

Functionalization of Single-Walled Carbon Nanotubes “On Water”

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Abstract: Single-walled carbon nanotubes (SWNTs) are exfoliated and functionalized into small bundles and individuals by vigorous stirring “on water” in the presence of a substituted aniline and an oxidizing agent. This is an example of an “on water” reaction that leads to functionalized SWNTs, and it represents a “green”, or environmentally friendly, process. A variety of reaction conditions were explored. The products were analyzed with Raman, UV–vis–NIR, and X-ray photoelectron spectroscopies, atomic force and transmission electron microscopies, and thermogravimetric analysis.

Introduction

The use of water as a solvent has been shown to increase the rate and yield of many organic reactions.^{1–3} Even reactions with water-insoluble solids have generated successful results, proving water solubility is not necessary.² It is thought that the increased rate and yield are due the hydrophobic nature of the reagents, since their repulsion from water would increase the collisions between organic molecules and increase their ground-state energies, leading to an increase in the rate of the reaction.² If a reaction proceeds “on water”,^{1,2} then replacement of environmentally unfriendly, potentially dangerous, and/or expensive organic solvents with water would be beneficial.

In this work we explore the “on water” functionalization of bundled SWNTs. We and others recently reviewed the covalent functionalization of SWNTs,⁴ and numerous protocols for the covalent and noncovalent functionalization of SWNTs have been published,⁵ including several that produced water-soluble functionalized SWNTs^{5a–c} or SWNTs wrapped with surfactants to produce individual water-soluble SWNTs for further reactions.^{5e} However, no conditions had been developed in which the functionalization of nonsurfactant-wrapped SWNTs could be

carried out “on water”. The method described here provides SWNTs that are functionalized to similar degrees as provided by previously disclosed routes;^{4,5} however, water can now be substituted for any organic solvent formerly used in the diazonium-based processes (Scheme 1). Functionalization of SWNTs can greatly enhance their utility in the formation of composites by aiding in dispersability and ensuring efficient interactions between the SWNTs and the host materials.^{4,5f}

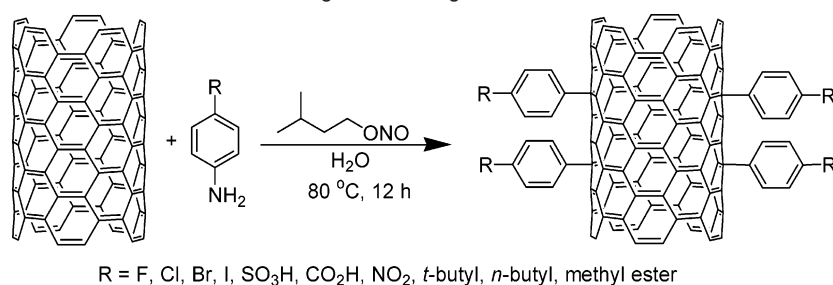
Results

In a typical experiment, purified SWNTs⁶ (10 mg) and deionized water (30 mL) were added to a 100 mL round-bottom flask. The contents were homogenized⁷ using an adjustable speed Dremel tool (model 400 XPR) fitted with a standard capacity rotor–stator generator (Cole-Parmer part no. A-36900-62) at the medium setting for 30 min, and then the homogenizer was removed. The reaction flask was heated to 80 °C in an oil bath. The aniline (4 equiv per SWNT C) and isoamyl nitrite (2 equiv per SWNT C) were then added, and a condenser was attached. The mixture was stirred vigorously with a Pyrex-coated stirbar (Scienceware spinbar, 1 in. × 3/8 in.) at 80 °C overnight. The contents were allowed to cool to room temperature and were then filtered on a Teflon filter (0.45 μm). The filter cake was washed with deionized water and acetone until the filtrate was clear. The product was removed from the filter and sonicated (Cole-Parmer ultrasonic cleaner, model 08849-00, 12 W) for 10 min in DMF (25 mL) to remove any remaining unreacted organics. The solid was collected by filtration using a Teflon filter (0.45 μm) and rinsed with acetone.

The weight of the functionalized material collected after workup was much higher than expected. The excess weight was

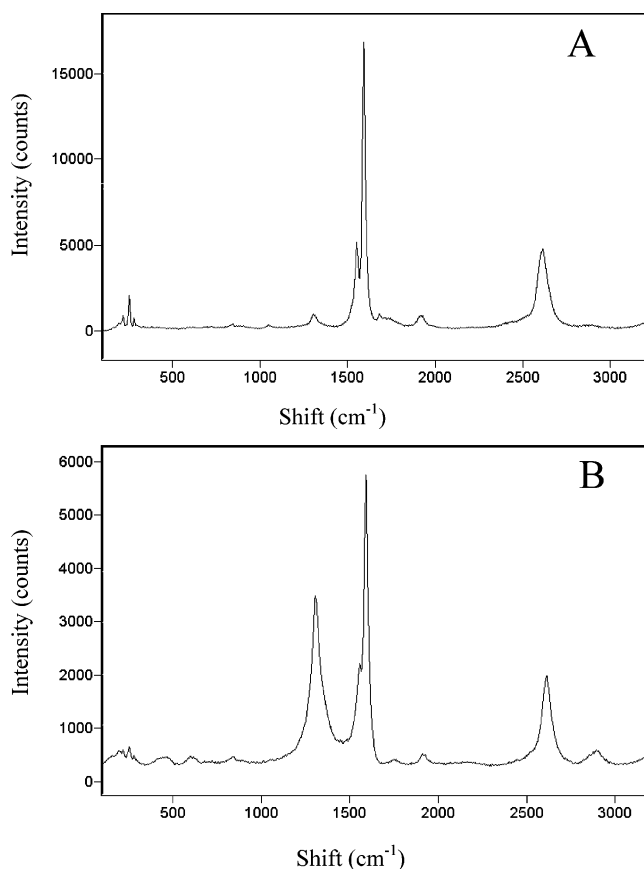
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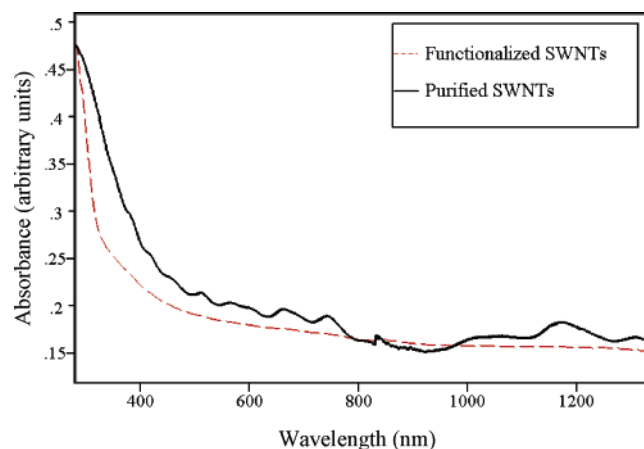
Scheme 1. Functionalization of SWNTs “On Water” with Vigorous Stirring**Table 1.** Calculated *D/G* Ratios from Raman Spectra^a

R group	<i>D/G</i> ratio
F	0.35
Cl	0.60
Br	0.30
I	0.29
SO ₃ H	0.54
CO ₂ H	0.23
NO ₂	0.22
<i>tert</i> -butyl	0.35
<i>n</i> -butyl	0.31
COCH ₃	0.20

^a The spectra were taken at 633 nm excitation, and the intensity values were averaged over 5–6 scans.

**Figure 1.** Raman (633 nm, solid) of (A) purified SWNTs and (B) SWNTs functionalized with 4-chloroaniline and isoamyl nitrite “on water”.

first thought to be unreacted organic material, but the weight did not decrease with additional rinsing with water and organic solvents. It was then thought that the weight gain might be due to polyarylene formation on the sidewalls of the SWNTs from addition of the aryl radical intermediates to the initially formed sidewall functional groups, but elemental analysis was incon-

**Figure 2.** UV-vis-NIR absorption spectra in DMF of purified SWNTs and 4-chloroaniline “on water” functionalized SWNTs. The solid and dashed lines represent purified and functionalized SWNTs, respectively.

clusive due to the high carbon content of the materials and hence their inefficient combustion. After the reactions, it was noted that the Pyrex stirbar and round-bottom flask showed signs of wear. The amount of wear was different for each sample and was due to the friction between the glass-coated stirbar and round-bottom flask during stirring. The increased weight of the products was found to be due to powdered glass. The glass was removed from the 4-chloroaniline-functionalized material by stirring the product in hydrofluoric acid (10% for 10 min in a polypropylene container). Extreme caution should be taken when using hydrofluoric acid. Proper safety procedures should be practiced at all times.⁸ X-ray photoelectron spectroscopy (XPS) confirmed the silicon was removed from the material (see the Supporting Information). The resulting overall weight gain in the product was comparable to prior results using alternative solvent systems, namely, 20–30% weight increases.^{5b} This value also correlated with the thermogravimetric analysis (TGA) weight losses (10 °C/min to 850 °C, Ar).^{4a}

When attempting to optimize the experiment, several known methods for functionalizing SWNTs using diazonium chemistries⁹ were surveyed. In an attempt to duplicate the functionalization of surfactant-wrapped SWNTs, we added isolated

- (8) From an MSDS for 40% hydrofluoric acid (Sigma-Aldrich): “Highly toxic. Hydrofluoric (HF) burns require immediate and specialized first aid and medical treatment. Use only in a chemical fume hood (in a lab equipped with a) safety shower and eye bath.” Wear a rubber apron, compatible chemical-resistant gloves, chemical safety goggles, and a face shield.
- (9) (a) Dyke, C. A.; Stewart, M. P.; Maya, F.; Tour, J. M. *SynLett* **2004**, 155. (b) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156. (c) Bahr, J. L.; Tour, J. M. *Chem. Mater.* **2001**, *13*, 3823. (d) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536. (e) Dyke, C. A.; Tour, J. M. *Chem. Eur. J.* **2004**, *10*, 11158. (f) Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H. W.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science* **2003**, *301*, 1519.

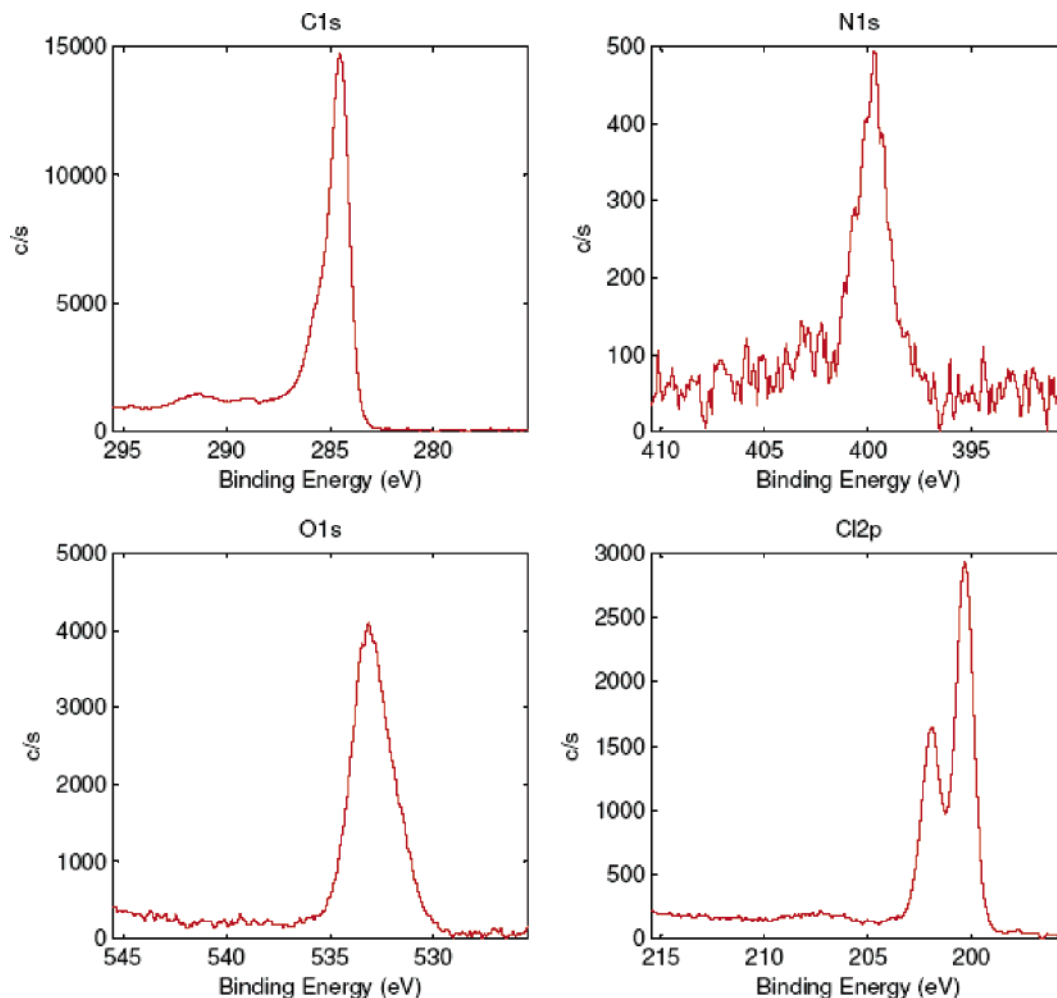


Figure 3. XPS analysis of 4-chloroaniline-functionalized SWNTs. The XPS beam size was 100 μm with a 45° takeoff angle and a pass energy of 26.00 eV.

diazonium salts to the bundles "on water" at an elevated pH with some success. However, the "on water" formation of the diazonium species through the oxidation of the aniline produced a higher degree of functionalization and better reproducibility. Another functionalization method used sodium nitrite as an oxidizing agent under acidic conditions.^{5c} We attempted using sodium nitrite under aqueous neutral or acidic pH conditions "on water" and found that the acidic system produced functionalized SWNT with a moderate level of success as judged by the Raman spectral analysis. This is probably due to the increased rate of formation of the nitrosonium species in acid to eventually form the diazonium species in situ. Another oxidizing agent used in solvent-free functionalization of SWNTs is isoamyl nitrite,^{9b} which we found to give the highest degree of functionalization in these "on water" reactions. Ethyl nitrite and *tert*-butyl nitrite were evaluated but gave lower degrees of functionalization.

Other experimental conditions were examined, but none increased the degree of functionalization. A biphasic system of water and chloroform was attempted and produced a low degree of functionalization when compared to results obtained in a water-only system. Increasing the pH of the system with NaOH increases the solubility of the SWNTs functionalized with acidic moieties, but we did not see an enhancement in functionalization. The use of brine instead of water gave no improvement in functionalization. Homogenization during the reaction^{5a} or the

use of AIBN as a radical initiator^{5ac} did not improve the degree of functionalization. A temperature study between room temperature and 100 °C indicated the optimal temperature for the reaction was 80 °C. The procedure produced functionalized SWNTs at higher and lower temperatures, but with decreased *D/G* ratios. The use of the Pyrex-coated stirbar was helpful because the Teflon-coated stirbars became caked with the nanotube products, lowering the degrees of functionalization and making product recovery more difficult.

The functionalized SWNTs (Scheme 1) were characterized using spectroscopic and microscopic methods commonly utilized in SWNT analysis.⁴ The Raman spectra of the purified SWNTs starting material show a disorder mode (diamondoid or D-band) with a very low intensity at 1290 cm^{-1} . Spectra of the functionalized materials show an increased intensity in the disorder mode, indicating functionalization of the SWNTs. The increase in the D-band is attributed to the sp^3 carbons present in the SWNTs after functionalization.^{5g} The relative degrees of functionalization were determined by dividing the intensity of the disorder mode by the intensity of the tangential mode (graphitic or G-band) at 1590 cm^{-1} (Table 1). It is significant to observe the resonance Raman enhancement of the pristine SWNT spectrum when compared to that of the functionalized material (Figure 1); the loss of the resonance enhancement is diagnostic of the sidewall functionalization.^{5g} This is characteristic of all samples obtained here.

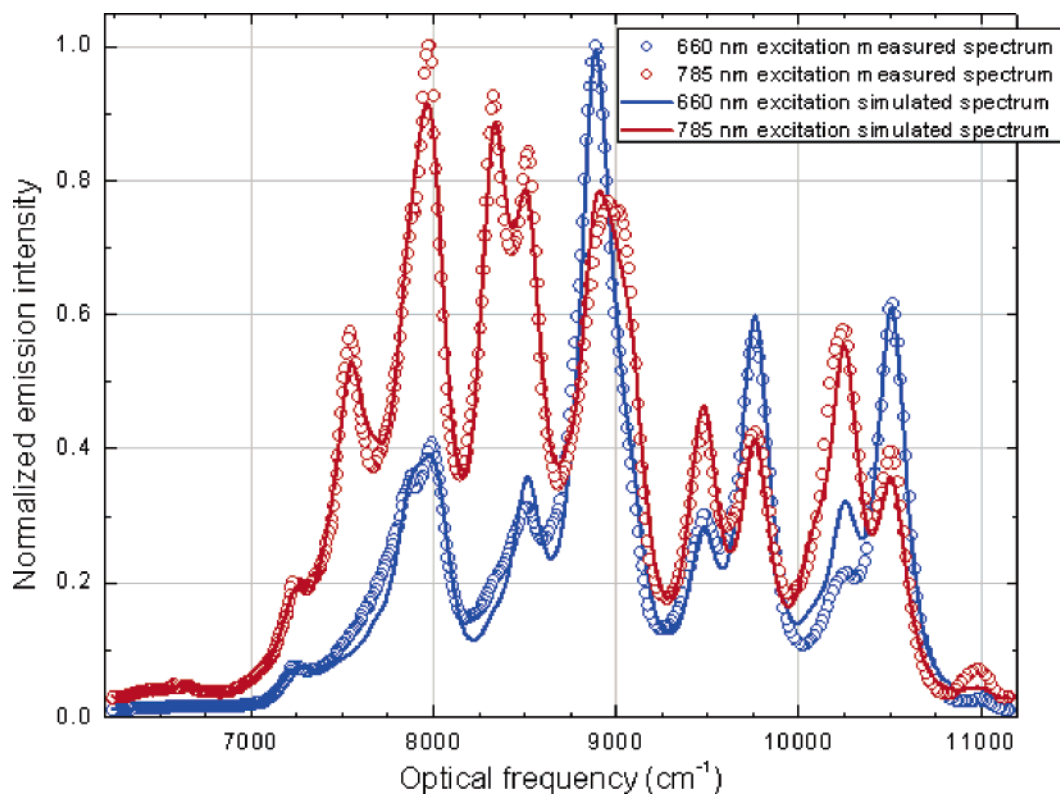


Figure 4. Excitation spectra (660 and 785 nm) of crude SWNTs using an NS1 NanoSpectralyzer. The 660 nm spectrum is blue, and the 785 nm spectrum is red. The circles represent the actual data points measured, and the lines represent the simulated spectra.

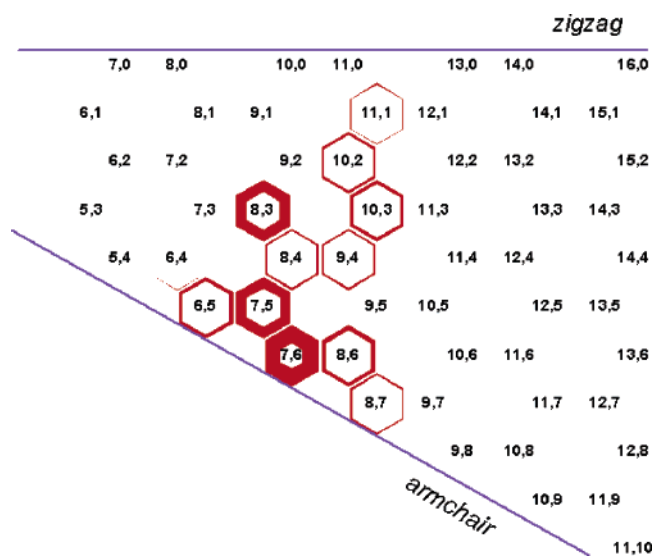


Figure 5. Illustration of the relative amounts of each (n,m) of the semiconducting SWNTs present in the sample. The intensity of the hexagon represents the relative number of SWNTs of that chirality in the sample.

UV–vis–NIR was also performed to characterize the SWNTs. The absorption spectrum of pristine SWNTs shows the characteristic van Hove singularities, while the spectra of functionalized material showed a dramatic decrease in the van Hove singularities diagnostic of sidewall covalent bonding (Figure 2).^{5g}

X-ray photoelectron spectroscopy (XPS) was performed on all products from reactions listed in Scheme 1. As noted above, XPS of the 4-chloroaniline-functionalized SWNTs prior to the hydrofluoric acid rinse showed the presence of silicon. Analysis of the same sample after acid exposure found no silicon present

(see the Supporting Information). Otherwise, each sample had the appropriate elements present. The 4-chloroaniline-functionalized SWNTs data is shown in Figure 3. The presence of each of the elements further confirms the successful functionalization of the SWNTs. The presence of nitrogen and oxygen can be attributed to commonly observed surface contamination.^{9a}

An NS1 NanoSpectralyzer was used to characterize the semiconducting SWNTs in the unfunctionalized SWNTs starting material using near-IR fluorescence spectroscopy.¹⁰ The SWNTs used in these experiments were produced using gas-phase catalytic growth from carbon monoxide (HiPco).¹¹ It is known that SWNTs prepared by this method are in many assorted diameters and chiralities. To define and characterize a SWNT's diameter and vector, the integers n and m are used. The metallic SWNTs ($n - m = 0$) have a band gap of 0 eV, and the semiconducting SWNTs ($n - m \neq 3q$, where q is an integer $\neq 0$) have a band gap of ca. 0.8–1.4 eV.^{5g} The semimetallic SWNTs ($n - m = 3q$ and $q \neq 0$) have a band gap of 10–20 meV. Semiconducting SWNTs fluoresce,¹² while the metallic and semimetallic SWNTs do not.

The SWNTs (1.5 mg) were sonicated (Misonix Microsor ultrasonic cell disruptor XL2000, 7 W) for 5 min in 1 wt % sodium dodecylbenzenesulfonate (SDBS) in water. The best results were achieved using crude rather than purified unfunctionalized SWNTs. The NanoSpectralyzer measured the fluorescence (integration time 200 ms) using 660 and 785 nm lasers. Figure 4 shows the excitation spectra of a sample of crude

(10) Information on the NanoSpectralyzer can be found at <http://www.applied-nanofluorescence.com> (accessed 1 March 2006).

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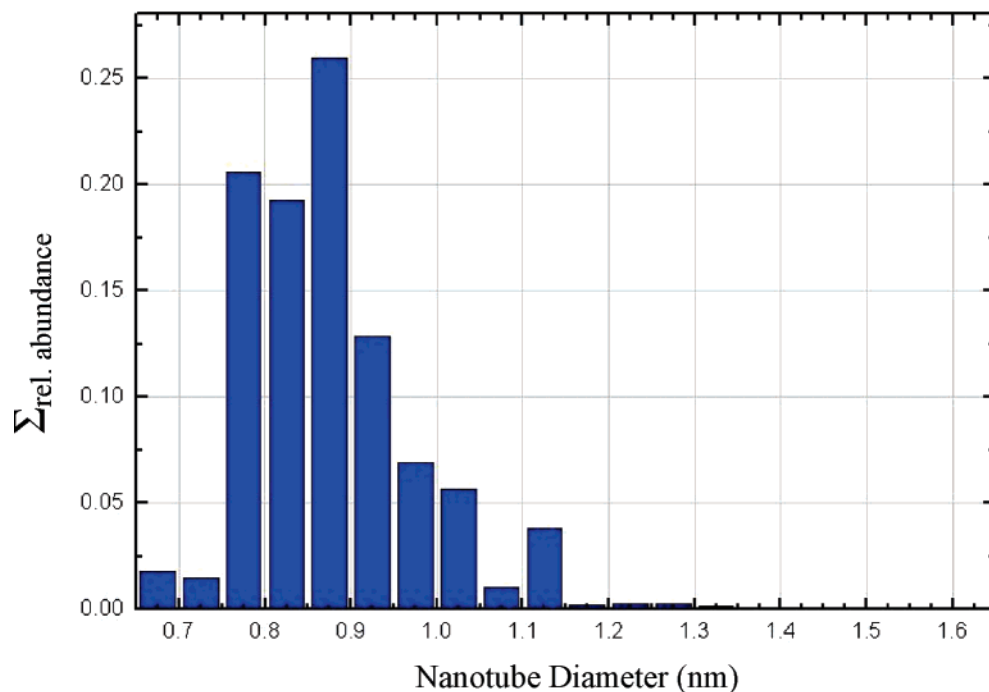


Figure 6. Histogram of the relative abundance of the SWNTs diameters present in the sample. Each (n,m) species has a known diameter. The relative abundances as displayed in Figure 5 can then be summed over diameter steps of 0.05 nm to produce the distribution above.

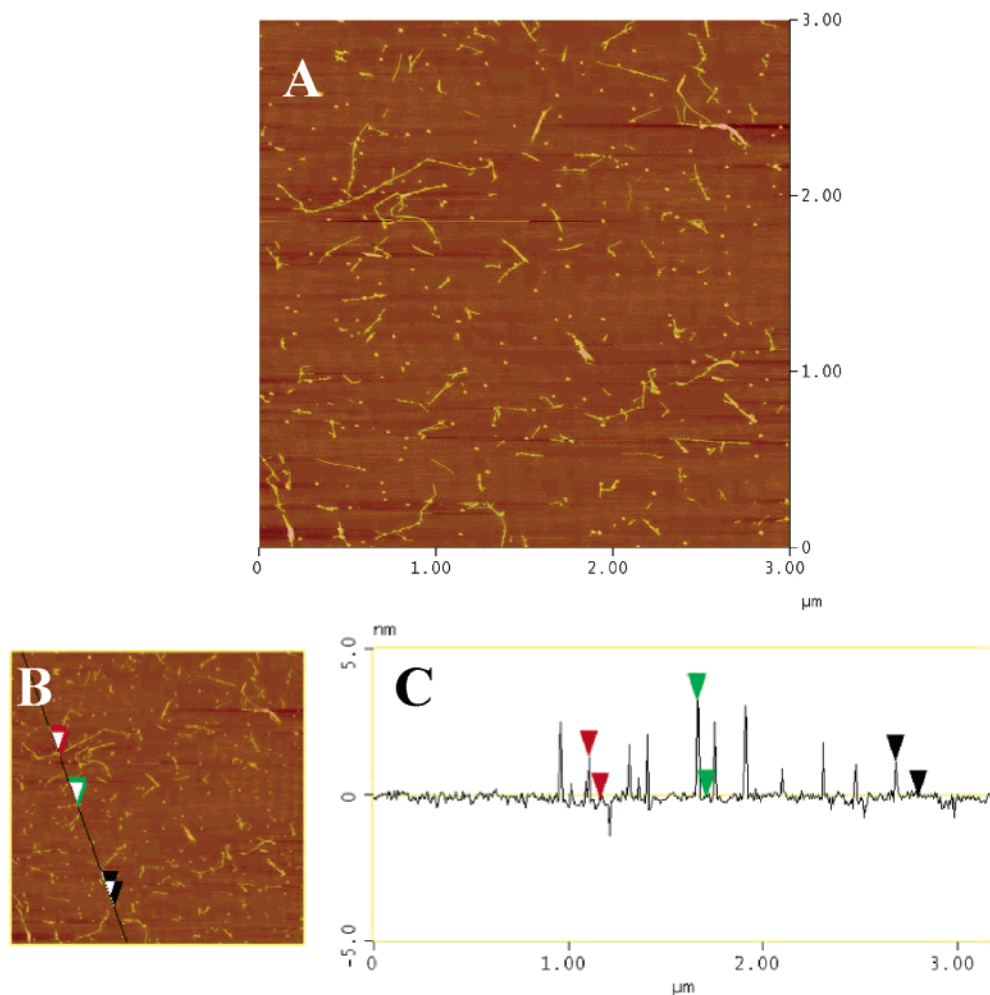


Figure 7. (A) AFM analysis (spin coated onto freshly cleaved mica in DMF) by height of 4-chloroaniline-functionalized SWNTs in water. (B) The sectional analysis across the black line illustrates the height data in nanometers (C) of the functionalized SWNTs. The vertical distances range between 1.1 and 5.0 nm. This range corresponds to small bundles (individual SWNTs are less than 1.4 nm) (ref 5c) of SWNTs.

SWNTs from the same batch of SWNTs from which a portion was purified and used for the “on water” functionalization reactions. From this spectral data, the relative abundance of the different semiconducting tubes can be addressed.

Figure 5 illustrates the relative amount of each type of semiconducting SWNT by (n,m) value, with the $(7,6)$ species being the most abundant in this batch.

Figure 6 is a histogram of the relative abundance of each SWNT diameter generated from the spectral data. About 80% of the SWNTs in this sample were found to be between 0.75 and 0.95 nm in diameter. These values can be used, in turn, to estimate the number of SWNTs in a bundle whose height is measured by atomic force microscopy (AFM).

AFM and transmission electron microscopy (TEM) showed that the functionalized SWNTs are present as individuals as well as in small bundles. Tapping mode was used to obtain images by AFM (Figure 7). The height data showed measurements between 1.1 and 5 nm. With the use of the data for SWNT diameters obtained from the NS1 NanoSpectralyzer, these heights correspond to a few individual SWNTs and bundles of up to five SWNTs. TEM images agreed with the AFM findings as Figure 8 shows a small bundle of functionalized SWNTs as well as an individual functionalized SWNT. TEM images of unfunctionalized SWNTs are known to have smooth sidewalls.^{5g} The image in Figure 8 shows bumps along the sidewalls of the SWNTs, indicative of the functional groups.^{5g} Without the functional groups present, the SWNTs would rebundle due to their 0.5 eV/nm intertube attractive forces.

Conclusion

Running reactions “on water” could reduce harmful waste and reaction times while increasing yields and reaction rates, which would increase overall efficiency.^{1–3} In an environmentally friendly process, the reaction of SWNTs “on water” in the presence of a substituted aniline and an oxidative species yields functionalized material. The functionalized SWNTs were characterized using spectroscopic and microscopic methods, which indicated the product existed as individuals and small bundles. Spectroscopy confirmed the findings of microscopy as UV–vis–NIR results showed the absence of von Hove

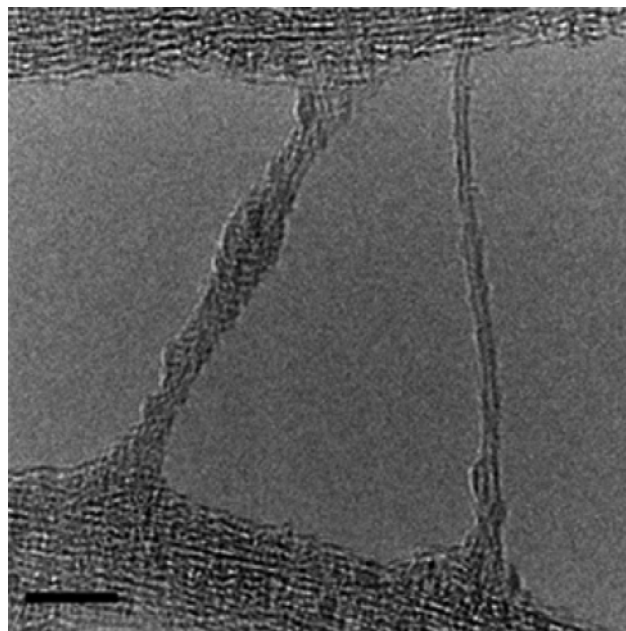


Figure 8. TEM image (on a lacy carbon grid) of SWNTs functionalized with 4-chloroaniline in water. A small bundle of functionalized SWNTs can be seen on the left, and an individual functionalized SWNT is on the right. The scale bar is 10 nm. Functional groups can be seen along the sides of the SWNTs. The top and bottom structures are characteristic of the lacy carbon.

singularities and Raman spectra displayed elevated D/G ratios. Fluorescence data assisted in the determination of the number of SWNTs present in the bundles observed in AFM images.

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Supporting Information Available: XPS of 4-chloroaniline SWNTs before and after HF treatment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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