

## Surface Reconstructions and Dimensional Changes in Single-Walled Carbon Nanotubes

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Dimensional stability is crucial to possible applications of single-walled nanotubes, as their properties are linked to size and topology. We observe nanotubes responding to uniform atom loss, through surface reconstruction and drastic dimensional changes. Experiments using electron irradiation evidence nanotube diameters shrinking from  $\sim 1.4$  to  $0.4$  nm. Molecular dynamics simulations show that surface reconstruction and size reduction occur through dangling bond saturation, forming nonhexagonal rings and 5-7 defects in the lattice. Nonuniform atom removal results in inhomogeneous tube deformations and local necking, and formation of linear atomic carbon chains in the nanotube body. [S0031-9007(98)06926-9]

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Single-walled carbon nanotubes represent ideal surface crystals made of hexagonal graphite honeycomb lattice of monoatomic layer thickness [1]. These structures possess unique electronic and mechanical properties due to their small diameters and lattice orientation [2]. The dimensional stability of these structures would be central to any possible applications of this material in the future. It is interesting to ask, what will be the effect of atom loss from the lattice of such a surface crystal, or in general, how would a structure constructed from a perfect monolayer lattice of atoms respond to loss of atoms which could happen through, for example, irradiation? We answer this question through observations of experimental electron microscopy and molecular dynamics simulations, of a freestanding nanotube subjected to continuous atom removal from its lattice.

The singlewalled nanotubes used in the experiments were synthesized by the recently reported electric arc technique using a Ni-Y catalyst in the anode [3]. A collar of carbon material formed around the cathode is broken down by brief agitation in a sonic bath and dispersed onto empty microscopy grids. Several regions in the sample have high density of ropes of nanotubes [4] and individual nanotubes crossing these ropes. Our observations were focused on these segments of individual tubes. Imaging and irradiation were done in a 200 keV high resolution TEM (JEM 2010) equipped with a Gatan Imaging Filter and all images were recorded digitally. The tubes were examined using a highly defocused electron beam, with intensity much lower than those typically used in high resolution transmission electron microscopy or scanning transmission electron microscopy studies. The approximate electron flux at the sample measured corresponds to current densities of  $1-0.1$  A/cm<sup>2</sup>, which is 1 to 2 orders of magnitude lower compared to typical imaging conditions.

Earlier experiments on singlewalled nanotubes had shown that tubes can be severely locally deformed and broken during exposure to focused electron irradiation.

The results showed that the tube develops several necks along the body (appearing like stringed fullerene beads), leading to fracture at the necks [5]. Irradiation (electrons here) effectively removes carbon atoms from the surface of the nanotube by knock-on displacement; for  $sp^2$  bonded carbon, knock-on of atoms from the lattice occurs for electron energies greater than 120 keV [6]. Under focused irradiation at high fluxes, it may be assumed that the atom extraction occurs rapidly and nonuniformly.

Under uniform irradiation conditions, as reported here, atom removal from the irradiated nanotubes occurs at a slower rate, as long as irradiation persists. Atom loss creates vacancies which could further cluster into larger holes in the structure, and due to the dangling bonds associated with these defects, the system will become energetically unstable. Continuous atom removal from the surface of a nanotube could hence either leave highly unstable nanotube structure of the original diameter or

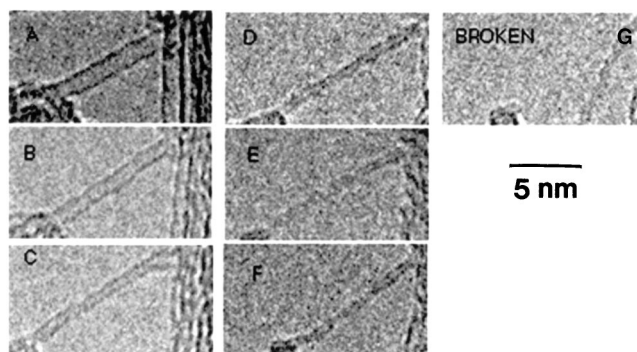


FIG. 1. Controlled electron irradiation of a singlewalled nanotube segment bridged between a hole in a carbon grid. The time difference between each frame of this sequence is about 5 min. The diameter of the original nanotube (a) is approximately 1.4 nm. Notice that the tube has shrunk drastically in diameter during the irradiation. Image in (f) shows the smallest diameter ( $\sim 0.4$  nm) that was visible before the tube broke (g).

could shrink by mending these holes through atomic rearrangements which should necessarily be constrained to the monoatomic layer. Our experimental observations of several single shell tube segments under low fluxes of irradiation strikingly show that the latter is the case. In Fig. 1, the images illustrate the irradiation sequence of a typical tube. In about half an hour of irradiation, the tube has shrunk from an original diameter of 1.4 nm to an incredible value of 0.4 nm. Nanotubes of such small diameters have never been observed before, but our experiments clearly suggest that such structures are indeed stable. Small deformations can be observed in the images of the irradiated tube (Fig. 1), although the roughness on the scale of atomic bond lengths will be difficult to quantify and compare with the shapes of the simulated tubes. But the overall shape of the tube remains cylindrical, even for the smallest tube observed. Continued irradiation results in the breakage of the tube

[Fig. 1(g)]. We speculate that the limiting case of this observation is the formation of atomic chains made of linear arrays of carbon atoms as evidenced in simulations discussed below. But this structure will never be observed in a TEM since displacement of any one atom from the chain (occurring on time scales much shorter than the observation times) will break the chain.

One obvious way in which the defects in an irradiated nanotube can be reconstituted and the energy lowered is by dangling bond saturation and Stone-Wales type transformation. The latter is a C-C bond rotation mechanism which is assumed to be present in many carbon nanostructures [7]. In order to understand the nature of surface reconstructions in singlewalled nanotubes during atom removal from the surface, we have performed tight-binding molecular dynamics simulations (TBMD) [8]. In this approach, we used an energy functional and parametrization which proved to be successful in the modeling of the

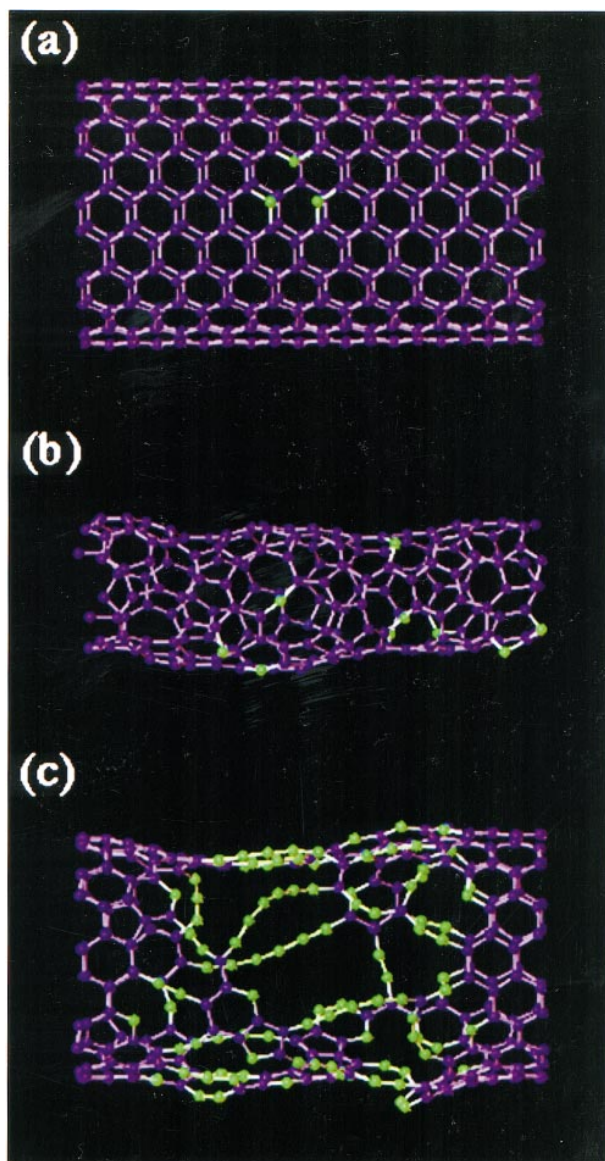


FIG. 2(color). Surface reconstruction of a (10,10) singlewalled carbon nanotube (diameter: 1.36 nm) after atom extraction. The simulation starts with a first vacancy in the (10,10) nanotube (a) as a model of knock-on atomic displacement on the tube surface through irradiation. The unit cell contains 399 carbon atoms (blue or green spheres, illustrating an atomic coordination of 3 and 2, respectively). Periodic boundary conditions are imposed along the nanotube axis. In each simulation, the nanotube was gradually heated up to a temperature of 700 K in order to accelerate the surface reconstruction process. TBMD calculations were performed using a time step of 0.7 fs, to assure optimal integration of equations of motion and energy conservation, and for a total simulation time of 70 ps. (b) Surface reconstruction of the nanotube after a random extraction of 200 carbon atoms along the entire surface. Although the reconstructed surface is highly deformed, the carbon system is still a rough cylinder with diameter value averaged around 0.7 nm. Although each vacancy creation produces three two-coordinate carbon atoms (in green), their number is very small after the reconstruction, illustrating its stability as a nearly pure  $sp^2$  disordered carbon network. (c) Surface reconstruction of the nanotube after an extraction of 80 carbon atoms in a localized region of the cylinder (center of the image). Linear atomic chains of carbon are bridging the two opposite undefected parts of the nanotube.

different allotropic forms of carbon and various carbon-based systems [9]. Although the TBMD is not as accurate as *ab initio* molecular dynamics calculations [10], it allows the treatment of bigger systems since the computational effort is significantly reduced. In addition, such a simulation tool does contain the essential physics and chemistry of the directional covalent C-C bond, and therefore properly describes both  $sp$ ,  $sp^2$ , and  $sp^3$  hybridizations.

The first simulation consists in homogeneously extracting carbon atoms from a perfect (10,10) carbon nanotube [Fig. 2(a)], which is supposed to be a predominant constituent of the ropes as synthesized in the present work [3]. The rate of extraction is 5 atoms/ps. During the course of the simulation, most of the holes, produced by vacancy creation in the lattice, mend as two-coordinate carbon atoms [in green, Fig. 2(a)] and try to recombine, thus forming a mainly three-coordinate highly defective carbon network. Nonhexagonal rings like squares, pentagons, heptagons, octagons, nonagons, and decagons were observed at certain stages of the surface reconstruction. However, the unstable high-membered rings are found to disappear by Stone-Wales mechanism, thus leading the structure to be mainly constituted of five-, six-, and seven-membered rings. Figure 2(b) presents the reconstructed rough surface of the (10,10) nanotube when half of the atoms in the original model were extracted. Fifteen (5-7)-like defect pairs are present in this final topology. The spontaneous formation of Stone-Wales defects and its role in the strain relief mechanisms of a plastically deformed nanotubes have been recently discussed [11], suggesting the role of such defects in responding to topological and dimensional changes in singlewalled nanotubes. In the present simulation, the diameter of the tube shrinks from 1.36 nm [Fig. 2(a)] to an average value of 0.7 nm [Fig. 2(b)]. Although the original hexagonal network is highly defected, the cohesive energy of this reconstructed narrow nanotube is reduced only by 0.55 eV/atom compared to a perfect (5,5) honeycomb lattice nanotube of the same diameter.

Taking a closer look at the reconstructing nanotube lattice in the simulations, a peculiar microscopic mechanism at the atomic scale is frequently observed (Fig. 3). As the removal of any C atom in a hexagonal network is energetically unstable and implies the creation of three two-coordinate C atoms, two of these “dangling bond” (DB) atoms often recombine, thus creating a pentagon [Figs. 3(a) and 3(b)]. This dominant scenario makes the tube shrink. As the reconstituted surface is quite stable, it can either wait for a second extraction of C atom in the neighborhood, or the remaining DB atom [in green, Fig. 3(b)] can attach to the opposite pentagon, thus creating a metastable situation where a C atom is  $sp^3$  at a sharing edge between two pentagons [in red, Fig. 3(c)]. Depending on which C-C bond breaks, one of the two pentagons is destroyed, thus leading the topology similar to the starting point [Fig. 3(b) or Fig. 3(d)]. In the lat-

ter case the global result is a motion of a DB atom at the nanotube surface, a process which increases the radius of interaction for the surface reconstruction in regions with large numbers of defects. The creation of heptagons close to pentagons (also observed in the simulation) comes mainly from reconstructions when more C atoms are extracted close to existing pentagons. This observation is very interesting since during the growth of a nanotube, a mistake (vacancy) in the growing lattice can instantaneously lead to the formation of a pentagon which would be the starting point of tube closure.

When inhomogeneous carbon extraction is performed on the perfect (10,10) nanotube, the defective surface is not able to reconstruct in a disordered  $sp^2$  network, but rather creates atomic linear chains of carbon [Fig. 2(c)], also called “carbynes” ( $C_n$ ,  $n = 2$  to 6), connecting undefected regions of the nanotube. This topology is 0.68 eV/atom less stable than the original perfect (10,10) nanotube. Earlier simulations have shown that a similar situation can result if a nanotube is pulled in tension, which leads finally to the formation of atomic wires in the necked region [12]. Such linear carbon chains have also been observed previously during the unraveling of the open edges of the graphene wall layers of a nanotube by the force of the electric field [13].

Both our experimental results and simulations show that an ideal shell structure like the singlewalled nanotube will respond to atom loss by reconstructing its surface. In carbon structures, this happens through dangling bond saturation and Stone-Wales mechanism. Surprisingly, the

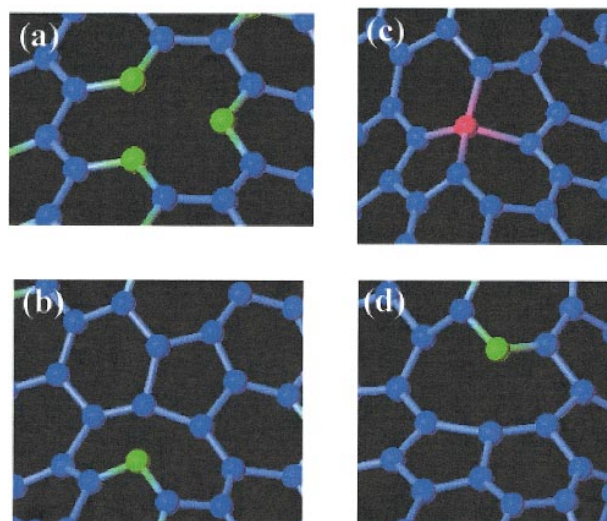


FIG. 3(color). Microscopic mechanism for dangling bonds saturation after atom extraction, illustrated at the surface of a (10,10) nanotube (red, blue, and green spheres, corresponding to an atomic coordination of 4, 3, and 2, respectively). (a) Vacancy creation; three two-coordinate carbon atoms are produced. (b) Pentagon creation; two two-coordinate atoms recombine. (c) Creation of a  $sp^3$  carbon atom which completely connects the network (metastable state), before leading to (d) the motion of the pentagon (of the two-coordinated carbon atom) at the nanotube surface.

process continues until nanotubes of very small diameters ( $\sim 0.4$  nm) are produced. If atom extraction occurs nonuniformly, the structure undergoes severe local deformation and necking, resulting in extreme cases of atomic wires bridging parts of the nanotube body. The results could have implications in the growth models of these structures, which are still far from clear. During growth, when several of the bonds are in a state of constant formation and reevaporation, it can be assumed that the many reconstruction sequences lead to the final nanotube lattice structure. This could imply that the surfaces of the as-grown nanotubes may contain odd-membered ring defects which are observed in our simulations, and suggested in previous works for multiwalled tubes [14]. Singlewalled nanotubes frequently appear (in images) nonuniform (and noncylindrical) in diameter and topology [15], indicating the presence of topological defects, although none of these defects have ever been found in atomically resolved images of nanotube lattice [16]. This could be a challenge for future scanning tunneling microscopy studies.

The shrinking of nanotubes we have observed here is also relevant to an earlier observation of compression in carbon onions [17] which once again results from the loss of atoms during electron irradiation and subsequent shrinkage of individual shells. Such a process has been recently addressed, at the microscopic level, as due to the dynamic nature of topological defects in these structures during the surface reconstructions that stabilize the structure kinetically [18].

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