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Communication

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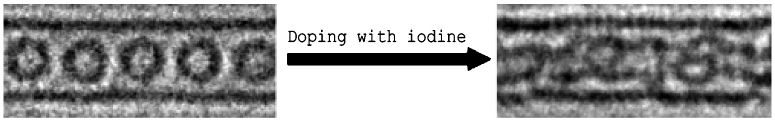

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COMMUNICATIONS

Coalescence of C_{60} Molecules Assisted by Doped Iodine Inside Carbon Nanotubes

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It is of great importance to understand the formation of one-dimensional (1D) C_{60} polymer.[1] Molecular arrays of C_{60} fullerenes can be encapsulated in single-walled carbon nanotubes (SWNTs) to form a 1D hybrid nanostructure, the so-called carbon nanopeapods (C_{60}@SWNTs).[2] This nanostructured material is an ideal subject for studying the 1D polymerization of fullerenes. Bandow et al. have reported that C_{60} molecules inside the host SWNTs coalesce to form a concentric SWNT at ~1200 °C.[3] Britz et al. have found that SWNTs can template polymerization of $C_{60}O$ to form $(C_{60}O)_n$.[4] Nanopeapods can be chemically doped in both intratubular and intertubular sites.[5−7] Recent theoretical calculations revealed that doped (or added) atoms can dramatically decrease the energy barrier of C_{60} polymerization.[8] However, there is a lack of experimental data to explore the adatom-assisted structure transformation of C_{60} molecules. Here we present a study on the coalescence of C_{60} molecules assisted by intratubular doped iodine atom(s) inside SWNTs. The high-resolution transmission electron microscope (HRTEM) and Raman spectroscopy results reveal that the doped iodine atoms (even one atom) can assist the structure transformation of C_{60} fullerenes inside SWNTs.

In this study, SWNTs were filled with C_{60} fullerenes by a gas-phase method.[9] The C_{60} peapods were immersed in molten iodine in an evacuated glass tube at 150 °C over 24 h for doping. The sample was characterized by field emission TEMs and Raman spectroscopy.

Figure 1 shows typical HRTEM images of the C_{60}@SWNTs before and after doping. The HRTEM image of an intact C_{60}@SWNT in Figure 1a shows that C_{60} molecules are regularly arranged with an intermolecular distance of ~1.0 nm inside the host SWNT of 1.3−1.4 nm in diameter. After doping with iodine, some dark spots (indicated by arrows), which could not be detected in the intact peapods, appear at the interfullerene sites inside the SWNTs of 1.3−1.4 nm in diameters (Figure 1b). The schematic structures (Figure 1c) are quite similar to the potassium-doped C_{60}@SWNTs in our previous studies.[5] Recent results have verified that iodine species (I_3^- and I_5^-) could be doped inside the SWNTs and adopt a bent arrangement.[10,11] As shown in Figure 1d and the corresponding schematic model (Figure 1e), when a host SWNT of larger diameter (~1.6 nm) can provide enough space to accommodate the iodine species, some chainlike structures, which are ascribed to the doped iodine species, appear inside the nanopeapod.

Iodine is frequently absent in the interfullerene sites inside the SWNT, indicating that the doping nanopeapods with iodine is inhomogeneous. The iodine-doped peapods are more sensitive to electron beam irradiation compared with the intact peapods. Under electron beam irradiation for tens of seconds, the rearrangement of C_{60} molecules began to occur. The cages of C_{60} molecules near the entrapped iodine atom first began to fuse or coalesce and eventually formed the fullerene polymer. In the intact C_{60}@SWNTs, the C_{60} peas inside the SWNTs pods also coalesced and polymerized,[12] but the structure transformations required a longer irradiation time (typically several hundred seconds) under the same electron dose (see Supporting Information for more details). By comparing a doped peapod with an intact peapod under the same HRTEM observation conditions, we conclude that the intratubular doped iodine atoms assist the coalescence of C_{60} molecules inside SWNTs.

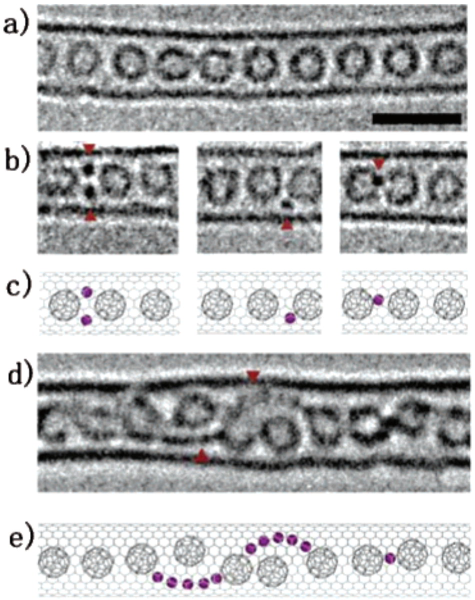

Figure 1. (a) An HRTEM image of the intact C_{60} peapods; (b) HRTEM images of the iodine-doped C_{60} peapods with low doping ratio, the black spots (indicated by arrows) are ascribed to the doped iodine atoms; (c) the best fit schematic model (purple, iodine; gray, carbon); (d) an HRTEM image of the iodine-doped C_{60} peapods with higher doping ratio, the bent chains (indicated by arrows) are ascribed to the doped iodine species; (e) the schematic model. Scale bar = 2 nm.

To verify the assistant effect of the doped iodine, we performed a vacuum heat treatment on both the intact C_{60} peapods (as reference) and their iodine-doped counterparts at 550 °C for 24 h. The temperature we chose was below the reported minimum coalescence temperature (800 °C) of the intact C_{60}@SWNTs. As expected, the intact C_{60}@SWNTs remained unchanged after heating at 550 °C for 24 h. However, for the iodine-doped C_{60}@SWNTs, after the heat treatment, a prominent structure transformation was revealed by the Raman spectra and HRTEM observation.

Figure 2 shows the Raman spectra taken from the iodine-doped C_{60}@SWNTs before and after heat treatment. Noticeable changes

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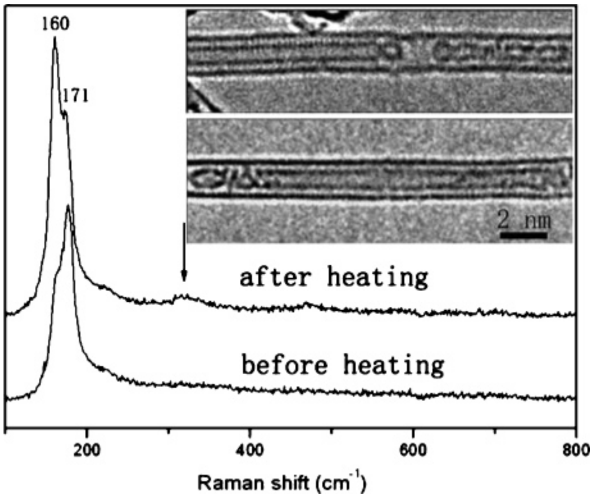

Figure 2. Raman spectra of the iodine-doped C_{60}@SWNTs before and after heat treatment. The arrow indicates the newly appearing RMB mode as the result of heat treatment. Inserted are typical HRTEM images of the iodine-doped C_{60}@SWNTs after heating.

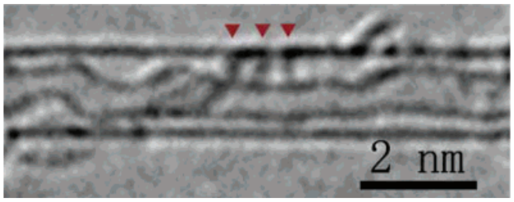

Figure 3. An HRTEM image of the iodine-doped peapod after heat treatment. The arrows indicate the intercalated iodine atoms between the inner and outer tubes.

in the Raman spectra as the result of heat treatment appear in the radial-breathing mode (RBM) frequency region. The diameters of SWNT are known to scale with RBM frequency ω by the relation ω (cm^{-1}): d (nm) $= 224/(\omega - 14)$.[13] Before heating, a single prominent peak can be observed, and this peak is actually represented by a superposition of at least two components (peaks centered at 160 cm^{-1} and 171 cm^{-1}), which are attributed to the RBM mode of the host SWNTs. After heat treatment, the relative intensities of the two components change, but the peak positions do not shift. A new broad peak (indicated by an arrow) appears around 320 cm^{-1}, which is ascribed to the newly formed SWNTs of 0.7−0.8 nm diameter resulting from the heat treatment (see Supporting Information for more details). The inserted HRTEM images in Figure 2 also reveal that the C_{60} molecules have transformed into a tubular structure after heat treatment. We could not find this kind of structure transformation in intact C_{60}@SWNTs after heat treatment. The results provide direct evidence that the doped iodine can assist the coalescence of C_{60} molecules inside SWNTs.

Another interesting thing we should mention here is that after heat treatment, some iodine atoms appear between the outer host SWNTs and the newly formed inner SWNTs. Figure 3 shows an HRTEM image of an iodine-doped peapod after heat treatment. The arrows indicate iodine atoms intercalated into a double-walled nanotube (DWNT) derived from the iodine-doped fullerene peapod. The average spacing between the outertube and the innertube was measured as ∼0.5 nm, considerably larger than the interlayer distance (∼0.35 nm) of graphite sheets and multiwalled carbon nanotubes. Iodine is known not to be intercalated into bulk graphite sheets.[14] However, recent Raman results proposed that it can be intercalated into nanographite.[15] Our HRTEM image presented direct evidence to reveal it. The iodine-doped peapods actually acted as the starting material for iodine-intercalated DWNTs.

In summary, we have demonstrated that iodine atoms/ions can be doped at the intratubular position in the C_{60} peapods. Heating the iodine-doped peapod at 550 °C induces the transformation of C_{60} into a tubular structure, and the doped iodine atoms can be intercalated between the outer host SWNT and the newly formed inner SWNT. The observed reaction inside the SWNT and the plausible charger transfer between the fullerene molecules and the doped atom(s) provide challenging subjects for further experimental and theoretical studies.

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Supporting Information Available: Synthesizing iodine-doped C_{60} peapods; HRTEM images of the doped peapod and the intact peapod. This material is available free of charge via the Internet at http://pubs.acs.org.

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