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Functionalization and Dissolution of Nitric Acid Treated Single-Walled Carbon Nanotubes

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Abstract: We report an investigation of the nature and chemical functionalization of nitric acid treated single-walled carbon nanotubes (SWNTs). SWNTs washed with diluted sodium hydroxide solutions were characterized by near-IR, mid-IR, and Raman spectroscopy as well as TEM, and the remaining carboxylic acid content was determined to assess the effect of base washing on the removal of carboxylated carbon fractions, which are generated by the nitric acid treatment. It was found that even after exhaustive washing with aqueous base the purified SWNTs contain carboxylic acid groups in sufficient quantity to prepare high quality soluble SWNT materials by covalent functionalization with octadecylamine.

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1. Introduction

While there has been substantial progress in the purification of single-walled carbon nanotubes (SWNTs),[1−18] outstanding questions remain and the resolution of this issue constitutes one of the most serious obstacles to the realization of high quality SWNT specialty chemicals and to the exploitation of the unique properties of this material.[19−21] The contaminants in the as-prepared materials (AP-SWNTs) are comprised of residual metal catalysts and carbonaceous byproducts including amorphous carbon (AC) and graphitized carbon nanoparticles (CNPs), which are generated by the various preparative techniques (electric arc, CVD, laser oven). Oxidative procedures are often employed as a first step in the removal of these impurities,[13,20] and the most common technique involves a reflux of the AP-SWNTs in nitric acid.[1,2,22] This treatment reduces the metal content, but it is known to consume some of the SWNTs and to produce additional carbonaceous impurities, commonly referred to as carboxylated carbons (CCs).[1,2,22−25] The nature of this problem was first recognized by the Smalley group who identified the CCs as polycyclic aromatic sheets, edge terminated with carboxylates (carboxylated carbon fragments, CCFs) together with cross-linked structures (carboxylated amorphous carbon, CAC).[1,2] While filter washing with mildly basic solution was shown to be effective in removing the CCs on a small scale, these workers noted that the process could not be scaled due to the tendency of the retained SWNTs to pack together and inhibit the filtration process as they accumulate deposited CCs.[2] The large scale purification of the nitric acid treated SWNTs utilized centrifugation followed by cross-flow filtration and an additional "polishing" step.[1,2]

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Shortly thereafter we introduced soluble SWNTs by chemically functionalizing the carboxylic acid groups that are introduced by nitric acid treatment with octadecylamine to produce SWNTs terminated with long chain amides (SWNT-CONH$(CH_2)_{17}CH_3$).[26] Given the presence of CCs, we were curious about the nature of the soluble SWNTs and undertook a number of studies to clarify the role of carboxylated impurities in the dissolution process. We began by analyzing the amount of end-group and defect sites present in nitric acid treated SWNT samples;[23−27] this was accomplished by converting the carboxylic acid groups to octadecylamide (SWNT-CONH$(CH_2)_{17}$-CH_3) and octadecylester (SWNT-COO$(CH_2)_{17}CH_3$) groups via the acylchloride. We found that the loading of octadecylamide (ODA) and octadecyloxy (ODO) groups present in the sample was higher than the expected value of 0.25 mol percent functionality which would be characteristic of a perfect 100 nm long (10,10) SWNT, which is cut perpendicular to the nanotube axis and terminated with carboxylic acid groups.[23,27] This result indicated that contaminating CCs could be retained in the samples that were produced during the nitric acid treatment, together with end- and defect-functionalized SWNTs.

The presence of highly carboxylated contaminants in the nitric acid treated SWNTs was further supported by the high acid content determined by acid−base titrations, which exceeded the theoretical value (above) by an order of magnitude in some cases.[24] The titration experiments were carried out in two steps: (1) a forward titration with base in which the conjugate base of the SWNT-COOH material was isolated by filtration, (2) a reverse titration step with acid neutralization of the conjugate base (SWNT-COO$^-$ Na$^+$) isolated in the first step. In general it was found that the acid content determined in the forward step (1) was higher than that in the reverse step (2), and the difference was attributed to the partial purification which is achieved in the basic titration as a result of dissolution of the CCs in step (1).[24]

We used chromatography to investigate the nature of the material that was taken into solution by the ODA functionalization; due to the high solubility of ODA functionalized SWNTs, this material could be separated on HPLC columns resulting in fractions of SWNT-CONH$(CH_2)_{17}CH_3$ and CC-CONH$(CH_2)_{17}CH_3$ that were characterized by AFM, UV−vis absorption and emission, near IR, and Raman spectroscopy.[28,29] The fact that the SWNT-CONH$(CH_2)_{17}CH_3$ fraction which separated on the column was recovered in high yield from the HPLC experiment suggested that this material maintained its solubility in the absence of functionalized CCs.

Recently there has been a resurgence of interest in this issue, and several groups have reported the removal of CCFs by washing nitric acid treated carbon nanotubes with NaOH.[30−34] In some cases it was found that the majority of the carboxylic acid functionality was present on the CCFs and that this contaminant must be removed prior to chemical functionalization.

Surfactants[2] and side-wall functionalization[35−40] have been extensively employed to disperse SWNTs, but noncovalent interactions and π-stacking routes for the dissolution of SWNTs have also become well developed.[41−48] It is therefore plausible that it is the adsorption of the functionalized CCFs on the SWNT surface that is responsible for the dissolution of materials such as SWNT-CONH$(CH_2)_{17}CH_3$.[30−33]

There have been substantial advances in the analysis and postprocessing of nitric acid treated SWNTs so that it is now possible to contemplate the essentially complete removal of the CCs which we take to be comprised of CAC and CCFs.[1−3,13,20,22,49−51] Thus it seemed worthwhile to revisit this issue, and in the present study we base washed nitric acid treated electric arc SWNTs (SWNT-COOH) that had been purified by low speed centrifugation,[22,50] before functionalization with octadecylamine (ODA), and fully characterized both materials (SWNT-COOH and SWNT-CONH$(CH_2)_{17}CH_3$). It is the purpose of the present manuscript to investigate the removal of the CCs and the role of this contaminant in the dissolution of SWNTs chemically functionalized with long chain amides (SWNT-CONH$(CH_2)_{17}CH_3$). The results lead to a consistent picture of the effect of base washing on SWNTs, the presence of residual carboxylic acid functionality, and the role of CCs in the solubility of functionalized SWNTs.

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2. Experimental Section

As prepared SWNTs, produced by electric arc discharge, were obtained from Carbon Solutions, Inc. (www.carbonsolution.com). The SWNTs were refluxed in concentrated nitric acid for 1.5 h and then purified by low speed centrifugation.[22,50] Other chemicals were purchased from Aldrich and used without further treatment. The sonication of samples was performed in a VWR Ultrasonic Bath sonicator (model 550HT). Solution phase near-IR data were collected in a quartz cell of 1 cm path length on a Varian Cary 5000 spectrophotometer. The mid-IR spectra of the materials were obtained from thin films on a ZnSe substrate using a Nicolet Nexus FT-IR spectrometer at a resolution of 8 cm^{-1}, and the spectrometer chamber was purged with nitrogen during the spectra collection. TGA was performed at a heating rate of 5 °C/min in air using a Pyris 1 thermogravimetric analyzer (Perkin-Elmer). Raman spectra of the starting material and products were collected from a Bruker RFS 100/S type FT-Raman spectrometer using a Nd:YAG laser excitation source with a wavelength of 1064 nm and a resolution of 8 cm^{-1}. Images from a high resolution transmission electron microscope (TEM) were obtained from a Technai 12 instrument operating at a 120 kV accelerating voltage.

The optimal concentration of the NaOH solution for base washing the SWNT-COOH material was determined by conducting a series of experiments to measure the amount of CCs that were removed in a single wash. For these experiments, 100 mg of purified, nitric acid treated SWNT-COOH (0W) were dispersed in 100 mL of 0.001, 0.01, 0.1, or 1 M NaOH by sonication (~30 min) in a polyethylene container; this mixture was allowed to stir for 48 h under argon. The black mixture was filtered through a Millipore Durapore membrane with a pore size of 0.22 μm and a diameter of 90 mm supported on a stainless steel frit. The filtrate was then diluted to 500 mL, and the absorbance at 550 nm was measured and normalized by the concentration ($A \times 0.5$ L/0.1 g).

Once the concentration of the base was optimized, successive base washings were performed in a Teflon beaker: 500 mg of 0W SWNT-COOH were dispersed in 500 mL of 0.01 M NaOH by sonication for 30 min followed by stirring for 1 h. To facilitate the filtration, which is very slow in the presence of high concentrations of CCs,[2,20] the mixture was divided into two equal portions which were processed in separate filtering stations comprised of a Millipore Durapore membrane with a pore size of 0.22 μm and a diameter of 90 mm supported on a stainless steel frit. The material was recombined, and either the solid was neutralized (1W) or the previous steps were repeated two more times (3W) or until the filtrate was colorless (FW). All samples were neutralized by addition of 500 mL of 0.01 M HCl. These mixtures were filtered using 0.4 μm polycarbonate membranes and were washed with DDI water until the filtrate was pH neutral. Each material was collected, dried, and fully characterized before undergoing functionalization.

The acid content was determined by directly neutralizing each of the materials with NaOH.[52] Briefly, 100 mg of SWNT-COOH material were combined with 25 mL of 0.0125 M NaOH in a sealed polyethylene container. After 48 h of stirring under Ar, the pH was measured with a Corning pH meter 445, and this value was compared to a blank solution (without SWNT material) that underwent the same process.

Functionalization of the carboxylic acid groups of the washed samples (1W, 3W, and FW) and the starting material (0W) was achieved by use of the 1,3-dicyclohexylcarbodiimide (DCC) coupling reaction. Approximately 100 mg of material were sonicated in 100 mL of anhydrous *N*,*N*-dimethylformamide (DMF, DrySolv) for 10 h. In an argon atmosphere, the homogeneous suspension was then combined with 1 g of DCC and was stirred for 30 min at room temperature. Then 1 g of octadecylamine (ODA) was added, and the reaction temperature was raised to 120 °C. After 6 days, the resulting solution was cooled to room temperature and filtered on a 0.2 μm Millipore Fluoropore membrane. The material was redispersed in DMF and filtered repeatedly until the filtrate was colorless; this step was repeated with ethanol. The resulting black solid was dried at room temperature under vacuum in a desiccator (yield by weight was 100−110%).

The solubility of the functionalized material in tetrahydrofuran (THF) was estimated from a saturated dispersion: 50 mg of the functionalized material and 5 mL of THF were sonicated for 6 h, and the resulting suspension was allowed to stand overnight at room temperature. Then 50 μL of the upper layer were carefully removed by syringe and further diluted to 25 mL with THF. The concentration of the dispersions was calculated by estimation of the extinction coefficient at 550 nm, using a previously described procedure.[53]

3. Results and Discussion

We began by determining the optimum pH for the extraction of the CCs by base washing nitric acid treated electric arc SWNTs (SWNT-COOH) that had been purified by low speed centrifugation,[22,50] while recognizing that this was unlikely to lead to a single step process for removal of the CCs (at least on any useful scale).[2,20] Thus we examined the effect of a single base washing step over a range of pH values using aqueous solutions of NaOH with concentrations from 0.001 to 1 M. As noted by a number of authors, the color of the filtrate is an indication of the amount of material that is being removed in the washing step; the darker and, consequently, the higher the absorbance of the filtrate, the more concentrated the CC extract.[30−32] Thus we monitored the efficiency of the process by spectroscopy (experimental section), by measuring the normalized absorbance of the extract at 550 nm. As may be seen from Figure 1A, the maximum absorbance of the filtrate from a single NaOH extraction occurred in the vicinity of pH 12 and presumably represents a compromise between a number of factors including the pK_a of the acid functionalities present in the CCs, the solution ionic strength, zeta potentials, and the filtration process. As explained below, this latter factor is the most important in determining the efficiency of the process.[2]

We examined the removal of CCs by serial base washings (NaOH solution, pH = 12) to investigate the convergence of this technique. By using spectroscopic techniques we were able to detect the continued removal of CCs until washing number 15 (Figure 1B). As noted previously, simple base washing is not a practical technique for the large scale purification of nitric acid treated SWNTs,[2,20] because the SWNTs pack together as the volume of the dispersion is reduced in the filter funnel resulting in a nanotube cake that acts as a second membrane which hinders the separation of the CCs and dramatically slows the permeation rate of the NaOH solution; thus the area of the filter membrane is the critical parameter.[2]

We characterized the base washed SWNT-COOH material at various stages of the procedure: 0 washings, 1 washing, 3 washings, and full (15) washings (when no more material was observed to be removed), hereafter referred to as 0W, 1W, 3W, and FW, respectively. The acid content of each of these samples was determined, the purity assessed by near-IR absorption spectroscopy, and the Raman spectrum obtained. Samples of each material were then functionalized with ODA, and the ODA loading in the SWNT-CONH$(CH_2)_{17}CH_3$ product was estimated by mid-IR absorption.[23]

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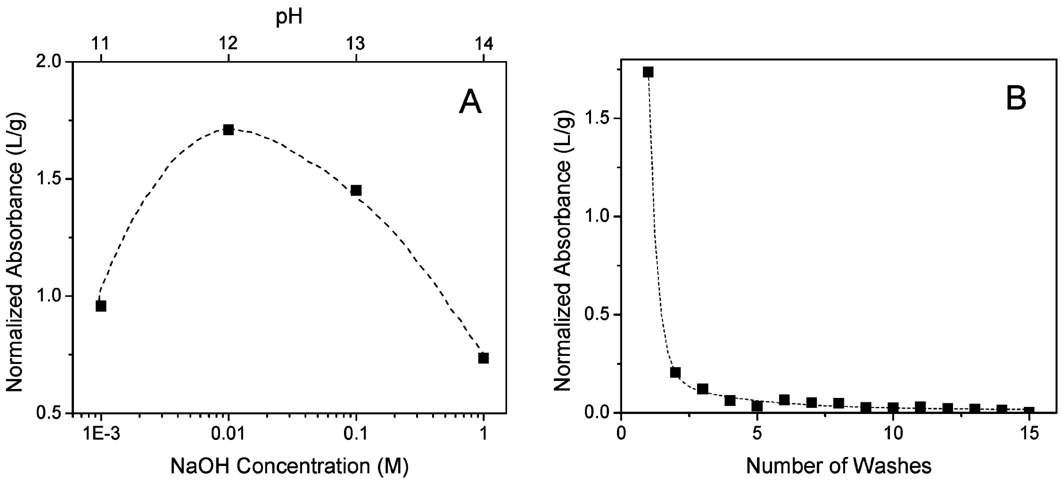


Figure 1. Normalized absorbance at 550 nm of the filtrate after base washing of nitric acid treated SWNTs. (A) Single washing with 0.001, 0.01, 0.1, and 1 M NaOH; (B) serial washing with 0.01 M NaOH.

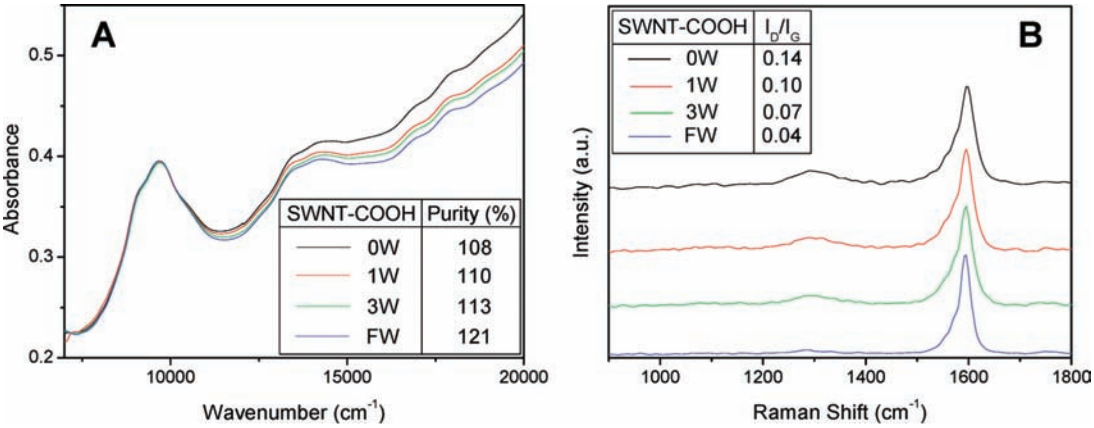
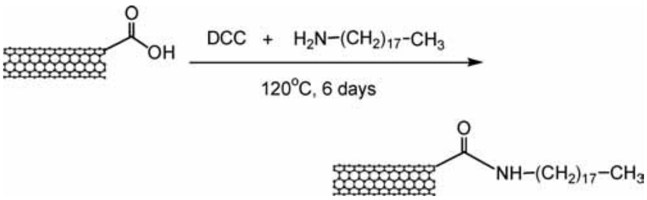


Figure 2. (A) Near-IR spectra and relative carbonaceous purities, (B) Raman spectra and I_D/I_G values of SWNT-COOH materials (0W, 1W, 3W, and FW correspond to 0, 1, 3, and full washes). Raman spectra are normalized at the G-band and shifted vertically for clarity.

The relative carbonaceous purity of each sample of the base washed SWNT-COOH materials was characterized by use of near-IR spectroscopy;[21,54] the relative purity of the SWNTs increased monotonically with the number of base washing cycles performed on the starting material (Figure 2A) presumably because the removal of the CCs decreases the background absorption of the carbonaceous impurities which underlies the S_{22} interband transition.[53,55] The higher relative carbonaceous purity with increasing base wash cycles measured by near-IR analysis is supported by Raman spectroscopy (Figure 2B). As seen in previous studies,[30−32] the intensity ratio, I_D/I_G, is reduced upon base washing and the evolution toward an increasingly pure product from 0W to FW is observed.

Functionalization of each material (0W, 1W, 3W, and FW) was accomplished by a DCC coupling reaction that resulted in the attachment of ODA through an amide linkage to give SWNT-CONH(CH$_2$)$_{17}$CH$_3$,[23,25,26,56−58] as seen in Scheme 1.

Scheme 1



Prior to functionalization, it is important to achieve a well dispersed mixture of SWNTs in DMF. For the reactions, a 10 h sonication treatment was employed to ensure that the material was fully dispersed within the solvent. Poor dispersions inhibit access of the reagents to the SWNT-COOH acid sites, which ultimately results in incomplete functionalization. After completion of the functionalization reaction, initial filtration of the reaction mixture gave rise to a dark filtrate which is due to the presence of the functionalized impurities previously isolated by chromatography.[28,29]

The removal of acid sites and the occurrence of the functionalization reactions are supported by mid-IR spectroscopy. The broad peak centered at 1741 cm^{-1}, which is assigned to the C=O stretch of the carboxylic acid groups, decreases with base washing (Figure 3A). Upon formation of the amide linkage, well-defined peaks are observed (Figure 3B); the prominent bands at 2920 and 2850 cm^{-1} are due to the symmetric and

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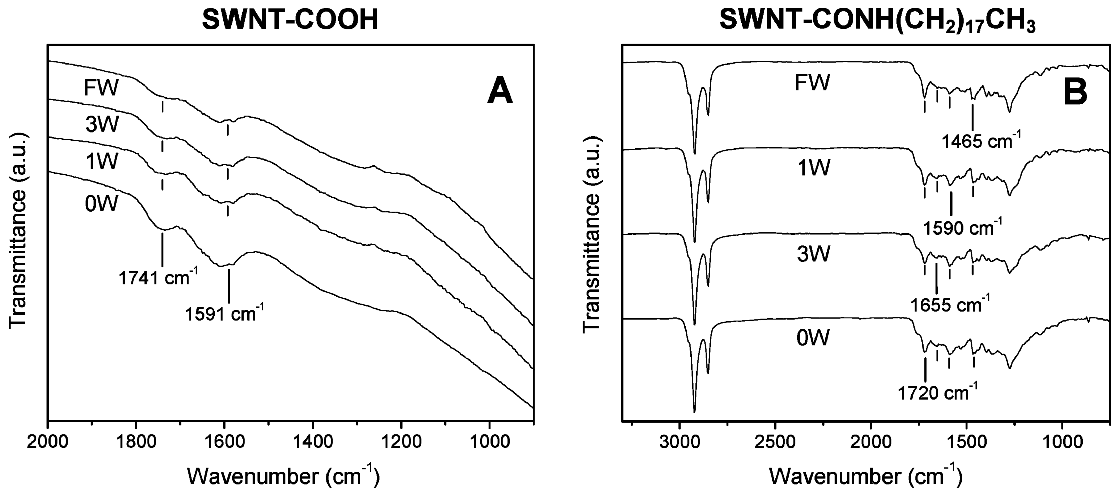

Figure 3. Mid-IR transmittance spectra of thin films of (A) unfunctionalized SWNT-COOH material and (B) SWNT-CONH(CH$_2$)$_{17}$CH$_3$ material (baseline corrected spectrum) deposited on a ZnSe substrate (0W, 1W, 3W, and FW correspond to 0, 1, 3, and full washes).

asymmetric vibrations of the C−H groups, and the shift of the C=O stretch to 1655 cm^{-1} supports the conversion of the carboxylic acid group to an amide.[23] The peaks at 1590 and 1465 cm^{-1} may be attributed to the C=C stretching of the polyaromatic backbone of the nanotubes. The peak at 1720 cm^{-1} may be assigned to the presence of residual lactones or anhydrides[59] that remain after functionalization.

Identifying the oxidation temperatures of the individual components of carbon nanotube materials from a TGA scan is complicated by the interaction between the components - particularly the nature and quantity of metallic catalyst impurities. Due to the interaction between the components, the TGA usually consists of overlapping peaks that appear over a broad temperature range as shown in the TG derivative data.[60] In Figure 4, the sharp peak at 480 °C for the unwashed SWNT-COOH materials is evidently associated with the CCs due to its gradual disappearance with base washing. While this peak is prominent in the 0W material, it is estimated to be associated with no more than 17% of the total starting material by weight; this is comparable to the total weight of CCs removed at FW. The CC peak has an overlapping peak at about 515 °C seen in the 0W SWNT-COOH material. With continual base washing, the this peak gradually shifts to 535 °C as the CCs are completely removed. This peak and the broad peak at 700 °C may be attributed to residual SWNTs and other large graphitic structures such as CNPs. When functionalized, a peak at 345 °C appears, indicating the presence of the ODA in the samples. This peak is observed to be the largest in 0W SWNT-CONH(CH$_2$)$_{17}$CH$_3$ material, indicating a higher loading when compared to the other functionalized materials.

We have previously shown that solution phase mid-IR spectroscopy may be used to determine the loading of the ODA functionality present in the SWNT-CONH(CH$_2$)$_{17}$CH$_3$ material based upon the measured absorbance of the C−H stretch of a sample with known concentration.[23] The reduction in the degree of functionalization of the SWNT-CONH(CH$_2$)$_{17}$CH$_3$ material with base washing of the starting material suggests that under standard washing conditions some of the CCs become functionalized and are retained in the final product. In our previous determination of the acid content of the SWNT-COOH material we utilized an acid−base titration sequence as discussed above.[24,61] However this method involves the filtration of a basic dispersion of the SWNT-COOH material, and we have already reported that it removes CCs in the first step of the procedure;[24] thus in the present work we employed direct base titration experiments to determine the acid content.[52] If none of the CCs

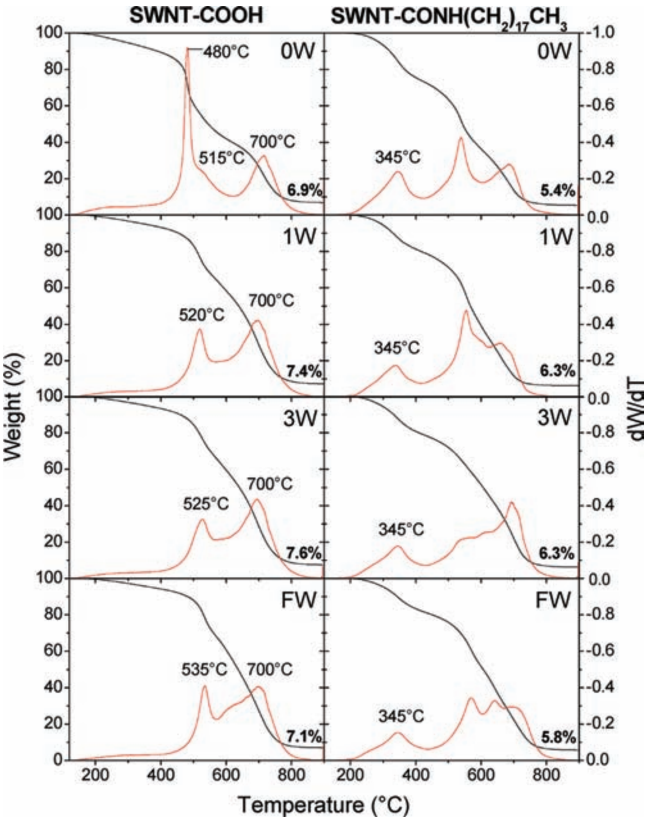

Figure 4. TGA measurements showing weight change (black line) and its derivative (red), together with residual metal oxide: base washed samples (left column, SWNT-COOH) and functionalized samples (right column, SWNT-CONH(CH$_2$)$_{17}$CH$_3$) (0W, 1W, 3W, and FW correspond to 0, 1, 3, and full washes).

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Table 1. Estimated ODA Loading (Weight Percent) in SWNT-CONH$(CH_2)_{17}CH_3$ Materials Calculated from Solution Phase Mid-IR and Acid Content Data[a]

	mid-IR data			acid content data		
sample	sample weight (mg)	ODA weight (mg)	ODA loading (%)	acid content of starting material (mol %)	acid content of starting material (meq/g)	theoretical ODA loading (%)
0W	1.0	0.33	33	2.9	2.4	39
1W	0.9	0.22	25	1.9	1.6	30
3W	1.0	0.24	24	1.6	1.4	27
FW	1.0	0.20	20	1.2	1.0	21

[a] 0W, 1W, 3W, and FW correspond to 0, 1, 3, and full washes; details of these calculations are given in the Supporting Information.

were removed during functionalization, the loading of ODA determined for the SWNT-CONH$(CH_2)_{17}CH_3$ material would be identical to the values obtained from the acid content data in the SWNT-COOH starting material (Table 1); the fact that the degree of functionalization is always less than the acid content data suggests that the filtration with DMF and then ethanol during the workup of the reaction is partially effective in removing the functionalized CCs.

As seen in Table 1, there is a gradual decrease in the degree of functionality for both the starting material and functionalized samples as a function of the number of base wash cycles. The analysis shows that the amount of acid sites is reduced from 2.4 to 1.0 meq/g; this is still higher than the value of 0.25 mol percent functionality (0.21 meq/g), which would be characteristic of a perfect 100 nm long (10,10) SWNT, which is cut perpendicular to the nanotube axis.[23,25] Nevertheless this value represents a theoretical minimum for SWNTs of this length, and given the damage that is apparent after nitric acid treatment,[57,62] it may be that this result is characteristic of such samples.

TEM images verify the effectiveness of functionalization and the base wash in purifying nitric acid treated SWNTs (Figure 5). In the SWNT-COOH starting material (0W), the nanotubes have a web-like coating along the side walls which presumably corresponds to the CCs. After several washes with dilute NaOH, the material is freed from this coating and well-defined side walls become visible (FW). Upon functionalization the final SWNT-CONH$(CH_2)_{17}CH_3$ materials are indistinguishable, and it is apparent that the careful workup of functionalized SWNTs and exhaustive base washing of the starting SWNT-COOH material are effective in producing high quality materials.

Finally, the solubility of each of the functionalized materials was evaluated by using the extinction coefficients calculated for each material at 550 nm. The solubility of SWNT-CONH$(CH_2)_{17}CH_3$ was found to be approximately constant at 7 g/L (Table 2), and thus the CCs retained in the samples exert a relatively minor effect on the dissolution of this material. These SWNT derivatives dissolve in organic solvents in much the same way as high polymers to give extremely viscous solutions. This result serves to emphasize the ability of chemical functionalization to modify and enhance the properties of single-walled carbon nanotubes and encourages the view that SWNT specialty chemicals are within reach.

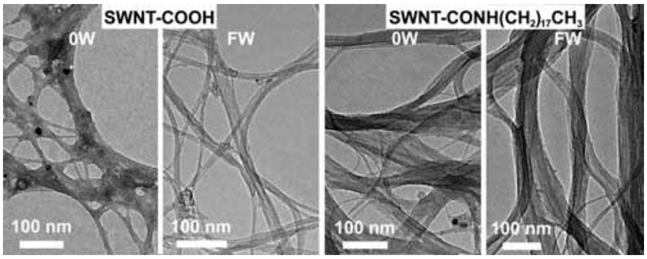

Figure 5. TEM images of unfunctionalized (SWNT-COOH) and functionalized SWNT-CONH$(CH_2)_{17}CH_3$ samples (0W and FW correspond to 0 and full washes).

Table 2. Solubility Data of Functionalized Material Calculated from the Respective Extinction Coefficient[a]

SWNT-CONH$(CH_2)_{17}CH_3$	ϵ (L/g · cm)	solubility (g/L)
0W	19	7.6
1W	21	7.6
3W	21	7.0
FW	20	6.6

[a] 0W, 1W, 3W, and FW correspond to 0, 1, 3, and full washes.

Conclusions

Nitric acid purification of SWNTs generates carboxylic acid functionalized carbon nanotubes and carbon fragments. The degree of functionalization and the concentration of the carboxylated carbons in the final product are dependent on the nature of the acid treatment and the postprocessing of the SWNT product. However, even after exhaustive base washing, the SWNTs contain detectable amounts of acid functionality which are susceptible to covalent chemical functionalization reactions in quantities that are sufficient to modify the material properties and, in the case of octadecylamine functionalization, to produce compounds that are soluble in organic solvents.

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Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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