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Water-Soluble, Exfoliated, Nonroping Single-Wall Carbon Nanotubes

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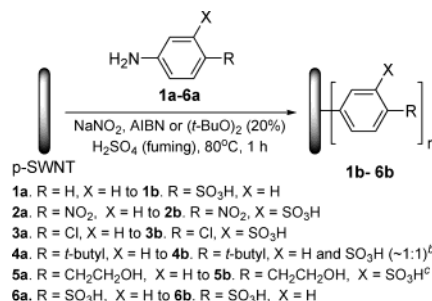
This paper describes the covalent functionalization of single-wall carbon nanotubes¹ (SWNTs) in fuming sulfuric acid to afford unbundled individual SWNT-arylsulfonic acids that are soluble in water; the process does not require surfactant or polymer-based prewrapping, centrifugation, or sonication. SWNTs are promising building blocks for high-performance composite materials.² An obstacle to fully exploiting the materials properties of SWNTs is their tendency to spontaneously form bundles and/or flocculate in their unfunctionalized state due to the extraordinary 0.5 eV/nm intermolecular cohesive interaction between neighboring SWNTs.³ Several methods have been used to functionalize SWNT bundles,³ even with water-solubilizing addends;⁴ however, they generally do not exfoliate the bundles^{3d} to produce individually functionalized nanotubes. We recently disclosed an exception⁵ where individually functionalized SWNTs could be obtained; however, the process suffered from the required sequence of (a) surfactant treatment of the SWNTs, (b) extended sonication, and (c) multiple centrifugations, all of which are difficult to scale; yields of only ca. 15 mg of material could be obtained in 12 h.

It has recently been reported that SWNTs disperse as individuals in superacids with SWNT concentrations of up to 10 wt %.⁶ Exploiting the solubility of SWNTs in oleum (H₂SO₄, 20% free SO₃), we have modified the diazonium functionalization chemistry⁷ to produce efficient functionalizations of nanotubes in that solvent. The aryl rings sulfonate under the reaction conditions, thereby imparting the unusual water solubility to the final compounds. Note that sulfuric acid is an inexpensive and commonly used industrial solvent for processing of Kevlar, for example, and removal of trace water from H₂SO₄ by addition of SO₃ is all that is required for the process described here.

We achieved the functionalization using sodium nitrite and diverse anilines to covalently attach arenes to the HiPco-produced⁸ purified SWNTs (heated in a water-rich atmosphere at 220 °C followed by HCl extraction)⁹ (p-SWNTs). This method is different than previous diazonium functionalization methods⁷ in that it requires the presence of a radical source for functionalization to ensue. Previous diazonium mechanistic work has indicated that functionalization initially occurs via the injection of an electron from a SWNT into the aryldiazonium salt, releasing N₂ and forming a reactive aryl radical that then reacts with the SWNT to form a new SWNT–arene bond.^{5b} In superacids, it is proposed that SWNTs are surrounded by a double layer of protons and counterions;⁶ thus the tube is unlikely to inject an electron into the diazonium salt. However, in the presence of a radical initiator,¹⁰ the superacid-based reaction affords a degree of functionalization similar to that achieved via previous diazonium methods and produces mostly individual SWNTs instead of bundles.

A typical experiment (Scheme 1) consisted of dispersing p-SWNT (50 mg, 4.2 mequiv C) in oleum (50 mL, 20% free SO₃, Aldrich) with magnetic stirring (3 h).⁶ Sodium nitrite (1.16 g, 16.8 mmol) was added followed by 4-chloroaniline (**3a**) (2.14 g, 16.8 mmol) and azobisisobutyronitrile (AIBN) (0.14 g, 0.84 mmol)

Scheme 1. Functionalization of SWNTs Dispersed in Oleum^a



^a XPS was used to determine the relative amount of sulfonation relative to the easily observed nitro and chloro moieties in **2b** and **3b**, respectively, and this was further correlated with the XPS data of the other products to show that in all cases, except **4b**, there was approximately one SO₃H group per aryl addend. ^b SO₃H regiochemistry (2- or 3-position relative to the nanotube) is not known, and alkyl migrations are possible. ^c Cyclization to the six-membered sulfonate ester is presumed to ensue.

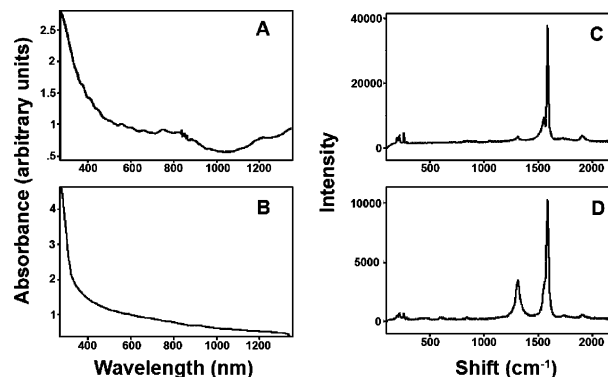


Figure 1. Absorption spectra of (a) p-SWNT in DMF. (b) **3b** in DMF. Raman spectra (solid, median scan of five different areas per sample, 633 nm) of (c) p-SWNT and (d) **3b**.

(AIBN and di-*tert*-butylperoxide produced similar results). The reaction was stirred at 80 °C for 1 h and then *carefully* poured into water, and the suspension was filtered through a polycarbonate membrane (0.22 μm). The filter cake was washed with water and acetone and then dried (55 mg of **3b**). The solid could be dispersed as individuals (unroped) in a variety of solvents including water, DMF, and EtOH (0.24, 0.16, and 0.06 mg mL⁻¹, respectively) using the dissolution/filtration protocol outlined previously.^{7d} Scales as large as 1.5 g of p-SWNTs in 500 mL of oleum yielding 2.0 g of functionalized tubes have been executed with similar results. Higher concentrations can be used; however, mechanical stirring is needed due to the high-viscosity solutions. Several controls were also carried out on the above-described conditions: (a) without AIBN, (b) without aniline, and (c) without nitrite, AIBN, and aniline. Under all of the control conditions, no sidewall functionalization was observed by Raman spectroscopy (no D-band increase, *vide infra*).

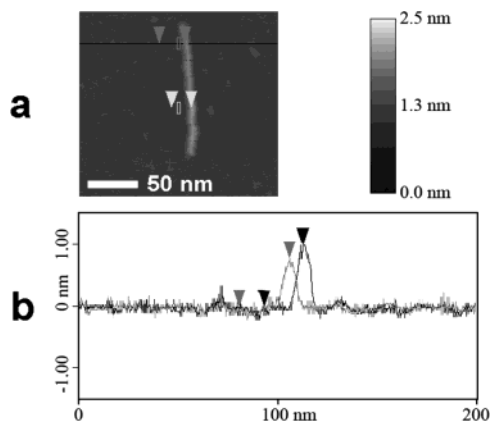


Figure 2. AFM analysis (on mica) of **3b**. Section analysis of an individual 140-nm-long SWNT performed at (a) a low spot and high spot, and (b) the resulting cross-sections, which show heights of 8 and 10 Å.

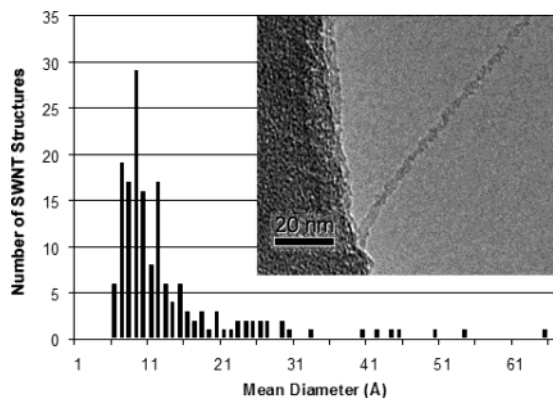


Figure 3. AFM-derived histogram (mica) of nanotube tube/bundle mean diameters present in a typical sample of **3b**. Bundles begin to appear at 15 Å. Over 160 structures were sampled, and the results are characteristic of those obtained from the other products shown in Scheme 1. The nanotubes were generally short, exhibiting a mean length of 100 nm. Note that the starting nanotube lengths could not be obtained due to their existence as roped structures. (Inset) TEM of **3b** suspended from the lacy carbon TEM grid (20 nm bar).

Figure 1a, shows the characteristic van Hove singularities^{7d} of the starting material p-SWNT. Figure 1b shows the loss of those transitions in product **3b**, which is confirmation of covalent functionalization, and this was characteristic of all the products obtained (**1b–6b**).⁷ Likewise, in Figure 1c, the Raman spectrum of the starting p-SWNT shows a very small disorder mode (D-band) at 1290 cm⁻¹. In Figure 1d, the spectrum of the functionalized material, there is a significant increase in the disorder mode relative to the large tangential mode (G-band), consistent with a high degree of functionalization. Similarly, the Raman resonance enhancement seen in Figure 1c is suppressed after functionalization, consistent with covalent attachment.^{7d}

Thermogravimetric analysis (TGA) of **3b** (Ar, 10 °C/min to 800 °C) showed a weight loss of 22%, which corresponds to ca. 1 functional group per 30 nanotube carbons.⁷ Although sulfonated aromatic pyrolysates can be carbonaceous, thereby complicating the TGA data, Raman D- to G-band intensities are similar to those of known material of that degree of functionalization.^{7d}

The presence of individual SWNTs was confirmed via Tapping-Mode atomic force microscopy (AFM). Height data were used to assess tube diameters for numerous experimental products and controls. Figure 2a is an image of an individual SWNT sample of **3b**.

The height, and thus diameter, of the tube ranges from 7 to 10 Å, with a mean diameter of 8 Å; this is consistent with the diameters of typical HiPco-produced tubes¹¹ but also with small perturbations due to addend-based surface roughening.¹² Individual SWNTs were the dominant feature in over 90% of the cases, but small bundles, typically 2–3 nm in diameter, were also observed (Figure 3).

Finally, transmission electron microscopy (TEM) revealed the presence of unbundled (throughout their entire length), surface-roughened, functionalized SWNTs (Figure 3 inset).⁷ Further desulfonation and sulfonyl derivatization (to sulfonic esters and amides) processes are being explored.

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