Experimental observation and quantum modeling of electron irradiation on single-wall carbon nanotubes.

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ABSTRACT

In situ experiments, based on electron irradiation at high temperature in a transmission electron microscope, are used to investigate isolated, packed and crossing single-wall nanotubes. During continuous, uniform atom removal, surfaces of isolated single-wall nanotubes heavily reconstruct leading to drastic dimensional changes. In bundles, coalescence of single-wall nanotubes is observed and induced by vacancies via a zipper-like mechanism. "X", "Y", and "T" carbon nano-structures are also fabricated by covalently connecting crossed single-wall nanotubes in order to pave the way towards controlled fabrication of nanotube based molecular junctions and network architectures exhibiting exciting electronic and mechanical behavior. Each experiment is followed by quantum modeling in order to investigate the effect of the irradiation process at the atomic level.

1. INTRODUCTION

Single-wall carbon nanotubes represent ideal surface crystals made of hexagonal graphite honeycomb lattice of mono-atomic 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? This question is answered through observations of experimental electron microscopy and quantum molecular dynamics simulations of a free standing nanotube subjected to continuous atom removal from its lattice, but also from nanotubes in bundles, as well as from crossing tubes.

Under more 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. Isolated nanotubes, ropes of single-wall tubes and couple of randomly-oriented crossed tubes are also investigated theoretically at the atomic level. In order to understand the effect of electron irradiation in single-wall nanotubes, we have performed tight-binding molecular dynamics simulations (TBMD) [3]. In this approach, we used an energy functional and parametrization which proved to be successful in the modeling of the different allotropic forms of carbon and various carbon-based systems [4]. Although the TBMD is not as accurate as *ab initio* molecular dynamics calculations [5], 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.

2. SURFACE RECONSTRUCTION OF NANOTUBES

Continuous atom removal from the surface of an isolated nanotube could hence either leave highly unstable nanotube structure of the original diameter or could shrink by mending these holes through atomic rearrangements which should necessarily be constrained to the mono-atomic layer. Our experimental observation [6] 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. 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 to compare to the shape of the simulated tubes. But the overall shape of the tube remains cylindrical,

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even for the smallest tube observed (Fig.1e). Continued irradiation results in the breakage of the tube (Fig.1f). We speculate that the limiting case of this observation is the formation of atomic chains made of linear arrays of carbon atoms. 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.

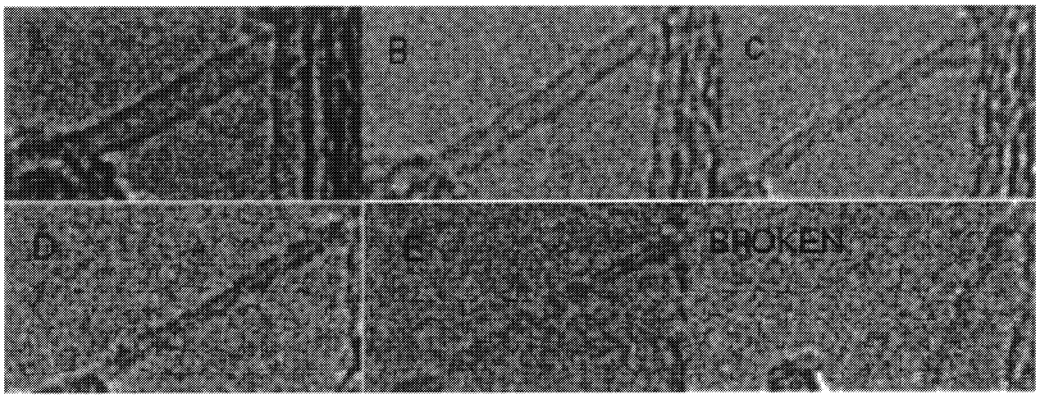

Figure 1: Controlled electron irradiation of a single-wall nanotube segment bridged between a hole in a carbon grid. The time difference between each frame of this sequence is about 5 minutes. The diameter of the original nanotube (a) is approximately 1.4 *n*m. Notice that the tube has shrunk drastically in diameter during the irradiation. Image in (e) shows the smallest diameter (~0.4 nm) that was visible before the tube broke (f).

The first quantum molecular dynamics simulation consists in homogeneously extracting carbon atoms from a perfect (10,10) carbon nanotube (Fig.2a). The rate of extraction is 5 atoms per picosecond. During the course of the simulation, most of the holes, produced by vacancy creation in the lattice, mend as two-coordinate carbon atoms (in black, Fig.2a) try to recombine, thus forming a mainly three-coordinate highly defective carbon network. Non-hexagonal rings like squares, pentagons, heptagons, octogons, nonogons, 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 [7], thus leading the structure to be mainly constituted of 5-, 6-, and 7-membered rings. Figure 2b 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.

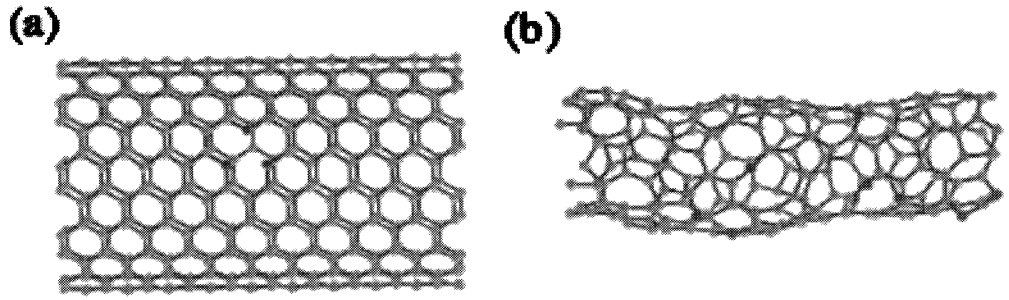

Figure 2: Surface reconstuction of a (10,10) single-wall carbon nanotube (diameter: 1.36 *n*m) after atoms extraction. The simulation starts with a first vacancy in the (10,10) nanotube (a) as a model of knock-on atomic displacement on the tube surface through irradiation. The unit cell contains 399 carbon atoms (gray, or black spheres, illustrating an atomic coordination of 3 and 2, respectively). Periodic boundary conditions are imposed along the nanotube axis. The nanotube was gradually heated up to temperature of 700K 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 higly defected, the carbon system is still a rough cylinder which diameter value is averaged around 0.7 *n*m. The number of two-coordinate carbon atoms (in black) is very small, illustrating the stability of the reconstruction as a nearly pure sp^2 disordered carbon network.

The spontaneous formation of Stone-Wales defects and its role in the strain relief mechanisms of a plastically deformed nanotubes have already been discussed [8], suggesting the role of such defects in responding to topological and dimensional changes in single-wall nanotubes. In the present simulation, the diameter of the tube shrinks from 1.36 *n*m (Fig.2a) to an average value of 0.7 *n*m (Fig.2b). Although the original hexagonal network is highly defected, the cohesive energy of this reconstructed narrow nanotube is only reduced 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 simulation (video sequences) we find a a peculiar reconstruction which appears very often (Fig.3). The removal of any C atoms in a hexagonal network implies the creation of 3 two-coordinated C atoms (in black, Fig.3a). This situation is really unstable, and most of the time two of these "dangling bond" (DB) atoms recombine, thus creating a pentagon (Fig.3b). This is really frequent, and it is clearly a dominant scenario that makes the tube shrink. This reconstituted surface is quite stable, and can wait for a second extraction of C atom from the neighborhood. Or, the last remaining DB atom can attach to the opposite pentagon, thus creating a metastable situation (Fig.3c) where a C atoms is four-fold coordinated. This situation is clearly unstable. The DB atom can either directly come back to the starting point (Fig.3b) or move at the surface of the nanotube (as in Fig.3d) by destroying and reforming a pentagon.

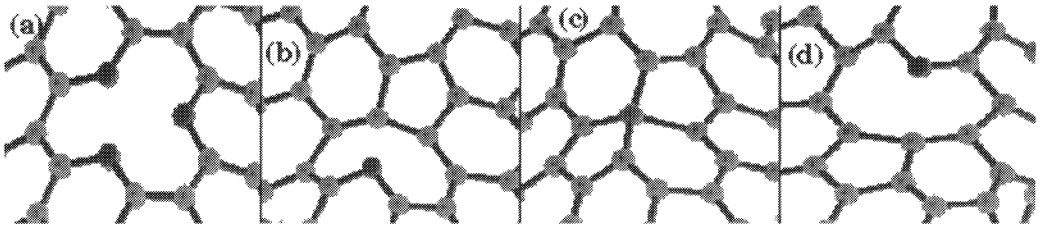

Figure 3: Microscopic mechanism for dangling bond saturation after atom extraction, illustrated at the surface of a (10,10) nanotube (dark grey spheres corresponding to dangling bonds). (a) Vacancy creation: three dangling bonds are produced. (b) Pentagon creation: two dangling bonds recombine. (c) Creation of a four-coordinate carbon atom which completely connect the network (transition state), before leading to (d) the motion of the pentagon at the nanotube surface.

This motion of DB atoms is really interesting because it increases the radius of interaction for the surface reconstruction in regions with large number 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 already 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 the tube closure [9]. If atom extraction occurs nonuniformly, the structure undergoes severe local deformation (necking) that will be useful in nano-welding as explained in section 4.

3. COALESCENCE OF NANOTUBES

Single-wall carbon nanotubes are large molecular assemblies consisting of several thousand atoms, which basic structure is made of seamless cylinders of sp^2-like carbon. The driving force for coalescence of supramolecular structures is the reduction in surface and strain energy, however high energy barriers may have to be overcome, particularly in the case of supramolecular systems where factors such as bond rigidity and rotation, structural geometry and atomic mobility play an important role. However, the possibility of coalescence between these massive molecular structures when they are annealed at high temperatures in the presence of hydrogen has been suggested [10]. In this paper, the coalescence of single-wall carbon nanotubes by in-situ irradiation and heating in a high resolution transmission electron microscope (HRTEM) is considered in detail, as well as the possible atomisitic mechanisms leading to the merger.

In our HRTEM experiment [11], the coalescence was promoted by electron irradiation and observed instantaneously on various occasions. In some cases, the events occur faster than the time resolution (approximately 1/10 seconds) of the real time TV-rate video camera of the electron microscope. In Fig.4, two of the several nanotubes present in the bundle coalesced rapidly into a larger diameter cylinder of nearly double the circumference (four times the cross section). Such processes were frequently observed at the edge of a bundle, probably because free space is needed to establish the merger. It is also hard to observe clearly any coalescence taking place in the interior of the bundles due to nanotube multidirectional overlapping, which reduces image contrast during observation.

In an earlier report of nanotube coalescence [10] it was suggested that the hydrogen present during annealing attacks the sides of the nanotubes, thus breaking a C-C bond and producing defective sites (vacancies and dangling bonds) which join together locally forming a seamless bridge. The propagation of this bridge would then open up the tube like a zipper [10]. In our experiments there are no gaseous species present but alternatively electron irradiation produces vacancies in the network which are responsible for promoting tube coalescence.

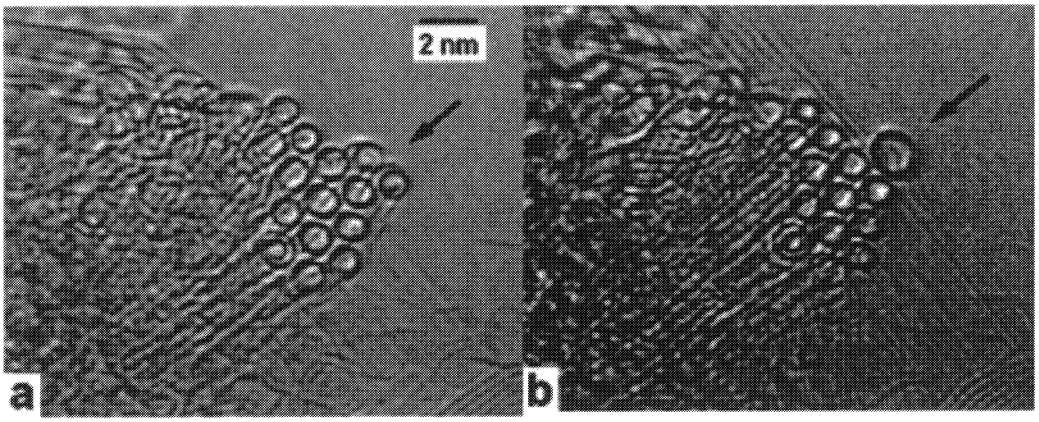

Figure 4: HRTEM images of a SWNT rope cross-section, consisting of *ca.* 15 nanotubes. The cross-sections of the tubes are seen where the tube axis is aligned along the viewing direction (direction of the electron beam). (a) Starting bundle and (b) bundle after a few seconds of high intensity electron irradiation (1.25 MeV) at 800°C. In (b) two of the outer tubes (each approximately 1.1 – 1.2 nm diameter) have coalesced into a larger one of *ca.* 1.8 – 2.0 nm diameter.

Tight-binding molecular dynamics calculations [3,4] were performed to investigate the structural stability and dynamical behavior during nanotube coalescence. Two adjacent (10,10) nanotubes, containing random vacancies and dangling bonds, along the nearest-neighboring edge, coalesced into a unique single-wall tube at 1000°C (Fig.5). The simulation starts with the creation of vacancies in two adjacent nanotubes so that coalescence is stimulated (Fig.5a). In this case, the number of vacancies is only about 2.5 % of defects within the cell, which can be easily produced in our irradiation experiments. The two adjacent tubes were heated up to 1000°C so that the creation of tube interconnections on their surface is accelerated. After 100 ps, a connection between the two tubes was established (Fig.5b) and a zipper-like mechanism proceeded to anneal the structures. Figure 5c reveals that the tubes have coalesced after 150 ps into a larger tubule of about 2.6 nm diameter. The reconstructed surface after coalescence contains some remaining vacancies (dangling bonds), but the time scale of our simulation prevented us from studying the further evolution of the atomic structure of this coalesced tube. In addition, the small number of two-coordinate (12 dangling bonds) and four-coordinate (only 1) carbon atoms demonstrate the stability of this nearly pure sp^2 cylindrical carbon network.

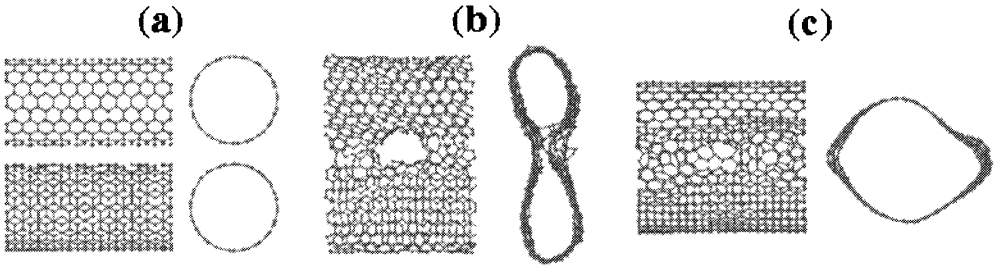

Figure 5: Sequences of coalescence (side and sectional views) between two adjacent (10,10) carbon nanotubes (diameter: 1.36 nm) into a unique single-wall tube of larger diameter. The simulation starts with the creation of 20 vacancies in the lattices of the two tubes (about 2.5 % of defects within the cell), in a localized neighboring region, in order to promote coalescence (a). The unit cell contains 820 carbon atoms. Periodic boundary conditions are imposed along the nanotube axis. 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 150 ps. The two nanotubes were gradually heated up to temperature of 1000°C in order to accelerate the creation of inter-links and the surface reconstruction. (b) After 100ps, the connection between the two carbon networks has been formed and the "zipping" mechanism is proceeding. (c) After 150ps, the coalescence is completed. The carbon system is now a cylinder with a diameter about 2.6 nm.

In our experiments, electron irradiation removes carbon atoms from their lattice sites in the nanotube by knock-on displacements [6,12]. Under the conditions of the present experiment, each carbon atom is displaced approximately every 100 seconds. The atoms can either be ejected from the tube or migrate as interstitials along the inner or outer surface. The high specimen temperature in this experiment ensures a high mobility of interstitials and hence rapid annealing of defects. The process of radiation damage and annealing kinetics in carbon nanostructures is described in detail in Ref. [12]. Due to the dangling bonds associated with the radiation induced vacancies, the carbon system will become energetically unstable. If the irradiated tube is isolated, it will shrink by mending these holes through atomic rearrangements, leading to surface reconstruction and dimensional changes [6], as illustrated in section 2. On the other hand, when assembled in bundles, the irradiated tube(s) will establish links in order to satisfy most of the dangling bonds. This coalescence phenomenon is also driven by strain energy minimization so that stable tubules of larger diameter are created [13]. Our TBMD simulations confirm that coalescence is catalyzed by the presence of dangling bonds and follows a "zipping" process.

4. NANO-WELDING OF CARBON NANOTUBES

Due to the remarkable electronic and mechanical properties of single-wall carbon nanotubes [2], various applications for these in nanoscale devices have been described [14]. However, little progress has been reported on techniques related to connecting such tubular structures. The latter is a key issue because both electronic devices and strong nano-mechanical systems need connections among the tubes. In particular, theory predicts that a "Y" or a "T" junction could act as multi-terminal electronic device involving single-wall nanotubes [15]. Therefore, it is imperative to join and connect nanotubes in a controllable way. In this account, controlled electron beam exposure at elevated temperatures is shown to be capable of forming "X", "Y", and "T" nanotube molecular junctions [16].

In our experiments, single-wall nanotubes were dispersed ultrasonically in ethanol and deposited onto holey carbon grids for transmission electron microscopy (TEM) observations. Observations were performed under a high-voltage of 1.25MeV at specimen temperatures of 800°C. From the random criss-crossing distribution of individual nanotubes and nanotube bundles on the specimen grid, several contact points could be identified where tubes were crossing and *"touching"* each other. These arrangements were selected and observed under controlled electron beam conditions. After a few minutes of irradiating two crossing tubes (Fig.6a), their merging was observed at the point of contact, resulting in the formation of a junction with an "X"-shape (Fig.6b). In other words, the tubes were welded together under the influence of electron irradiation and annealing at their contact region. During the junction formation, the upper "arms" of the X-junction cross over and protrude out of the plane. This is depicted schematically in the inset of Fig.6. From our direct observations, we conclude that it is possible to join two SWNTs of different diameter perfectly through the formation of a stable junction. Further manipulation of the ready-formed "X-junctions" is thus used to create "Y" (Fig.6c) and "T" (Fig.6d) molecular connections. By using careful conditions of irradiation, we are able to remove one of the "arms" of "X" junction in order to create a "Y" or "T" molecular device. This indicates that controlled electron irradiation is able to tailor the transformation of the junction geometry; this tool may be used to generate "nano-devices" with three, four or more terminals. It needs to be pointed our that the angle between the tubes cannot be measured directly here because we obtain only a projection of the junction in the image plane. It is noteworthy that these molecular geometries remain stable over a surprisingly long period of irradiation. We should also note that the tube diameters within the junction are different.

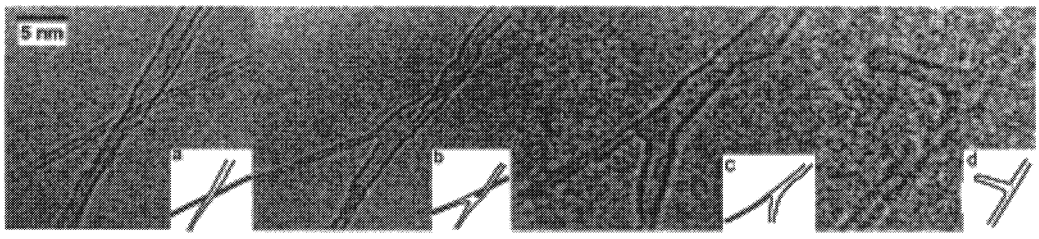

Figure 6: HRTEM images of single-wall nanotubes welding under intense electron beam. (a) A SWNT of *ca.* 2.0 nm diameter (running from bottom-left diagonally towards top right) crossing with an individual SWNT of *ca.* 0.9 nm in diameter. (b) 60 seconds of electron irradiation promote a molecular connection between the thin and the wide tubes, forming an "X" junction. Schematics are illustrated below in order to show that this junction is twisted out of the plane. (c) a "Y" junction is created following a controlled irradiation of the "X" nano-structure. One of the arms of the "X" junction vanished due to continuous sputtering under the electron beam, and a three-terminal junction remained. Note that the junction clearly exhibits tubes of different diameters, which are molecularly joint. (d) a "T-like" junction is formed after irradiating a preformed "Y" junction.

Since the merging of crossing tubes did not occur in the absence of irradiation, we conclude that electron beam effects are responsible for the formation of the junctions. It is well known that knock-on displacements of carbon atoms, *i.e.*, the formation of vacancies and interstitials, are responsible for structural re-arrangements within graphite-like structures under high-energy particle irradiation [12]. At the high specimen temperature of 800°C in these experiments, carbon interstitials are highly mobile, leading to the annealing of vacancy-interstitial pairs before interstitial agglomerates can form. It is important to emphasize that electron irradiation at room temperature would rapidly lead to a total loss of the tubes. It has already been demonstrated in the previous section that the coalescence of individual SWNTs placed in parallel, within a bundle, can occur when vacancies are present in the tubes. Thus, we assume that in our experiments the presence of irradiation-induced vacancies within the tubes is also responsible for the formation of molecular junctions (see theoretical results below). Dangling bonds around vacancies at the point of contact of the two tubes can serve as bridges for the merging process. Rearrangement of the carbon atoms occurs so as to form heptagonal or octagonal rings introducing negative curvature regions at the common surfaces (Fig.6).

In order to understand the formation mechanism of these molecular junctions, we have carried out tight-binding molecular dynamics calculations [3,4]. The simulation of two crossing tubes under irradiation at 1000°C reveals the nanotube merging process, resulting in an almost perfect molecular junction (Fig.7). In our experiments, focused electron irradiation is known to displace carbon atoms from the tube lattice by knock-on effects. In order to include these irradiation effects in the modeling, 20 atoms were removed randomly from the lattices of the two nanotubes (Fig.7a), thus creating vacancies in the crossing region. After 10 picoseconds (ps), the crossing tubes approach each other and the dangling bonds start to connect via carbon chains. After 100 ps, the connection between the crossing tubes is clearly established, although both four-coordinate atoms and dangling bonds are still present at the intersection (Fig.7b). After 220 ps, a complete surface reconstruction takes place, leading to the creation of an "X" junction, mainly constituted by three-coordinate carbon atoms (Fig.7c). Both heptagons and octagons are observed in the reconstructed surface. The key role played by these rings is certainly to increase the energetic stability of the structure when compared to that shown in Fig.7b, as well as to introduce a smooth negative curvature in both hexagonal carbon networks. The present simulation provides a clear picture of an intermediate state of the "welding" process. The experimentally observed merging occurs on time scales of seconds or even minutes, and the calculation of the whole process, until the arrangement has reached a final and stable configuration, is too extensive to be carried out within a reasonable time scale. However, our tight binding molecular dynamics calculations confirm that vacancies and interstitials, formed under controlled electron beam exposure, trigger the formation of molecular junctions with negative surface curvature.

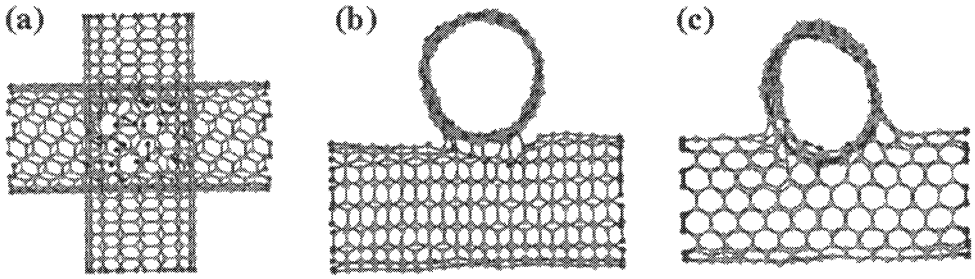

Figure 7: Sequences of merging between two crossing (8,8) carbon nanotubes (diameter *ca.* 1.1 nm) into a unique "X-like" junction. (a) The simulation starts with the random creation of 20 vacancies in the lattices of the two tubes, in the localized neighboring region, in order to promote connection (top view). The unit cell contains 860 carbon atoms (dark grey spheres indicate dangling bonds). Periodic boundary conditions are imposed along both nanotube axes. 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 220 ps. The two nanotubes were heated up to a temperature of 1000°C in order to accelerate the creation of inter-links and the surface reconstruction. (b) After 100 ps, the connection between the two tubes is established, although some four-coordinbate atoms and dangling bonds are still remaining (side view). (d) After 220 ps, a surface reconstruction occurs and the carbon system is now an "X" junction. The reconstructed surface after connection is a pure sp^2 carbon network, containing six heptagons, one octagon, one pentagon and two dangling bonds.

5. CONCLUSION

Both experimental and theoretical results indicate that an ideal shell structure like the single-wall nanotube will repond to atom loss by reconstructing its surface. In carbon structures, this happens through the familiar Stone-Wales mechanism [7]. Surprisingly, the process continues untill nanotubes of very small diameters (~0.4 nm) are produced. This 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 / 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 Stone-Wales-like and odd-membered ring defects which are seen in our simulations. The shrinking of nanotubes 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 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.

Nanotube coalescence involves various phenomena which must simultaneously occur: (a) defect generation or the presence of reactive surface sites (such as vacancies, interstitials, dangling bonds and Stone-Wales defects); (b) surface and atom reconstruction by chemical reactions (that could involve hydrogen termination) or electron irradiation processes; and (c) thermal annealing (zipping). It is highly likely that nanotubes contain as grown or irradiation induced 5-7-7-5 or similar topological defects on their surface. These regions can be easily damaged producing vacancies (dangling bonds) which will be the reactive sites that trigger coalescence; this process involves a zipping mechanism if the tubes possess the same chirality. In tubes with different chiralities, coalescence is unlikely because a large number of rearrangements of atoms needs to take place along the tube lattice. Coalescence seems thus to be restricted to tubes with the same chirality, explaining the low frequency of occurrence of this event. However, local polymerization (topologically connected structures) results in such cases. Thermal processes and sufficient available kinetic energy (through annealing) are crucial both for coalescence and the formation of interconnections between nanotubes. Therefore, controlled irradiation, or well-designed chemical reactions on carbon nanotube aggregates, followed by heat treatments, may generate fascinating interconnections.

I*n-situ* experiments demonstrate that junctions are established between individual single-wall nanotubes. Such junctions have been predicted in various theoretical works, and can indeed be fabricated using high temperature electron beam nano-welding of crossed tubes. The junctions between extremely small nanotubes are created via vacancies and interstitials, induced by the focused electron beam, that promote the formation of inter-nanotube links and negative curvature between the networks of the adjacent nanotubes. The results presented here suggest that it is now possible to construct novel nanotube networks by growing cross-linked single-wall nanotubes followed by controlled electron irradiation at high temperature. Our quantum molecular dynamics simulations of two crossing tubes demonstrate the atomic reconstructions that occur during the welding process. Finally, we believe that the nanotube network architectures, consisting of covalently joined single-wall nanotubes, may constitute the key components of carbon nanodevices and may form the ultimate carbon-carbon composites for the fabrication of fascinating carbon structures such as foams and light-weight fabrics.

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