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C$_{60}$ modified single-walled carbon nanotubes

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Abstract

Single-walled carbon nanotubes (SWNTs) can react with C$_{60}$ through simple solid-phase mechanochemical reaction at room temperature under nitrogen atmosphere to produce C$_{60}$ modified SWNTs.
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1. Introduction

Since their discovery in 1991 [1], single-walled carbon nanotubes (SWNTs) have attracted much interest in nanoscience and nanotechnology due to their novel and structure-dependent properties [2,3]. For endowing SWNTs with ultimate new characteristics, considerable attention has been focused on the chemical modification of SWNTs [2,4–6]. Such modification is interesting since fundamental knowledge of the chemical properties of SWNTs is thus accessible and chemical connection of other functional molecules will ultimately lead to new property profiles [5]. In the meantime, fullerenes have been continuously attracting strong interest from many areas of science and technology, owing to their unique chemical and physical properties [7–9]. It can be expected that nanomaterials combined of SWNTs and fullerenes will lead to novel electronic and optoelectronic properties for the extensive potential application. In this context, C$_{60}$ encapsulated SWNTs (bucky-peapods) was synthesized and raised the exciting possibility of a nanoscale material having a tunable structure that can be tailored to a particular electronic functionality [10,11]. In this Letter, we report the first approach of synthesis and characterization of C$_{60}$ covalently modified SWNTs via a simple mechanochemical reaction.

2. Experimental

SWNTs used in our experiments were purified HiPco SWNTs from Carbon Nanotechnologies, Inc., USA. C$_{60}$ was purchased from SES Research,

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USA. Typically, 5 mg of SWNTs, 25 mg of [60]fullerene, and 100 mg of potassium hydroxide were weighted into a stainless steel capsule containing a stainless steel milling ball and then vigorously shaken for 50 minutes under nitrogen atmosphere at room temperature using a commercial Wig-L-Bug (Bratt 3110-B). Thereafter, the reaction mixture was washed with a large excess of toluene followed by centrifugation until the excessive precursor of [60]fullerene was removed. The resulting black solid was further washed with excess of o-dichlorobenzene to remove any C_{60} oligomers completely, if there are any. The insoluble residue was washed with deionized water and centrifuged repeatedly until the water solution became neutral to ensure a complete removal of the excessive potassium hydroxide. As a final step, the remaining solid (denotes as SWNT-C_{60}) was dried in a vacuum oven at 50 °C overnight.

UV–vis spectra were obtained using a computer-controlled Simadzu UV-2501PC Spectrophotometer. FT-IR spectra were collected using a Bio-Rad FTS600 Spectrometer. The samples were homogeneously dispersed in KBr pellets. Raman spectroscopy was measured using Renishaw RM 2000 Micro-scopic Raman Spectrometer at an excitation wavelength of 632.8 nm (He–Ne laser). Transmission electron microscopy (TEM) was performed on a Hitachi H-800 transmission electron microscopy instrument at an accelerating voltage of 100 kV.

3. Results and discussion

Mechanochemical reaction refers to processes in which mechanical motions/energy control chemical reactions [12]. This reaction technique can generate local high-pressure spots and has been presumed to bring the reacting species into the closest contact to cause novel chemical reactions to occur [13,14]. Very recently, we [15] used high-speed vibration mill (HSVM) technique and obtained single-walled carbon nanotubols – multiple hydroxyl groups direct-modified SWNTs by simply milling SWNTs and KOH together in a Wig-L-Bug. HSVM technique and similar solid-state reaction techniques have also been used

successfully to make bulk quantity of fullerene oligomers such as C_{60} dimer C_{120} [14,16], C_{60}–C_{70} cross-dimer C_{130} [17], C_{70} dimer C_{140} [18,19], and also C_{60} trimer C_{180} [20] from the corresponding parent fullerenes (which are poorly soluble in common organic solvents) and various potassium salts such as potassium cyanide and potassium hydroxide, through a proposed electron transfer mechanism [16]. All of these fullerene oligomers are difficult to make from ordinary 'wet chemistry' technique. Since SWNTs are scarcely soluble in any of the common solvents, the solvent-free reaction [21] or/and solid-phase reaction methods should also have privilege in the modification of SWNTs.

The SWNT-C_{60} was first characterized by UV/vis absorption spectroscopy together with that of pristine SWNTs (Fig. 1). The featureless absorption of SWNT-C_{60} is an indication of the successful functionalization of SWNTs, in which the introduction of sp^3-hybridized carbon atoms disrupts the extended π-network of the bare sp^2-hybridized nanotubes [22,23]. There is also an additional peak at 326 nm, suggesting the existence of C_{60} cages in the sample [24]. While the FT-IR spectroscopy of the pristine SWNTs does not show any meaningful peaks as reported before (Fig. 2, dash line) [25], the spectrum of SWNT-C_{60} exhibits
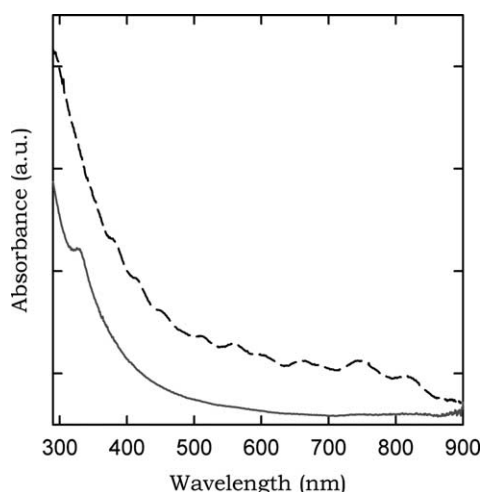

Fig. 1. UV/vis absorption spectra of pristine SWNT (dash line) and SWNT-C_{60} (solid line) in DMF.
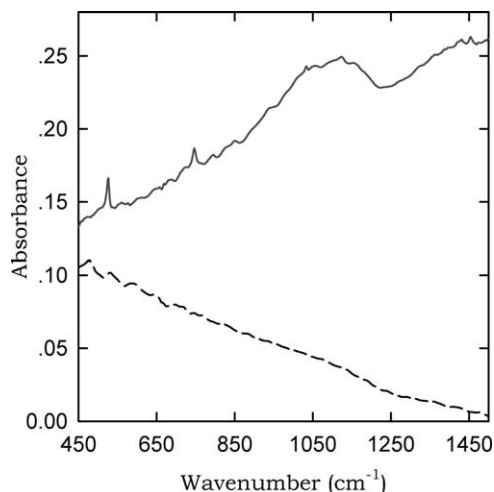
Fig. 2. FT-IR spectra of pristine SWNTs (dash line) and SWNT-C_{60} (solid line).

two clear absorptions at 526, and 746 cm^{-1}, respectively (Fig. 2, solid line). Although a broad band at ∼1050 cm^{-1} is observed, which is similar to the FT-IR spectra of polyfullerenes reported before [26,27], the FT-IR spectrum of SWNT-C_{60} is significantly different from those of C_{60} polymers [26–29] as well as SWNT polymers [30]. The absorption at 526 cm^{-1} is corresponding to the strongest intramolecular F_{1u} mode of C_{60}, which is indicative of the remaining of C_{60} cages in the sample. The peaks at 1124 and 1431 cm^{-1} may be derived from other F_{1u} modes of C_{60} at 1182 and 1428 cm^{-1}, respectively. The relative shifts of the peaks should be due to the functionalization of the C_{60} cages, most probably, by SWNTs.

Further evidence for the covalent attachment of C_{60} to SWNTs was obtained from Raman spectroscopic measurements. As can be seen from Fig. 3, the Raman spectrum of the pristine SWNTs 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 line). The Raman spectrum also shows clear characteristic peaks (192, 217, 257, 282 cm^{-1}, respectively) in the radial breathing mode (RBM) spectral region. The corresponding Raman spectrum for SWNT-C_{60} (Fig. 3, solid line), however, reveals an E_{2g} tangential mode at 1590 cm^{-1} and a relatively strong D line at 1308 cm^{-1}, which arises from the
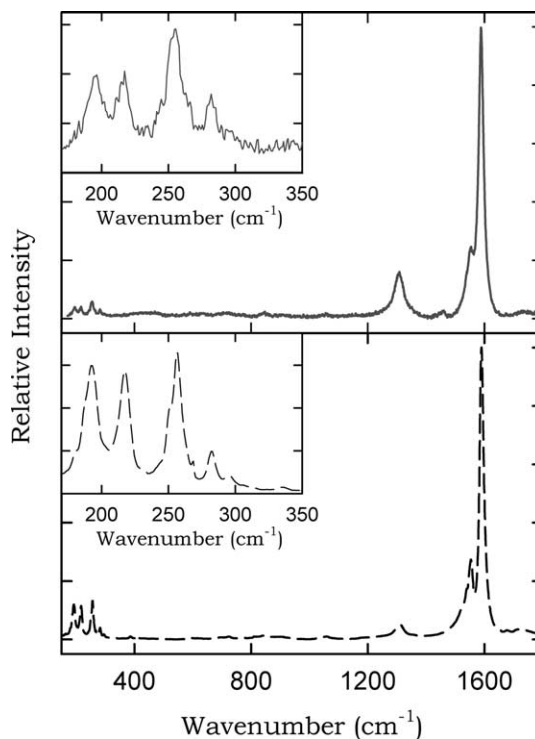

Fig. 3. Raman spectra of pristine SWNTs (dash line) and SWNT-C_{60} (solid line). The insets show the enlarged RBM regions.

disordered structures. The relative intensity ratio of the tangential mode to the disordered mode decreases significantly from 20:1 for the pristine SWNTs to 7:1 for SWNT-C_{60}. This is an expected result of the introduction of covalently bound moieties (i.e., C_{60} groups in this study) to the SWNTs framework, wherein sp^2 carbons have been inevitably converted to sp^3 hybridization [23]. The Raman spectrum of SWNT-C_{60} also shows clear characteristic peaks (196, 217, 255, 282 cm^{-1}, respectively) in the radial breathing mode (RBM) spectral region, which strongly suggests the remaining of the tubular structures in the SWNT-C_{60} sample [15]. Moreover, a small but clear peak centered at 1459 cm^{-1} can be revealed. This peak should correspond to the $A_g(2)$ peak of C_{60} cage [26], which strongly suggests the covalent binding of C_{60} to SWNTs.

More direct evidence for the attachment of C_{60} to SWNTs was obtained by transmission electron

microscopy (TEM). The pristine SWNTs show an average diameter of 10–30 nm with clean surfaces (Fig. 4, up), just as reported before [22]. However, the TEM image of SWNT-C_{60} gives a different vision. While the average diameter of the tubes remains unchanged, some clusters with $\sim$5 nm diameters can be observed clearly on the surface of the tube (Fig. 4, down). As the size of a single C_{60} molecule is below 1 nm, we suggest these clusters are C_{60} polymers attached on the surface of SWNTs. Together with the spectroscopic results, it is most likely that the mechanochemical reaction processes in the following way. At the beginning, C_{60} molecules react with SWNTs to form C_{60} bounded SWNTs at those sites on the surface of SWNTs where the reaction is easier to take place. Because C_{60} moieties are more reactive than SWNTs, the additional free C_{60} molecules will react with the already bounded C_{60} to form C_{60} polymers, thus resulting the C_{60} cluster-modified SWNTs. This can be illustrated by Scheme 1.

In summary, we have demonstrated that C_{60} direct-modified SWNTs can be produced via a simple solid-phase mechanochemical reaction. The application of this reaction to SWNTs and other members of the fullerene family (for example, C_{70}), as well as fullerene derivatives, is expected to lead to other fullerene modified SWNTs. In view of the unique properties of both SWNTs and fullerenes, these novel materials could conceivably exhibit unique electronic and optical properties which
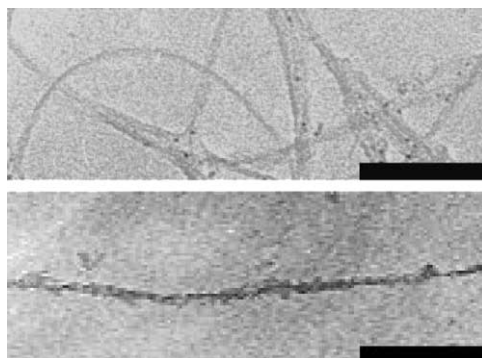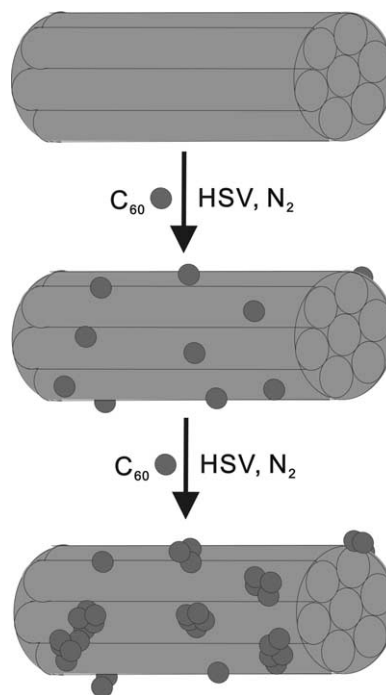

Scheme 1. Proposed reaction route to SWNT-C_{60}.

may pave the way for the extensive potential application in nanoscience and nanotechnology.

Acknowledgements

Fig. 4. Typical TEM images of pristine SWNT (up, scale bar: 200 nm) and SWNT-C_{60} (down, scale bar: 300 nm).

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