Capturing the Motion of Molecular Nanomaterials Encapsulated within Carbon Nanotubes with Ultrahigh Temporal Resolution

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ABSTRACT We use *in situ* low-voltage aberration corrected high resolution transmission electron microscopy with a temporal resolution of 80 ms to track the motional dynamics of nanostructures encapsulated within carbon nanotubes. Two different nanostructures are examined and both are produced by electron beam irradiation of peapods containing La@C_{82} metallofullerenes. The first novel nanostructure consists of a LaC_2 metal cluster attached to carbon nanotube inside a nanotube host. It exhibits repeated nanopiston-like behavior over a 5 min duration, driven by energy supplied by electron beam irradiation. Interaction of the metal cluster with the nanotube host is also examined, revealing that the metal cluster can open up the nanotube sidewall, exit, and then seal the hole in the wall back up with carbon from the surrounding region. Finally, the intrinsic motional dynamics of an isolated single fullerene within a SWNT is captured and we report velocities up to 112 nm/s.

KEYWORDS: aberration-corrected · HRTEM · nanotubes · peapods · nanomaterials

The interaction between catalytic metal nanoparticles and sp^2 graphitized carbon is fundamental for understanding the growth dynamics of carbon nanotubes.[1] High resolution transmission electron microscopy enables the atomic structure of graphene-based carbon nanomaterials to be imaged.[2,3] *In-situ* high-resolution transmission electron microscopy using environmental holders has been used to study the growth of single-walled carbon nanotubes and multiwalled carbon nanotubes.[4,5] However, they are often limited in their resolution, and resolving the C−C bond necessary to obtain the full atomic structure of the carbon nanomaterials has proven to be difficult.

Rodriguez-Manzo *et al.* used *in situ* HRTEM to study the nucleation of carbon nanotubes by the injection of carbon atoms into metal particles.[6] Advances in low-voltage aberration corrected HRTEM now permit the study of carbon nanomaterials at accelerating voltages as low as 80 kV and often with angstrom resolution.[7−12] Recently, Jin *et al.* examined the enlargement of fullerenes by catalytic metal atoms using HRTEM.[13] We have recently shown that electron beam irradiation of SWNT peapods filled with La@C_{82} using an accelerating voltage of 80 kV can lead to the coalescence of the fullerenes and the formation of an inner nanotube within the host SWNT.[14] This was extended to double-walled nanotubes (DWNTs) and triple-walled nanotubes (TWNTs).[14] During the coalescence procedure the La metal atoms are mobile within the interior and if the diameter of the nanotube is sufficient the La atoms eventually aggregate to form clusters.[14]

The motional dynamics of molecular material encapsulated within carbon nanotubes has been previously investigated using time-series of HRTEM images.[14−21] This has revealed interesting properties such as the rotation of metallofullerenes in carbon nanotube peapods,[19] cork-screw rotation and translational motion of larger C_{300} nanostructures within nanotubes,[16] conformational changes in molecules,[17] and the oscillation of small nanotubes back and forth.[21] Theoretical calculations by Somoda and co-workers indicate that thermal energy not only activates motion of capsules inside nanotubes but can also induce deformation of the nanotube host that hinders continual motion.[21]

While the spatial resolution in the studies of carbon nanomaterials has been high when aberration corrected HRTEM is used, the temporal resolution is often low. The

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time between frames of HRTEM images is typically on the order of 1−5 s. Improving the temporal resolution for *in situ* HRTEM imaging of material encapsulated inside carbon nanotubes will enable more details about the motional dynamics to be elucidated and provide more accurate determination of kinetic quantities such as velocity and rotation rates. Significant advances have been made in ultrafast electron microscopy using pulsed electron sources,[22] but the resolution is not sufficient to resolve the atomic structure of carbon or study the detailed motion of small molecular materials.

Here, we use *in situ* low-voltage aberration corrected high resolution transmission electron microscopy with an ultrafast temporal resolution of 80 ms to study the motion of molecular material within the confined space inside carbon nanotubes. This is achieved by optimizing the read-out conditions of the CCD array to provide fast-frame rate HRTEM imaging at high magnification, with the capabilities to resolve atomic structure. We use this to monitor the motional dynamics of two novel nanostructures formed inside nanotube hosts. We show that small metal clusters attached to carbon nanotubes can be formed inside peapods containing La@C_{82} metallofullerenes after being exposed to 80 kV electron beam irradiation for 20 min. The motional dynamics of this novel structure are captured and show rapid nanopiston-like behavior for extended periods of time. Electron beam driven interaction between the metal cluster and the nanotube is observed, leading to substantial structural changes. We demonstrate that metal clusters can escape from the interior of carbon nanotubes. They can do this by first opening the sidewalls of a carbon nanotube, moving from inside to the outer surface of the nanotube, sealing the hole back up, detaching from the nanotube, and then rolling away. Finally, we examine a single isolated fullerene trapped within a small sealed 10 nm section of a nanotube. The absence of other fullerenes enables the true dynamics of single fullerene motion to be captured for the first time. The velocity of the fullerene is measured and reported.

RESULTS AND DISCUSSION

We exposed a large 4×10^4 nm^2 region of La@C_{82}:SWNT peapods with an 80 kV electron beam irradiation for 20 min in order to create novel molecular structures inside the nanotube host. We found the metallofullerenes in densely packed areas often coalesced to form narrow inner SWNTs within the larger SWNT host (*i.e.*, double-walled carbon nanotube), similar to previous reports.[14] Novel complex nanostructures were observed next to regions of empty space inside the SWNTs. These regions are attributed to peapods that were originally only partially filled with La@C_{82}. The presence of empty space at the end of a chain of La@C_{82} enables the accumulation of La metal atoms in this region during the electron beam irradiation. Figure 1i shows a novel structure formed in the interior of a partially filled La@C_{82}:SWNT peapod. This structure contains a crystalline lanthanum carbide (LaC_2) head (indicated with red bracket), and a SWNT body attached to the back (indicated with a yellow bracket. This structure is one entity and the SWNT attached to the LaC_2 head has a spherical end-cap. Figure 1ii,a shows a HRTEM image of the structure, presented in false color ("fire" color LUT used) to enhance the visibility and contrast. A schematic representation is presented below in Figure 1ii,b, illustrating the LaC_2 head and SWNT body. Analysis of the crystal lattice shows a match with the tetragonal LaC_2 crystal structure with, space group *I*4/*mmm*, $a_0 = 4.00$ Å, and $c_0 = 6.58$ Å.

The chirality of the SWNT containing the novel nanostructure was index as (13,10) by directly imaging the carbon atomic structure of the SWNT and analyzing the 2D fast Fourier transform (FFT) and diameter.[24,25] The green box in Figure 1iii,a indicates the region used for the FFT analysis, presented in Figure 1iii,b. The FFT shows two sets of six spots that are slightly rotated with respect to each other, corresponding to the graphitic structure of front and back layers of the nanotube. In Figure 1iii,c a red hexagon is overlaid on one set of six spots, and in Figure 1iii,d a green hexagon is overlaid on top of the other set of six spots. A reconstructed image is presented in Figure 1iii,e and is produced by including only the six spots within the green hexagon and also the inner region. A similar reconstructed image is produced from the red hexagon spots in Figure 1iii,f. Structural diagrams of the respective front and back walls of a (13,10) SWNT matching the reconstructed images are presented in Figure 1iii, panels g and h.

The vacant space inside the SWNT allows the novel LaC_2-nanotube structure to demonstrate mobility and pump back and forth, operating like a nanopiston for least 25 times over 5 min. Figure 2i presents a series of HRTEM images showing the LaC_2-nanotube structure at various positions in the nanotube host, 0.5 s acquisition times were used. Figure 2i shows the nanostructure has a length of 8.1 nm and moves back and forth over a distance of up to 6 nm. A movie with 12 frames per second was taken and captured the nanopiston operation on a time scale of 80 ms for over 4 min (see Supporting Information). The movement of the piston was generally rapid between the two end points of fixed stability. The motion is driven by the electron beam by either the transfer of thermal energy to kinetic energy or from charging effects. We find that increasing the beam current density leads to more movement of the nanopiston back and forth within the host nanotube. Figure 2ii presents eight sequential frames of HRTEM images extracted from the movie, with 80 ms between each frame. In Figure 2ii,a the LaC_2-nanostructure is located on the right-hand side. In the next frame, Figure 2ii,b, it is found on the left-hand side. The movement was faster than our 80 ms resolution, since no intermediate position was observed. In Figure

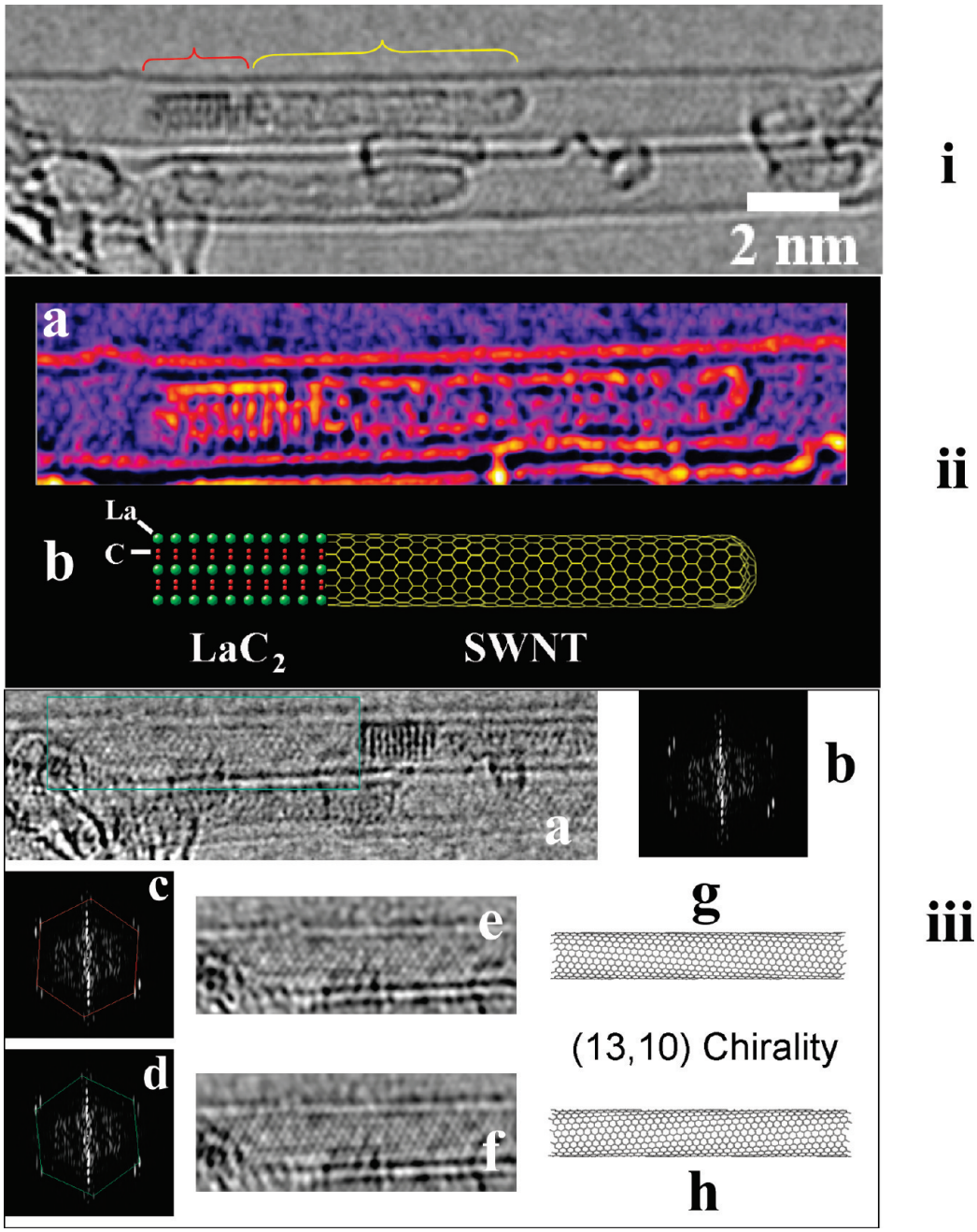

Figure 1. (i) HRTEM image of the LaC_2 cluster (red bracket) attached to a carbon nanotube (yellow bracket) inside a SWNT host. Taken with an exposure time of 0.5 s. (ii) (a) HRTEM image of the LaC_2-nanotube structure in color for enhanced contrast ("fire" LUT color scheme used); (b) structural schematic of the LaC_2-nanotube structure. (iii) (a) HRTEM image showing atomic structure of the carbon nanotube containing LaC_2-nanotube, indicated with green box; (b) FFT from the green box region in part a; (c) red hexagon overlaid on the FFT to highlight one set of six spots associated with the graphene lattice structure; (d) green hexagon overlaid on the FFT to highlight the other set of six spots associated with the graphene lattice structure; (e) reconstructed HRTEM image obtained by removing the six spots in the green hexagon in part d. (f) reconstructed HRTEM image obtained by removing the six spots in the red hexagon in part c; (g) atomic structural representation of one wall of a (13,10) SWNT matching the HRTEM image in part e; (h) atomic structural representation of the other wall of a (13,10) SWNT matching the HRTEM image in part f.

2ii,d the LaC_2-nanotube structure has moved back to its original location to the right-hand side. Figure 2ii,e shows it rapidly moving back to the left and by Figure 2ii,f it has returned again back to its original position on the right-hand side. This shows two full oscillations have occurred in less than the time it took for one image acquisition in Figure 2i of 0.5 s. We measured a maximum velocity of 75 nm/s and this was primarily limited by the acquisition time of the HRTEM images and the distance available for the movement within the interior of the SWNT.

After 10 min of continuous motion the nanostructure finally lost its mobility. The freedom of the LaC_2-nanotube structure to move back and forth dissipates

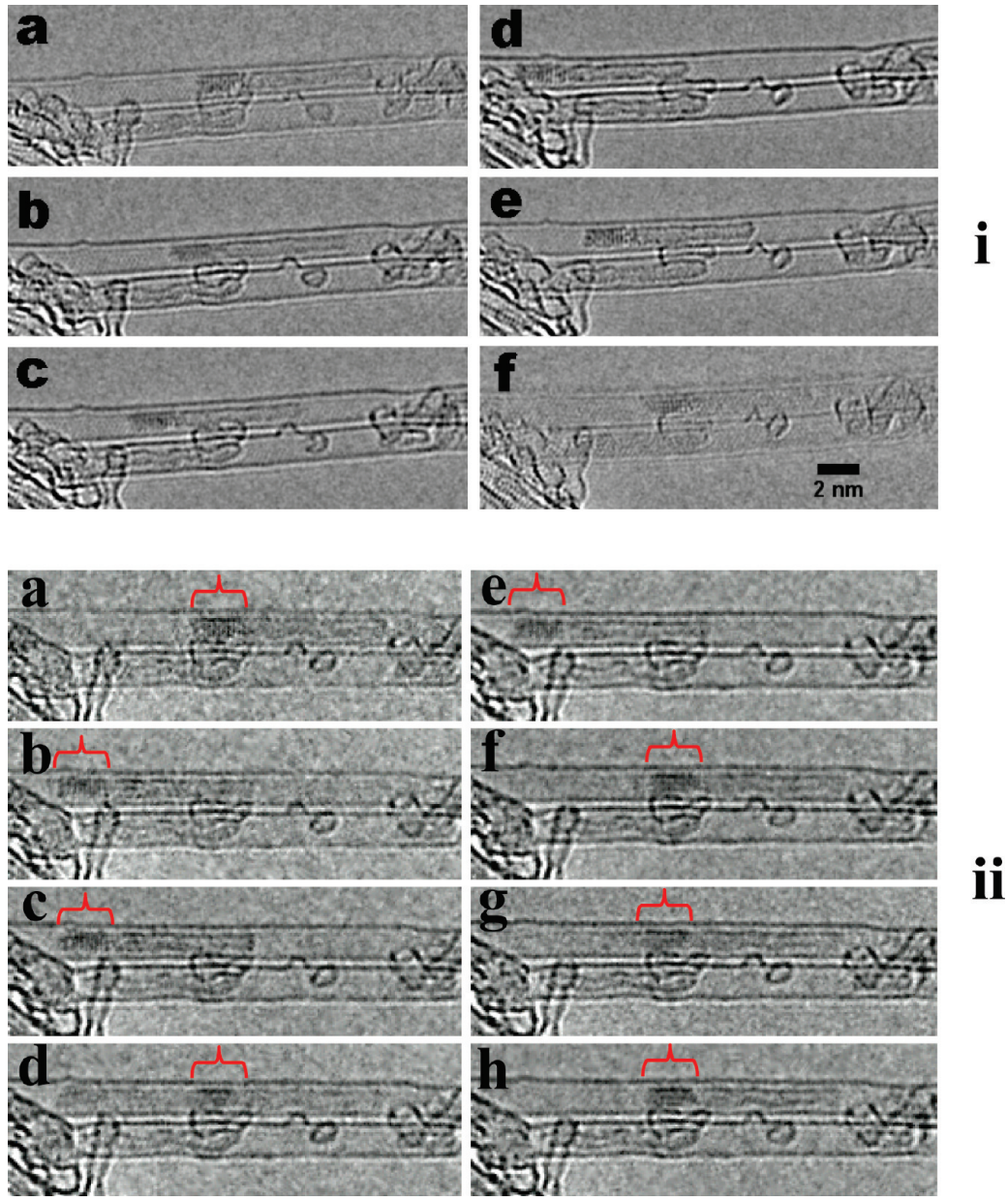

Figure 2. (i) Series of HRTEM images showing the LaC_2-nanotube nanostructure at various positions within the nanotube host: 0.5 s acquisition time. (ii) Time-series of HRTEM images showing rapid oscillations of LaC_2-nanotube structure. Time between frames is 80 ms. Red bracket indicates position of LaC_2 cluster.

energy gained from the electron beam irradiation. The loss of motion may be due to the LaC_2-nanotube reacting with the nanotube sidewalls and becoming fixed. Figure 3i shows the LaC_2 crystal opening up the sidewall of the SWNT and entering the other SWNT next to it. The time between each frame is 5 s Finally by Figure 3i,f the LaC_2 nanocrystal has detached from its carbon nanotube body and fully entered the neighboring nanotube. It has been suggested that molecules are capable of exiting from the interior of SWNTs through the sidewalls,[23] and recently Sato *et al*. showed Cs^+ ions escaping from the sidewalls of a SWNT using HRTEM.[24] However, HRTEM images were taken using an accelerating voltage of 120 kV, which is more than sufficient to produce holes or defects in the sidewalls of the SWNTs. Figure 3i provides direct evidence that metal carbide particles are capable of escaping from SWNTs and sheds light on the recent work by Shiozawa *et al*., where they found iron crystals on the outside of the SWNTs after the transformation of SWNTs encapsulated with ferrocene to DWNTs.[23]

Figure 3ii shows the LaC_2 cluster seals the hole it created in the sidewall of the SWNT. Throughout this sequence the length of the carbon nanotube inside the SWNT gradually gets smaller and smaller. The opening of the side-wall of the nanotube will expose several carbon atoms which have dangling bonds and are highly reactive. For the hole to seal back up, extra carbon is needed. The LaC_2 cluster assists in using the carbon atoms from the inner encapsulated nanotube and to re-

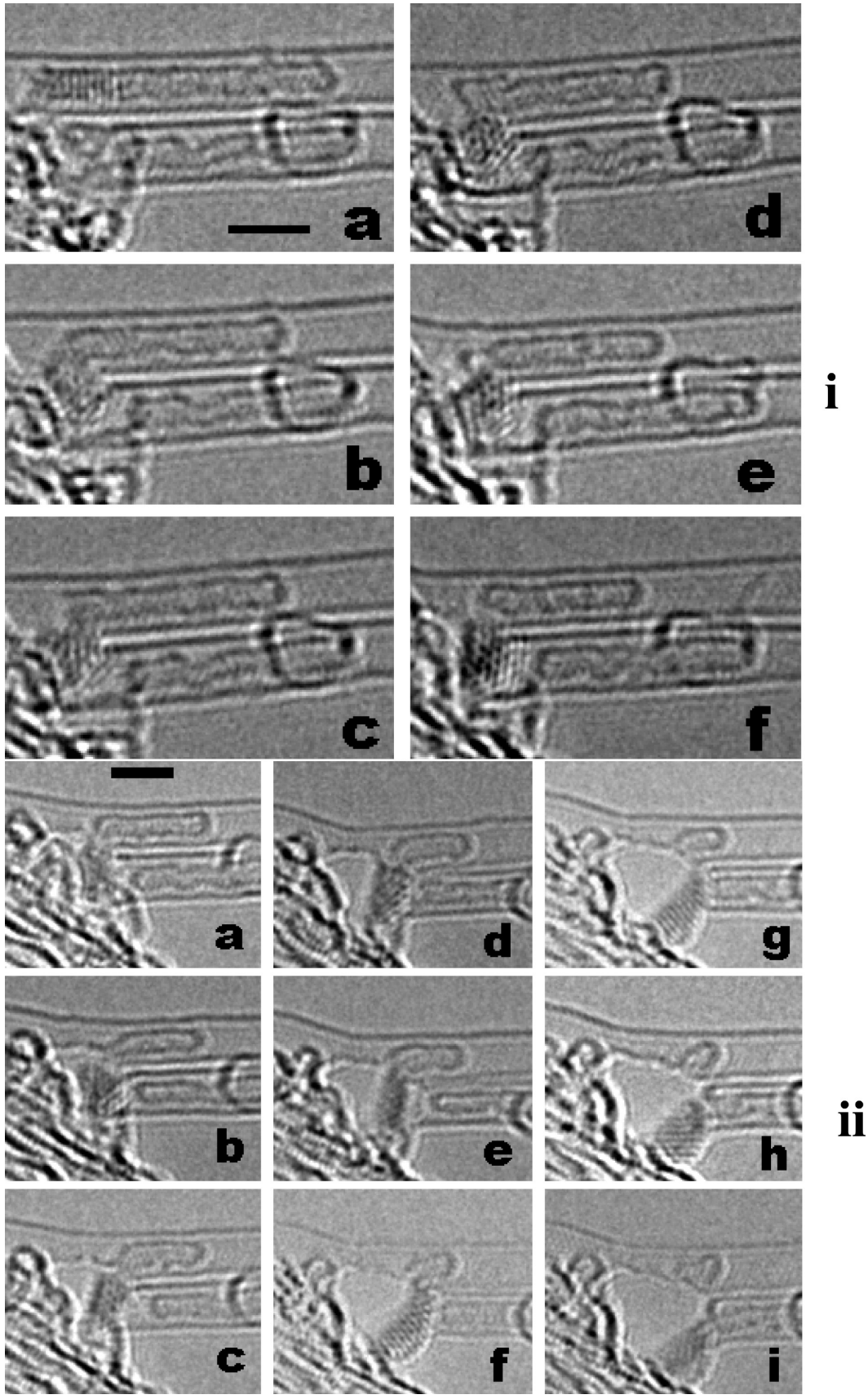

Figure 3. (i) Sequence of HRTEM images showing the LaC_2 cluster opening up the sidewall of a SWNT and exiting into another neighboring SWNT and detaching from its carbon nanotube body. Scale bar indicates 2 nm. (ii) Sequence of HRTEM images showing the LaC_2 cluster using the attached carbon nanotube to seal the hole in the SWNT it exited. Scale bar indicates 2 nm.

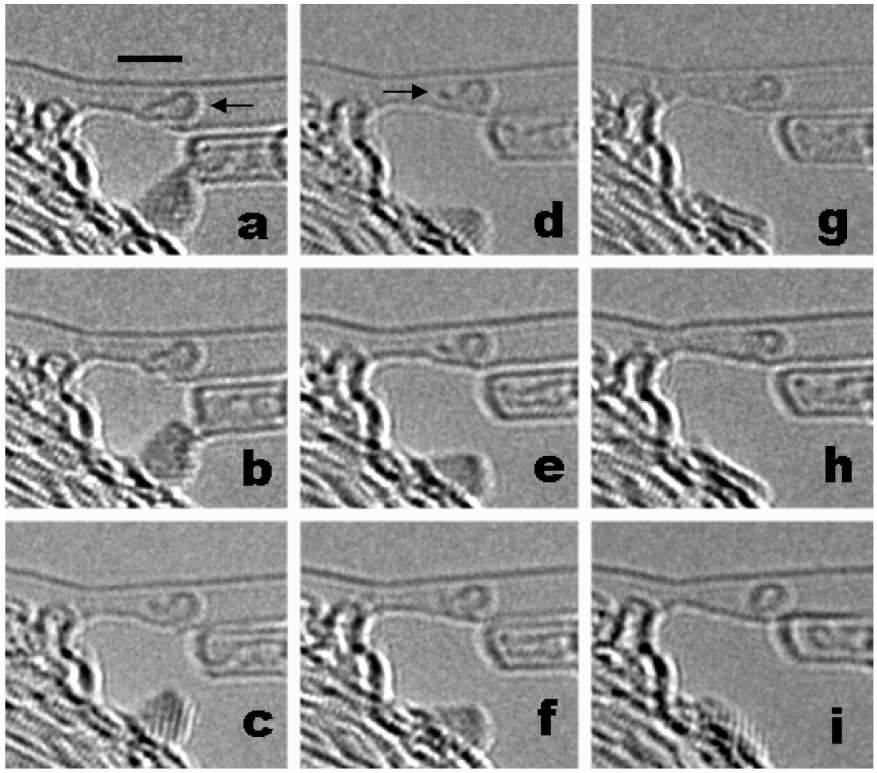

Figure 4. Sequence of images showing a fullerene being formed from a SWNT and the LaC_2 cluster completely detaching from the nanotubes and rolling away. Time between frames is 1 s. Scale bar is 2 nm.

construct the side-wall. This process may be similar to the way carbon nanotubes and graphitic shells are formed around catalytic metal particles through precipitation of carbon atoms with sp^2 bonding. The region where the hole in the side-wall was formed continues to reconstruct and smooth itself out even after the LaC_2 cluster has left, indicating that electron beam irradiation also plays a major role in the process. The LaC_2 cluster breaks the second SWNT off from the support on the left-hand side, shown in Figure 3ii,d onward. In Figure 3ii,h the LaC_2 cluster is completely detached from the SWNT it was originally encapsulated in and the sidewall has been totally sealed up. The LaC_2 cluster now remains attached to the end of the second SWNT it has broken off.

Figure 4 shows that the inner carbon nanotube that was used to seal the hole in the top SWNT has almost been used up with a small fragment remaining, which contains the spherical end-cap of the original nanotube, indicated with an arrow in Figure 4a. Figure 4a shows the fragment is still attached to the sidewall of the SWNT. Figure 4d shows that this end-cap fragment breaks off from the sidewall and closes its shell to form a fullerene with an extra piece of carbon sitting next to it on the left-hand side, indicated with an arrow. In Figure 4f the fullerene opens up and the extra piece of carbon becomes incorporated into the fullerene. By Figure 4i the fullerene has a closed shell and the side walls of the SWNT are smoothed out. The LaC_2 cluster completely detaches from the second SWNT leaving it with a smooth round end-cap and rolls away from the SWNTs. This demonstrates that LaC_2 clusters are capable of completely exiting SWNTs from within. These images show a fullerene being formed from a SWNT under intense electron beam irradiation and confirm its structural stability at 80 kV.

The fullerene formed inside the SWNT is trapped in a small capsule with a round sealed end to the right and a narrow bottleneck to the left. This provides an isolated environment free from other fullerenes and allows the true dynamics of a single individual fullerene within a SWNT to be studied under electron beam irradiation. The encapsulation of a fullerene inside a carbon nanotube capsule has been the basis for a proposed bucky-shuttle nanomechanical memory device.[25] Previous examination of fullerene movement in peapods has always involved more than one fullerene along with the movement of the entire chain within the SWNT.[19] The presence of other fullerenes can lead to electron beam induced dimerization and coalescence and this has prevented the real dynamics of individual fullerene motion in peapods to be elucidated over long time periods.[16,26] A line profile was taken across the fullerene in Figure 4a and revealed a diameter of 0.7 $\pm$ 0.04 nm, suggesting it could possibly be a C_{60} fullerene. However, unambiguous assignment of the fullerene structure is difficult. Figure 5 shows the fullerene is free to move back and forth within this SWNT capsule. The position of the fullerene was monitored with a temporal resolution of 80 ms, and over 1300 images were acquired to track the motion over a 105 s period. Figure 5ii plots the position of the fullerene as a function of time and shows the movement is sporadic and typically results in large jumps between positions of fixed stability. A maximum velocity of up to 112 nm/s was measured, which again was limited by the distance free to move and the time resolution of image acquisition.

We found the fullerene occupied most time at the far left-hand side of the capsule near the bottleneck, spending 67% of the time in this position. The movement of the fullerene also seemed to be affected by the SWNT next to it. The fullerene was trapped several times in the center of the SWNT, when the neighboring SWNT was in close contact, shown in Figure 5i,c. This may be due to either changes in the local van der Waals forces or simply constriction of the nanotube containing the capsule by its neighbor. The neighbor-

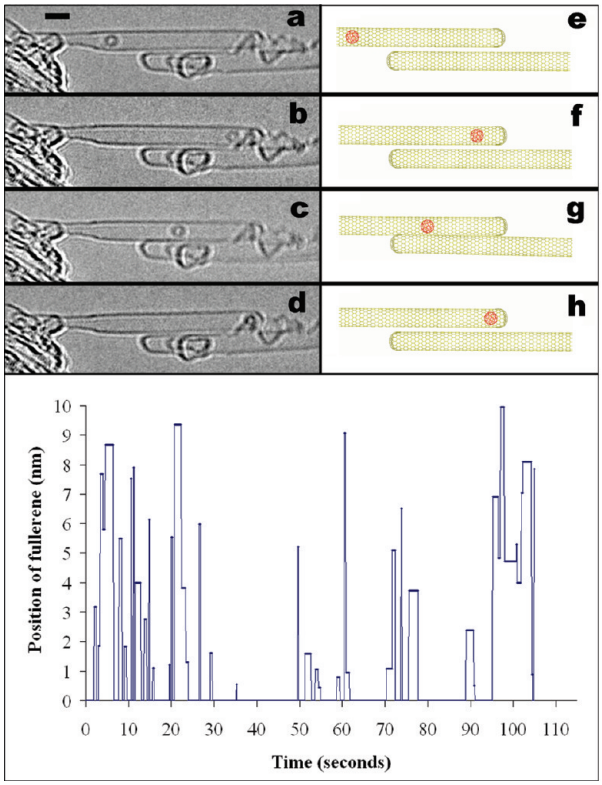

Figure 5. (i) (a−d) Sequence of TEM images showing the oscillation of a single isolated C_{60} in a sealed SWNT capsule. (e−f) Schematic illustration of the movement of the C_{60}. (ii) Plot of the location of the C_{60} as a function of time. The location is measured every 80 ms for 1312 frames.

ing SWNT may change the van der Waals forces locally in the contact region and give rise to a potential well that can trap the oscillating fullerene momentarily. It is also possible that the neighboring SWNT induces structural distortion when making contact, which blocks the passage of fullerene beyond this point. The ability to perform switching of the position of the fullerene within the SWNT capsule using only electron beam irradiation, indicates sufficient energy is being supplied to overcome the attractive van der Waal forces and enable the fullerene to break free and propagate along the SWNT. The fullerene then becomes trapped again by strong van der Waals interactions either at the end, where the fullerene curvature matches the SWNT curvature or in the middle, where the presence of another SWNT on the exterior alters the van der Waals forces along the SWNT. We also observed the elastic distortion of the shape of the fullerene as it was drawn into the narrow neck region of the SWNT capsule, changing from spherical soccer ball to oval rugby ball and returning back to the original shape upon leaving the region.

CONCLUSION

We have shown that increasing the temporal resolution for aberration-corrected low-voltage high resolution transmission electron microscopy enables the detailed kinematics of molecules and nanomaterials encapsulated inside carbon nanotubes to be captured. This enabled velocities of up to 112 nm/s to be recorded, which were limited primarily by the space available to move in and the temporal resolution. This approach can be extended to other molecules, encapsulated inside carbon nanotubes and possibly to molecules situated on the surface of graphene. This technique has limitations in that it cannot be used to study motion under ambient conditions (*i.e.*, without electron beam irradiation). The observation of metal nanoparticles escaping the carbon nanotubes and leaving no holes behind may shed light on the mechanisms behind the removal of metal catalyst particles using high temperature annealing. Observing a single fullerene inside a nanotube for up to 10 min of constant electron beam irradiation indicates that they are structurally stable at an accelerating voltage of 80 kV, when protected inside the nanotube.

EXPERIMENTAL METHODS

Arc-discharge SWNTs were purchased from Carbolex. The SWNTs were purified before use, by heating to 350 °C for 2 h in air, followed by refluxing in HCl acid for 8 h. The SWNTs were then heated to 400 °C for 10 min prior to peapod formation to remove functional groups at the ends of the nanotubes that may prevent fullerenes from entering. La@C_{82} was produced using an arc-discharge apparatus and purified using HPLC. Peapods were formed using the hot vapor phase filling technique. The SWNT:La@C_{82} composite was heated under static vacuum for 4 days at 450 °C. The peapods were dispersed in methanol using an ultrasonic bath, and a lacey-carbon-coated TEM grid was dipped into the solution. TEM was performed using a FEI Titan^3 operating at 80 kV with spherical aberration correction. A CCD (Gatan US1000 2k×2k Camera, 9.5 counts per electrons) was used for image acquisition. Fast temporal resolution was achieved by using 6 pixel binning of the CCD with an overall system magnification of 2.6×10^6. The CCD acquisition time was then reduced to 0.06 s. An electron beam density of up to 0.1 pA/nm^2 was used. Camtasia Studio 5 screen recorder software was used to record the live CCD display and capture HRTEM images at 12 frames per second data rate.

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Supporting Information Available: Movies. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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