

Solvent-Free Functionalization of Carbon Nanotubes

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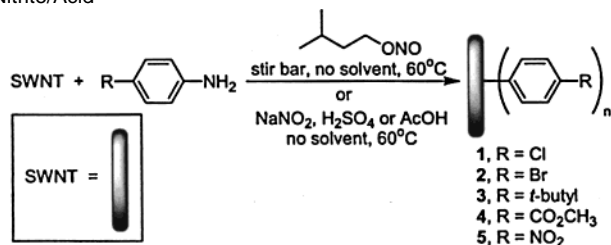
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Since their discovery,¹ carbon nanotubes and the single-walled carbon nanotubes (SWNTs) in particular, have attracted considerable attention due to their unique chemical and physical properties as well as their promise in the area of materials chemistry.^{2,3} For their full potential to be realized, the intrinsic van der Waals forces^{4,5} must be overcome for high degrees of sidewall functionalization, thereby generating compounds that are more compatible with composites and more soluble. We have shown that the electrochemical reduction of diazonium salts⁶ and thermally generated diazonium compounds⁷ will readily functionalize SWNTs. However, a severe limitation of all processes thus far has been the extraordinary amounts of solvent needed (~ 2 L/g coupled with sonication in most cases) for the dissolution or dispersion of the SWNTs. We report here that solvent-free techniques⁸ produce functionalized nanotubes, thereby leading the way for large-scale functionalization of the materials and providing a fundamentally different approach when considering reaction chemistry on these unique materials.

The initial solvent-free functionalizations were performed on HiPco-produced,⁹ purified¹⁰ SWNTs in an inert atmosphere. In a typical experiment (see Scheme 1), SWNTs (6 mg, 0.5 mmol of

Scheme 1. Solvent-Free Functionalizations Performed with Various 4-Substituted Anilines and Isoamyl Nitrite or Sodium Nitrite/Acid



carbon) and 4-substituted aniline (4 equiv/mol of carbon) were added to a flask equipped with a reflux condenser and a magnetic stir bar. After the cautious, slow addition of isoamyl nitrite (0.32 mL, 4.8 equiv/mol of carbon) via syringe, heating (60 °C) and vigorous stirring (magnetic stir bar) of the paste were commenced. After a time (vide infra), the paste was diluted with DMF and filtered through a PTFE (0.45 μ m) membrane. The collected solid was washed with DMF until the filtrate became colorless. Dispersing the solid in DMF by sonication followed by filtration afforded purified functionalized nanotubes. Sonication was only used here to ensure that occlusion of small organics was not occurring to afford proper analyses; it is not required for the overall process. DMF was removed by washing with ether, and compounds **1–5** were dried in a vacuum oven (65 °C) overnight and characterized. In all cases, the mass of the product was greater than the mass of the starting nanotubes.

Compounds **1–5** were characterized by UV/vis/NIR absorption spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TGA), with findings similar to those previously reported when

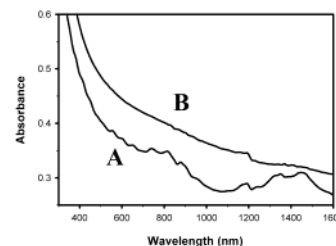


Figure 1. Absorption spectra in dimethylformamide of (A) pristine SWNTs and (B) aryl chloride **1** synthesized utilizing the solvent-free technique.

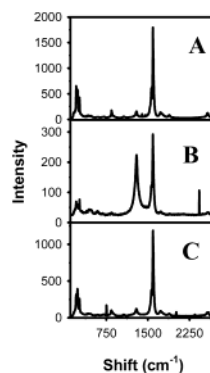


Figure 2. Raman spectra (780.6 nm excitation) of (A) pristine SWNTs, (B) solvent-free product **1**, and (C) product **1** after TGA (10 °C/min to 750 °C) in argon.

large volumes of solvent (~ 2 L/g) were used.^{2a,6,7} The absorption spectrum of **1** (Figure 1), which is nearly identical to the spectra of **2–5**, displays a loss of features compared to the SWNT spectra, indicating a disruption in the electronic structure of nanotubes. The Raman spectrum of **1** (Figure 2) is also considerably altered compared to the spectrum of pristine SWNTs, in that the radial breathing (230 cm^{-1}) and tangential (1590 cm^{-1}) modes characteristic of SWNTs are present, but the disorder (1290 cm^{-1}) mode in the spectrum of compound **1** is greatly enhanced. Both the loss of structure in the absorption spectrum and the increased disorder mode in the Raman spectrum are indicative of covalent functionalization.^{2a}

We previously showed⁶ that heating functionalized nanotubes in an inert atmosphere removes the organic moieties and restores the pristine nanotube structure (Figure 2); therefore, TGA could be a measure of the degree of functionalization.² Observed percent weight loss from TGA (10 °C/min to 750 °C in argon) of compounds **1–5** is as follows: 22% (**1**), 30% (**2**), 34% (**3**), 25% (**4**), and 25% (**5**). These results are comparable to our former electrochemical and solvent-based thermal techniques and suggest a high degree of functionalization.^{6,7}

Infrared spectroscopy (ATR-IR) indicates the presence of the functional addends: **3** has strong C–H stretching from the *tert*-butyl moiety at 2954 cm^{-1} ($\Delta\nu = -5$), **4** has the strong carbonyl

at 1722 cm^{-1} ($\Delta\nu = 41$), and **5** has the expected aromatic nitro group at 1516 and 1339 cm^{-1} ($\Delta\nu = 43$ and 15 , respectively) ($\Delta\nu$ signifies the change in the absorbance frequency relative to the starting aniline).

The levels of solubility achieved were analogous to what we obtained previously with the solvent-based techniques.^{6,7} For example, the solubility of **3** was 0.03 and 0.4 mg/mL in THF and 1,2-dichlorobenzene, respectively, while the same material prepared using the former derivatization method showed 0.05 mg/mL solubility in THF.

Another solvent-free functionalization technique we investigated was ball milling. The Raman spectrum (Supporting Information) suggested a high degree of functionalization, although much of the SWNT structure could be compromised by the high shear, pulverizing action of the process as described by Li et al.¹¹ The intensity of the Raman-disorder mode might suggest tube destruction or a very high degree of functionalization, but since AFM analysis showed no rope-like structure, the tube scaffold was probably compromised.

Using the same solvent-free (stir bar) conditions except substituting multi-walled carbon nanotubes (MWNTs) for SWNTs also produced functionalized material. TGA analysis using the 4-chlorophenyl-substituted system gave 8% weight loss, while the pristine MWNTs gave no weight loss under identical TGA conditions ($10\text{ }^\circ\text{C/min}$ to $750\text{ }^\circ\text{C}$ in argon). The lower functionalization percentage in the MWNTs is likely due to their larger outer diameter causing them to be less reactive than the smaller-diameter HiPco tubes. Second, the sheathed nature of MWNTs renders many of their sidewalls inaccessible.

The same reaction to form aryl chloride **1** (Scheme 1) was performed for three different times (1 h, 1 d, and 3 d). The isolated products were spectroscopically identical, and the TGA data were similar: 1 h (20%), 24 h (19%), and 72 h (22%). Hence, the reaction is complete after 1 h at $60\text{ }^\circ\text{C}$.

In addition to short reaction times, the utility of diazonium chemistry was also observed by generating **1** from sodium nitrite (4.0 equiv/mol of carbon) and an acid (4.8 equiv/mol of carbon) as shown in Scheme 1. Both sulfuric acid and acetic acid promoted the formation of **1** according to UV/vis and Raman spectroscopy, and the degree of functionalization according to TGA (sulfuric acid (20%), acetic acid (22%)) was equivalent.

Benzynes addition (from anthranilic acid and isoamyl nitrite)¹² was also attempted, utilizing solvent-free conditions. The ATR-IR spectrum of the product exhibited a weak carbonyl stretch (1676 cm^{-1}) although it was not as intense as the strong carbonyl stretch (1722 cm^{-1}) observed for carboxylic ester **4**. Hence, the major product formed could be the benzyne adduct with some of the ortho acid. However, when 2-(trimethylsilyl)phenyltrifluoromethanesulfonate was treated with TBAF, which has been shown to give benzyne,¹³ unfunctionalized SWNTs were isolated. Furthermore, the Prato reaction,¹⁴ nitrile oxide,¹⁵ quinodimethane via α,α' -dibromo-*o*-xylene/zinc wetted with THF,¹⁶ and ethyl bromomalonate/NaH¹⁷ all failed to produce functionalized nanotubes under solvent-free or even slightly organic solvent-wetted paste-like reaction conditions.

For functionalization of nanotubes to occur, the bundles must be partially de-rope prior to reaction; initial reactions can then

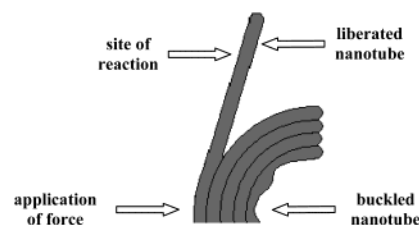


Figure 3. Schematic of the functionalization of carbon nanotubes without solvent. A mechanical force (stir bar) is applied to a nanotube bundle, which distorts the bundle causing bending, buckling, and sites for the reaction to occur.

cause further de-rope. This partial de-rope is typically achieved by sonicating dilute solutions of nanotubes. With solvent-free techniques (Figure 3), however, initial de-rope is probably effected by mechanical means.

In conclusion, this fundamentally new approach to carbon nanotube derivatization paves the way for the large-scale functionalizations for use in materials studies, for example, wherein the surface bonding groups cause load transfer to the nanotubes in polymer blends; a phenomenon that is not observed with the pristine nanotube blends.¹⁸

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Supporting Information Available: Raman spectrum after ball-milling, results of NMR analyses, and IR spectra of **3–5** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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