

Synthesis and TEM structural characterization of C₆₀-flattened carbon nanotube nanopeapods

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ABSTRACT

A fully flattened carbon nanotube (FNT), a graphene nanoribbon (GNR) analogue, provides a hollow space at edges for endohedral doping. Due to the unique shape of the hollow space of FNTs, novel types of low-dimensional arrangements of atoms and molecules can be obtained through endohedral doping into FNTs, which provides a new type of nanopeapods. FNT-based nanopeapods have been synthesized through endohedral doping of C₆₀, and their structural characterization with transmission electron microscopy (TEM) performed. The doping of C₆₀ into the inner hollow space of FNTs has been carried out via the gas-phase filling method, where open-ended FNTs are sealed in a glass ampoule and heated at 723–773 K for two days. TEM observations show that most of the encapsulated C₆₀ molecules align as single molecular chains along the edges of FNTs and that some of the C₆₀ forms two-dimensional close-packed structures inside FNTs.

1 Introduction

Discoveries of a new type of carbon nanostructures, including nanopeapods [1], carbon nanotubes [2] and fullerenes [3], have driven nanoscience forward. For example, the discovery of nanopeapods [1] has stimulated a wide range of researchers. A large number of structural investigations of peapods have revealed that various one-dimensional atomic or molecular arrangements, including C₆₀ [4], C₇₀ [5], metal sulfides [6], endohedral metallofullerenes [7] and rare earth metal atoms [8, 9] can be realized in

the inner space of CNTs, providing a new type of CNT-based hybrid nanostructures [10]. Through the huge amount of work on nanopeapods reported, important findings, such as bandgap modulation by encapsulated molecules [11], control of field-effect transistor characteristics [12] and formation of atomic nanowires in CNTs [8, 9], have appeared. This clearly illustrates the significance of finding and creating of a new form of carbon nanostructures.

Recently, we reported a synthesis of fully flattened CNTs (FNTs), which possess an inner space with a unique shape, using solution-based extraction of

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large-diameter CNTs from multi-wall CNTs (MWCNTs) [13]. At the time of the inner CNTs extraction from MWCNTs, large-diameter (most outer) CNTs are spontaneously flattened to form FNTs due to attractive van der Waals interaction between the upper and lower walls of CNTs. FNTs thus provide a unique low-dimensional nanospace with a dumbbell-like cross section that is significantly different from that of CNTs. This new type of nanospace provides the ability to align atoms or molecules in not only a one-dimensional way but also two-dimensional fashion, creating a brand new class of FNT-based hybrid nanostructures such as FNT peapods. We report here the synthesis of FNT-based C_{60} nanopeapods, C_{60} @FNT, and transmission electron microscopy (TEM)-based structure characterization of low-dimensional arrays of C_{60} .

2 Experimental

C_{60} @FNTs samples were synthesized by gas-phase encapsulation of C_{60} into FNTs. Details of the preparation of FNTs have been reported previously [13]. Briefly, open-ended MWCNTs were sonicated in 1,2-dichloroethane or water-containing surfactant for typically 1 hour; this procedure produces high-quality FNTs in relatively high yield. The so-prepared FNTs were dispersed in 1,2-dichloroethane and then dropped onto a TEM grid (a Si membrane grid). The TEM grid was then heated at 473 K under vacuum for 1 hour to remove residual solvent. Before the encapsulation of C_{60} , the FNTs on the TEM grid were exposed to a mild-condition hydrogen plasma to remove amorphous carbon attached to the outer surface of FNTs. The clean open-ended FNTs and C_{60} powders were vacuum sealed in a clean Pyrex ampoule under 10^{-7} Torr, and the ampoule was placed in an electric furnace at 723–773 K for two days. Before TEM observation, amorphous impurities and C_{60} molecules attached to the outer surface of FNTs were removed with vacuum heating and hydrogen plasma treatment in mild conditions. This cleaning process ensures TEM observations of encapsulated C_{60} .

TEM observations were carried out using a high-resolution field-emission gun TEM (JEM-2100, JEOL) operated at 80 kV at room temperature and under a

pressure of 10^{-6} Pa. TEM images were recorded with a charge coupled device with an exposure time of typically 1 s. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations and electron energy loss spectroscopy (EELS) experiments were performed by using a JEOL-ARM200F, fitted with EELS detector (Gatan Image Filter) and CEOS image and probe aberration correctors, operating at 80 kV.

3 Results and discussion

Figures 1(a) and 1(b), respectively, show a high magnification TEM image and close-up TEM image of a six-layer FNT (a fully flattened triple-wall CNT) on the TEM grid before C_{60} doping. The close-up TEM image shows three linear contrasts at one edge, which is similar to the folded edge of three-layer graphene; the edge is visible by the (002) graphene lattice fringe in the case of folded graphene [14]. In the corresponding HAADF-STEM image (Fig. 1(c)), the circles show the positions of EELS measurements of the edge (position 1, blue circle) and flat area (position 2, red circle).

Typical EELS spectra recorded from the edge and flat area of the FNT are shown in Fig. 1(d), where the carbon K (1s) absorption edge (~ 285 eV) is clearly observed. The carbon K edge in the two spectra exhibits a sharp π^* peak and a large hump in the σ^* region (~ 299 eV). These transition can be assigned to electronic transitions from the 1s core orbital of carbon to valence π^* and σ^* bands. The observed spectral shape of the π^* and σ^* peaks in FNTs is characteristic of sp^2 hybridization of carbon atoms. It is worth noting that the intensity of the π^* peak is much weaker and the σ^* fine structure is more rounded in the flat area (red) of the FNT compared to that in the edge (blue). This is consistent with a previous reports in which p-orbital direction was shown to cause an intensity change of the π^* peak and a difference in curvature causes the changes in the σ^* fine structure [15]. This provides clear evidence of the dumbbell-like cross section of FNTs, with a one-dimensional hollow space present at the edges.

Figures 2(a) and 2(b) show a high magnification TEM image and a close-up TEM image of FNTs after

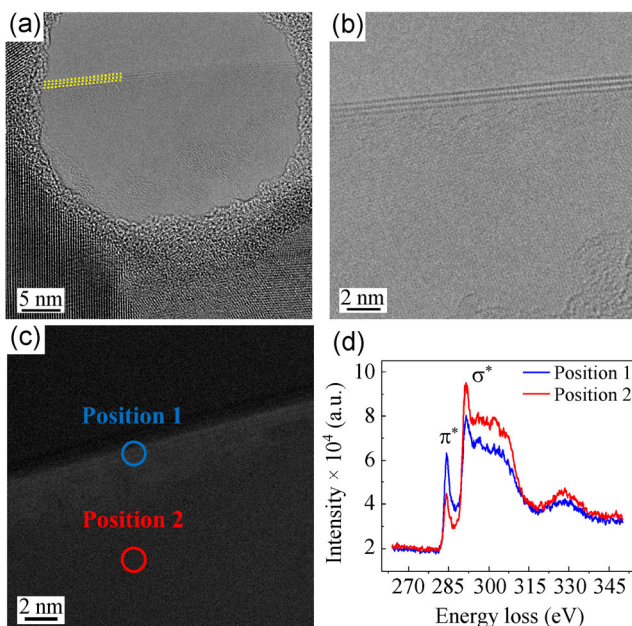


Figure 1 (a) High magnification TEM image and (b) close-up TEM image of a six-layer FNT (a fully flattened triple-wall CNT) on the TEM grid before C_{60} doping. (c) The corresponding HAADF-STEM image of the same FNT. The circles show the positions of EELS measurements: blue circle, position 1, the edge; red circle, position 2, the middle flat area. (d) A typical EELS spectra recorded from position 1 and 2, involving carbon K-absorption edges (~ 285 eV).

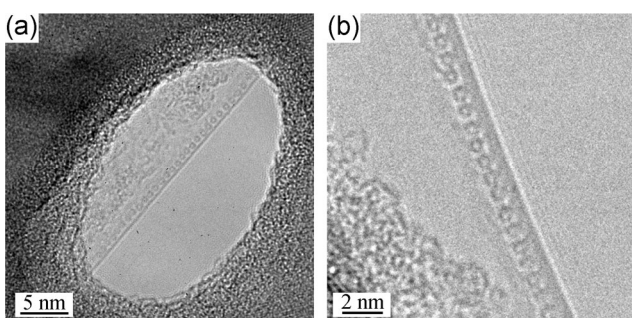


Figure 2 (a) High magnification TEM image of a two-layer FNT (a fully flattened single-wall CNT) on the TEM grid after the C_{60} encapsulation. (b) Close-up TEM image of a four-layer FNT (a fully flattened double-wall CNT) on the TEM grid after C_{60} encapsulation. One-dimensional alignment of circular contrasts exists along the edge of the FNT, which probably corresponds to a linear alignment of the encapsulated C_{60} molecules.

the C_{60} encapsulation, respectively. Linear contrasts are observed at the edges, which correspond to one of the closed edges of the FNT. Due to the closed edge rounded structure, the density of carbon atoms along the e-beam direction at the closed edge is

higher than that of middle flat part, which leads to the observed strong linear contrasts at the edge of the FNT. As clearly seen in the figure, a one-dimensional alignment of circular contrasts exists along the edge of the FNT, which corresponds to a linear alignment of the encapsulated C_{60} molecules. The average inter-circle distance is 1.0 nm, which is almost the same as the C_{60} - C_{60} intermolecular distance observed in C_{60} -peapods [4, 5]. Furthermore, the contrasts of the circles are similar to that of the rounded edge of the FNT, confirming that the constituent atoms are carbon rather than a heavier element.

To confirm the validity of the proposed structure of C_{60} @FNT, we have performed TEM image simulations based on the multi-slice method. In the multi-slice method, samples are divided into several slices along the e-beam direction, and the electrostatic potential within each slice is projected onto a two-dimensional plane [16]. Electron waves propagate through these planes, and the propagation is treated by the small angle approximation. In this calculation, we divided the unit cell into 10 slices and the defocus value, spherical aberration coefficient, beam convergence and defocus spread were set to 73 nm, 0.9 mm, 1.0 mrad and 5 nm, respectively. We limited the structure model around one of the edges of FNT for computational reasons. Figures 3(a) and 3(c), respectively, show the structure model and the corresponding simulated image of C_{60} @FNTs. As can be clearly seen, the simulated image well reproduces the main features of the observed image of C_{60} @FNT, i.e., a high linear contrast at the edge part and one-dimensionally aligned circular contrasts adjacent to the edge. The simulated image also reproduces the relative intensity of the linear and circular contrasts. We have, therefore, concluded that the proposed structure model is appropriate and that C_{60} molecules align in a one-dimensional fashion along the rounded edge of FNT, forming C_{60} -FNT-nanopeapods.

Furthermore, we found that FNTs can provide a nanospace where molecules can align not only in a one-dimensional but also in a two-dimensional manner. The flattened structure of FNTs is formed through the spontaneous deformation (flattening) of large diameter CNTs due to the attractive van der Waals

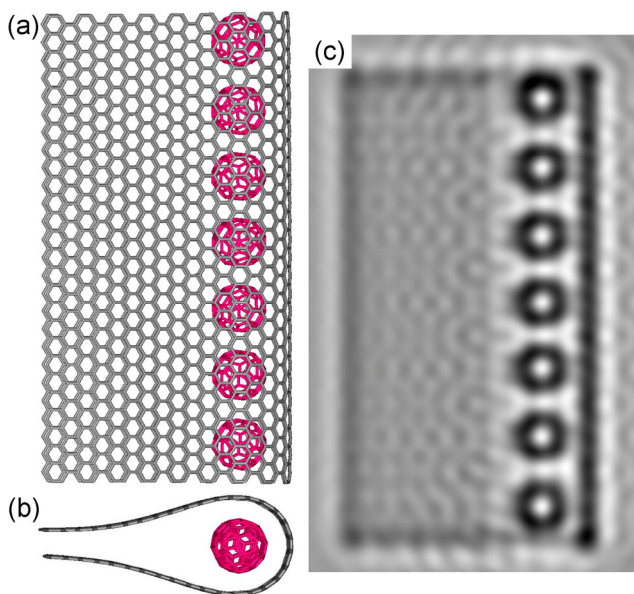


Figure 3 Structure model of one edge of a FNT with linear C_{60} molecules intercalated in the edge: (a) top view; (b) cross section; (c) the corresponding simulated TEM image.

force exerted between tube walls of CNTs [13, 17]. Because the van der Waals interaction is not robust and the interaction between C_{60} molecules and the walls of FNTs is comparable in magnitude to wall-to-wall van der Waals interaction in FNTs, C_{60} molecules can be intercalated into both edge and flat area of FNTs. This provides opportunity to align C_{60} molecules in a two-dimensional manner that is distinctly different from the one-dimensional alignment of C_{60} in nanopeapods.

Figure 4(a) shows a TEM image of a FNT with full C_{60} intercalation, where C_{60} molecules are packed in a two-dimensional manner. The width of the observed structure is about 10 nm, and we can exclude the possibility that the observed structure is not a FNT but actually a large diameter CNT; the threshold diameter of flattening deformation is about 4 nm which is smaller than the observed width [18]. The parallel linear contrasts correspond to the edges of a four-layer FNT (a fully flattened double-wall CNT), and between the linear contrasts, there are ten columns of circular contrast approximately 0.7 nm in diameter, and the edge columns of C_{60} lie about 0.3 nm away from the FNT walls (Fig. 4(a)). The average inter-circular distance is 1.02 nm (with a standard deviation of 0.011), which is consistent with the

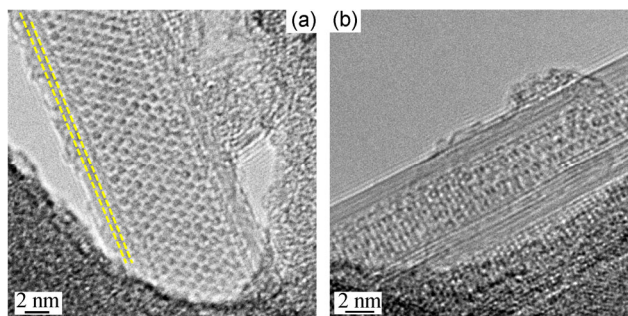


Figure 4 (a) High magnification TEM image of a four-layer FNT (a fully flattened double-wall CNT) with complete C_{60} intercalation, where C_{60} molecules are packed in a two-dimensional manner. (b) High magnification TEM image of a MWCNT with three-dimensional packing of C_{60} molecules intercalation.

molecular size of C_{60} [5]. For comparison, a TEM image of C_{60} @MWCNT, where C_{60} molecules are packed in a three-dimensional manner in a MWCNT (a four-wall CNT), is shown in Fig. 4(b). The diameter of the inner CNT of the MWCNT is larger than 4 nm and three-dimensional packing of C_{60} is therefore feasible.

As seen in the figure, circular contrasts significantly overlap with each other, which results in complicated image contrasts in the MWCNT. Due to the three-dimensional packing structure of C_{60} , the number of encapsulated C_{60} molecules along the e-beam direction is not one, but a maximum of 4–5 [5], leading to the complicated superimposed image contrast as shown in Fig. 4(b). The observed clear array of circular contrasts (Fig. 4(a)) is, therefore, considered to arise from two-dimensional packing of C_{60} molecules in C_{60} @FNT.

Based on the TEM image shown in Fig. 4(a), we have constructed a possible structure model of the C_{60} @FNT (Fig. 5(a)); for simplicity, we have employed a smaller width of the FNT in the structure model. In the structure model, C_{60} molecules are closely packed in a two-dimensional manner that is identical to the structure of the (111) plane of the face-centered-cubic (fcc) structure; the fcc structure is known to be the stable crystal structure in bulk C_{60} at room temperature. Figure 5(c) shows simulated TEM image based on the structure model. As can be clearly seen, the simulated image well reproduces the observed image, which supports the validity of our proposed structure model.

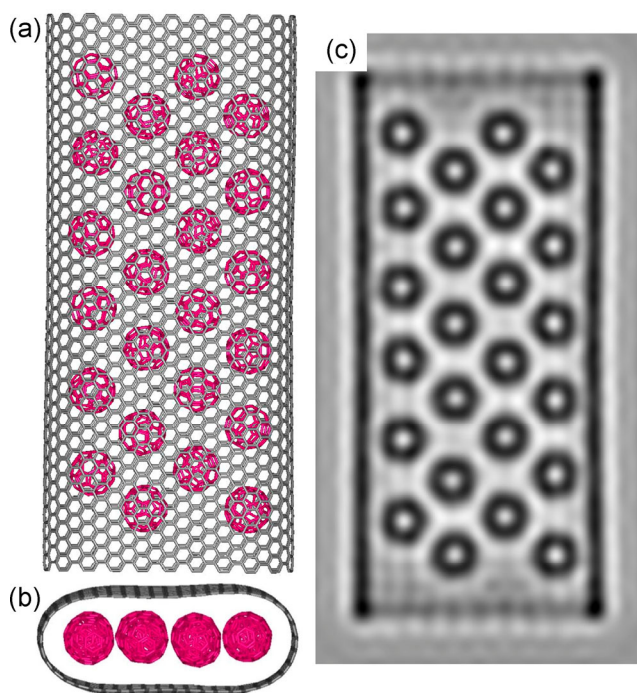


Figure 5 Structure model of a FNT with two-dimensional packing of intercalated C_{60} molecules: (a) top view; (b) cross section; (c) corresponding simulated TEM image.

4 Conclusions

We have reported a new hybrid material composed of FNTs (flattened CNTs) and C_{60} fullerenes with unique structures. TEM observations and EELS measurements of the FNT showed clear evidence of the presence of a rounded hollow space at the edges. The encapsulation of C_{60} molecules into the edge space provides a brand new hybrid material (C_{60} @FNT) with one-dimensional C_{60} alignment at the edge. We also synthesized C_{60} @FNT that possesses two-dimensional packing of C_{60} on the flattened area of FNTs. These structures were characterized by TEM observations and image simulation based on the multi-slice method. The two-dimensional packing of C_{60} molecules has been achieved for the first time in this study. The brand new class of nanocarbon materials have structures which are quite intriguing and well-characterized by TEM observations. In addition, our work indicates that various atoms and molecules can be encapsulated in FNTs, opening up the possibility of producing a new class of novel hybrid materials based on FNTs.

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