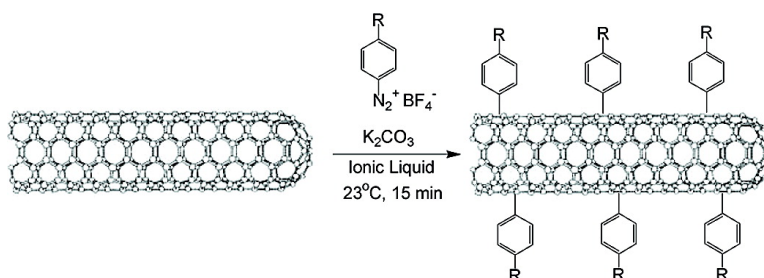


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Green Chemical Functionalization of Single-Walled Carbon Nanotubes in Ionic Liquids

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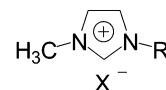
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Abstract: Single walled carbon nanotubes (SWNTs) are exfoliated and functionalized predominantly as individuals by grinding them for minutes at room temperature with aryldiazonium salts in the presence of ionic liquids (ILs) and K_2CO_3 . This constitutes an extremely rapid and mild green chemical functionalization process for obtaining the individualized nanotube structures. A number of ILs and various reaction conditions were surveyed. Raman, XPS, UV/vis/NIR spectroscopies, thermogravimetric analysis, and atomic force and transmission electron microscopies were used to characterize the products.

Introduction

Single walled carbon nanotubes (SWNTs) have the potential to make vast improvements in numerous applications because of their electrical and mechanical properties.¹ To more fully exploit their properties for composite and other materials applications, SWNTs must be unbundled into individuals.² This is difficult because of the high intermolecular cohesive forces (0.5 eV/nm) between SWNTs. The majority of functionalization procedures afford predominantly bundled SWNT products.^{1,2} A few protocols have recently been discovered that exfoliate and functionalize SWNTs while also producing individuals and small bundles.³ These procedures require harsh solvents such as fuming sulfuric acid^{3a} or liquid ammonia,^{3b} or expensive equipment with extended reaction times to produce small amounts of product.^{3c} We report here a new method, functionalization in ionic liquids (ILs), resulting in exfoliation of the ropes and derivatization as predominantly individual SWNTs that do not rebundle due to the addends. The reaction occurs in minutes at room temperature using only a mortar and pestle to mix the reactants (Scheme 1).

The interest in ILs has grown dramatically in the past decade as their unique properties have been exploited.⁴ These unique properties that allow processes to be designed such that the ILs are recyclable consist of the following: they are salts that are liquids at room-temperature having boiling points over 200 °C, and they are nonvolatile.⁵ It has been reported that SWNT bundles can be exfoliated in ILs to form relaxed bundles.⁶ We



EMIBF ₄	R = C ₂ H ₅	X = BF ₄
BMIBF ₄	R = <i>n</i> -C ₄ H ₉	X = BF ₄
HMIBF ₄	R = <i>n</i> -C ₆ H ₁₃	X = BF ₄
OMIBF ₄	R = <i>n</i> -C ₈ H ₁₇	X = BF ₄
BMIPF ₆	R = <i>n</i> -C ₄ H ₉	X = PF ₆

Figure 1. Structures of ILs used in this work.

Table 1. Calculated D/G Ratios from the Raman Spectra^a

IL	R group (Scheme 1)	D/G ratio ^b
BMPBF ₄	Cl	0.29
BMIBF ₄	<i>tert</i> -butyl	0.16
BMIBF ₄	I	0.36
BMIBF ₄	Br	0.27
HMIBF ₄	CCH	0.40
BMIPF ₆	Cl	0.51
HMIBF ₄	F	0.33
HMIBF ₄	NO ₂	0.36
OMIBF ₄	COCH ₃	0.21

^a Excitation at 633 nm on the solid. ^b Averaged over 5–6 different scan positions.

have combined our diazonium functionalization chemistry⁷ with the desirable properties of ILs such that an extremely rapid and mild green chemical⁸ functionalization process results. The presence of the IL leads to exfoliation of the SWNTs ropes, with subsequent addition of functionalized aryl groups to the sidewalls of the SWNTs, providing functionalized SWNTs that remain predominantly as individuals.

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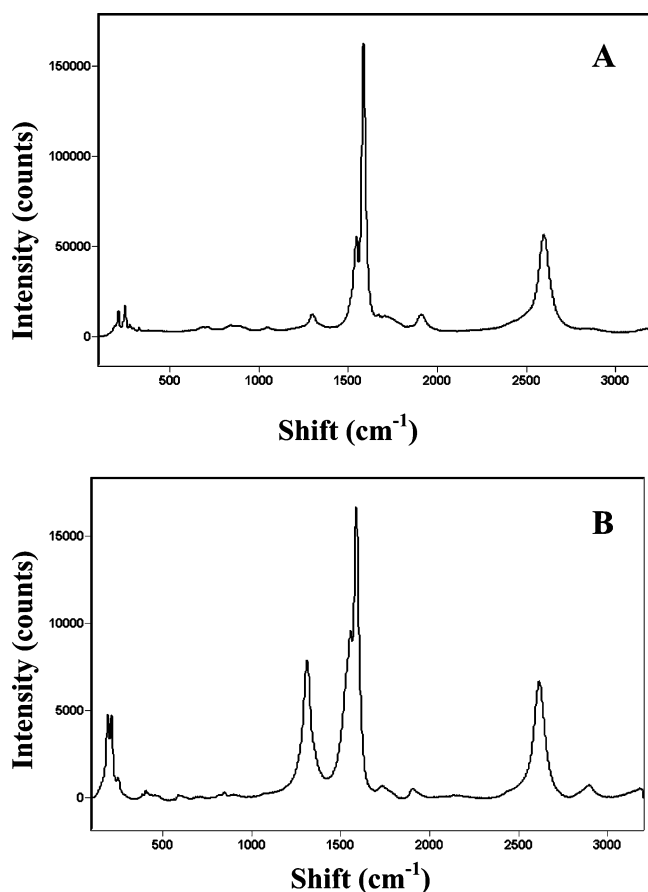


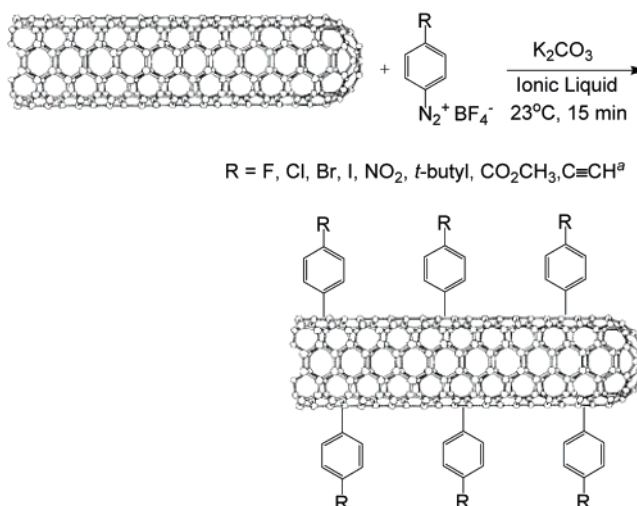
Figure 2. Raman (633 nm, solid) of (A) purified SWNTs and (B) SWNTs functionalized with 4-chlorobenzenediazonium tetrafluoroborate in BMIPF₆.

Results

Our work centered on the use of imidazolium-based ILs with various alkyl branch lengths (Figure 1). A pyridinium-based IL, 1-butyl-4-methylpyridinium tetrafluoroborate (BMPBF₄), was tried for comparison purposes with little observed difference in the degree of functionalization. Except for 1-ethyl-4-methylimidazolium tetrafluoroborate (EMIBF₄), which produced the lowest degree of functionalization, the length of the alkyl branch on the IL did not markedly affect the dispersion and degree of functionalization of the SWNTs (Table 1). In our work, the counterion (BF₄⁻ or PF₆⁻) did not influence the degree of functionalization of the SWNTs; however, the literature indicates that the counterion can affect the recovery and recycling of the IL.^{5,9}

In a typical experiment, purified HiPco SWNTs¹⁰ (2 mg) and the diazonium salt (1 mmol per mequiv C) were ground by hand in an agate mortar and pestle with the IL (0.4 mL) for 10 min. The base, K₂CO₃ (5 mg, 0.2 equiv), was then added, and the mixture was ground for an additional 5 min. The sides of the mortar were scraped down with the pestle during grinding to

Scheme 1. Functionalization of SWNTs in Ionic Liquid Using a Mortar and Pestle



^a The alkyne moiety was *meta*-substituted relative to the diazonium functionality.

ensure complete mixing. The mixture was washed from the mortar and pestle using acetone, and the resulting suspension was filtered on a Teflon filter (0.45 μm). The filter cake was washed with acetone and DMF to remove the ionic liquid, followed by a water wash to dissolve excess base. The solid was removed from the filter and sonicated (Cole-Parmer Ultrasonic Cleaner, model 08849-00, 12 W, 10 min) in DMF (5 mL) and isolated by filtration.

The functionalized SWNTs were then characterized using spectroscopic and microscopic methods along with thermogravimetric analysis (TGA). The Raman spectrum of the starting material shows a minimal disorder mode (diamondoid or D-band) at 1290 cm⁻¹. A spectrum of functionalized product shows a higher D-band corresponding to functionalization of the SWNT (Figure 2), and this increase is due to an increase in the number of sp³-carbons that are formed on the SWNT during functionalization.¹ The intensity of the D-band was divided by intensity of the tangential mode (graphitic or G-band) at 1590 cm⁻¹ (Table 1), and this ratio provides a good indication of the relative degree of functionalization.¹ Additionally, as expected, the resonance Raman enhancement seen in the pristine SWNT spectrum is markedly suppressed in the functionalized material.¹

A UV/vis/NIR absorption spectrum of the starting material displays the characteristic van Hove singularities (Figure 3). The spectrum of the functionalized SWNTs shows the lack of the van Hove transitions, consistent with covalent functionalization of the SWNTs.¹ All products had similar spectral features.

Functionalization of the SWNTs with 4-chlorobenzenediazonium tetrafluoroborate in HMIBF₄ showed a 21% increase in the weight of the isolated material. TGA of the material (Ar, 10 °C/min to 800 °C) showed comparable weight loss that is calculated to be ca. one functional group in 44 nanotube carbons.

Microscopy confirmed the findings of the Raman, UV/vis/NIR absorption spectra and TGA. Using the tapping mode in atomic force microscopy (AFM), individual tubes (6–12 Å) and a few small bundles (up to 27.5 Å) were observed, and height data was used to determine the diameter of the tubes. An AFM image of 4-chlorobenzenediazonium tetrafluoroborate-

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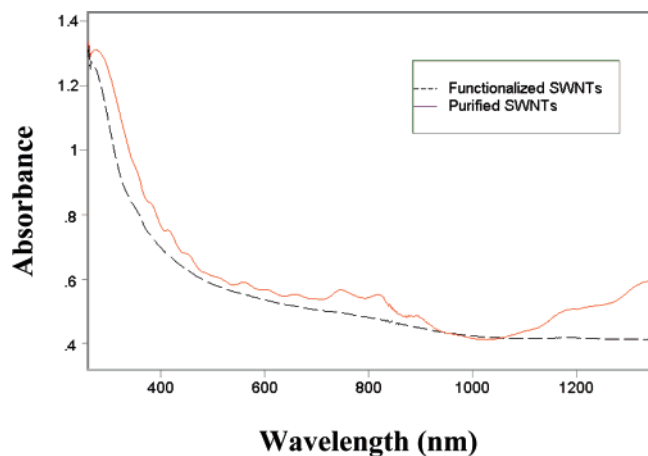


Figure 3. UV/vis/NIR absorption spectra (absorbance scale is in arbitrary units) in DMF of purified SWNTs and SWNTs functionalized with 4-chlorobenzenediazonium tetrafluoroborate in BMIBF₄.

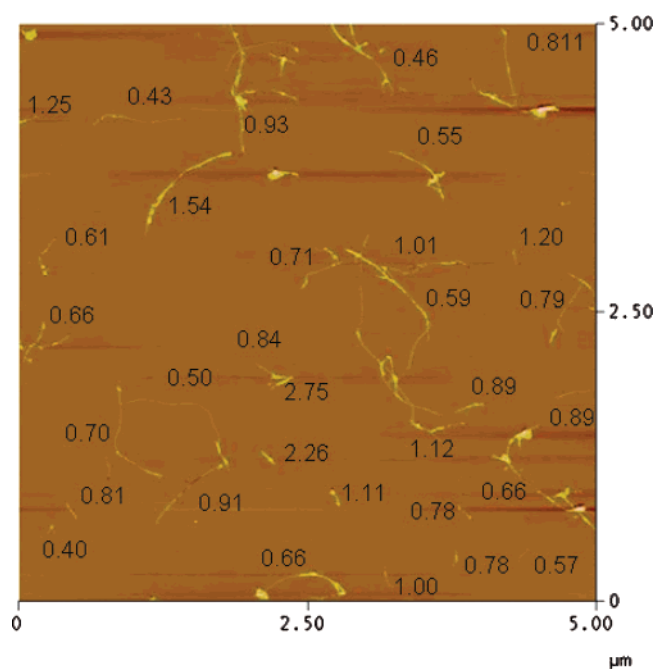


Figure 4. AFM analysis (spin-coated onto freshly cleaved mica in DMF) by height of SWNTs functionalized with 4-chlorobenzenediazonium tetrafluoroborate in OMIBF₄. The sectional analysis shows the height data in nanometers of the functionalized SWNTs. The vertical distances measured (shown as numbers, in nm, on the micrograph) are predominantly <1.4 nm, therefore indicating individual SWNTs.

functionalized SWNTs is shown with height data in nanometers in Figure 4. Figure 5 shows SWNTs that were processed with the same method but without the diazonium salt addition. Clearly, the functionalized SWNTs remain predominantly as individuals (<1.4 nm) (Figure 4) while the unfunctionalized SWNTs rebundled extensively (Figure 5). Transmission electron microscopy (TEM) showed individual SWNTs with functional groups appended to their sidewalls (Figure 6). Hence the microscopy studies are consistent with the spectroscopic analyses.

X-ray photoelectron spectroscopy (XPS) of SWNTs functionalized using 4-chlorobenzenediazonium tetrafluoroborate salts in BMIBF₄ showed the presence of chloride, but no fluoride was detected even in the multiplex spectrum. Hence, there was no remaining IL in the material. XPS was also done of SWNTs

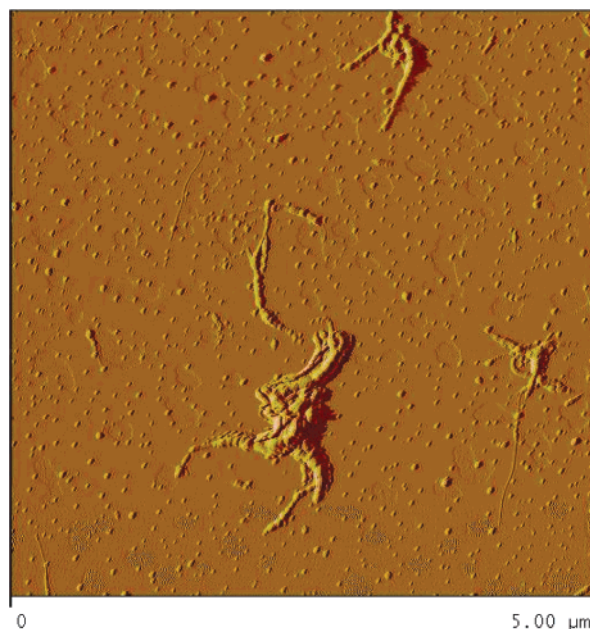


Figure 5. AFM analysis (spin-coated onto freshly cleaved mica in DMF) by amplitude of SWNTs that had undergone IL treatment and grinding with K₂CO₃ but without the diazonium salt addition. The sectional analysis measured the height data of the SWNTs and found the vertical distances measured to be as high as 45 nm.

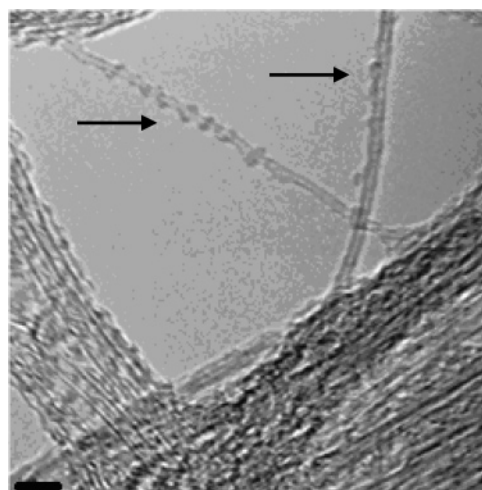


Figure 6. TEM image (on a lacey carbon grid) of SWNTs (arrows) functionalized using 4-chlorobenzenediazonium tetrafluoroborate salts in BMIBF₄. The scale bar is 5 nm. The functional groups can be seen as bumps along the sides of the individualized SWNTs.

functionalized using 4-nitrobenzenediazonium tetrafluoroborate salts in HMIBF₄. A distinct peak at 405.9 eV (NIST XPS Database) confirms the presence of the nitrobenzene groups on the SWNTs (Figure 7).

The following control experiments were also run: SWNTs and IL only, without base, with NaOH instead of K₂CO₃, without diazonium salt, with 1-methylimidazole as the solvent (synthetic precursor of IL), and with AIBN as a radical initiator.^{3a} When no base was present, the degree of functionalization was not as high as with base. The use of NaOH instead of K₂CO₃ was found to give lower yields, possibly due to degradation of the diazonium salt through hydroxide substitution of the diazo moiety. In the other controls, no or minimal functionalization was observed. Thus, basic conditions aid in the diazonium-induced functionalization of the SWNTs as we

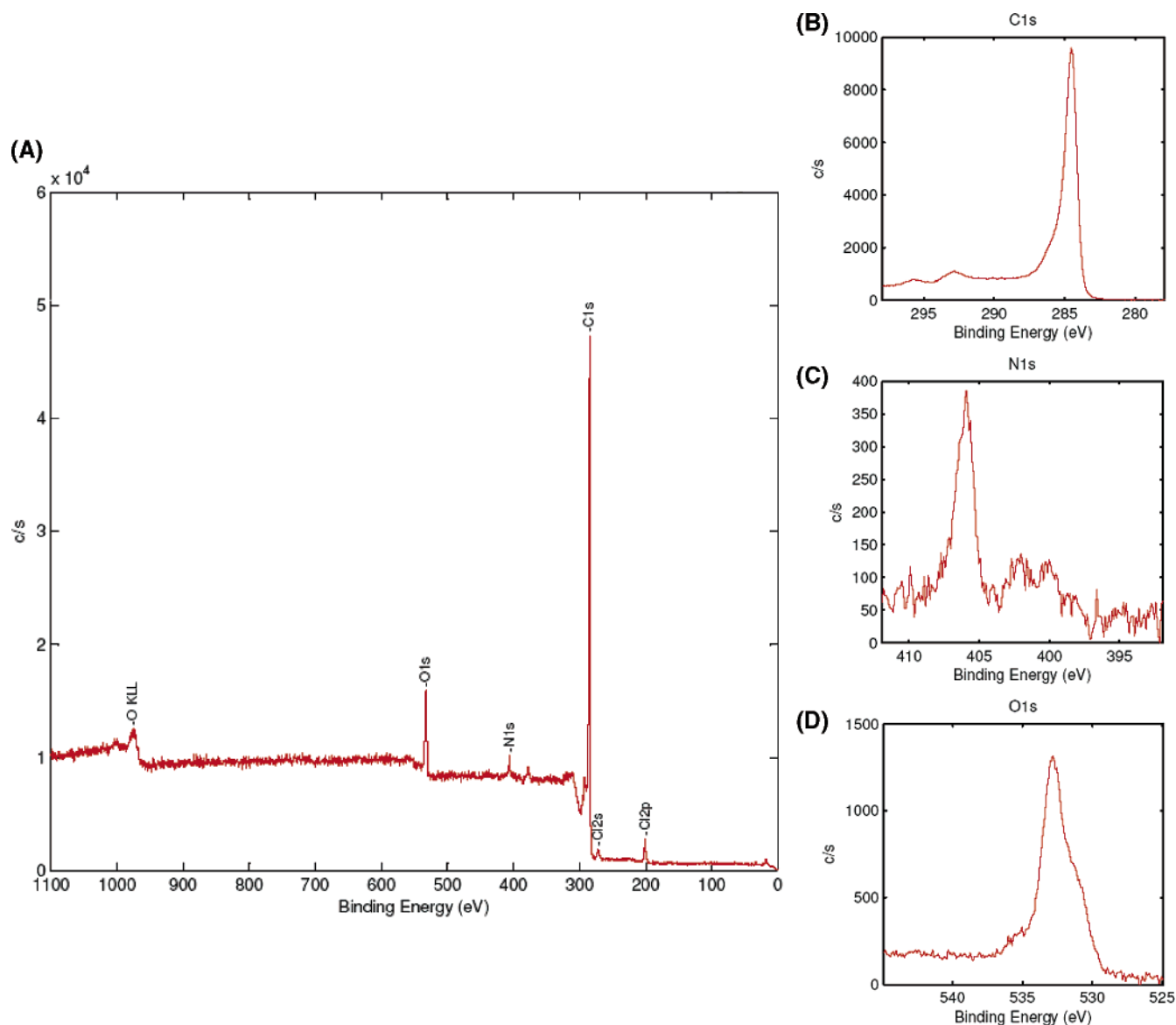


Figure 7. XPS analysis of SWNTs functionalized using 4-nitrobenzenediazonium tetrafluoroborate salts in HMIBF₄. XPS data were acquired on a Physical Electronics (PHI QUANTERA) XPS/ESCA system. The base pressure of the system is at 5×10^{-9} Torr. A monochromatic Al X-ray source at 100 W was used with a pass energy of 26 eV and with a 45° takeoff angle. The beam diameter was 100.0 μ m. Binding energy values were referenced externally to a gold 4f peak at 84.00 eV and internally to a carbon 1s binding energy of 280.50 eV (NIST XPS Database). The XPS analysis consisted of (A) survey of the spectral region from 0 to 1100 eV, (B) the carbon 1s region, (C) the nitrogen 1s region, and (D) the oxygen 1s region. The nitrogen region peak at 405.9 eV confirms the presence of nitrobenzene groups within the sample.

have seen in solution-phase reactions,^{7c} and the IL is necessary for functionalization of individual SWNTs to occur.

Conclusion

Reaction of SWNTs with aryldiazonium salts in ILs results in the production of functionalized individuals; the products are comparable to those derived from other processes using harsh reaction conditions.³ The method utilizes the unique properties of ILs. It does not require adverse solvent conditions, and it is complete in minutes at room temperature. This method thereby paves the way for a green chemical functionalization protocol to exfoliate SWNTs which are optimal for materials applications.¹

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