Observation of Ordered Phases of Fullerenes in Carbon Nanotubes

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(Received 21 January 2004; published 18 June 2004)

We have assembled molecular arrays of C_{60} inside double-walled carbon nanotubes (DWNTs) with internal diameters of 11–26 Å and directly observed the existence of different crystalline phases of C_{60} previously predicted theoretically. The structure of the encapsulated C_{60} crystal is defined by the internal diameter of the DWNT, as the molecules adjust their packing arrangement in order to maximize van der Waals interactions. We have also shown that fullerenes in C_{60}@DWNT interact with the outer layer of DWNTs, as demonstrated by the efficient filling of DWNTs with internal diameters of less than 12 Å.

DOI: 10.1103/PhysRevLett.92.245507 PACS numbers: 81.05.Tp, 81.07.Nb

The packing of hard macroscopic spheres in cylindrical cavities represents an interesting mathematical problem that has been only recently solved [1]. Fullerenes, C_{60} (with a van der Waals diameter of about 10 Å), can be considered as nanoscale spheres. In much the same way as macroscopic spheres, they may be inserted in nanoscale cylindrical containers, such as nanotubes, as demonstrated for the first time by Smith *et al.* [2]. The resulting structures, molecular arrays of fullerenes in single-walled carbon nanotubes (SWNTs) known as "peapods," have been studied extensively [3]. The diameters of commonly available SWNTs vary over a relatively narrow range, and consequently the positions of the fullerenes are generally constrained to form linear chain structures C_{60}@SWNTs [Fig. 1(a)]. We have previously demonstrated that orientations of ellipsoidal fullerene molecules such as C_{70} are strongly dependent on the nanotube diameter, so that even small changes in SWNT diameter can alter the geometry of fullerene arrays [4]. We report herein the first experimental study of molecular packing of C_{60} in single- and double-walled carbon nanotubes with a wide range of internal diameters. We demonstrate that the geometry of the molecular array is precisely controlled by the nanotube diameter.

Recent theoretical calculations by Hodak and Girifalco [5] predict that C_{60} molecules in carbon nanotubes of a wide range of diameters can form a variety of packing arrangements, in some ways analogous to those observed for macroscopic hard spheres [1]. They studied packing arrangements of fullerene C_{60} inside carbon nanotubes with diameters between 12.54 and 27.14 Å and predicted ten different crystalline phases of C_{60}. According to their calculations the type of the phase is strictly defined by the size of the nanotube cavity, so that each phase can exist only in nanotubes within a certain narrow range of diameters. Our experiments richly confirm these predictions, where we directly observe four of the ten predicted phases: linear one-dimensional chains, achiral zigzags, chiral double helices, and achiral two-molecule layers.

Double-walled carbon nanotubes (DWNTs) can be viewed as pairs of coaxially arranged SWNTs whose radii differ by a distance similar to the graphitic interlayer spacing [6,7]. Owing to their structural rigidity [8] DWNTs can support larger internal cavities than SWNTs [7,9]. Advances in nanotube synthesis [9] have allowed the preparation of clean DWNTs of a high quality on a large scale. However, the functional properties of DWNTs still remain largely unexplored. In our study we have used DWNTs [chemical vapor deposition (CVD), *Nanocyl*] with internal diameters 10.0–26.0 Å. This sample consists of mostly double-walled nanotubes, some triple-walled, and a very few single-walled nanotubes. Raw as-received nanotubes were heated in 5*M* HNO_3 under reflux for 2 h in order to open their ends, then washed with deionized water, dried, and annealed at 430 °C for 40 min in air shortly before mixing with fullerene. DWNTs were filled with C_{60} in the gas phase by mixing nanotubes with a threefold excess of C_{60} and heating the mixture at various temperatures in the range

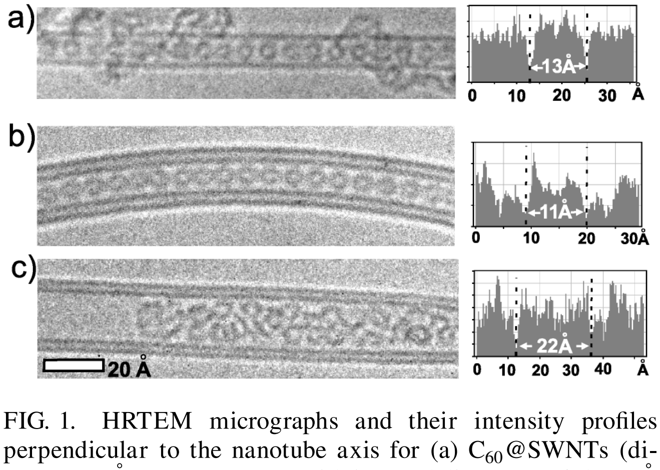

FIG. 1. HRTEM micrographs and their intensity profiles perpendicular to the nanotube axis for (a) C_{60}@SWNTs (diameter 13 Å); C_{60}@DWNTs with internal diameters of (b) 11 Å and (c) 22 Å. The wide DWNT (c) is only partially filled with an amorphous phase of C_{60}.

of 200–520 °C in 5×10^{-5} Torr vacuum over 48 h. C_{60}@DWNT structures were formed in 20%–50% yields depending on the temperature. The packing arrangements of the molecules inside DWNTs were imaged by high-resolution transmission electron microscopy at ambient temperature (HRTEM, JEOL4000EX, LaB_6 filament, operated at 100 kV).

In DWNTs with internal diameters smaller than 15 Å, fullerene molecules form straight chains [Fig. 1(b)] that have the same structure as C_{60}@SWNT peapods [10]. We find that both SWNTs [4] and DWNTs containing straight chains of C_{60} tend to be filled uniformly, without gaps. If the nanotube diameter is large enough to accommodate C_{60}, the nanotube is filled completely; if the diameter is too small, the tube remains completely empty. Sparsely filled DWNTs are rarely found. This observation is consistent with the fact that insertion of C_{60} in carbon nanotubes with diameters matching the van der Waals size of C_{60} is a highly exothermic process with an energy of about 3 eV per C_{60} [11,12]. This is substantially larger than the cohesive energy of C_{60} in a crystal [13], and consequently, the insertion of fullerenes in nanotubes is spontaneous and irreversible. The smallest diameter of SWNT capable of hosting C_{60} is above 12.5 Å [14–16], and insertion of C_{60} in SWNTs narrower than 12.5 Å is strongly endothermic because it requires a distortion of the nanotube. Thus the spontaneous formation of peapods in narrow SWNTs is prohibited, and our attempts to insert C_{60} in SWNTs with diameters 11–12 Å (CVD grown) did not yield any detectable quantities of peapods.

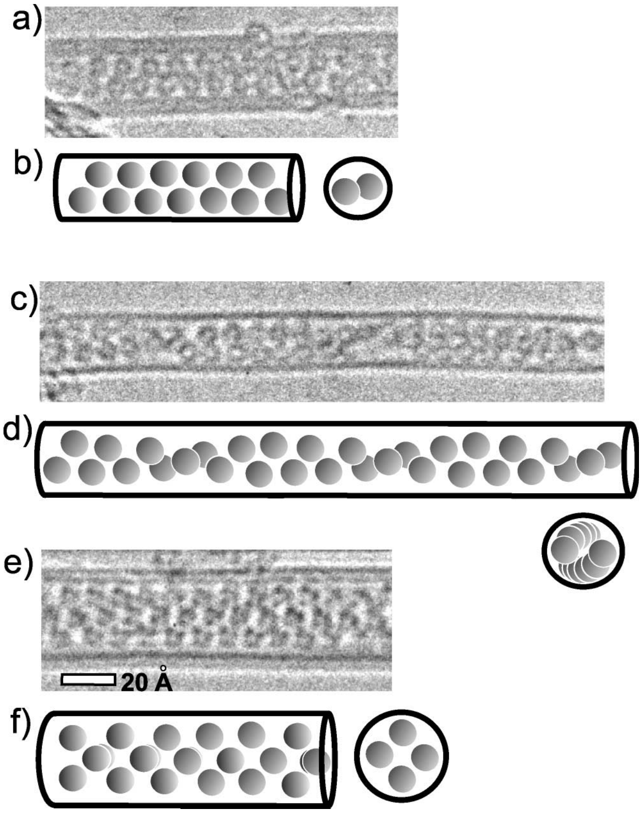

FIG. 2. HRTEM micrographs and schematic representation of (a),(b) C_{60}@DWNTs zigzag phase; (c),(d) C_{60}@SWNT chiral phase; (e),(f) two-molecule layer phases.

Surprisingly, for DWNTs the threshold diameter for filling with C_{60} is narrower than for SWNTs; all observed DWNTs with inner diameters between 10.9 ± 0.5 and 12.6 ± 0.5 Å, and with an average diameter of 11.3 Å, were found to be effectively filled with fullerenes [Fig. 1(b)]. The difference in behavior between DWNTs and SWNTs can be attributed to the presence of the second graphene layer in DWNTs, which can contribute to the attractive part of the van der Waals interaction. This substantial contribution to the C_{60}-nanotube binding energy allows the insertion of fullerene in DWNTs with inner diameter <12 Å, which would be a forbidden endothermic process for SWNTs of such diameters. The presence of a second graphene layer in a multiwalled nanotube has the greatest stabilizing effect; increasing the number of nanotube walls beyond two has little effect on the C_{60}-nanotube potential [5]. We find that fullerenes encapsulated in such narrow DWNTs appear to be axially deformed, which was predicted by calculations for narrow SWNT peapods by Rochefort [14].

Hodak and Girifalco predict a transition of the straight chain phase of C_{60} to a zigzag phase [Figs. 2(a) and 2(b)] when the nanotube diameter reaches 14.5 Å [5]. The zigzag phase is expected to be more abundant than the other nine phases of C_{60} as it can exist for the widest range of nanotube diameters (14.5 to 21.6 Å). The majority of DWNT inner diameters used in our study fall in this range. HRTEM imaging revealed a large proportion of DWNTs filled with the zigzag phase of C_{60} [Fig. 2(a)]. As predicted for this range of diameters the zigzag arrays in DWNTs are achiral (i.e., no helical pitch is observed), and the length of the repeating unit of the zigzag depends on the diameter of the nanotube.

Several chiral phases of C_{60} can form in DWNTs with an inner diameter wider than 21.6 Å [Figs. 2(c) and 2(d)] [5]. The helical shapes of the chiral phases cause a complex overlap of projections of the fullerene cages in HRTEM. This makes the micrographs difficult to interpret especially for double-walled nanotubes where the chiral arrays of fullerenes are surrounded by two layers of graphene. However, we found that the chiral phase can be clearly observed in SWNTs of a similar diameter [Fig. 2(c)].

We have also demonstrated the existence of complex achiral (nonhelical) phases forming ordered arrays over distances of 200–500 Å in wider nanotubes, such as a two-molecule layer phase formed in a 26 Å DWNT [Figs. 2(e) and 2(f)]. Such structures appear to maintain order even in imperfect DWNTs whose internal diameters vary by 2–3 Å along the visible length. Similar packing geometries have also been observed in boron nitride multiwalled nanotubes [17].

Many DWNTs with diameters greater than 15 Å appear to be only partially filled at temperatures 200–250 °C [Fig. 1(c)]. Using HRTEM at room temperature we observe that C_{60} in such partially filled nanotubes tends to be disordered [Fig. 1(c)]. This confirms the results of Monte Carlo calculations [18] predicting that the ordered phases of C_{60} in wide nanotubes with filling factors below 90% transform into an amorphous phase at temperatures above −123 °C. The same calculations suggest that the ordered phase is stabilized at higher temperatures if the nanotube is almost 100% filled with fullerenes. Increasing the nanotube filling temperature to 450–520 °C improves the filling factor of wide DWNTs, and HRTEM indicates that in this case most nanotubes are filled with ordered phases (Fig. 2) that exhibit some degree of tolerance to the presence of intermolecular gaps within the array and nanotube defects.

In conclusion, we have shown that DWNTs form effective containers for molecular arrays of C_{60}, and that the C_{60}-DWNT interaction is substantially different from the more extensively studied C_{60}-SWNT case, as demonstrated by our observation of the formation of peapods in DWNTs with an internal diameter of less than 12 Å. Our detailed HRTEM experimental study demonstrates unambiguously the existence of ordered and amorphous phases of C_{60} in carbon nanotubes for the first time; our observations are in good agreement with theoretical calculations. We have shown experimentally that C_{60}@DWNTs structures, and thus the properties of the encapsulated molecular arrays, can be tailored by choosing nanotubes of suitable diameters. We are currently exploring applications of DWNTs for assembling ordered molecular arrays of fullerene dimers and endohedral fullerenes.

The work described here is supported through the Foresight LINK Award *Nanoelectronics at the Quantum Edge*, funded by DTI, EPSRC (GR/R66029/01), and Hitachi Europe Ltd. D. A. B. thanks the Overseas Research Student Scheme. A. A. is supported by the Royal Society.

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