Individualized Single Walled Carbon Nanotubes from Bulk Material Using 96% Sulfuric Acid as Solvent

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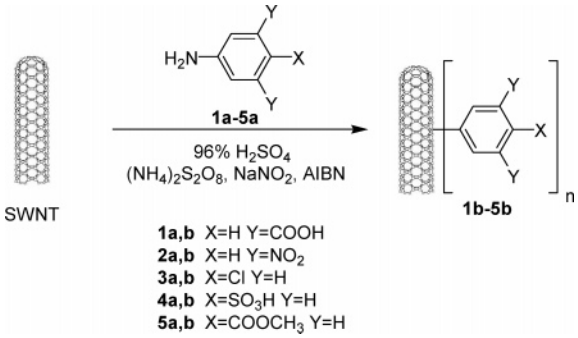
Single walled carbon nanotubes (SWNTs) have been functionalized in a mixture of 96% sulfuric acid and ammonium persulfate, using sodium nitrite to produce intermediate diazonium salts from substituted anilines. These afford unbundled functionalized SWNTs from bulk bundled SWNTs. This new process eliminates the need for corrosive and more expensive oleum solvent, as described in prior work, and therefore also reduces the formation of sulfonated products.

Introduction

The functionalization of single walled carbon nanotubes (SWNTs) is a popular research area. Several methods for the functionalization of SWNTs have been developed which give either individualized or bundled SWNTs. Functionalized SWNTs in bundles can be formed electrochemically,[1] in organic solution,[2] or in the dry state.[3] Individualized SWNTs have been functionalized in aqueous solution[4] via surfactant wrapping, via the Billups method using lithium and ammonia,[5] and in oleum[6] to produce SWNTs that are water soluble.[7] We have recently reviewed the functionalization of SWNTs for applications in materials chemistry.[8]

The oleum method[7] achieves high yields of single tubes due to the ability of oleum to disperse purified SWNTs into solution before functionalization and the low tendency of functionalized SWNTs to rebundle after workup. However, in a side reaction, the appended aromatic SWNT substituents are heavily sulfonated by the excess SO_3 in oleum, giving SWNTs with sulfonated sidewall functionalities. While this side reaction produces water and alcohol soluble tubes, a new method is described here to produce exfoliated individually functionalized tubes that avoids significant sulfonation of the products and does not require oleum. In this case, aromatic amines are diazotized using sodium nitrite in 96% sulfuric acid containing ammonium persulfate. Persulfate salts have been shown to cause SWNTs to disperse well in concentrated sulfuric acid.[9] This added dispersion helps to separate the SWNT bundles, thereby making more SWNT surface area available for functionalization. Thus the method described here produces functionalized, individualized tubes in inexpensive, less hazardous sulfuric acid without the sulfonation side reactions seen in the oleum-based protocol.

Scheme 1. Functionalization of SWNTs with Aniline Derivatives in 96% H_2SO_4 and Ammonium Persulfate



Results

A mixture of 96% sulfuric acid and ammonium persulfate is also known as Caro's acid, a peroxymonosulfuric acid.[10] Similar to the previously proposed mechanism,[11] we propose that the functionalization occurs when a SWNT donates an electron to the formed aryl diazonium salt. This results in the expulsion of N_2 and creates a highly energetic aryl radical species which then adds directly to the tube, thus creating a new covalent SWNT−aryl bond (Scheme 1). With the 96% sulfuric acid/ammonium persulfate mixture, reactions proceed best when the ammonium persulfate is added in molar excess of the water present, and the reactions are heated for 3 h at 80 °C. Although not essential, a radical initiator, 2,2′-azobis-(isobutyronitrile) (AIBN), was generally used to facilitate the reaction and increase the degree of functionalization in some cases. Likewise, without ammonium persulfate, the

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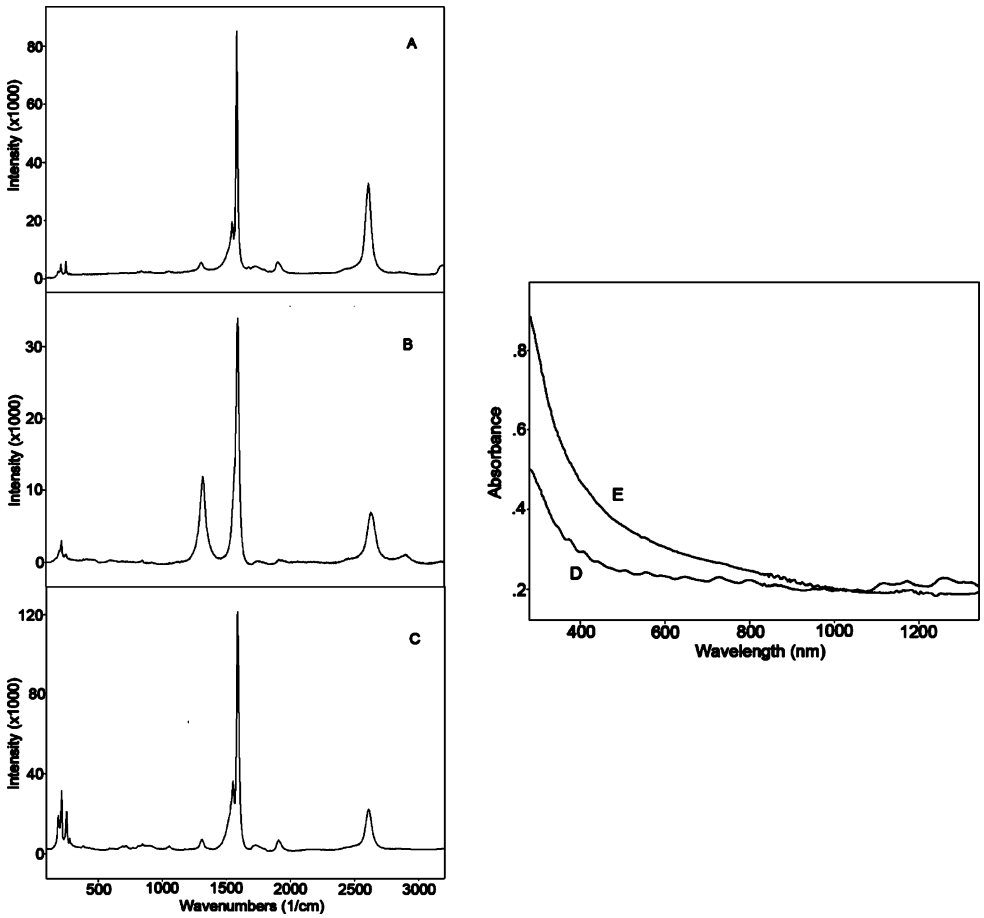

Figure 1. (A) Raman spectrum of pristine SWNTs (solid scan, median of five area scans per sample at 633 nm). (B) Raman spectrum of functionalized product **2b.** (C) Raman spectrum of product **2b** after 850 °C TGA treatment in argon at 10 °C/min. (D) UV−vis of pristine SWNTs. (E) UV−vis of **2b** showing loss of the van Hove singularities.

degree of functionalization was always depressed, possibly due to the lack of dispersion of SWNTs, thereby allowing less surface area for radical attachment (see Experimental Section for details). Functionalized SWNTs **1b** and **2b** showed the greatest overall functionalization by Raman spectroscopy and thermogravimetric analysis (TGA).

Functionalization of SWNTs by the method disclosed here gave tubes with aromatic pendant groups that were not heavily sulfonated, therefore reducing their solubility in water as compared to those produced in the oleum process. However, water solubility can still be achieved with a polar pendant group, such as the disubstituted carboxylic acid functionalized SWNT product **1b** and, to a lesser degree, the monosulfonic acid, **4b**.

Recently, it has been shown that piranha solution will cause oxidation and sidewall damage of SWNTs.[12] However, similar oxidative sidewall damage is not seen using 96% sulfuric acid containing ammonium persulfate in the absence of an aniline. SWNTs were suspended in this mixture at 80 °C and the Raman data showed no increase in the D-band, suggesting that there was very little, if any, sidewall damage caused by the oxidative mixture.

Characterization

As shown by the Raman spectral data in Figure 1A, unfunctionalized pristine SWNTs have a very small disorder mode (D-band, 1290 cm^{-1}) compared to the tangential mode (G-band, 1594 cm^{-1}); the ratio of these two intensities is known as the D/G ratio.[8] As compared to Figure 1A, the functionalized tubes **2b** in Figure 1B had an increase in the D/G ratio that indicates a significant degree of functionalization. The Raman D/G ratio, TGA-determined weight loss, and calculated functionalization coverage for all five products are given in Table 1. Calculated coverages were determined by assuming that the weight loss measured in the TGA was due only to the loss of the functional addend.[8] This is an estimate of the numbers of addends per carbon atom on the SWNT.

Table 1. Raman D/G Ratio, TGA-Determined Weight Loss, and Calculated Functionalization Coverage for All Five Products

product	Raman D/G[a]	TGA wt loss[b] (%)	calculated coverage[c]
1b	0.36	26	1/35
2b	0.33	28	1/35
3b	0.21	12	1/40
4b	0.18	23	1/50
5b	0.13	17	1/60

[a] Representative Raman D/G values averaged over five scans per sample. [b] TGA weight loss obtained by ramping at 10 °C/min to 850 °C in argon. [c] Coverage of arenes per nanotube carbon calculated by assuming all weight loss in TGA was due to addends and determining the amount of coverage along the SWNTs.

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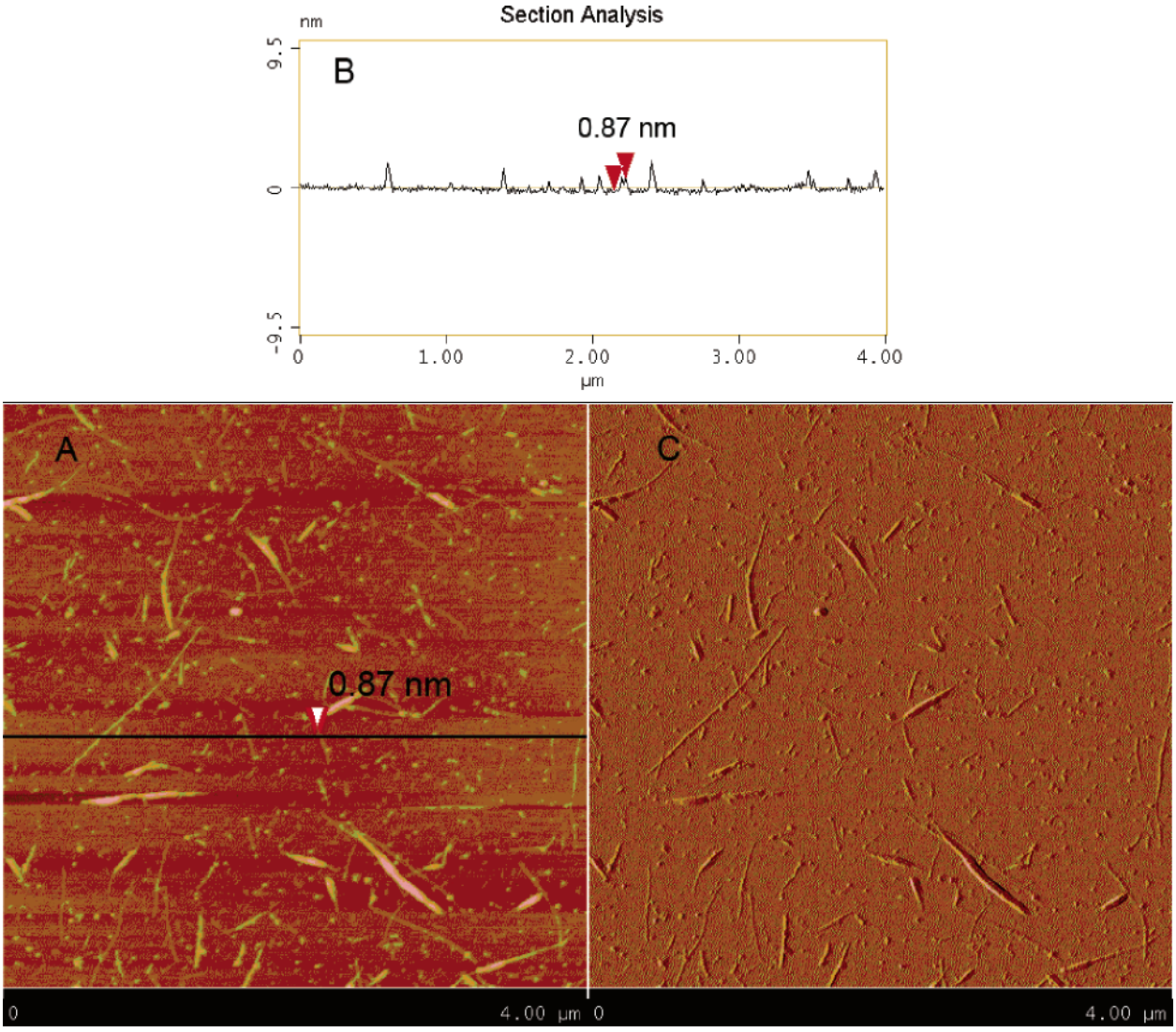

Figure 2. AFM analysis of **2b**. (A) Section analysis showing unbundled, single tube heights across the surface. (B) Section analysis plot for the black line in A. (C) Surface scan of height data showing individualized tubes with the presence of some small bundles.

The functionalization is corroborated by the UV−vis data in Figure 1E showing the loss of van Hove singularities[13] from the functionalized product **2b**, compared to the pristine SWNT starting material seen in Figure 1D. Figure 2 shows AFM analysis of **2b** dispersed on mica after sonication in DMF. Though a few bundles of SWNTs are present, the majority of functionalized SWNTs are found as singles on the surface (0.7−1.3 nm). The presence of some larger diameter SWNTs may be due to only two or three nanotubes in a bundle.[14]

In our experience, X-ray photoelectron spectroscopy (XPS) carbon data can be skewed in functionalized SWNTs due to surface contamination.[12] However, XPS analysis of **3b** confirmed the presence of chlorine (Cl 2p). XPS also indicated the presence of sulfur (S 2p) and nitrogen (N 1s) in all cases, which could be due to traces of sulfuric acid or ammonium persulfate used in the functionalization protocol. The XPS analysis showed approximately 1 sulfur atom for every 80 carbon atoms of the SWNT. The oleum functionalization protocol shows approximately 1 sulfur atom for every 30 carbon atoms, or one for every arene addend on the SWNT.[7] Since we would also expect **3b** to be soluble in water had the aromatic addends been heavily sulfonated, the corroborating evidence indicates that the presence of the sulfur in the XPS analysis is not due to significant addend sulfonation.

Conclusion

This use of 96% sulfuric acid/ammonium persulfate has been shown to produce bulk functionalized single SWNTs without the use of hazardous oleum or the production of heavily sulfonated products, thus expanding the diversity of functionalized SWNTs available to chemists and materials scientists. Raman, TGA, XPS and UV−vis data confirm the high degree of functionalization, supported by AFM data which shows a large degree of individual functionalized SWNTs.

Experimental Section

All TGAs had a 30 min isothermal treatment at 120 °C to remove small amounts of adsorbed water and DMF. Weight loss beyond

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this point was then recorded up to 850 °C in argon at a ramp rate of 10 °C/min.

General Procedure for Functionalization of SWNTs in 96% H_2SO_4. A mixture of 96% H_2SO_4 (30 mL, 66 mmol H_2O) with SWNTs (10 mg, 0.8 mmol) and $(NH_4)_2S_2O_8$ (20 g, 87 mmol) was homogenized[15] using an adjustable speed Dremel tool (model 400 XPR) at the lowest setting utilizing a standard-capacity rotor-stator generator (Cole-Parmer part #A-36900-62). Once the mixture was visibly dispersed (usually 2 h before no large particulates were visible), the substituted aniline derivative (1.6 mmol) was added and homogenization was continued for 10 min in order to effectively disperse the aniline throughout the mixture. This was followed by addition of solid $NaNO_2$ (0.11 g, 1.6 mmol) and *slow* addition of AIBN (0.06 g, 0.4 mmol). *(CAUTION: During the addition of AIBN in reactions **3b** and **4b**, a fire started in the reaction flask due to too rapid of an addition. To reduce the risk of fire, the subsequent reactions were run by slowly adding AIBN. The AIBN was split into two portions. Each portion was added to the reaction while the homogenizer was off. Once added, the mixture was homogenized for 2 min allowing the AIBN to mix thoroughly. Once both portions were added, homogenization continued throughout the reaction.)* The mixture was then placed in an oil bath at 80 °C and homogenization was continued for 3 h. The suspension was poured over 100 g of ice, and the melted mixture was filtered using a 1 μm polycarbonate filter. The bucky paper filter cake was then dispersed in acetone using sonication (Cole-Parmer 12 W, 55 kHz) and subsequently filtered and collected as a bucky paper on a 0.2 μm PTFE filter membrane after washing with acetone. The bucky paper was removed and again dispersed, with sonication, in DMF and collected as a bucky paper, after washing with fresh DMF, on a 0.2 μm PTFE filter, and then dried.

3,5-Isophthalic Acid SWNT (1b). The general reaction procedure was followed. 5-Aminoisophthalic acid (0.29 g, 1.6 mmol) was the aniline used in the process. The product **1b** was isolated as a bucky paper (13 mg). Raman D/G 0.36, TGA mass loss 26%. XPS analysis: C 1s 76.7%, N 1s 4.2%, O 1s 18.1%, S 2p 1.0%. Without the use of ammonium persulfate, the Raman D/G ratio was 0.18.

3,5-Dinitrophenyl SWNT (2b). The general reaction procedure was followed. 3,5-Dinitroaniline (0.29 g, 1.6 mmol) was used in the process. The product **2b** was isolated as a bucky paper (14 mg). Raman D/G 0.33, TGA mass loss 28%. XPS analysis: C 1s 67.0%, N 1s 8.3%, O 1s 22.8%, S 2p 2.4%. Without the use of ammonium persulfate the Raman D/G ratio was 0.21.

4-Chlorophenyl SWNT (3b). The general reaction procedure was followed. 4-Chloroaniline (0.20 g, 1.6 mmol) was used in the process. The product **3b** was isolated as a bucky paper (12 mg). Raman D/G 0.21, TGA mass loss 12%. XPS analysis: C 1s 80.9%, N 1s 2.0%, O 1s 15.07%, S 2p 1.3%, Cl 2p 0.6%. Without the use of ammonium persulfate the Raman D/G ratio was 0.09.

4-Benzenesulfonic Acid SWNT (4b). The general reaction procedure was followed. 4-Aminobenzenesulfonic acid (0.28 g, 1.6 mmol) was used in the process. The product **4b** was isolated as a bucky paper (12 mg). Raman D/G 0.18, TGA mass loss 23%. XPS analysis: C 1s 70.4%, N 1s 4.7%, O 1s 21.8%, S 2p 3.1%. Without the use of ammonium persulfate the Raman D/G ratio was 0.11.

4-Methyl Benzoate SWNT (5b). The general reaction procedure was followed. Methyl 4-aminobenzoate (0.24 g, 1.6 mmol) was used in the process. The product **5b** was isolated as a bucky paper (10 mg). Raman D/G 0.13, TGA mass loss 17%. XPS analysis: C 1s 81.1%, N 1s 2.2%, O 1s 15.8%, S 2p 0.8%. Without the use of ammonium persulfate the Raman D/G ratio was 0.09.

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