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### Synthesis and TEM Structural Characterization of C$_{60}$-Flattened CNT Nanopeapods

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The unique shape of the hollow space of FNTs provides the ability of endohedral doping of C$_{60}$ molecules into FNTs, in which most of the encapsulated C$_{60}$ molecules align as single molecular chains along the edges of FNTs and some of the C$_{60}$ forms two-dimensional-closed-packing structures inside FNTs.
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ABSTRACT

The fully flattened carbon nanotube (FNT), a graphene nanoribbon (GNR) analogue, provides a hollow space at edges for endohedral doping. Due to its 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 are synthesized through endohedral doping of C\textsubscript{60}, and their structural characterization with transmission electron microscopy (TEM) is performed. The doping of C\textsubscript{60} into the inner hollow space of FNTs is 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 C\textsubscript{60} molecules align as single molecular chains along the edges of FNTs and that some of the C\textsubscript{60} forms two-dimensional closed-packing 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 nanopeapod [1] has stimulated a wide range of researchers. A large number of structural investigations on peapods have revealed that various one-dimensional atomic or molecular arrangements, including C\textsubscript{60} [4], C\textsubscript{70} [5], sulfide [6], endohedral metallofullerenes [7] and rare earth metal atoms [8, 9] have been realized in the inner space of CNTs, providing a new type of CNTs-based hybrid nanostructures [10]. Through the huge amount of works on nanopeapods reported, important findings, such as bandgap modulation by encapsulated molecules [11], control of field effect transistor characteristics [12] and formation of atomic nanowire in CNTs [8, 9], have been appeared. This fact 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 inner space with unique shape, using solution-based extraction...
of 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 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 one-dimensional way but also two-dimensional fashion, creating a brand new class of FNTs-based hybrid nanostructures such as FNT peapods. We report here the synthesis of FNTs-based C_{60} nanopeapods, C_{60}@FNT, and TEM-based structure characterization of low-dimensional array 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 were 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 transmission electron microscopy (TEM) grid (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 was exposed to mild-condition hydrogen plasma to remove amorphous carbon attached to the outer surface of FNTs. The clean open-ended FNTs and C_{60} powder were vacuum sealed in a clean Pyrex ampoule under 10^{-5} 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.

![Figure 1](image)

**Figure 1** (a) (b) 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; (c) The corresponding HAADF-STEM image of the same FNT. The circles show the positions of EELS measurement: 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 with carbon K-absorption edges (~ 285 eV).

3 Results and discussion

Figures 1(a) and (b) show high magnification TEM image and close-up TEM image of a six-layer FNT (a fully flattened triple-wall CNT), respectively, on the TEM grid before C_{60} doping. The close-up TEM image shows three liner 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 measurement of the edge (position 1, blue circle) and flat area
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 σ* region (~299 eV). These transition can be assigned to electronic transition from 1s core orbital of carbon to valence π* and σ* bands. The observed spectral shape of π* and σ* peaks is characteristic to sp² hybridization of carbon atoms in FNT. It is worth noting that the intensity of 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 the previous result in which p-orbital direction causes intensity change of π* peak and difference in curvature causes the changes of σ* fine structure [15]. This provides clear evidence of the dumbbell-like cross section of FNTs with one-dimensional hollow space present at the edges.

Figure 2 (a) High magnification TEM image of a two-layer FNT (a fully flattened single-wall CNT) on the TEM grid after the C₆₀ encapsulation; (b) Close-up TEM image of a four-layer FNT (a fully flattened double-wall CNT) on the TEM grid after C₆₀ encapsulation. One-dimensional alignment of circular contrasts exists along the edge of the FNT, which probably corresponds to a liner alignment of the encapsulated C₆₀ molecules.

Figures 2 (a) and (b) show a high magnification TEM image and a close-up TEM image of FNTs after the C₆₀ encapsulation, respectively. The 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 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, one-dimensional alignment of circular contrasts exists along the edge of the FNT, which corresponds to a liner alignment of the encapsulated C₆₀ molecules. The average inter-circle distance is 1.0 nm, which is almost the same as the C₆₀-C₆₀ intermolecular distance observed in C₆₀-peapods [4, 5]. Furthermore, the contrasts of the circles are similar to that of the rounded edge of the FNT, and thus the constituent atoms are carbon rather than a heavier element.

To confirm the validity of the proposed structure of C₆₀@FNT, we have performed TEM image simulations based on the multi-slice method. In multi-slice method, samples are divided into several slices along e-beam direction, and electrostatic potential within each slice is projected onto two-dimensional plane [16]. Electron wave propagates through these planes, and the propagation is treated by small angle approximation. In this calculation, we divided the unit cell into 10 slices and 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 have limited the structure model around one of the edges of FNT for computational reasons. Figures 3(a) and (b), respectively, show the
structure model and the corresponding simulated image of C_{60}@FNTs. As 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 the one-dimensional fashion along the rounded edge of FNT, forming C_{60}-FNT-nanopeapod.

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 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 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 two-dimensional manner that is distinctly different from 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 a large diameter CNT; the threshold diameter of flattening deformation is about 4 nm that is smaller than the observed width [18]. The parallel linear contrasts correspond to the edges of a four layers FNT (a fully flattened double-wall CNT), and between the linear contrasts, there are ten columns of circular contrast with 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 (standard deviation is 0.011), which is consistent to the molecular size of C_{60} [5]. For comparison, a TEM image of C_{60}@MWCNT, where C_{60} molecules are packed in three-dimensional manner in a MWCNT (four-wall CNT), is shown in Figure 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 a complicated image contrasts in the MWCNT. Due to the three-dimensional packing structure of C_{60}, the
number of encapsulated C$_{60}$ molecules along e-beam direction is not one but 4–5 at largest [5], leading to the complicated superimposed image contrast as shown in Fig. 4(b). The observed clear array of circular contrasts (Fig. 4a) 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 (111) plane of 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(b) shows simulated TEM image based on the structure model. As clearly seen, the simulated image well reproduces the observed image, which supports the validity of our proposed structure model.

4 Conclusions

In conclusion, we 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 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 with TEM observations and image simulation based on the multi-slice method. The two-dimensional packing of C$_{60}$ molecules has been achieved in this study for the first time. They are a brand new class of nanocarbon materials whose structure is quite intriguing and well-characterized by TEM observations. In addition, the present finding 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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