

Carbon Nanotubols from Mechanochemical Reaction

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) can react with potassium hydroxide through a simple solid-phase mechanochemical reaction at room temperature to produce single-walled carbon nanotubols (SWNTols) – multiple hydroxyl groups direct-modified SWNTs. The SWNTols are highly soluble in water and can be readily self-assembled into aligned arrays through strong surface hydrogen bond interactions.

The chemical modification of single-walled carbon nanotubes (SWNTs) is of great current interest. Such functionalization is necessary to access the fundamental chemistry of SWNTs, to modify their chemical and physical properties, and to endow SWNTs with ultimate new characteristics.¹ In addition to the noncovalent approaches to modifying SWNTs such as polymer wrapping,² biomolecule binding,^{3,4} and metal ion binding,^{5,6} considerable effort has been made through covalent modification. For example, Haddon⁷ first synthesized solubilized SWNTs through the amidation reaction of long chain amine with carboxylic acid groups activated by SOCl₂ on the surface of SWNTs. Margrave et al.⁸ obtained fluorinated SWNTs by taking elemental fluorine as the fluorinating agent at temperatures ranging from 150 to 600 °C. Subsequently, Tour et al.⁹ reported that aryl diazonium compounds could react with SWNTs both electrochemically and thermochemically to produce aryl-modified SWNTs through presumable aryl radical intermediates. Very recently, Prato et al.¹⁰ have shown that the covalent modification of SWNTs can be achieved through 1,3-dipolar addition of azomethine yields. Other covalent modifications of SWNTs through carbenes,^{11,12} radicals,¹¹ nitrenes,¹² and electrophiles¹³ were also reported. The organization of chemically modified carbon nanotubes^{14,15} as well as shortened carbon nanotubes¹⁶ with certain substrates was also demonstrated.

In this communication, we report a novel approach to modify SWNTs through simple solid-phase mechano-

chemical reaction at room temperature. Commercially available SWNTs can react with potassium hydroxide to produce single-walled carbon nanotubols (SWNTols), which are multiple hydroxyl group directly modified SWNTs that are soluble in water and can be readily self-assembled into compact aligned arrays.

Mechanochemistry refers to processes in which mechanical motions/energy control chemical reactions.¹⁷ Specifically, the solid-phase mechanochemical reaction involves highly reactive centers generated by the mechanical energy imparted to the reaction system. Certain organic reactions have been demonstrated to take place efficiently in the solid-state phase.¹⁸ Such technique has also been successfully used to make fullerene derivatives such as bucky dumbbell C₁₂₀ from the parent fullerenes, which are poorly soluble in common organic solvents.¹⁹

In our experiment, a piece of buckypaper¹⁴ which was made from the SWNT suspensions of Tube@Rice was used as starting material. Typically, 10 mg of SWNTs and 200 mg of potassium hydroxide were weighted into a stainless steel capsule containing a milling ball. The capsule was then vigorously shaken for 2 h in air at room temperature using a Wig-L-Bug (Bratt 3110-B). Thereafter, the reaction mixture was dissolved in 10 mL of water and precipitated into 100 mL of methanol. Precipitation was repeated until the methanol solution became neutral to ensure a complete removal of potassium hydroxide residues, if any. After centrifuging, the upper layer of liquid was removed and the resulting black solid was readily soluble in water (up to 3 mg/mL). Different from other solubilized CNTs, the SWNTols thus prepared are insoluble in common organic solvents such as dichlorobenzene, chloroform, etc., which implies a highly hydrophilic nature.

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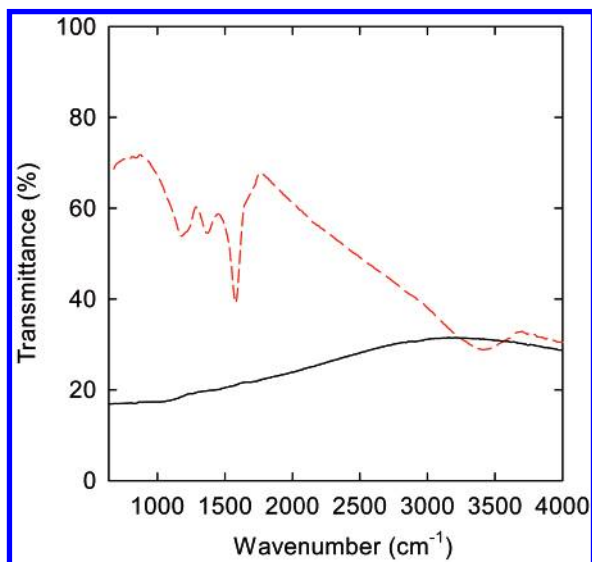


Figure 1. FTIR spectra of the pristine SWNTs (solid curve) and the SWNTols (dash curve).

The resulting SWNTols were studied by micro-FTIR spectroscopy. As can be seen in Figure 1, SWNTols show a remarkably different FTIR spectrum from that of pristine SWNTs. Consistent with previously reported data,²⁰ no detectable transmission band was observed for the pristine SWNTs in the wavenumber range covered in this study (solid line, Figure 1). In contrast, the corresponding FTIR spectrum for SWNTols (dash line, Figure 1) shows a very broad transmission band centered at 3405 cm^{-1} , characteristic of hydrogen bonded -OH . The band at 1177 cm^{-1} is corresponding to the stretching band of C-O , while the band at 1372 cm^{-1} can be interpreted to the bending stretching band of hydroxyl groups. The strong transmission band at about 1580 cm^{-1} can be attributed to the stretching mode of -C=C- in an enol form. The above FTIR results are consistent with the introduction of -OH groups into the nanotube structure, which is supported by the following XPS measurements.

Figure 2a,b shows the XPS C 1s spectra of the pristine SWNTs and SWNTols, respectively. Figure 2a shows a spectrum similar to that of graphite,²¹ along with weak signals for C-O (286.4 eV) and C=O (288.0 eV). The low contents of C-O (3.4%) and C=O (4.4%) deduced from the curve fitting could indicate an incorporation of a trace amount of oxygen-containing impurities into the nanotube sample, as carbon nanotubes are known to be susceptible to gas adsorption.^{22,23} Comparing with Figure 2a, Figure 2b shows a significant increase in the percentage content of C-O (286.4 eV) from 3.4% to 14.9%, clearly indicating the introduction of hydroxyl groups. The increased value of ca. 11% C-O corresponds to a grafting density of ca. 1 OH group per 10 carbon atoms in the resultant nanotubols.

Further evidence for the formation of SWNTols comes from Raman spectroscopic measurements (Renishaw RM 2000, 632.8 nm from He-Ne laser). As seen in Figure 3, the Raman spectrum of the pristine SWNTs (solid curve) shows an intense peak at 1591 cm^{-1} , attributable to the E_{2g} tangential mode, with a small disordered-induced peak at 1309 cm^{-1} (D lines).²⁴ The Raman spectrum also shows clear

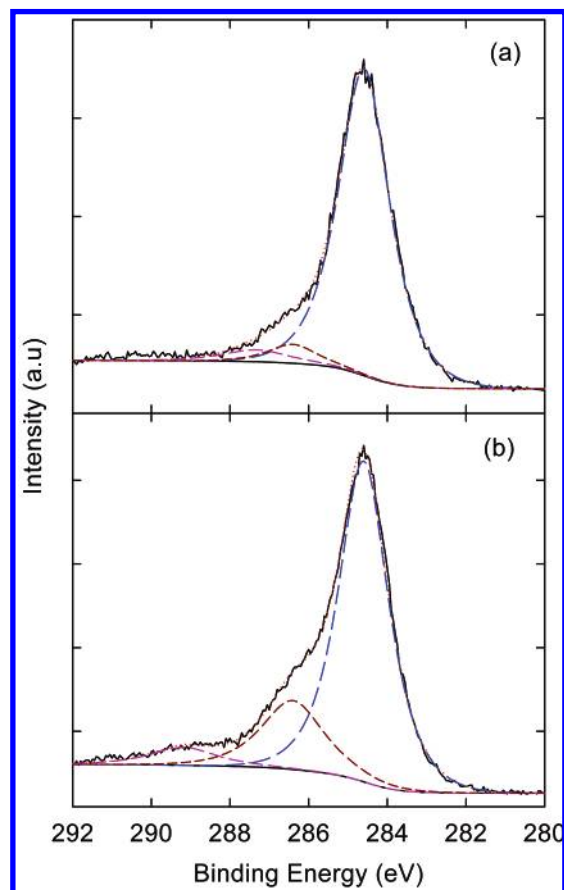


Figure 2. XPS C 1s spectra of (a) the pristine SWNTs and (b) the SWNTols.

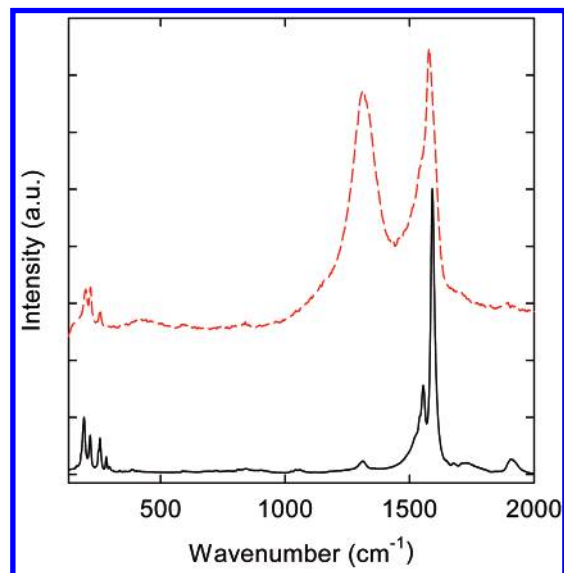


Figure 3. Raman spectra of the pristine SWNTs (solid curve) and the SWNTols (dash curve).

characteristic peaks in the radial breathing mode (RBM) spectral region. The corresponding Raman spectrum for SWNTols (dash curve, Figure 3), however, reveals a strong peak around 1323 cm^{-1} , arising from disordered structures. The relative intensity ratio of the tangential mode to the disordered mode decreased from 18:1 for the pristine SWNTs to 1.2:1 for SWNTols. As expected, the introduction of

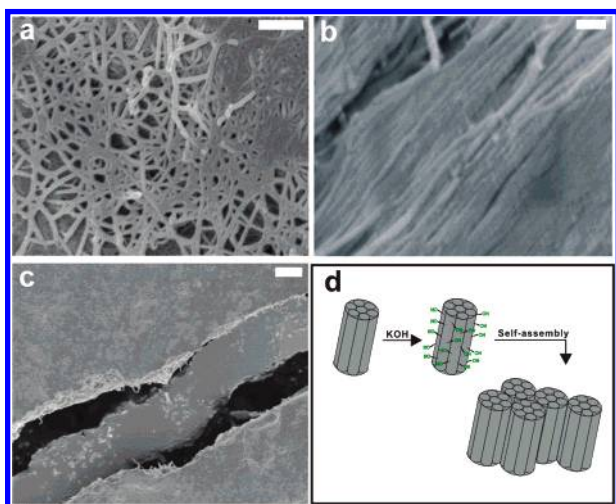


Figure 4. SEM images of (a) the starting SWNT sample (scale bar, 100 nm); (b) cross-section view of the self-assembled SWNTol sample shown in (c) (scale bar, 100 nm); (c) top view of the self-assembled SWNTol sample (scale bar, 1000 nm); and (d) schematic representation of the self-assembling process.

covalently bound moieties (i.e. $-OH$ groups in this study) to the SWNT framework will inevitably change the sp^2 carbons into sp^3 hybridization.⁹ The existence of a RBM Raman line of the nanotubol sample in the low-frequency range strongly suggests the remaining of the tubular structures of the carbon nanotubols. The significant increase in the sp^3 population revealed by the Raman spectra is consistent with the high percentage of hydroxyl groups introduced into the nanotube structure, as indicated by the XPS results.

A solid-state mechanochemical reaction of C_{60} with potassium cyanide or potassium hydroxide under nitrogen atmosphere has been previously reported to produce dumbbell-shaped C_{120} through a nucleophilic addition, followed by an intermolecular electron-transfer reaction.¹⁹ However, the solid-state mechanochemical reaction of [60]fullerene with potassium hydroxide in air produced [60]fullerols with about 27 hydroxyl groups on the surface of each [60]fullerene with no other detectable products.²⁵ It was believed that the oxygen played an important role in the formation of [60]-fullerols. The nucleophilic attack of hydroxide onto the [60]-fullerene was also involved in the reaction. The functionalization described here is probably initiated in a manner similar to the formation of [60]fullerols. Considering the relative low reactivity of SWNTs compared to that of [60]-fullerene, the SWNTols thus prepared contain less hydroxyl group percentage (1 OH group per 10 carbon atoms) than does [60]fullerols (1 OH group about 2 carbon atoms).

The high content of OH groups in the nanotubol structure, together with the strong FTIR absorption for hydrogen bonding, suggest a strong intermolecular interaction between SWNTols. Therefore, self-assembling of SWNTols can be expected. As shown in Figure 4, the SEM image for the starting SWNTs (Figure 4a) shows a randomly entangled morphology. In contrast, the cross-section SEM image of a mashed solid sample of SWNTols²⁶ reveals a well-aligned self-assembled structure (Figure 4b). Figure 4c shows a large-

area flat surface for the nanotubol film, indicating the occurrence of a large-scale self-assembling process. As schematically illustrated in Figure 4d, the strong hydrogen bonding interaction between the nanotubols is believed to be the driving force for the formation of the highly oriented, self-assembled nanotubol arrays.

In summary, we have demonstrated a novel approach for functionalization of SWNTs with multiple hydroxyl groups via a simple solid-phase mechanochemical reaction with potassium hydroxide. The resulting SWNTols show a strongly intertube interaction through hydrogen bonding that facilitates the nanotubols to self-assemble into aligned arrays. The simple solid-phase mechanochemical reaction for chemical modification of SWNTs, coupled with the rich chemistry for further chemical derivatization through reactions characteristic of functionalities introduced by the solid-state reaction, could make the methodology developed in this study as a simple, but versatile, approach toward large-scale production of functionalized SWNTs and self-assembled SWNT films with ordered structures attractive for many potential device applications ranging from nanotube electronics to sensor chips.

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