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Environmentally friendly functionalization of single walled carbon nanotubes in molten urea

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ABSTRACT

Using molten urea as the solvent, single walled carbon nanotubes (SWCNTs) are dispersed and functionalized with arenediazonium salts in less than 15 min to afford predominantly unbundled functionalized SWCNTs. This technique provides a rapid and economically viable route to produce covalently functionalized nanotubes in large amounts with an industrially friendly method.

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1. Introduction

Single walled carbon nanotube (SWCNT) composites promise to offer toughened materials for future high performance applications [1]. A common problem in preparing SWCNT composites is the dispersion of the individual SWCNTs into the polymer matrix and maintaining efficient interactions between the nanotubes and the host material. There is ~ 0.5 eV/nm of cohesive interaction between any two tubes, [2] so one needs a solvent that will liberate portions of individual tubes while permitting addend formation to the nanotube sidewalls, thereby inhibiting the nanotubes from reforming bundles. The nanotube–host dispersion difficulty can be similarly overcome through covalently functionalizing the sidewalls of the nanotubes with moieties that render the SWCNT more compatible with the matrix while promoting good interfacial adhesion through dipolar interactions, π – π attractions, hydrogen bonds or covalent bonds to the matrix [2]. Although some environmentally sound protocols have been developed by us including the use of ionic liquids [3] and on-water [4] reactions, most other functionalization protocols require lengthy reaction times or utilize hazardous solvents [1,5–8]. Here we describe a facile route to functionalized SWCNTs with arenediazonium salts, formed in situ from anilines, using the environmentally benign solvent, urea.

2. Results and discussion

An illustrative functionalization of SWCNTs in urea was conducted as follows. To an oven-dried three-necked round bottom flask containing 60 g of urea was added 50 mg of purified SWCNTs (obtained by heating HiPco SWCNTs in a humid atmosphere at 220 °C followed by HCl extraction of the catalyst) [9] and the mixture was heated to 140 °C (Fig. 1). After the urea had become molten, the reaction was homogenized for 5 min using an adjustable speed Dremel tool (model 400xpr) equipped with a standard-capacity rotor–stator generator (Cole-Parmer No. A-36904-52) at the lowest setting. Once the SWCNTs were suspended in the molten urea, the aniline (2 M equiv per nanotube carbon) was added to the solution and allowed to homogenize for 5 min. Solid sodium nitrite (4 equiv) was added in one portion and rapid outgassing was observed. In some cases the functionalized SWCNTs floated to the surface of the molten reaction mixture. After 15 min, the mixture was poured into an Erlenmeyer flask containing 200 mL of DI water. The mixture was then filtered through a PTFE (0.45 μ m) membrane. Further purification was done by re-suspending the filter cake in ethanol and filtering over a PTFE membrane (2 \times) and then re-suspending the filter cake in DI water and filtering over a polycarbonate (0.22 μ m) membrane (2 \times). After the final water wash, the filter

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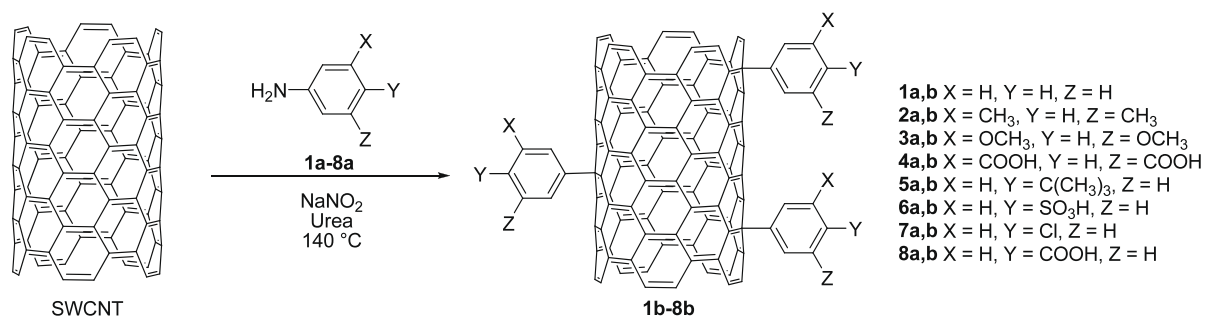


Fig. 1 – Functionalization of purified SWCNTs in molten urea by diazonium salts formed in situ.

cake was washed with 50 mL of acetone and allowed to dry under vacuum overnight to yield the final product.

It is known that urea reacts with nitrous acid under acidic conditions, [10] however in this case the urea appears to have no deleterious effect on the outcome of the reaction.

Raman spectra of solid SWCNT samples were collected before and after reaction using both 633 and 785 nm excitation on a Raman microscope (RM 2000, Renishaw Inc.). Visible and near-IR absorbance data (300–800 nm) were collected on the NanoSpectralyzer (10 spectral averages, 0.5 s acquisition time). Finally, atomic force microscopy (AFM) imaging and X-ray photoelectron spectroscopy (XPS) analyses were done.

A representative set of experimental spectroscopic data is shown in Fig. 2, which shows the common signs of covalent functionalization. The top trace (line 1) in Fig. 2a shows the characteristic van Hove singularities of pristine (unfunctionalized) material that disappear after functionalization [5] in the bottom trace (line 2). The loss of these transitions after the reaction (Fig. 2a line 2) confirms that covalent functionalization is occurring on the surface of the SWCNTs. Fig. 2b shows the Raman spectra of the nanotubes. The intensity of the ratio of the D-band (the region near 1370 cm⁻¹) to the G-band (region near 1590 cm⁻¹) increased markedly following reaction. Likewise, the Raman resonance enhancement seen in unfunctionalized SWCNTs was lost after the reaction. Such a loss of intensity is diagnostic of functionalization [11]. It is known that metallic tubes react more quickly than semiconductors with diazonium species, [12] however in this case the slow addition of reagents and careful temperature control that is necessary to preferentially react one species over the others was not done. XPS analysis of 6b (Fig. 3) confirms the presence of sulfur from the sulfanilic acid. The presence of the sulfur in combination with the loss of van Hove singularities and increased D to G ratio in the Raman lead to the conclusion that the reaction produced covalently functionalized SWCNTs. It is also worthy to note that the small shoulder at roughly 286.5 eV of the C1s spectra (Fig. 3) may be indicative of amide groups (sometimes referred to as ureido groups) from isocyanic acid addition to the carboxylic acids located at the ends of the oxidized tubes and on the functional groups of 4b and 8b. These trace amide groups may also explain some of the nitrogen impurity in the sample [13,14].

A range of anilines that formed products with SWCNTs as evidenced by the Raman D to G ratios is presented in Table 1.

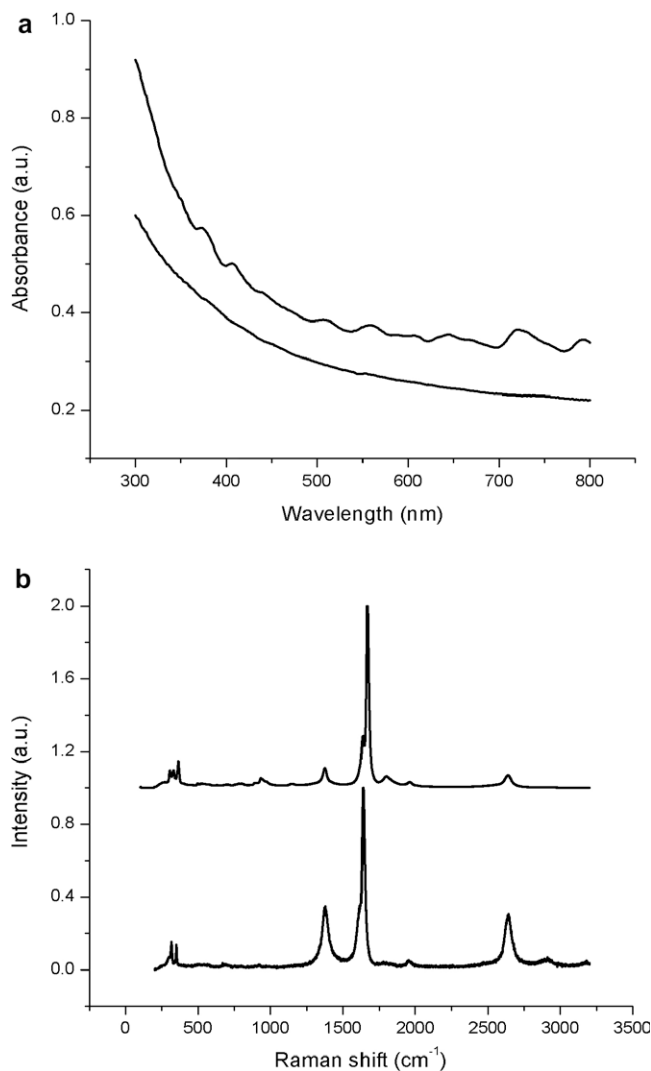


Fig. 2 – (a) Absorption spectra of pristine SWCNTs in DMF (top) and 6b in DMF (bottom). (b) Raman spectra of the starting SWCNTs (top) and 6b (bottom). Raman spectroscopy was carried out on solid samples using a 633 nm He-Ne laser.

Functionalization of the SWCNTs was successful with the exception of 4-nitroaniline (9a, entry 9 in Table 1).

The AFM image (Fig. 4) of 6b, which was taken from a DMF dispersion spin-coated on freshly cleaved mica, shows many

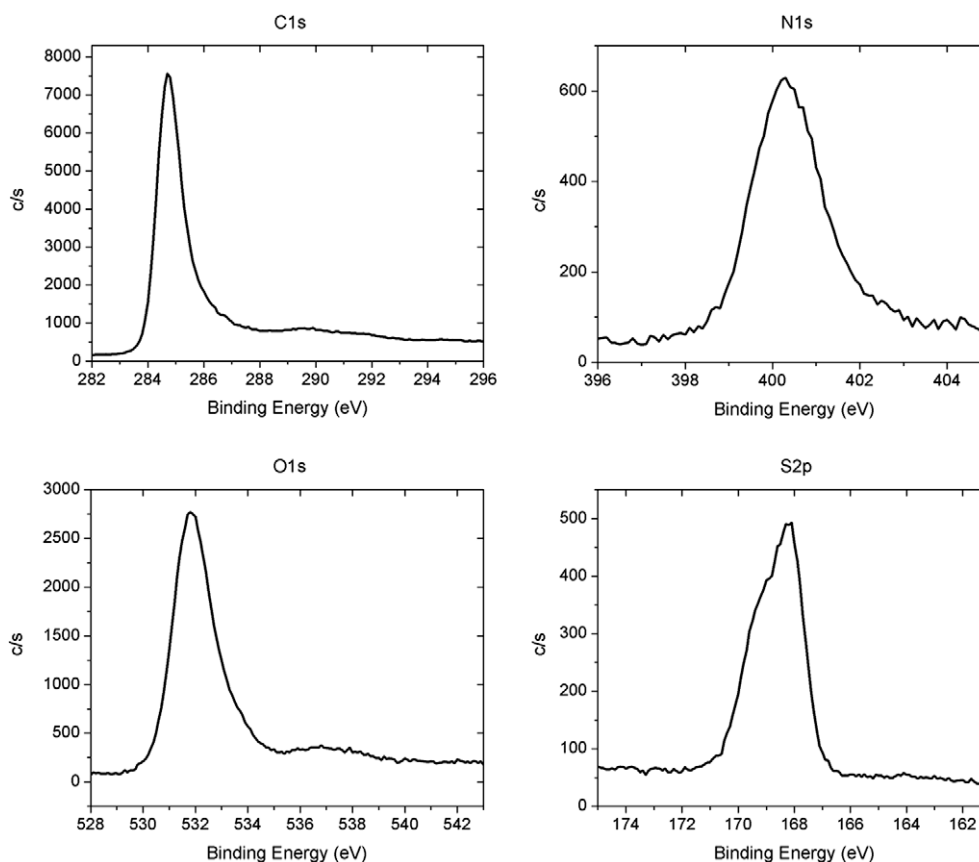


Fig. 3 – XPS analyses showing the elemental concentration from 6b; C = 77%; N = 5%; O = 15%; S = 3%. The base pressure of the system was at 5×10^{-9} Torr. A monochromatic Al X-ray source at 100 W was used with a pass energy of 26 eV and with a 45° takeoff angle. The beam diameter was 100.0 μm . Binding 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).

Table 1 – Raman D to G ratio (633 nm excitation) of SWCNTs after reaction with various anilines in molten urea.

Entry	Aniline	Raman D to G
1	Aniline (1a)	0.14
2	3,5-Dimethylaniline (2a)	0.21
3	3,5-Dimethoxyaniline (3a)	0.18
4	5-Aminoisophthalic acid (4a)	0.15
5	4- <i>tert</i> -Butylaniline (5a)	0.18
6	4-Aminobenzenesulfonic acid (6a)	0.32
7	4-Chloroaniline (7a)	0.38
8	4-Aminobenzoic acid (8a)	0.34
9	4-Nitroaniline (9a)	NR ^a

a No reaction.

individual functionalized SWCNTs with a few small bundles. In the section analysis, the individual functionalized tubes are about 1 nm in height. This is consistent with the typical diameters of HiPco-produced tubes [15]. While the bundled tubes may be functionalized, it is difficult to determine by AFM because the size of the bundles is comparatively much larger than any increases in size that may be due to functionalization. In addition, unfunctionalized individual tubes are expected to rebundle after quenching the reaction due to the cohesive interactions previously discussed.

3. Conclusion

In conclusion, SWCNTs can be functionalized in molten urea to afford products with an average Raman D to G ratio of 0.30 containing individual SWCNTs as well as some small SWCNT bundles. The products contain functional groups that are covalently bound with no detectable trace of urea attached to the SWCNTs. Furthermore, this process is inexpensive using a solvent that could be considered to be environmentally friendly.

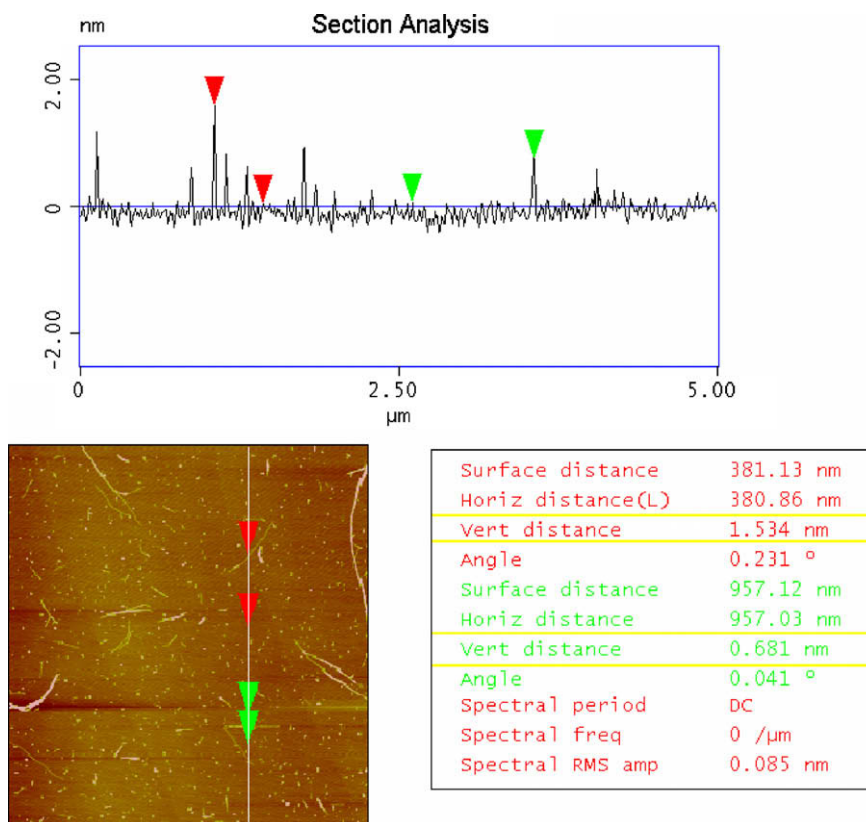


Fig. 4 – AFM analysis showing individual and bundled functionalized nanotubes 6b.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.07.035.

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