Two-Dimensional Coalescence Dynamics of Encapsulated Metallofullerenes in Carbon Nanotubes

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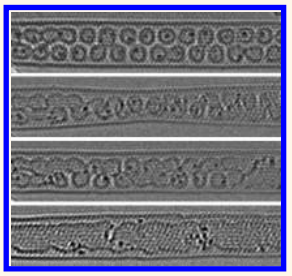
ABSTRACT We report on the coalescence of a two-dimensional (2D) chain of La@C_{82} metallofullerene molecules encapsulated inside a single-wall carbon nanotube (SWNT). 2D packing of metallofullerenes is known to adopt a zigzag arrangement and cause elliptical distortion to the cross-section of the SWNT host. We show that after coalescence of the metallofullerenes into an inner nanotube the carbon nanotube host returns to its original circular cross-section. This is due to a relaxation of the strain caused by the packing of the encapsulated La@C_{82} molecules into the nanotube. We identify the formation of some novel but transient fullerene-based structures formed during the intermediate stages of coalescence of the La@C_{82} into an inner nanotube. These results highlight the flexible nature of SWNTs and their ability to adapt their cross-sectional profile depending upon forces induced by material encapsulated within.



KEYWORDS: peapods · fullerenes · carbon nanotube · HRTEM · coalescence · aberration-corrected

The range of materials that can be encapsulated inside carbon nanotubes is broad and includes inorganic crystals,[1] biomolecules,[2,3] linear carbon chains,[4] graphene nanoribbons,[5] metals,[6] and fullerenes.[7] The nanotube host can also act as a confining container to enable chemical reactions and structural transformations of the encapsulated material to occur.[8] In some cases these changes are driven *in situ* by electron beam irradiation,[9] and in others simply the application of high temperature is sufficient to induce reactions.[10]

The precise mechanism for the structural transformation of an encapsulated fullerene molecule under electron beam irradiation is not fully understood. For the case of irradiation at electron energies in excess of the threshold energy of 86 keV knock-on damage is the primary cause.[11,12] It has been suggested that due to the high curvature of C_{60} molecules, knock-on damage can occur even at energies below this threshold.[13,14] At electron energies below 86 keV it is likely that changes are driven by a combination of contributions from a variety of interaction effects.

When fullerenes are encapsulated within single-walled nanotubes (SWNTs) with diameters of 1.4−1.6 nm, they form highly ordered 1D crystals.[15] Recently it was shown that when larger diameter carbon nanotubes are used (∼2 nm), the fullerenes no longer adopt the 1D packing, but instead form 2D zigzag structures.[15,16] In this context the term 2D is used to refer to the packing geometry of the fullerenes inside the carbon nanotube and helps to differentiate from the case where fullerenes form a three-dimensional packed structure. This 2D packing of fullerenes results in the SWNT becoming distorted due to the van der Waals forces at play. The cross-section of the SWNT becomes elliptical and can lead to wider projections in high-resolution transmission electron microscopy (HRTEM) of SWNT diameters, as well as shorter ones, depending on the relative orientation of the zigzag chain. Electron beam driven rotation of such zigzag chains also occurs and leads to both projections being visible within the same region during the time period of examination.[9] Examination of the structural transformations, such as electron beam induced coalescence, that may occur for 2D packed fullerenes has yet to be explored.

Coalescence dynamics of 1D packed fullerenes in nanotubes has been extensively examined using 80 kV electron beam irradiation.[14,17,18] It has been shown that metallofullerenes fuse together to form an inner carbon nanotube, with the metal atoms generally trapped within the inner space.[17] In some cases the metal atoms react with the host tube, leading to destruction,[18] while in other cases the metal

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atoms eventually aggregate together to form well-ordered nanocrystals that are mobile within the nanotube host.[19]

Here, we present the first examination of the coalescence dynamics of 2D packed metallofullerenes, La@C_{82}, in large-diameter SWNT hosts. We use low-voltage aberration-corrected HRTEM at an accelerating voltage of 80 kV. This energy of the electron beam is known for being ideal to induce coalescence to form well-defined inner structures from metallofullerenes while leaving the host SWNT undamaged.[17]

RESULTS AND DISCUSSION

Figure 1a shows a HRTEM image of a SWNT containing 2D packed La@C_{82} metallofullerenes. Contrast from individual heavy La atoms is seen as a dark spot within each fullerene. Figure 1b shows the 2D fast Fourier transform (FFT) of the real space image shown in Figure 1a. Measurements of the axial positions of the carbon nanotube layer lines (marked with black arrows in Figure 1b) normally allow the calculation of the ratio of the chiral indices (m, n).[20,21] Combined with an accurate measurement of the diameter of the tube, this, in principle, allows for the determination of the chiral indices of the carbon nanotube. However, the carbon nanotube is deformed to an elliptical shape due to the presence of the La@C_{82} molecules, and as such, the diameter measured from the real space image is not the true diameter of the SWNT. The red arrows in Figure 1b mark the lines associated with the periodic packing of the La@C_{82} molecules. The distance from the central line to the first of the La@C_{82} lines is equal to the reciprocal of the La@C_{82}–La@C_{82} repeat distance. The second and third La@C_{82} lines correspond to higher order reflections. Measurements of the distances of the La@C_{82} lines from the equatorial line give a La@C_{82} repeat distance of d1 = 1.10 ± 0.05 nm, which matches well with the case of 1D packing in peapods.[22] The radial spacing of the La@C_{82} molecules is measured from the HRTEM image (Figure 1a) to be d2 = 0.91 ± 0.05 nm. From these measurements we can construct a realistic atomic model of the La@C_{82}:SWNT, shown in Figure 1c. Figure 1d shows an atomic model of the 2D packing of the La@C_{82}.

Figure 2a–d show a time series of HRTEM images capturing the overall coalescence behavior of the peapod under the electron beam. The apparent diameter of the SWNT is monitored over time at several different locations, indicated by the colored lines in Figure 2a. Figure 2e plots the diameter of the SWNT measured at each of the five positions marked in part a against total time exposed to the electron beam. Between parts a and b in Figure 2 the two-dimensional array of La@C_{82} molecules has rotated about the nanotube axis, causing a deformation in the host nanotube, resulting in a large decrease in the projected

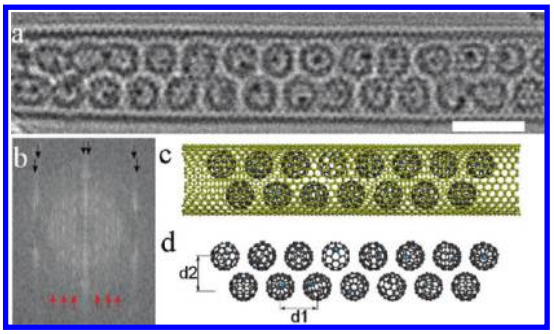

Figure 1. (a) HRTEM image of a SWNT containing 2D packed La@C_{82} metallofullerenes (the scale bar indicates 2 nm). (b) 2D FFT taken from part a showing SWNT layer lines (black arrows) and spots associated with the 2D periodicity of the La@C_{82} packing (red arrows). (c) Atomic model of the peapod, with the SWNT colored yellow for clarity. (d) Atomic model showing the arrangement of the La@C_{82} within the peapod structure. The structure of the tube and the axial spacing (d1) of the La@C_{82} were determined from part a. The orientation of the La@C_{82} is arbitrary.

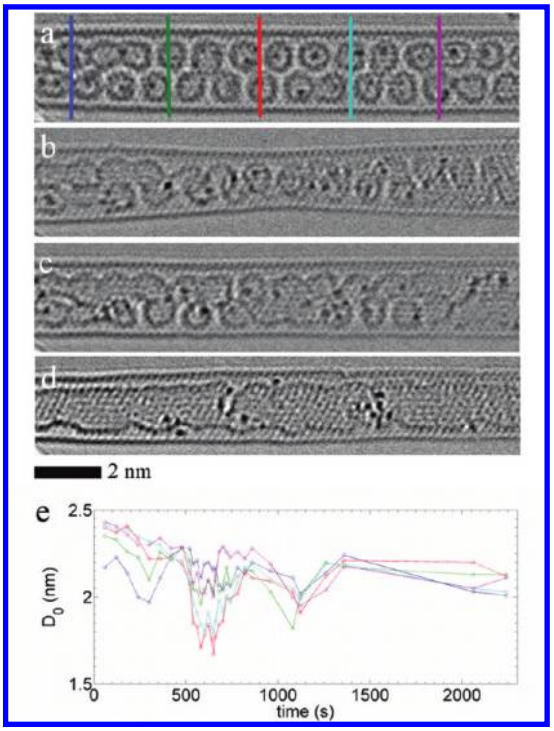

Figure 2. (a) HRTEM image of the carbon nanotube peapod in its initial state. The positions of the diameter measurements are marked by colored lines. (b–d) HRTEM images during rotation and coalescence of the C_{82} molecules corresponding to total exposure times of (b) 590 s, (c) 830 s, and (d) 2040 s. (e) Variation of the apparent carbon nanotube diameter with total exposure time. The plot colors correspond to measurements at the positions of the lines marked in part a.

apparent diameter of the SWNT (see Supporting Information Figure S1).[23] After the initial rotation there is a partial secondary rotation followed by the complete coalescence of the La@C_{82} molecules into an inner tube. During the initial rotation the apparent diameter of the SWNT decreases by as much as 30% (at the

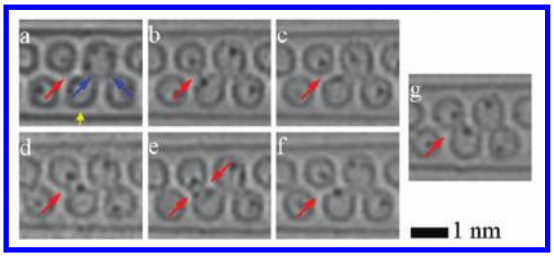

Figure 3. (a) HRTEM of a La@C_{82} molecule (yellow arrow) and its four nearest neighbors. The blue arrows highlight zigzag bonding between C_{82} molecules, and the red arrow highlights the absence of a bond. (b–g) Time series showing the making and breaking of zigzag bonds between adjacent C_{82} molecules. The red arrows indicate the positions of interest.

position marked in red in Figure 2a). Previous work has shown that under the influence of electron beam radiation a 2D zigzag chain of fullerene molecules encapsulated inside a SWNT can undergo a corkscrew-like rotation, causing deformation of the host SWNT.[16,23] A similar motion has also been observed in a zigzag chain of $Sc_3C_2C_{80}$ peapods, with a change in the diameter of the host SWNT of up to 17%.[9] Figure 2e shows that the diameter of the SWNT gradually decreases with time, indicative of the SWNT cross section reverting from elliptical to circular, as the strain is relieved by fullerene coalescence. The final diameter of the SWNT (~2.1 nm) lies halfway between the maximum (~2.5 nm) and the minimum (~1.7 nm), as one would expect for such a cross-sectional transition from elliptical to circular.

Next, we study the details of how the La@C_{82} fullerenes interact with their nearest neighbors during the coalescence. In the case of 1D packing, each La@C_{82} has only two nearest neighbors on opposite sides, whereas for the 2D packing, there are four nearest neighbors that complicate the coalescence dynamics. Figure 3 shows a time series of HRTEM images of the 2D packed La@C_{82}:SWNT peapod, with the lattice structure of the SWNT removed using a mask in the FFT and a three-pixel Gaussian blur applied.

In Figure 3a, a La@C_{82} with its four nearest neighbors is observed (yellow arrow), with the red arrow indicating a nonbonded neighbor and blue arrow a zigzag bonded neighbor. After approximately 40 s of electron irradiation, Figure 3b, a single bond forms catalyzed by the proximity of the La atom. By the following frame (there is approximately 10 s of irradiation between frames), Figure 3c, this bond has been destroyed and the La atom has migrated away from the bond position. One frame on, Figure 3d, the La atom has again catalyzed a single bond between the C_{82} molecules. A second bond is quickly formed and is seen in the following frame, Figure 3e. These two bonds do not last long, with both having been broken in two frames' time, Figure 3f. After a further three frames of irradiation the two molecules fuse (marked with a red arrow in Figure 3g), which marks the beginning of the coalescence of the two adjacent molecules. This making and breaking of bonds is similar to that observed in 1D packing.[14]

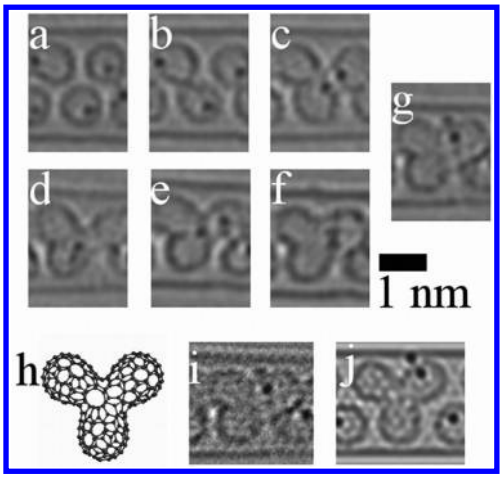

Figure 4. (a–g) Time series of HRTEM images showing the coalescence of three La@C_{82} to form a novel trilobate structure. (h) Atomic model of a trilobate structure formed from three C_{82} cages. (i) Raw HRTEM image of the trilobate structure and (j) image simulation utilizing the atomic model of trilobate in part h within a SWNT.

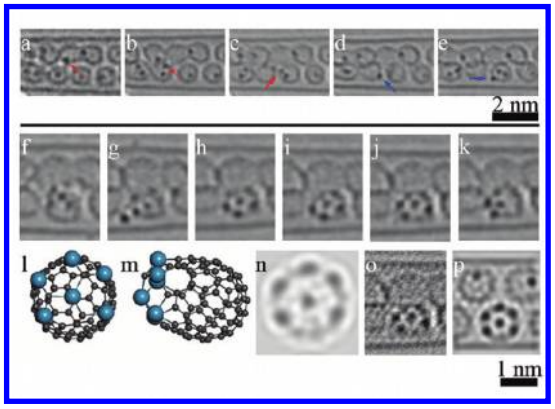

Figure 5. Formation of a La_5C_{77} molecule. (a–e) HRTEM time series tracking the migration of two La atoms (red and blue arrows) to join the resident La atom on a single host C_{82}. (f–k) Time series of the dynamics of six La atoms that have now aggregated about the C_{82} molecule. (l, m) Proposed structure for the La_5C_{77} molecule shown in the projection normal to the plane of the La atoms (l) and rotated by 90° (m). (n) Image simulation of the molecular model shown in part l. (o) Raw HRTEM image of the La_5C_{77} and an image simulation of the model within a SWNT (p). The 2 nm scale bar corresponds to images a–e. The 1 nm scale bar corresponds to images f–k, o, and p.

The 2D nature of the coalescence led to novel structures being formed that are not possible in the 1D packing scenario. Figure 4a–g present a time series of HRTEM images showing the formation of a novel trilobate structure through the coalescence of three La@C_{82}. An atomic model of a trilobate structure formed by three C_{82} cages is shown in Figure 4h. Figure 4i and j show a HRTEM image of the trilobate structure (i) and an image simulation (j) with good

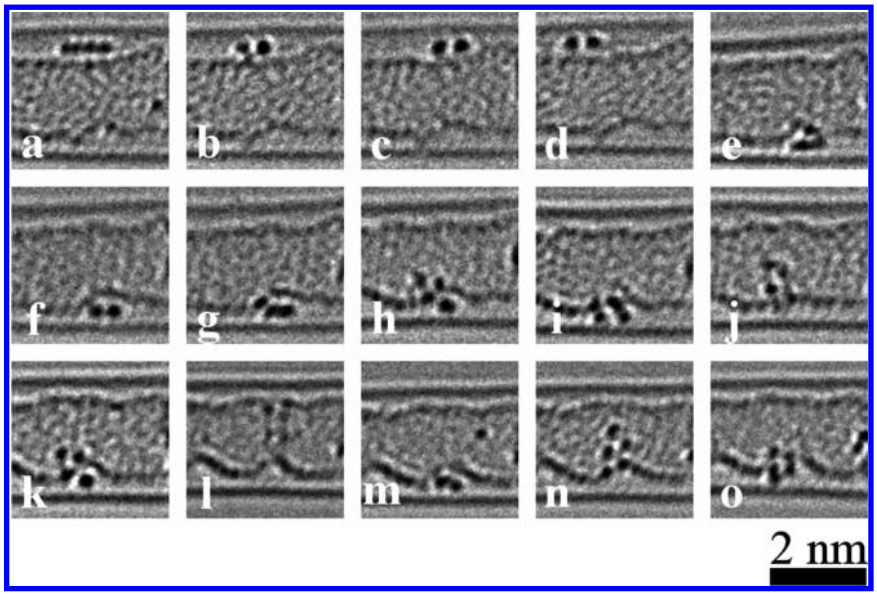

Figure 6. Time series of HRTEM images showing the dynamics of La atoms after complete coalescence of the C_{82} molecules. The lattice structure of the outer SWNT has been removed with a FFT mask.

agreement in the contrast profiles (the atomic model used for this simulation is shown in Supporting Information Figure S2).

The large diameter of the host SWNT (~2.1 nm), which enables the 2D packing of the La@C_{82}, also leads to a large-diameter inner tube being formed through the coalescence of the La@C_{82}. This increased inner nanotube diameter, compared to those formed from 1D coalescence, provides more space for the motion of La atoms to occur.

Figure 5 shows a time series of HRTEM images showing La atoms moving both parallel and perpendicular to the SWNT axis. The migration of La atoms from their original host C_{82} into neighboring C_{82} molecules is observed in Figure 5a–c. A La atom is tracked (red arrow) as it escapes from its initial C_{82} cage, migrating first into its southwest neighbor and then east into another C_{82}. Figure 5d and e show the tracking of another La atom (blue arrow) as it migrates from its host to join the La atom tracked in Figure 5a–c and the initial resident of the C_{82} molecule. Figure 5f–k show a continuation of the series, resulting in at least five La atoms clustering around a single C_{82} fullerene. Figure 5l shows a proposed atomic model of five La atoms attached to a C_{82} cage, with the side view shown in Figure 5m and the image simulation in Figure 5n. Figure 5o is the experimental HRTEM image of the five-atom cluster, and Figure 5p an image simulation of the proposed cluster model shown in part l placed within an appropriate nanotube structure. Good agreement is observed between the HRTEM image and simulation.

With prolonged electron beam exposure the C_{82} molecules fully coalesced to form a somewhat defective inner tube. Figure 6 shows the formation and evolution of a four-atom nanocrystal between the inner and outer tube walls. In Figure 6a a linear chain of four La atoms sits in the vacancy within the original host SWNT but outside the newly formed inner tube. Six frames later (Figure 6d) only two spots can be seen. The increased intensity suggests that each spot is due to two La atoms, one behind the other. This quartet of La atoms then translates horizontally between the inner and outer tube, remaining in the same orientation (b–d). On some of the intermediate frames between parts b and d ghosting of the rear La atoms can be seen (see Supporting Information movie SM1). The La atoms then suddenly (within one frame) flip to the opposite side of the tube, remaining between the inner and outer tube (e). They reside within a small cavity in the inner tube wall for 12 frames (e–g) before beginning to move vertically around the inner tube (h). At least one of the four La atoms appears to be pinned to the small cavity in the inner tube with the other three rotating around it (g–o). Occasionally all four atoms briefly escape from the cavity (l); however this lasts for only one frame and the blurred contrast indicates that the La atoms are transient during image capture. In Figure 6m a fifth atom joins the four La atoms and remains attached until the end of the series, forming of a five-atom nanocrystal.

The formation of other small nanocrystals around defect sites in the inner carbon nanotube was also observed (a four-atom nanocrystal is shown in Supporting Information Figure S3 and a 10-atom nanocrystal in S4). This suggests that a bond forms between a defect site in the inner carbon nanotube wall and at least one of the atoms in the nanocrystal. This small nanocrystal then acts as a nucleation site for the growth of increasingly large nanocrystals.

CONCLUSION

We have shown that the strain induced on a SWNT by the 2D packing of La@C_{82} can be relieved through coalescence. The large-diameter SWNT enabled a larger diameter inner nanotube to be formed than has been previously reported. This provided more room for La atom migration. Small clusters of La atoms were formed that adopted unusual orientations on C_{82} cages. During the first stages of coalescence, trilobate structures were observed, formed by the fusion of three nearest neighbor C_{82} cages. Prolonged exposure to the electron beam resulted in the full coalescence of the C_{82} molecules into an inner tube. The La atoms then aggregated to form nanocrystals consisting of just a few atoms, which remained tethered to defect sites on the inner tube but continued to change their conformation under exposure to the electron beam. These results provide a possible route toward fabricating large-diameter double-wall carbon nanotubes and interesting fullerene structures.

We have not, however, demonstrated any control over the nature of the intermediate products in the coalescence reaction. Recent work on tailoring the species inserted into carbon nanotube hosts to determine the products of coalescence[5] and detailed descriptions of the process of fullerene dimerization under electron beam irradiation[14] suggest that it may eventually be possible to deliberately create such structures as those reported in this work.

Radial deformation of a SWNT has been predicted to alter the band gap in semiconducting SWNTs and can cause the opening of a band gap in non-armchair semimetallic SWNTs.[24] The precise nature of this band gap change is strongly dependent on the structure of the nanotube and the details of its cross-section. The fabrication of a TEM-compatible La@C_{82}:SWNT electronic device would allow for the experimental investigation of these predictions and may also pave the way for the development of a novel carbon nanotube based nanomechanical transistor.

Future work will examine, in more detail, the possible varieties of La metal nanocrystals that may form within such larger diameter inner tubes and possible routes to the controlled formation of potentially interesting fullerene intermediaries.

METHODS

The peapods were prepared in a similar manner to our previous work on 2D packed peapods.[23] The La@C_{82} metallofullerenes were produced using arc-discharge with La-doped carbon rods and purified using HPLC. The carbon nanotubes used in this work were FH-P nanotubes obtained from Meijo Nanocarbon. This sample contains a mixture of large-diameter SWNTs, some double-wall carbon nanotubes, and triple-wall carbon nanotubes. The FH-P nanotubes were heated in air for 20 min at 350 °C and then cooled to room temperature before a CS_2 solution containing La@C_{82} was added dropwise to the buckypaper. The composite sample was then placed in a quartz tube, evacuated, sealed, and then placed in a furnace at 500 °C for 4 days to form peapods. TEM samples were prepared by sonicating the peapods in 1,2-dichloroethane for 20 min and drop casting onto lacey carbon TEM grids. HRTEM was performed using Oxford's OJ JEOL 2200MCO, with a CEOS probe and image aberration correctors operating at 80 kV. Image simulations were performed using supercells and the multislice approach in JEMS.

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Supporting Information Available: Molecular model of the deformed SWNT; molecular model of the trilobate structure encapsulated within a SWNT; further examples of the formation and dynamics of nanocrystals; HRTEM image sequence movie of La dynamics. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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