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Collapsing carbon nanotubes with an electron beam

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Abstract

We report the first in situ study of the dynamical behavior of carbon nanotubes. We have used high energy electrons to collapse multi-walled tubes in an atomic resolution transmission electron microscope. Our video recorded observations show the real time dynamics of collapse of the tubular structure. We propose that the orientation dependent damage and channeling effects of the incident 800 keV electrons enable the multi-walled tube to flatten parallel to the flow of electrons. Evidence is seen for a zipper-like closure effect initiated by van der Waals interactions between the inner tube walls.

The strong interatomic carbon bond present in nanotubes [1] suggests that these structures may constitute the strongest fibers possible [2]. Although nanotubes collapsed into flat ribbon-like structures have recently been observed, the reason for their collapse is still unknown and is presumed to be initiated by external mechanical deformation of the bulk material [3]. Due to their unique length scale, controlled manipulation of single nanotubes has been thus far unpredictable. We describe here the use of a high energy (800 keV) electron beam to induce collapse of a multi-walled carbon nanotube, allowing us to study the phenomenon of a collapsing tube in situ in a high resolution transmission electron microscope (HRTEM). Along with the tube walls becoming disordered, we observe the lattice fringes on either side of the hollow moving towards each other thus narrowing the gap in between. With continued electron irradiation, the gap completely disappears, signifying the full collapse of the tubular structure. We suggest that damage caused by the high energy electrons forms a collapsed tube oriented with its width parallel to the electron beam. From real time observations of a collapsing nanotube, we propose the van der Waals force is instrumental in a zipper effect which helps propagate the collapsing process down the entire length of the tube. The total collapse and destruction of the well-formed crystalline tube by the 800 keV electrons occurs in a matter of minutes.

Our multi-walled carbon nanotubes were synthesized in a conventional arc-discharge chamber and prepared for HRTEM as discussed elsewhere [3]. HRTEM has been instrumental in characterizing nanotubes, specifically in showing the inner diameter and number of walls of a given tube. The accelerating voltage most commonly used for HRTEM study of nanotubes is 200 keV [1]; electrons at this energy do not appear to affect the nanostructures, and the tubes can be conveniently studied for extended periods of time without any sign of damage. A 300 keV beam, however, does affect the fullerene nanostructures [4]. Using 300 keV electrons, Ugarte has transformed angular graphitic particles into rounded struc-

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tures by collapsing and reforming them into robust carbon onions [5]. We confirmed our sample as being multi-walled carbon nanotubes with crystalline walls using a JEOL JEM 200CX with a 200 kV accelerating voltage; then for the purposes of deforming, we used 800 keV electrons in the Berkeley Atomic Resolution Microscope (JEOL-ARM 1000, resolution 0.16 nm) to further study our samples.

Fig. 1 is a series of stills taken at different times from a continuous video recording of a collapsing multi-walled carbon nanotube. Fig. 1a, taken after 30 seconds of continuous exposure of the sample to the beam, shows the inner gap of the tube as being about 1.6 nm. Another multi-walled carbon nanotube lies to the left of this one, and thus there is a greater number of lattice fringes on one side (a dashed line distinguishes one tube from the other). Fig. 1b shows the same sample at $t = 60$ seconds. Here the gap has clearly decreased from that observed in Fig. 1a and the lattice fringes are no longer continuous walls but wiggly lines. The deterioration of the lattice fringes results from a breaking of carbon-carbon bonds in selected areas and a reduction of the order in the atomic arrangement. Also, the width of the inner diameter of the tube is no longer uniform down its length but varies from about 1.2 to 0.8 nm: this is indicated in Fig. 1b by white and black arrows, respectively. An interesting phenomenon is observed as the gap further decreases: once the inner walls in a particular region of the tube (black arrows) get close, the tube walls move closer in neighboring regions (white arrows) creating a zipper like effect, and the tube flattens down its entire length. This effect is strikingly revealed in real time viewing of the collapsing process on video. Fig. 1c shows the tube at $t = 165$ seconds at which time there is no gap

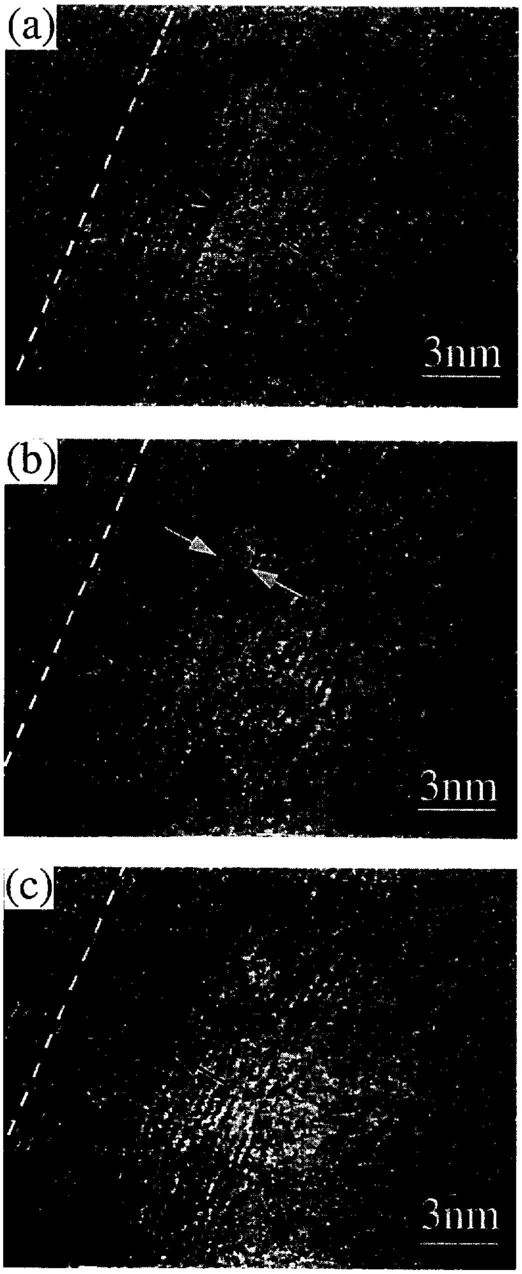


Fig. 1. A series of stills taken from a video recording of a collapsing carbon nanotube. (a) Taken at $t = 30$ seconds. This micrograph shows the crystalline lattice planes of a multi-walled tube; the dashed white line differentiates the tube on the left from the relevant one in the main region of the viewing screen. The arrows point to the gap corresponding to the hollow of the tube. (b) Taken at $t = 60$ seconds. The image reveals the effect of the 800 keV electrons, channeling through the planes. The narrowing of the gap is not uniform as pointed out by the white and black arrows which define the region of the 2 nm and 1 nm gap, respectively. The wiggly lattice fringes indicate the breaking of carbon bonds in the tube layers. (c) Taken at $t = 165$ seconds. The photograph shows the complete collapse of the tube where the gap disappears to a distance on the order of the van der waal separation between planes, as pointed to by the arrows. The structure becomes progressively more amorphous with continued exposure to 800 keV electrons.

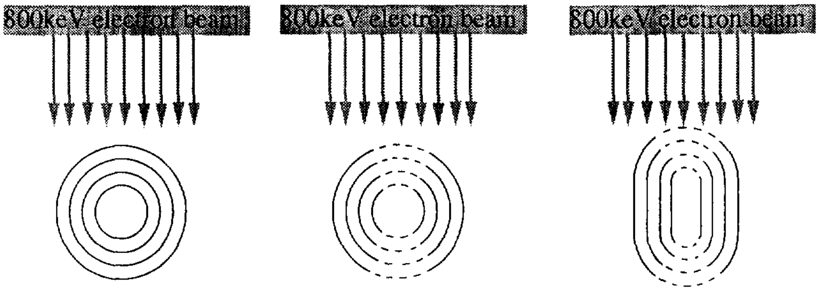
in the middle. This is the signature of tube collapse. The comparison of the lattice fringes observed in Figs. 1a and 1b with those seen in Fig. 1c reveals the progressive amorphization of the tube after continued irradiation. We observe that an 800 keV electron beam changes both the overall geometry of the tube and the local bonding of the structure in a matter of minutes.

Measurements taken from Figs. 1a and 1c of this multi-layered tube with 13 walls yield a lattice spacing of 0.338 nm from *both* images. This result agrees well with the graphite interplanar spacing seen in tubes and shows that the average distance between layers does not change throughout the collapsing process. Fourier analyses of Figs. 1a, 1b and 1c confirm that the periodicity in the lattice is the same in all images. This result excludes the behavior of the tube as being described simply as amorphous material filling in the hollow region during irradiation. Finally, consistent with a flattened nanotube, the width of the tube in Fig. 1a equals the width of the tube in Fig. 1c plus the initial gap of 1.6 nm.

Since the electron beam used in this study is of high energy, the major effect of irradiation is expected to be due to atomic displacements caused by direct collisions between the incident electrons and carbon atoms. Ionization effects are expected to be much less significant [6,7]. Because of the similar sp^2 bonding in graphite, it is instructive to compare our results on carbon nanotubes with studies of graphite under electron irradiation. In graphite, displacement damage due to irradiation by high energy electrons rapidly causes disruption of the basal planes, visible as a breakup of the ordered fringes in high resolution images [8]; this is very similar to the present observations. A proposed mechanism [8] for the breakup of the basal planes is based on the clustering of carbon interstitials and the subsequent interaction of a cluster with a (relatively immobile) vacancy in a basal plane. (In graphite, higher doses can cause remarkable dimensional changes of up to 300% strain in the graphite *c*-direction [8–10] and lead to amorphization. We did not observe significant strain, presumably because the planes in the carbon nanotubes are geometrically constrained.)

Irradiation effects have been observed in graphite after doses as low as 0.02 displacements per atom (dpa) [9,10]; complete amorphization occurs at around 1 dpa [9]. For graphite irradiation with electrons at energies above 200 keV, the cross section is $\sim 3 \times 10^{-27}$ m^2 per atom and thus amorphization requires a dose of the order of 3×10^{26} electrons m^{-2} [9]. For comparison, the present experiment was carried out using a beam current of 2×10^{23} electrons m^{-2} s^{-1}, and the dose corresponding to Fig. 1c is about 3×10^{25} electrons m^{-2}. The damage rates in the two materials are therefore similar.

The local rate of damage in a carbon nanotube might be expected to depend on the local electron density (as it does in other materials [6,7,11,12]). We propose that damage occurs at a higher rate at the



(a) (b) (c)

Fig. 2. Schematic (not to scale) view of changes in the nanotube during electron irradiation: (a) initial, tubular structure (b) an enhanced damage rate weakens the bonding in areas perpendicular to the beam (c) the less damaged parts of the tube relax towards a planar graphitic structure.

more 'exposed' sites on planes perpendicular to the beam, while atoms on the inclined surfaces are relatively protected because of channeling effects and 'shadowing' resulting from atomic alignment parallel to the beam direction. The strength and directionality of sp^2 bonds may be significant in causing this differential damage. A higher damage rate at the top and bottom of the tubes will allow the less damaged parts of the walls to relax towards the equilibrium planar graphitic morphology, allowing the tube to collapse to a ribbon (Fig. 2). Finally, the van der Waals interaction between interior surfaces will stabilize the tube in the collapsed state [3]. The final state is therefore expected to be a ribbon approximately parallel to the electron beam. However, it is known that small particles often adopt an exact on-axis orientation, believed to be due to momentum transfer from the electron beam [13]. We propose that this effect is instrumental in encouraging the final orientation of the collapsed tube to be exactly parallel to the electron beam.

Theoretical predictions indicate that the van der Waals force plays an important role in maintaining the collapsed tube as a flat structure [3]. Our video recorded observations suggest that the van der Waals force between the inner walls may be instrumental in the actual collapsing process. The following model describing the zipper effect may be a useful method of visualizing the collapse of tubular structures which have a van der Waals 'glue' spread inside the hollow center. In its original state, the inner diameter of carbon fibers or even nanotubes is outside the range of the van der Waals attraction so the hollow is maintained. If, however, the inner walls get closer (e.g. the tube pinches or is forcibly pushed flat), the van der Waals force draws them together until they have reached the graphite interplanar spacing of about 3.4 Å, after which it keeps the tube deformed. This deformation now starts the zipper effect because nearby regions are now within the range of the van der Waals force and are drawn together. Thus the deformation propagates down the length of the tube and flattens the entire structure.

This experiment uniquely follows the spatial and time evolution of a collapsing carbon nanotube. Our study shows the destruction of the crystallinity of multi-walled carbon nanotubes by 800 keV electrons and characterizes the collapsing process. Orientation dependent damage results in the straightening of the curved tube walls which narrows the inner diameter of the nanotube, initiating the van der Waals interaction between the inner layers which leads to the total collapse of the structure. This method potentially provides a controlled way of testing the strength of nanotubes and studying the mechanisms involved in shape changes. The structure of nanotubes lends itself naturally to further experimentation of electron-channeling effects of high energy electrons. The zipper effect outlined in this report can be more widely used as a model of collapse for structures which have a short range interaction between them. The capability of manipulating the geometrical structure of a single nanotube, as shown in this experiment, leads to the potential of producing other novel nanostructures with varying mechanical and electrical properties.

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