Inserting Fullerene Dimers into Carbon Nanotubes: Pushing the Boundaries of Molecular Self-assembly

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Abstract. Carbon nanotubes can encapsulate several molecular species forming one-dimensional crystals. Using previously reported methods we produced directly-bonded, asymmetric C_{60}-C_{70} dimers and oxygen-bridged dimers of the type C_{60}-O-C_{60}. We present here microscopic evidence of filling single-walled carbon nanotubes (SWNTs) with the above fullerene dimers. The most important filling constraint is found to be the nanotube size. SWNTs with diameters around 1.6 nm incorporate dimers considerably more easily than SWNTs with smaller diameters. This kind of molecular self-assembly opens up the potential for using nanotubes and fullerenes for nanodevices.

INTRODUCTION

Carbon nanotubes have been extensively studied due to their promising electronic, transport and mechanical properties [1]. Due to their tubular nature, carbon nanotubes have been found to encapsulate several molecular species, thus forming quasi one-dimensional crystals [2]. The discovery of “peapods” (carbon nanotubes filled with fullerene cages) [3] has attracted more research and expanded the potential applications of these molecular structures in the field of nanotechnology.

The vast majority of peapods studied so far involve the filling of single-walled carbon nanotubes (SWNTs) with fullerenes of different cage size (such as C_{60} and C_{70}) or with endohedral metallofullerenes of the type $M_x@C_{82}$ (where x = 1-4). In this paper we present the first evidence of filling SWNTs with directly-bonded and oxygen-bridged fullerene dimers.

EXPERIMENTAL

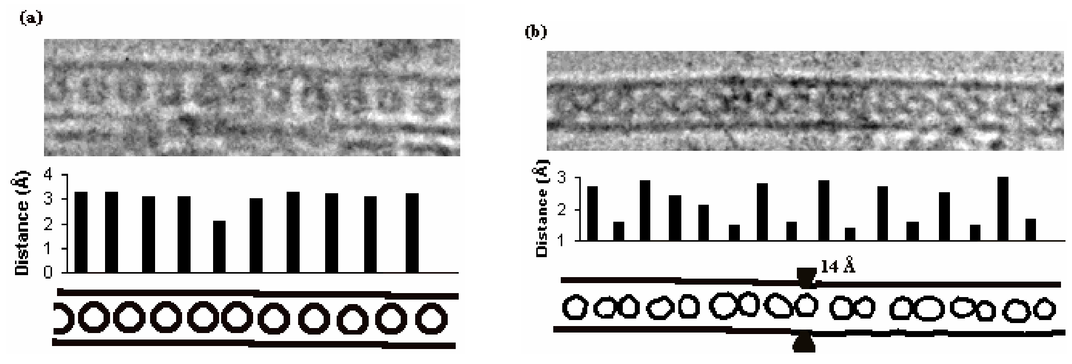
Several types of fullerene dimers have been reported in the literature [4]. Using the solid-state mechanochemical reaction of C_{60} and C_{70} with K_2CO_3 as catalyst, according to the high-speed vibration milling (HSVM) technique pioneered by Komatsu and co-workers [5], we produced asymmetric C_{60}-C_{70} dimers. We also produced oxygen bridged dimers of the type C_{60}-O-C_{60} by thermally reacting C_{60} and $C_{60}O$ [6].

The reaction products were purified by high performance liquid chromatography (HPLC) using a Cosmosil 5PYE column, 20 mm × 250 mm, with pure toluene eluent and flow-rate of 15 ml min^{-1}. A combination of HPLC, mass spectrometry and UV-Vis spectroscopy have confirmed the formation of the different isomers of fullerene dimers. Our characterisation results are in good agreement with the literature [7].

The fullerene dimers were inserted in SWNTs by mixing them with purified, open-end SWNTs (Aldrich, diameters = 13-16 Å) in a quartz ampoule and heating the mixture at 350ºC under $5 \cdot 10^{-6}$ Torr for several hours. Non-encapsulated dimers were removed by extensive washing with CS_2 and the remaining material was examined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-4000EX, LaB_6, information limit <0.12 nm). The imaging conditions were set to minimize knock-on damage commonly occurring in peapod structures under exposure to the electron beam [8]. The accelerating voltage was set at 100 kV, the beam current on the specimen was reduced to minimum and exposure times were 1-2 sec to minimise the damage. Imaging of C_{60}@SWNT under these conditions showed no structural changes in peapods over 10 minutes.

RESULTS AND DISCUSSION

Approximately 30% of the total sample of SWNTs were found to be filled with fullerene structures. HRTEM micrographs (Fig. 1) show SWNTs filled with C_{60}-C_{70} dimers.



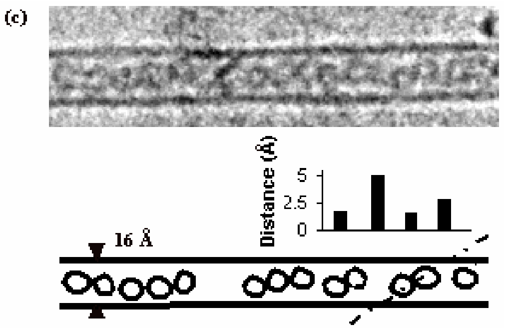


FIGURE 1. HRTEM micrographs of SWNTs filled with C_{60} and C_{60}-C_{70} dimers. The cartoons below each micrograph are used for clarity. The histograms show measured cage-to-cage distances between fullerene molecules. When the dimers have dissociated during filling, the nanotubes are filled with monomeric C_{60} or C_{70} molecules (a). In relatively narrow SWNTs the dimers are aligned with the nanotube axis (b). In wider SWNTs the dimers are tilted (as indicated by the dotted line) such that the van der Waals interactions between the molecules and the nanotube sidewalls are maximised (c).

Approximately 50% of the filled SWNTs appear to contain C_{60} or C_{70} molecules as in Fig. 1(a). Since there was no monomeric C_{60} or C_{70} in the purified dimer samples before filling, one must assume that some of the dimers have undergone dissociation during heating. Using differential scanning calorimetry, Wang *et al.* estimated the dissociation temperature of C_{120} to be between 150 and 175°C [9]. However, it seems that under our filling conditions some C_{60}-C_{70} dimers have remained intact. Indeed, extensive HRTEM imaging has shown that approximately 50% of the filled SWNTs contain dimers (Fig. 1(b) and 1(c)). Figure 1 shows clear microscopic evidence for the presence of fullerene dimers in SWNTs. In ordinary fullerene peapods, such as C_{60}@SWNT or C_{70}@SWNT, the typical van der Waals inter-fullerene spacing of ~ 3 Å is observed (Fig. 1(a)). When fullerene dimers are in the SWNTs, the constituent fullerene molecules of each dimer appear to be connected to each other by covalent bonds (Fig. 1(b) and 1(c)). We measured the cage-to-cage distance within a dimer to be 1.5±0.5 Å which is well below the van der Waals separation and corresponds to the length of a single C-C bond. Furthermore we observed that in relatively narrow SWNTs (d = 13-14 Å) the long axes of the dimers are aligned with the axis of the nanotube (Fig. 1(b)). In wider SWNTs (d = 16Å) the dimers are tilted such that the van der Waals SWNT···dimer interactions are maximised [10] (Fig. 1(c)). This tilting also indicates that the two fullerene cages comprising each dimer are linked by rigid chemical bonds. Both regular peapods and dimer-filled peapods were observed in the same sample using the same imaging conditions. Therefore, we cannot attribute the aggregated fullerenes to beam damage or transient charging effects seen in earlier peapod studies. Thus, these images show the first example of fullerene dimers inserted into SWNTs.

We employed a similar approach for filling SWNTs with oxygen-bridged C_{60}-O-C_{60} dimers. An excess of C_{60}-O-C_{60}, dissolved in CS_2, was dropped on freshly annealed SWNTs and the mixture was dried. It was then sealed in a quartz tube at 10^{-5} Torr and heated at 305°C for 3 days. Figure 2 shows a typical HRTEM micrograph of a SWNT containing C_{60}-O-C_{60} dimers.

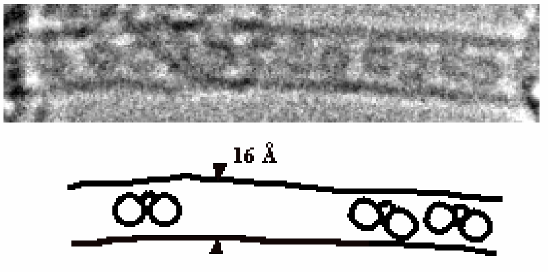


FIGURE 2. HRTEM micrograph of a SWNT containing C_{60}-O-C_{60} dimers. The dimers are tilted so that they retain the Van der Waals distance between them and the walls of the nanotube.

The oxygen-bridged dimers are more thermally robust than the directly bonded dimers and we observed that they do not dissociate as C_{60}-C_{70} does during filling. In a similar manner as the C_{60}-C_{70} dimers, the C_{60}-O-C_{60} dimers are tilted inside the nanotube so that the van der Waals distance between them and the walls of the nanotube is retained. Hence, it is shown that it is possible to fill SWNTs with molecules of relatively long aspect ratios. For dimers of both kinds, it appears that the most important constraint of the dimer peapod formation is the nanotube size. Wider SWNTs with diameters around 16 Å incorporate dimers more easily than SWNTs with diameters 13-14 Å. A likely explanation for this observation is steric hinderance due to the large size of the dimeric molecules.

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REFERENCES

1. M. Dresselhaus, G. Dresselhaus and P. Eklund, *Science of fullerenes and carbon nanotubes: their properties and applications*, Academic Press, 1996.
2. K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara and S. Iijima, *Phys. Rev. Lett.*, **85**, 5384, (2000).
3. B. W. Smith, M Monthioux and D. E. Luzzi, *Nature*, **396**, 323, (1998).
4. J. L. Segura and N. Martin, *Chem. Soc. Rev.,* **29**, 13, (2000).
5. K. Komatsu, G-W. Wang, Y. Murata, T. Tanaka and K. Fujiwara, *J. Org. Chem.*, **63**, 9358, (1998).
6. S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor and W. Kratschmer, *Tetrahedron Lett.*, **36**, 4971, (1995).
7. N. Tagmatarchis, G. S. Forman, A. Taninaka and H. Shinohara, *Synlett*, **2**, 235, (2002); N. Dragoe, H. Shimotani, J. Wang, M. Iwaya, A. Dias, A. L. Balch and K. Kitazawa, *J. Am. Chem. Soc.*, **123**, 1294, (2001).
8. B. W. Smith and D. E. Luzzi, *J. Appl. Phys.*, **90**, 3509, (2001).
9. G-W Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, **387**, 583, (1997).
10. M. Hodak, and L. A. Girifalco, *Phys. Rev. B*, **67**, 07541, (2003).