, TX, in a powder form, have also been used in some experiments. The fluoronanotubes **1** of approximately $C_{2.5}F$ stoichiometry have been prepared by direct fluorination of purified SWNTs at 150 °C according to the procedure earlier reported by our groups.[11] All other chemicals, such as alcohols **2a**−**f** and amino alcohols **2g**−**i**, used in further experimental steps to the synthesis of hydroxyl nanotubes were purchased from Aldrich.

Synthetic Procedures. *Method I.* For preparation of hydroxyl nanotubes by this method (Scheme 1) 10−15 mg of fluoronanotubes **1** were placed in a vial with 10 mL of corresponding diols or triols **2a**−**f** and sonicated (17 W/55 kHz Cole Palmer bath) for 30 min at 80−90 °C to achieve complete dispersion into a suspension solution. In a separate vial, 60−80 mg of LiOH (NaOH or KOH) were sonicated for 30 min in 10 mL of corresponding alkanol until complete dissolution. In the case of diols **2a**−**h** this procedure was carried out at room temperature, while in the case of more viscous glycerol **2f** sonication at elevated temperature (80−90 °C) was necessary. In the next step the solutions from both vials were combined and the resulting mixture was sonicated for about 1 h. Then the reaction mixture was filtered through a 1-μm pore size Cole Palmer Teflon membrane and washed with a large amount of ethanol and water to ensure complete removal of LiF (NaF or KF) and LiOH (NaOH or KOH) byproducts. The precipitated on a membrane black-colored films of hydroxyl nanotubes **3a**−**f** were peeled off and dried overnight in a vacuum oven at 70 °C. The EDX elemental analyses showed 3−5 at. % residual fluorine content in the samples of **3a**−**f** derivatives.

Method II. In these experiments (Scheme 2) fluoronanotubes **1** (10−15 mg) were sonicated in 30 mL of amino alcohols **2g**−**i** for 3 min. This resulted in complete dispersion of fluoronanotubes to form a black-colored solution. Thereafter, five drops of pyridine (Py) were added to the solution as a catalyst and the reaction mixture was stirred under a nitrogen atmosphere for 3 h at 80−90 °C. Then the reaction mixture was filtered through a 1-μm pore size Cole Palmer Teflon membrane with a large amount of ethanol to ensure complete removal of unreacted amino alcohol and reaction byproducts. The collected on a filter functionalized SWNTs **3g**−**i** were dried overnight in a vacuum oven at 70 °C. The detected by EDX analysis residual fluorine content in **3g**−**i** was 11−13 at. %.

Characterization. The Raman, ATR-FTIR, UV−Vis−NIR, TGA, SEM/EDX, AFM, and TEM methods were used for characterization of pristine SWNTs, fluoronanotubes, and hydroxyl nanotubes **3a**−**i** prepared in the present work. The Raman spectra for the samples placed on the top of a standard microscope slide were collected with a Renishaw 1000 microraman system operating with an AlGaAs diode 780-nm laser source. For the ATR-FTIR spectral measurements, a Thermal Nicolet Nexus 870 FTIR system with an ATR accessory was employed. The spectra in the UV−Vis−NIR range were taken using a Shimadzu 3101 PC UV/Vis/NIR spectrometer. The thermal degradation analyses were performed with a TA-SDT-2960 TGA-DTA analyzer. Scanning electron microscopy (SEM) was performed at 30-kV beam energy using a Phillips XL-30 field emission microscope equipped with an energy-dispersive X-ray (EDX) analyzer. A DI-MultiMode-SPM with 2570JV-Z scanner model was used for tapping mode atomic force microscopy analysis (AFM). Transmission electron microscopy (TEM) photoimages of specimen placed on lacey carbon-coated copper grids (size 200 mesh) were obtained with a JEOL JEM-2010 electron microscope operating at an accelerating voltage of 100 kV.

Results and Discussion

Reactions of Fluoronanotubes. Recent DFT calculations[12] implied that the fluoronanotubes are better electron acceptors than the naked carbon nanotubes and therefore they should more eagerly interact with strong nucleophilic reagents. These reactions are also facilitated by the weakened C−F bonds in fluoronanotubes relative to alkyl fluorides and thus fluorine could be more easily displaced. The solubility of fluoronanotubes in alcohols prompted the efforts to functionalize them by reactions with alkoxides. In a single example of this reaction documented prior to the present work, sonication of the fluoronanotubes ($\sim C_2F$) in methanol solution of sodium methoxide for 2 h was shown to produce the sidewall methoxylated tubes with the stoichiometry of $C_{4.4}F(OCH_3)_{0.25}$. The IR and variable temperature−mass spectrometry (VTP-MS) data as well as elevated oxygen content from the electron microprobe analysis confirmed the partial substitution of fluorine in fluoronanotubes and bonding of the methoxy groups to the nanotube side walls.[13,14] It is important to note that we have earlier found that sonication or refluxing of fluoronanotubes in

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(8) Stevens, J. L.; Kiny, V. U.; Huang, A. Y.; Chiang, I. W.; Derrien, G. A.; Khabashesku, V. N.; Margrave, J. L. *Proc. NanoTech* **2003**, *3*, 169−172.

(9) Zhang L.; Peng, H.; Margrave, J. L.; Khabashesku, V. N. *Rice Quantum Institute 17th Annual Summer Research Colloquium*, Aug 8, 2003; Abstr. p 5.

(10) Kini, V. U.; Khabashesku, V. N.; Margrave, J. L. *Rice Quantum Institute 16th Annual Summer Research Colloquium*, Aug 9, 2002; Abstr. p 25.

(11) Mickelson, E. T.; Huffman, C. B.; Rinzler, A. G.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *Chem. Phys. Lett.* **1998**, *296*, 188.

(12) Kudun, K. N.; Bettinger, H. F.; Scusseria, G. E. *Phys. Rev. B* **2001**, *63*, 45413.

alcohols (methanol, ethanol, 2-propanol, ethane diol, and glycerol) alone do not result in significant substitution or elimination of fluorine.[15] Therefore, in the present study alcohols, diols and glycerol, were used both as solvent media and as reagents to provide a surplus of hydroxyl-terminated monoalkoxides through the reactions with alkali bases (Scheme 1).

In the previous studies we have also demonstrated that terminal diamines, $H_2N(CH_2)_nNH_2$ ($n = 2, 3, 4, 6$), can dissolve the fluoronanotubes and under elevated temperatures (90−150 °C) chemically react with them in the presence of catalytic amounts of pyridine. The reactions resulted in almost complete removal and substitution of fluorine and produced the amino group-terminated functionalized SWNTs by creating a direct C−N bonding attachments to the sidewalls.[8,16−18] These results encouraged the analogous choice for the present study of amino alcohols as both solvents for fluoronanotubes and nucleophilic reagents expected to react in the presence of pyridine through their NH_2- rather than $OH-$ end groups and consequently yield the hydroxyl group-terminated SWNT derivatives according to Scheme 2.

Characterization of "Hydroxyl-Nanotube" Derivatives by Optical Spectroscopy. Raman spectroscopy provides essential and quick information for evaluation of the covalent sidewall modification of the nanotubes. The Raman spectra collected for the SWNT derivatives studied in the present work are shown in Figures 1−3. The observation of the peak in the 1285−1300-cm^{-1} region has been related to the sp^3 states of carbon and normally used as a proof of the disruption of the aromatic system of π-electrons on the nanotube sidewalls by the attached functional groups.[1−3] In the Raman spectra of fluoronanotubes **1** (Figure 1A) the observed high-intensity peak at 1293 cm^{-1} reflects the largest content of the sp^3-hybridized sidewall carbons (∼40%) among all functionalized SWNTs prepared in the present work. This high degree of sidewall modification in **1** causes complete disappearance of the typical for pristine SWNT breathing mode peaks at 200−260 cm^{-1} as well as broadening and weakening of the tangential mode peak which is red-shifted from 1594 cm^{-1} in naked nanotubes[1−3] to 1584 cm^{-1} in **1**. The observed in the Raman spectra of hydroxyl nanotubes **3a**−**i** sp^3 carbon peaks in the range of 1287−1293 cm^{-1} thus indicate the covalent functionalization. Lower relative intensity of these peaks than that in the Raman spectrum of fluoronanotubes **1** can be explained by the ongoing (along with fluorine substitution) side elimination of fluorine from **1** in the reactions studied (Schemes 1 and 2), which reduces the number of sp^3 carbon states and partially restores the sp^2-bonding on the nanotube side wall. Unlike **1**, the breathing mode peaks at 200−260 cm^{-1} become visible in the spectra of **3a**−**i** and exhibit higher intensities for SWNT derivatives **3a** and

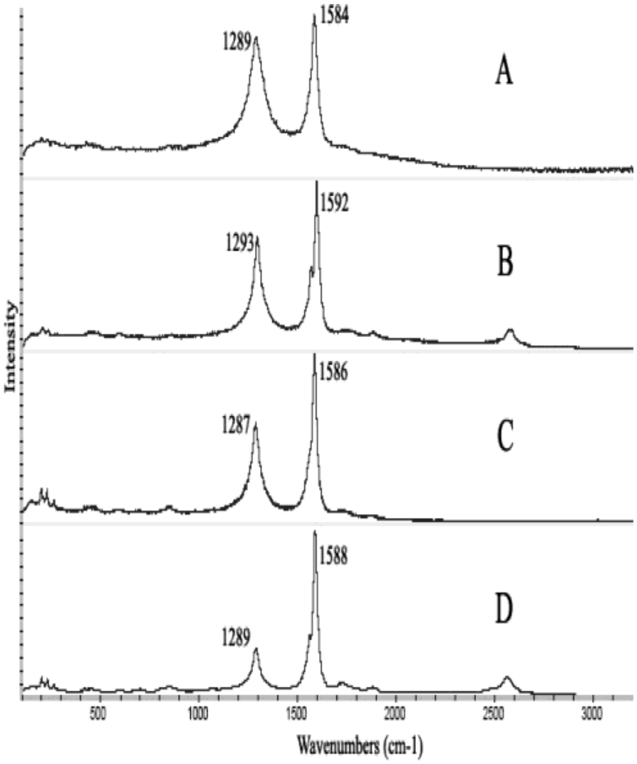

Figure 1. Raman spectra of SWNT materials: fluoronanotube **1** (A), "hydroxyl nanotubes" **3a** (B), **3b** (C), and residue after TGA of **3b** (D).

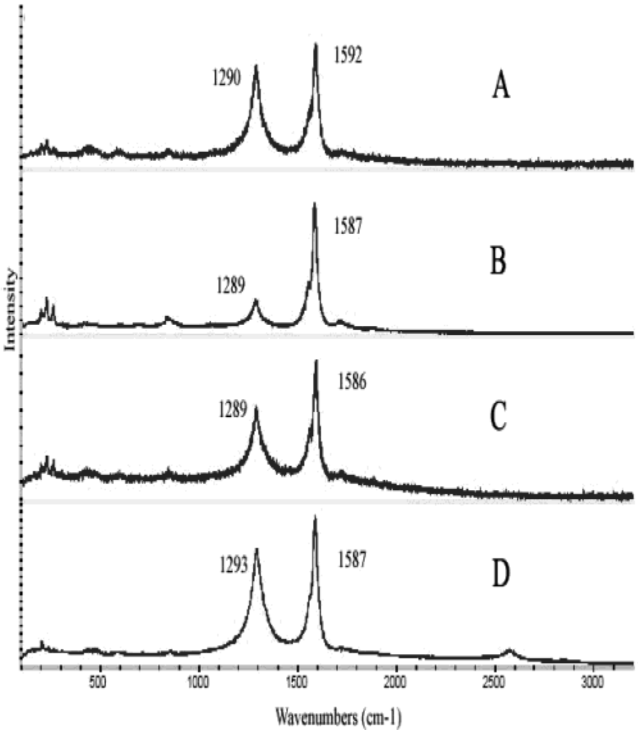

Figure 2. Raman spectra of "hydroxyl nanotubes": (A) **3c**, (B) **3d**, (C) **3e**, and (D) **3f**.

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(13) Mickelson, E. T. *Novel Chemistry of Elemental Carbon: Graphite, Fullerenes and Nanotubes*; Ph.D. Thesis, Rice University, Houston, TX, 1999.

(14) 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.

(15) Shukla, R.; McClain, B.; Khabashesku, V. N.; Margrave, J. L. *Rice Quantum Institute 15th Annual Summer Research Colloquium*, Aug 17, 2001; Abstr. p 19.

(16) Huang, A. Y.; Chiang, I. W.; Khabashesku, V. N.; Margrave, J. L. *Rice Quantum Institute 15th Annual Summer Research Colloquium*, Aug 17, 2001; Abstr. p 18.

(17) Stevens, J. L.; Huang, A. Y.; Peng, H.; Chiang, I. W.; Khabashesku, V. N.; Margrave, J. L. *Nano Lett.* **2003**, *3*, 331.

(18) Khabashesku, V. N.; Stevens, J. L.; Derrien, G. A.; Margrave, J. L. Sidewall Functionalization of Single-Wall Carbon Nanotubes Through C−N Bond Forming Substitutions of Fluoronanotubes. Patent application filed with the U.S. Patent and Trademark Office, Nov. 18, 2003.

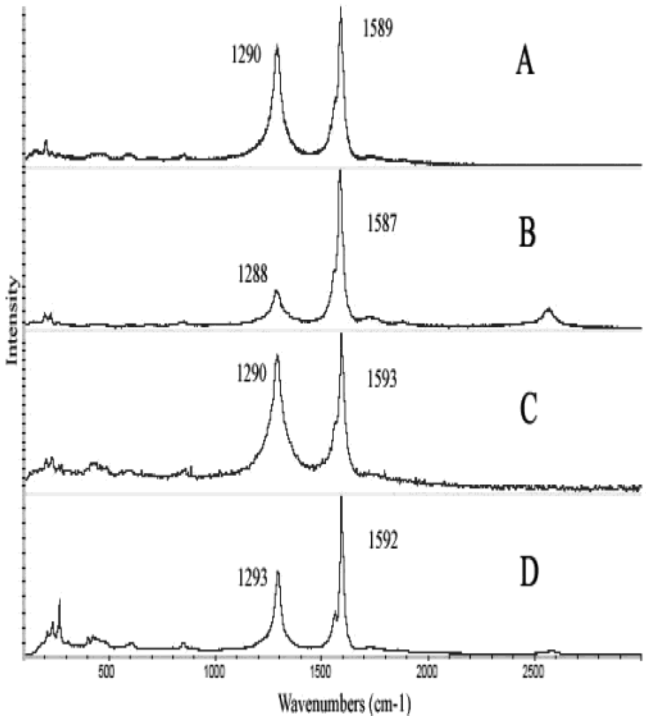

Figure 3. Raman spectra of SWNT materials: (A) **3g**, (B) residue after TGA of **3g**, (C) **3h**, and (D) **3i**.

3d, functionalized at the lowest degree (Figures 1B and 2F). This mode becomes weaker in derivatives **3b**,**c**,**e**−**i** with more attached sidewall groups, which very likely hinders the radial breathing oscillation of the nanotube.

The UV−Vis−NIR spectroscopy serves as another spectroscopic probing of the SWNT sidewall functionalization. In this case altering of the electronic structure instigates loss of the van Hove transition features routinely observed in the spectra of pristine nanotubes. In the present study this argument is illustrated by comparing in Figure 4 the UV−Vis−NIR spectra of pristine SWNT with those taken for fluoronanotube **1** and hydroxyl nanotubes **3f**,**g** in dimethylformamide solution. Unlike naked SWNT, van Hove singularities are completely absent in the spectrum of highly functionailized derivative **1**. Dramatical reduction in the intensities of van Hove singularities observed for **3f**,**g** made their UV−Vis−NIR spectra look typical for sidewall-functionalized SWNTs[1−3,8] and thus provide important evidence for the occurrence of chemical modification.

The ATR-FTIR spectra shown in Figures 5 and 6 were used to identify the hydroxyl group-terminated moieties, covalently bonded to the sidewalls of the SWNTs. The strong peak around 1140 cm^{-1}, characteristic of the C−F bond stretches in the fluoronanotubes **1** (Figure 5A), has disappeared after the reactions with diols, triol, and amino alcohols. This peak was replaced in the spectra of all hydroxyl nanotubes **3a**−**i** by peaks in the 1020−1070-cm^{-1} region, which we attributed to the C−O bond stretches of the nanotube-O−C and C−OH units. The new very broad bands in the range of 3000−3600 cm^{-1} are assigned to the O−H stretches, while the peaks in the 2800−3000- and 1360−1460-cm^{-1} region are assigned to the C−H stretching and deformation modes, respectively. The C−N stretching modes of the nanotube-N(H)−C or nanotube-N(C)−C structural units in the derivatives **3g**,**h** and **3i**, respectively, were observed in the spectral range of 1120−1210 cm^{-1} (Figure 6A−C), characteristic of the C−N modes in secondary and tertiary amines.[19] The activated C═C stretching mode peaks in **1** and **3a**−**i** were observed in the 1540−1580-cm^{-1} region.

Thermal Degradation Studies. These studies provided further evidence for covalent sidewall derivatiza-

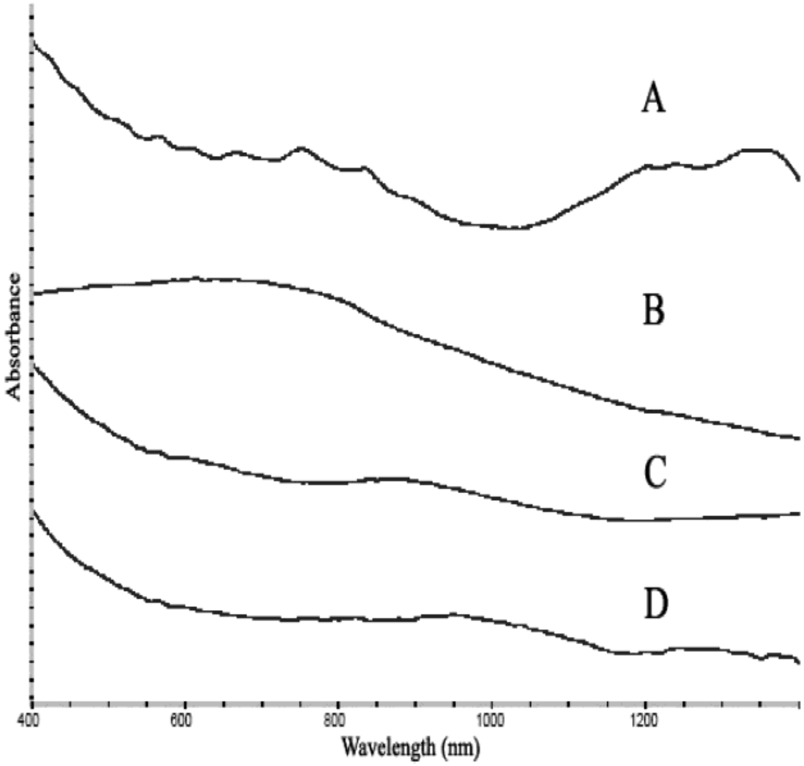

Figure 4. UV−Vis−NIR spectra of pristine SWNTs (A), fluoronanotubes **1** (B), and “hydroxyl nanotubes” **3f** (C) and **3g** (D).

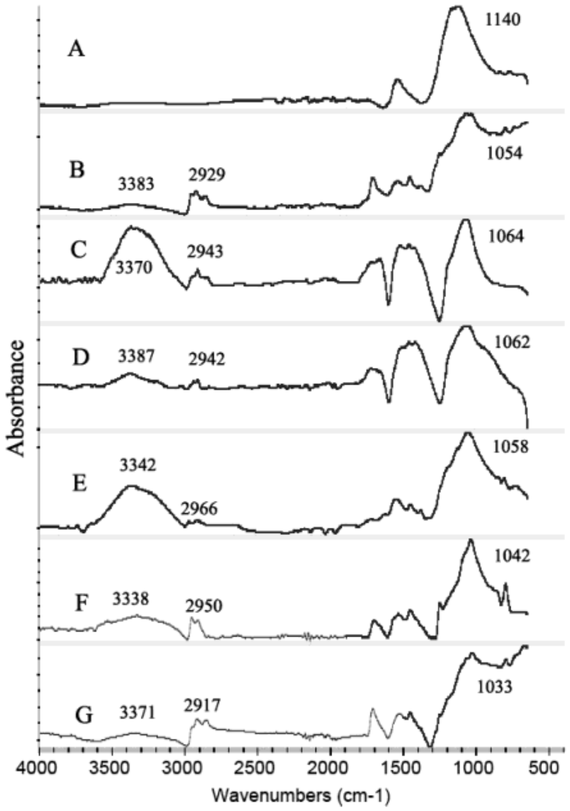

Figure 5. ATR-FTIR spectra of fluoronanotube **1** (A) and “hydroxyl nanotubes” (B) **3a**, (C) **3b**, (D) **3c**, (E) **3d**, (F) **3e**, and (G) **3f**.

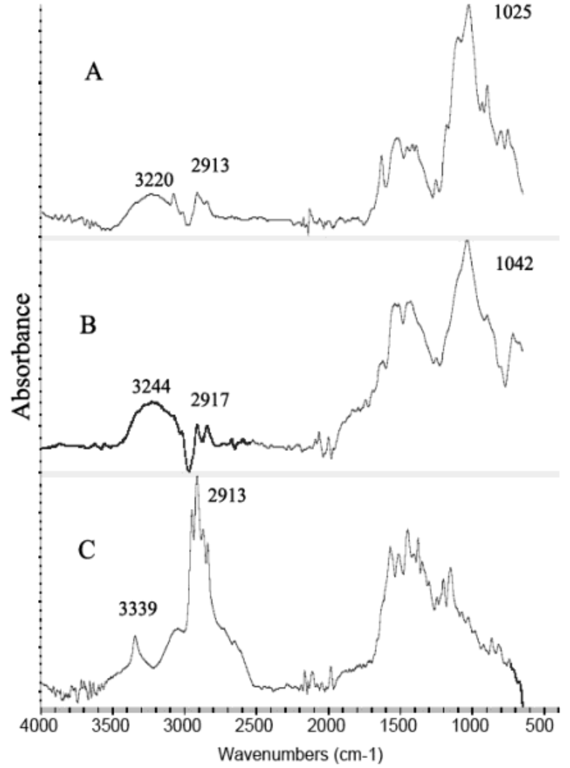

Figure 6. ATR-FTIR spectra of “hydroxyl-nanotubes”: (A) **3g**, (B) **3h**, and (C) **3i**.

tion of nanotubes. As examples, the TGA-DTA data plots obtained for samples **3b**, **3f**, and **3g** (Figures 7−9) show on derivative plots a major peak at 250 °C. The appearance of these peaks at such high temperatures indicates that the weight loss is caused by detachment and fragmentation of OH group-terminated moieties and not

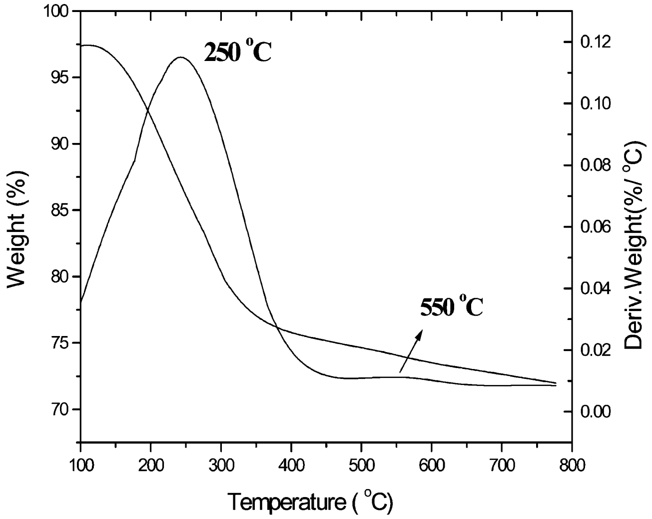

Figure 7. TGA-DTA of “hydroxyl-nanotubes” **3b**.

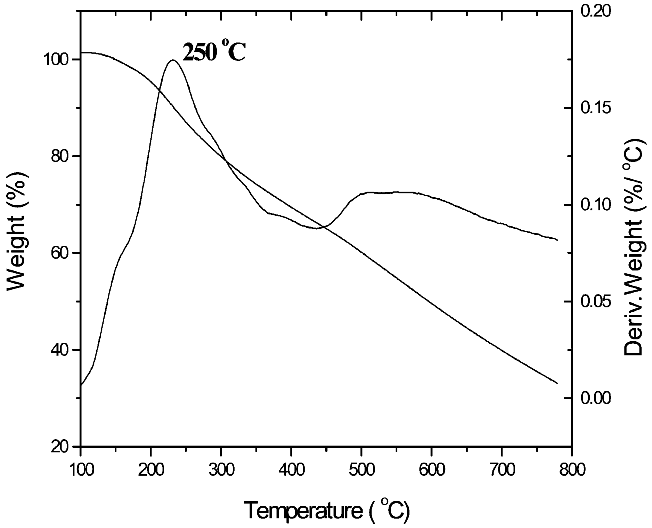

Figure 8. TGA-DTA of “hydroxyl-nanotubes” **3f**.

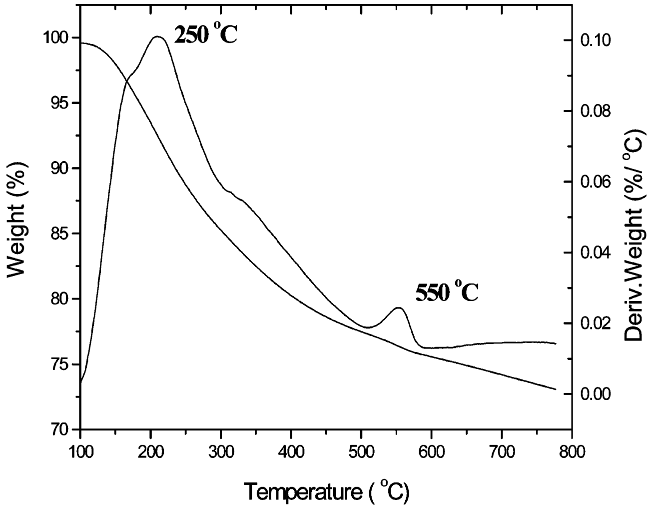

Figure 9. TGA-DTA of “hydroxyl-nanotubes” **3g**.

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(19) Lin-Vien, D.; Colthup, N. B.; Fatelley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press Inc.: San Diego, CA, 1991; p 299.

by desorption of physisorbed species from nanotubes. The second peaks observed on DTA plots for these SWNT derivatives at about 550 °C are due to elimination of residual C−F bonds,[2,14] correlating with the measured by EDX residual fluorine content. The minor character of these peaks shows that the majority of the C−F bonds in fluoronanotubes **1** have been efficiently replaced by the OH group-terminated moieties in the course of reactions (Schemes 1 and 2). The major peaks observed at 250 °C on TGA plots of **3b**, **3f**, and **3g** show the average weight loss of 20%, 35%, and 22%, respectively. By assuming that this weight loss is due to elimination of OH group-terminated moieties, the degree of sidewall functionalization in these derivatives can be roughly estimated as 1/25 in **3b**, 1/16 in **3f**, and 1/20 in **3g**.

The Raman spectra (Figures 1D and 3B) taken for residue materials after TGA of **3b** and **3g** derivatives, prepared by different methods (Schemes 1 and 2), both show a dramatic reduction in the intensity of the sp^3 carbon mode. These data indicate that the detachment of functional groups from nanotube side walls occurs in agreement with the previous observations of thermal degradation properties of other covalently functionalized SWNTs.[1−3,17,20,21]

The volatile species evolving during thermal degradation of SWNT derivatives have been analyzed by variable temperature pyrolysis-mass spectrometry (VTP-MS). The data obtained by VTP-MS for **3a**−**f** indicate a fragmentation of attached groups under vacuum conditions in the 300−550 °C temperature range, detected in mass spectra by peaks at *m*/*z* 44 (C_2H_4O) and 29 (HCO) in **3a** and **3d**−**f**, and additional groups of peaks at *m*/*z* 58, 57, 56, 55 (C_3H_6O through C_3H_2O) and *m*/*z* 72, 71, 70 (C_4H_8O to C_4H_6O) in **3b** and **3c**, respectively. The presence of sidewall C−N bonded groups in the derivative **3i** causes the appearance of a major peak at *m*/*z* 105 due to a detaching diethanol amine at temperatures in the 250−400 °C range.

Microscopy Analysis. The TEM allowed direct imaging of sidewall modification in the hydroxyl nanotubes. Figure 10 shows a TEM image of glycerol-functionalized SWNT **3f** specimen placed on a lacey carbon-coated copper grid. The inset clearly shows a "bumpy" surface of a single nanotube resulting from covalent alteration of the fraction of carbon−carbon bonds on the sidewall from shorter sp^2 to a longer sp^3 state carbon-formed linkages.

The atomic force microscopy studies of the **3f** derivative (Figure 11) revealed the significantly reduced in comparison with the pristine SWNT nanotube bundle sizes due to the sidewall functionalization. The pristine SWNTs are known to aggregate into bundles ranging from several tens to a hundred nanometers in diameter. The average bundle sizes in **3f** were measured to be only 3−6 nm in diameter. It is most likely that within those bundles the individual hydroxyl nanotubes are linked together through the hydrogen bonds formed by the terminal OH groups from the side chains. The tapping mode analysis of the backbone profile of the functionalized SWNT bundle shows the average height of 4.4 nm. The height difference (~0.8 nm) measured along the backbone area, free of amorphous carbon particle impurity, can probably be related to the approximate length of the $OCH_2CH(OH)CH_2OH$ chain attached to the nanotube sidewalls in a "stretched" fashion shown by the TEM image in the inset in Figure 10.

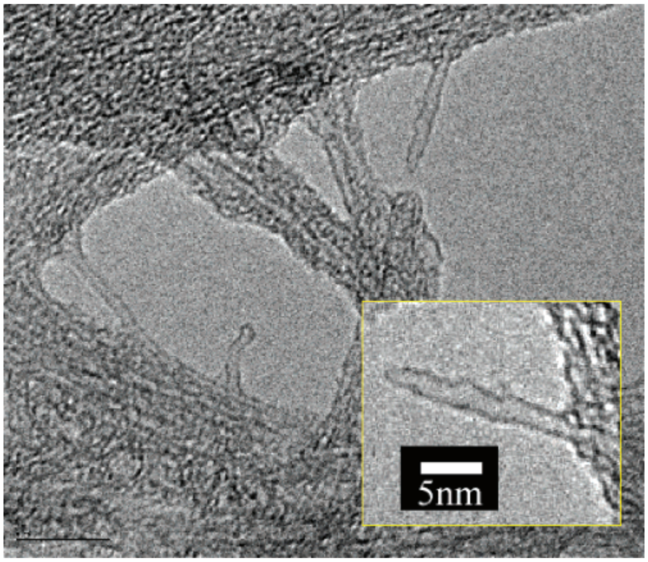

Figure 10. TEM image of the specimen of "hydroxyl nanotubes" **3f**. Inset shows a zoomed-on picture of a single functionalized nanotube.

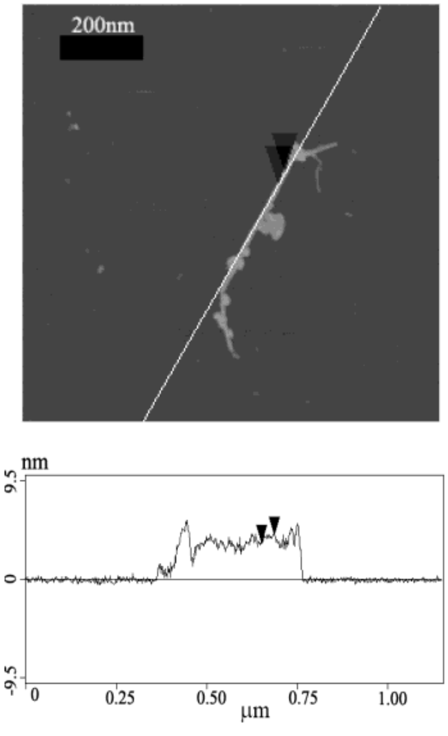

Figure 11. AFM image and height analysis along a backbone of a bundle of "hydroxyl-nanotubes" **3f**. The arrows point to a 0.8-nm height difference due to sidewall functionalization.

Solubility. All prepared hydroxyl-nanotube SWNT derivatives have shown an improved solubility in polar solvents as compared with pristine SWNTs (Figure 12A). The most stable solutions were obtained from the glycerol-derived SWNT material **3f**, probably due to the highest content of hydroxyl groups in the nanotube side

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(20) Peng, H.; Reverdy, P.; Khabashesku, V. N.; Margrave, J. L. *Chem. Commun.* **2003**, 362.

(21) Peng, H.; Alemany, L. B.; Margrave, J. L.; Khabashesku, V. N. *J. Am. Chem. Soc.* **2003**, *125*, 15174−15182.

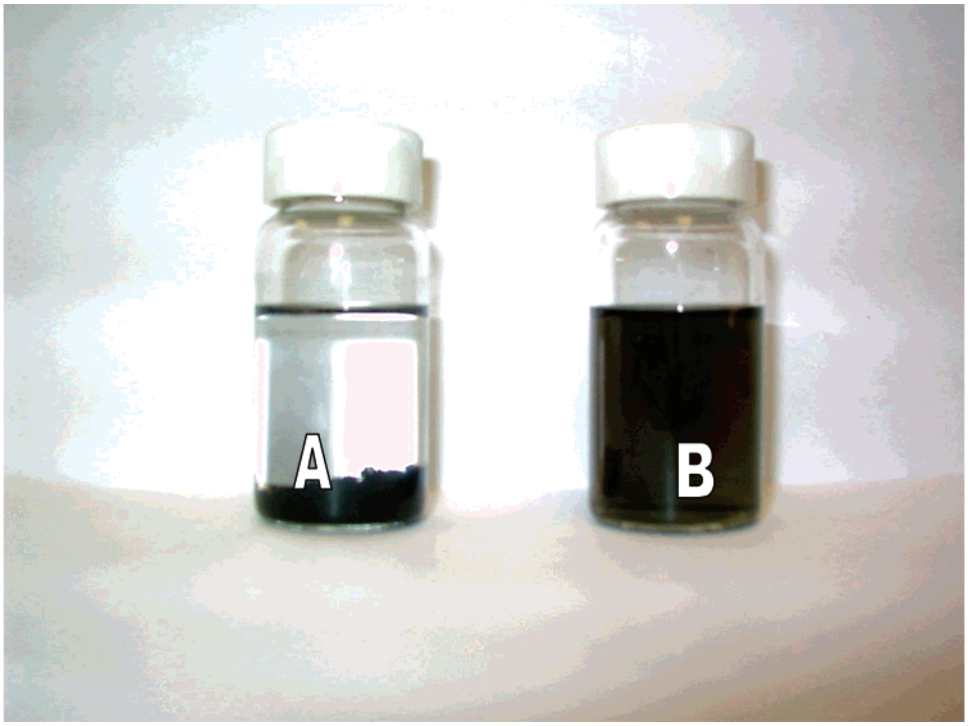

Figure 12. Photographs of the SWNT materials dispersion in ethanol: (A) pristine SWNTs and (B) glycerol-functionalized SWNTs **3f**.

chain. The solutions of **3f** in water (~40 mg/L) were stable for several days, while ethanol solutions (Figure 12B) with higher **3f** concentration (~80 mg/L) showed little precipitation only after several months.

Conclusion

We have developed two convenient and efficient methods for sidewall functionalization of single-walled carbon nanotubes with OH group-terminated moieties—"hydroxyl nanotubes". These functional groups have been attached to sidewalls either through the C−O or C−N covalent bonds. Both methods illustrated by Schemes 1 and 2 utilize mild reaction conditions and can be readily followed. The applications of SWNT derivatives prepared in the present work will be based on hydrogen-bonding ability and chemical reactivity of terminal hydroxyl groups in the side chain. The chemistry of the OH group is so abundant that the hydroxyl nanotubes can be used to produce covalently integrated nanotube-reinforced copolymers and ceramics as well as biomaterials. These studies are currently in progress in our laboratory.

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