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Self-healing in defective carbon nanotubes: a molecular dynamics study

Chen-Li Zhang and Hui-Shen Shen[1]

Department of Engineering Mechanics, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China

E-mail: hsshen@mail.sjtu.edu.cn

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Abstract

The self-healing phenomenon of defective single-walled carbon nanotubes (SWCNTs) is observed at the atomic level from a molecular dynamics (MD) simulation test. The ideal network of carbon nanotubes is unable to avoid damage under destabilizing loads at high temperature, leading to unforeseen patterns in bond breakages and vacancy defects on the wall. We observe that (10, 10) and (17, 0) carbon nanotubes containing such vacancies are energetically unstable. In the situation of unloading or increasing temperature, the local structures around the vacancies reconstruct through dangling bond saturation, forming non-hexagonal rings, 5–7–7–5 defects or an ideal graphite network. We find that a defective carbon nanotube with large vacancies is remendable, and the Stone–Wales (SW) construction is energetically preferred in self-healing processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotubes (CNTs) possess extremely high Young's modulus and strength as well as unique electronic properties due to their ideal lattice crystals of hexagonal network. These exceptional characteristics along with their low specific weight make CNTs stiff fibers for nanocomposites [1, 2] and ideal components for electromechanical devices [3, 4]. The outstanding characteristics hold for nearly perfect nanotubes. However, defects such as vacancies, dislocations and Stone–Wales (SW) constructions occur on the network, resulting in mechanical and physical degradation of CNTs to some extent. The first two defects can appear at the stages of CNT growth and purification [5, 6], and the last one is mainly observed in the CNTs under large tensile strain [7–9]. Moreover, under destabilizing loads of axial compression and/or torsion, nanotubes will suffer from plastic collapse in the form of atom rearrangements

[1] Author to whom any correspondence should be addressed.

and bond breakages, giving rise to various larger vacancies on the lattice. One can expect that the large vacancy defects on the atomic structure of CNTs will affect their characteristics more significantly compared to local point defects.

Experimental and theoretical studies have shown that the defective CNTs are energetically unstable [10–15]. The surface reconstruction and dimensional changes were observed through dangling bond saturation for an individual irradiated SWCNT [10]. It has been shown that electronic excitations can heal defects in nanotubes [12]. When assembled in bundles, the defective SWCNTs will establish links and subsequently coalesce into larger diameter nanotubes [13]. It is reported that the presence of SW sequences can cause coalescence of fullerene cages and CNTs [14]. Recent transmission electron microscope (TEM) observations indicated that nanotubes with defects of pentagons and heptagons could be cured under the excitation of current up to 2.4 μA nm^{-1} [15]. On the other hand, due to thermal oscillations of atoms and mechanical buckling, C–C bonds at high curvature on the nanotube wall are susceptible to breaking in the form of non-hexagonal vacancies and large holes. We need to know whether it is even possible for the CNTs to mend large vacancy defects in the atomic network automatically.

In the present study, molecular dynamics simulations are used to investigate the changes of the local structures around the vacancies under conditions of strain release and thermal excitation. We demonstrate self-healing of SWCNTs with defects of large holes.

2. Simulation model

In the framework of MD approaches, the interactions between carbon atoms are modeled with the reactive empirical bond order (REBO) potential [16]. This potential realistically describes binding energies, lattice constants and bond length of solid state carbon molecules. In order to obtain optimal integration of equations of motion and energy conservation, a velocity Verlet algorithm is used to integrate the equations of motion with a basic time step of 0.5 fs. We use the Nose–Hoover thermostat [17] to maintain the temperature of the nanotube system, which is suitable for the present problem since it provides good conservation of energy and leads to less fluctuation in temperature. The usage of this type of thermostat is available at a high temperature of 1800 K for strain release of carbon nanotubes [7].

The bond-breaking criterion is a crucial issue for the present study. In the original version of the REBO potential [16], energy calculations are limited for nearest-neighbor bonds by assuming the distance of 2.0 Å as the so-called cut-off distance, resulting in bond breakage for a pair of atoms with distance exceeding 2.0 Å. This cut-off scheme for CNTs works well for most equilibrium structures. However, the bond-breaking criterion is problematic in MD simulations of the fracture process since fracture properties are not usually included in a potential fitting database. Different values of cut-off distance for covalent C–C bonds in CNTs have been adopted in the literature, e.g. 1.71 Å [18], 1.77 Å [19] and a variable value between 1.8 and 1.9 Å [20], as well as different cut-off radii, 1.7, 1.95 and 2.05 Å [21]. Owing to our MD simulations, the cut-off problem of the REBO potential may result in non-physical behavior in fracture simulations; we adopt the cut-off distance as 1.85 Å [22, 23]. If a C–C bond is longer than 1.85 Å, it is assumed to be broken.

In the following, via molecular dynamics simulations, we show that SWCNTs with large vacancy defects possess an excellent self-healing mechanism. Both ends of the nanotube considered are held rigid, and the remaining atoms in the middle part are free to evolve in time. Based on studies of Mylvaganam and Zhang [24], the Nose–Hoover thermostat is applied to all atoms except the rigid ones of the nanotube so that the fluctuation in temperature is kept to within reasonable ranges. The nanotube is initially optimized and relaxed at zero temperature

to reach the minimum energy configuration. Then, in order to accelerate bond breakages and surface reconstruction processes, the nanotube is gradually heated up and allowed to move fully until the next stable configuration at 1500 K is found. An external load of axial compression or torsion is exerted on the relaxed structure to carry out the dynamic simulation, respectively, of which the variation of C–C bond lists has been carefully monitored.

3. Results and discussion

3.1. Self-healing of hole vacancies induced by buckling under axial compression

We show in panel (a) of figure 1 the postbuckling morphology of a (10, 10) armchair SWCNT that has radius 0.68 nm and length 9.26 nm. The present MD simulations give the critical buckling strain of 0.033 for a (10, 10) nanotube under axial compression at 1500 K. We observe a typical instability mode for the buckling process with three flattenings that are perpendicular to each other. As seen from panel (a), the nanotube rotates around the middle flattening at the moment of strain $\varepsilon = 0.089$, simultaneously giving rise to bond breakages in the position with high curvature. It can be seen that a 14-side vacancy is displayed on the network, resulting in the configurations with two-coordinate carbon atoms.

We first study the evolution of the structure around the vacancy under the condition of unloading. Simulation results are shown in panels (b)–(e) of figure 1. The defective (10, 10) nanotube is found to gradually return to its original length by relocating positions of carbon atoms. As the strain is reduced to 78% of the critical value (panel (b)), the vacancy structure varies by the formation of bond 1–3, transforming the 14-side hole into a heptagon connected with a nonagon vacancy. But this topological change is verified to be metastable in further formation. From stage (b) to (c), bond 1–3 as well as bonds 5–6 and 6–7 are broken, while the three bonds 2–3, 1–7 and 4–6 come into being accordingly. Then, just after the strain is reduced by 0.004, the pair of atoms 5 and 6 is observed to combine, that is shown in panel (d) (the strain is equal to 57% of the critical value). It is interesting to note that a pair of coupled pentagon–heptagons (5–7–7–5) structure is formed on the nanotube wall. This is the so-called Stone–Wales construction, which can be seen as the result of a C–C bond rotation by 90° that transforms four hexagons into two pentagons and two heptagons. This type of defect has been investigated previously [7–9, 18], and the results show that the carbon nanotube releases its excess strain via the formation of SW defects beyond a critical value of tension. In the present study, the SW construction acts as a spontaneous topological change for the repair of the vacancy. Finally, the (10, 10) tube readily recovers its straight axis while the SW construction remains unchanged after unloading, as shown in panel (e).

In the above process, the stored strain energy induces atom reconnections, forming pentagons and heptagons, thus heals the defective CNT. However, the transformation of the SW construction keeps permanent deformation in the resulting nanotube, indicating an important role of SW defects in the strain release process.

On the other hand, the large vacancy defect can be mended by thermal excitation, as shown in figure 2, of which the initial stage with a 14-side hole is equivalent to configuration (a) of figure 1. To begin with the MD simulation, both ends of the (10, 10) SWCNT for stage (a) in figure 1 are fixed to be restrained against displacement longitudinally. The tube is then relaxed at 1500 K for 40 ps. Afterward, the temperature is elevated to 1550 K and another 40 ps relaxation is carried out. Fortunately, surface reconstructions of the nanotube can be observed despite the small timescale of our MD calculations. For the simulation at 1500 K, the only change around the vacancy occurs at 36 ps by combination of atoms 1 and 3, just as for configuration (b) in figure 1. In the succeeding process at 1550 K, the nanotube is observed to

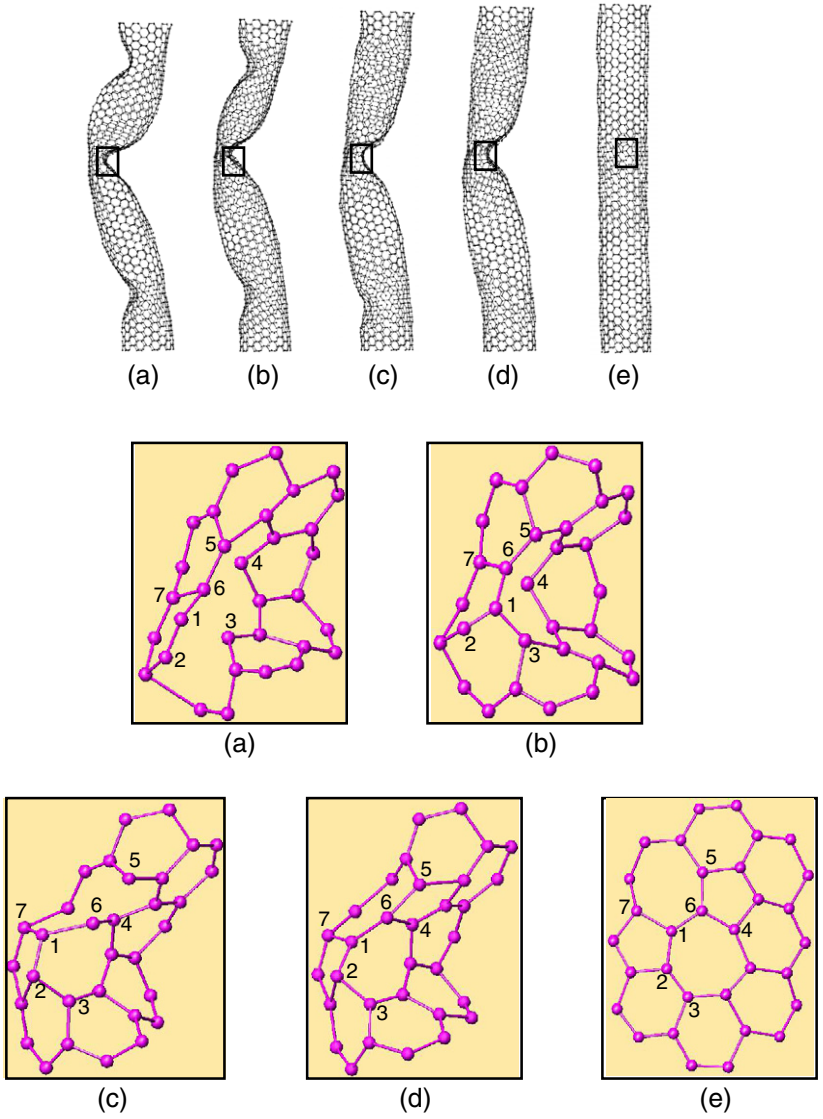

Figure 1. Self-healing of the large vacancy induced by compressive buckling during the unloading process for a (10, 10) SWCNT at 1500 K: (a) $\varepsilon = 0.089$; (b) $\varepsilon = 0.070$; (c) $\varepsilon = 0.055$; (d) $\varepsilon = 0.051$; (e) $\varepsilon = 0.0$. (a) corresponds to the postbuckling configuration with a 14-side large vacancy on the wall, (b)–(e) are the stages during the unloading process. The 14-side hole is mended and transformed to a 5–7–7–5 structure at stage (d); this structure remains unchanged until stage (e).

construct covalent bond between atoms 4 and 8 at 23 ps due to increased thermal energy, thus creating an interesting structure with bond 5–6 in front of bond 4–8 (panel (b)). Subsequently, this structure undergoes much more complex variations involving bond breakages and dangling bond saturation by sp^2 or sp^3 hybridization. Panel (c) reveals that the 14-side defect changes into a 5–7–7–5 structure after 38 ps at 1550 K, which is in the same configuration as the result in the unloading process. The nanotube framework with pure three-coordinated atoms is demonstrated to be stable during the remaining simulation time.

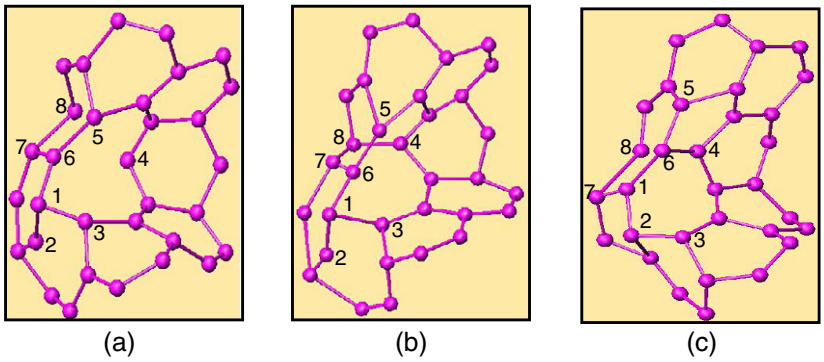

Figure 2. Self-healing of the large vacancy induced by compressive buckling under thermal excitation for a (10, 10) SWCNT: (a) 36 ps, $T = 1500$ K; (b) 23 ps, $T = 1550$ K; (c) 38 ps, $T = 1550$ K; a 5–7–7–5 structure is displayed on the tube wall. The strain is kept at $\varepsilon = 0.089$ throughout the simulation.

In order to gain more insights into the mechanism for SWCNTs to mend large vacancies, energies of different stages in figure 2 are calculated, of which the variation of energy is mainly caused by changes in the C–C bond list since the atomic coordinates are not rescaled in such simulations. At 1500 K, formation of bond 1–3 reduces the potential energy by 2.15 eV compared to the structure with a 14-side hole. At 1550 K, the energy of configuration (c) in figure 2 is lower than that of stage (b) by 4.74 eV. Accordingly, each bond recombination step decreases the total energy to reach the minimum energy structure. As expected, configuration (c) of figure 2 is the most stable one among any possible configurations with mainly three-coordinate atoms. The present simulation results demonstrate that postbuckled carbon nanotubes containing large vacancies exhibit an excellent self-healing mechanism. Induced by strain release or thermal excitation, the defective network of carbon nanotubes can be recombined and the total energy is reduced by dangling bond saturation and SW type transformation.

3.2. Self-healing of hole vacancies induced by buckling under torsion

In the buckling patterns induced by torsion deformation at 1500 K, tension conditions on the wall bulging outward will lead to a plastic phenomenon of C–C bond fracture. With definition of ϕ as the angle of twist per unit length, panel (a) of figure 3 shows the buckling configuration at the instant $\phi = 15.52^\circ$ nm^{-1} of the (10, 10) SWCNT under torsion, for which the critical angle is predicted to be 3.52° nm^{-1}. It is worth noting that the atomic network exhibits vacancies with two neighboring 10-side holes, and is linked by an atomic linear chain, thus creating the metastable situation.

From our MD simulation tests, these vacancy defects can also be mended during the unloading process, as shown in panels (b)–(d) of figure 3. Atoms 3 and 4 are combined first at the moment of $\phi = 8.85^\circ$ nm^{-1}, and bond 1–2 forms subsequently at $\phi = 4.06^\circ$ nm^{-1}, resulting in an SW type configuration on the tube wall (panel (c)). It is found that the SW construction remains unchanged until the torsional deformation is released completely. We find that the deformation and bucking behavior of SWCNTs under conditions of high temperature is beyond a reversible process. The (10, 10) nanotube readily recovers to its originally straight axis when starting the unloading after buckling, while the defects are healed by SW transformations instead of the ideal hexagonal network. This can be attributed to the

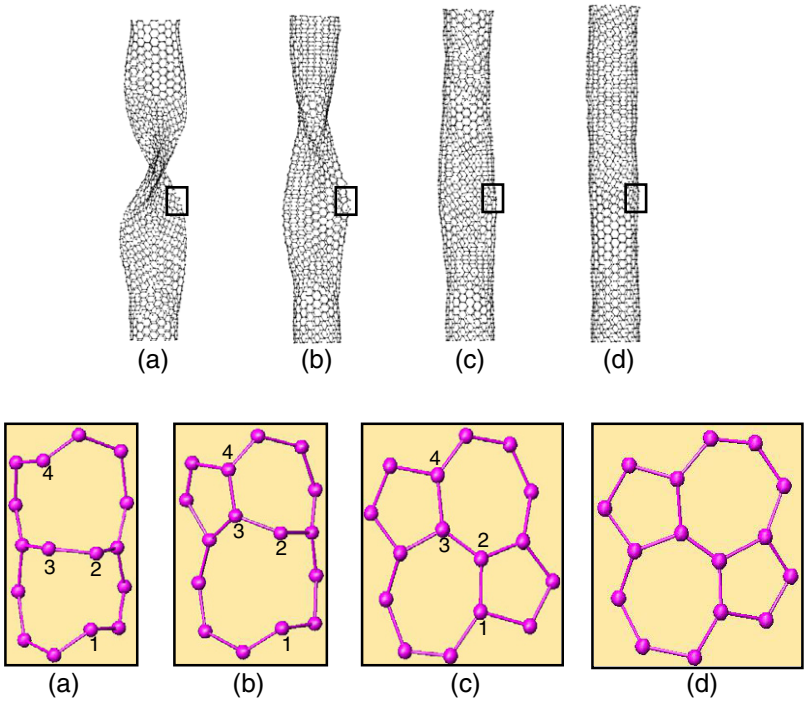

Figure 3. Self-healing of the large vacancy induced by torsional buckling during the unloading process for a (10, 10) SWCNT at 1500 K: (a) $\phi = 15.52°$ nm^{-1}; (b) $\phi = 8.85°$ nm^{-1}; (c) $\phi = 4.06°$ nm^{-1}; (d) $\phi = 0.0$. (a) corresponds to the postbuckling configuration with two neighboring 10-side large vacancies on the wall; (b)–(d) are the stages during the unloading process. The two 10-side holes are mended and transform to a 5–7–7–5 structure at stage (c); this structure remains unchanged until stage (d).

fact that the formation of SW type defects will release excess deformation for CNTs, which is in accordance with the studies of [7–9, 18].

When dynamic simulations with thermal excitation are performed on the defective (10, 10) tube after buckling under torsion, the evolution of two neighboring decagons is depicted in figure 4, where the initial defective configuration is equivalent to panel (a) of figure 3. For such a process, the defective construction becomes more metastable since increased thermal activity of carbon atoms will break the chain. However, the (10, 10) nanotube structure is stable for relaxation at 1500 and 1550 K, each for 40 ps. Thermal energy does not cause bond breakages to form larger vacancies. When the temperature is elevated to 1600 K, the nanotube begins to reconstruct covalent bonds in order to satisfy the structure. The first bond saturation happens at 20 ps. Subsequently, the defective structure transformed to an ideal hexagonal lattice at 32 ps, as shown in panel (b) of figure 4. This hexagonal network keeps unchanged for the remaining time. The variation of total energy involved in the formation of bond 2–4 is predicted to be -0.93 eV, and the reduction is 3.88 eV of configuration (b) in figure 4 compared to that of stage (a). Again, the results demonstrate that the SWCNT will respond to large vacancies by spontaneously constructing new covalent bonds to reach the minimum energy configuration.

3.3. Effect of helicity on self-healing mechanism

In order to show the effect of nanotube helicity on mending large vacancy defects, we study the zigzag (17, 0) SWCNT that has very close geometries with its counterpart (10, 10) nanotube. In

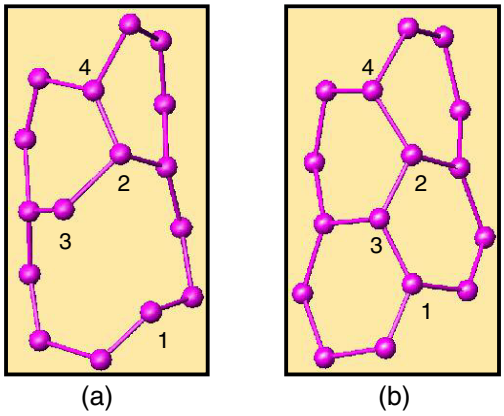

Figure 4. Self-healing of the large vacancy induced by torsional buckling under thermal excitation for (10, 10) SWCNT: (a) 20 ps, $T = 1600$ K; (b) 32 ps, $T = 1600$ K; the ideal hexagonal network is displayed on the tube wall. The twist angle is kept at $\phi = 15.52°$ nm^{-1} throughout the simulation.

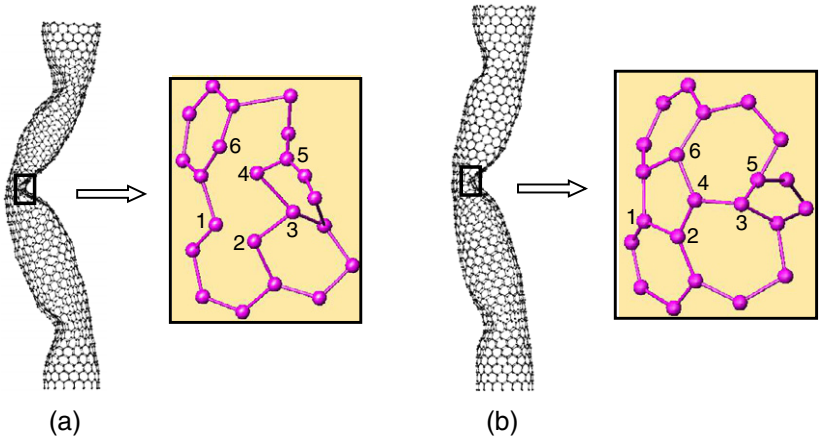

Figure 5. Self-healing of the large vacancy induced by compressive buckling during the unloading process for a (17, 0) SWCNT at 1500 K: (a) $\varepsilon = 0.098$; (b) $\varepsilon = 0.061$. (a) corresponds to the postbuckling configuration with a 14-side large vacancy on the wall. The 14-side hole is mended during the unloading process and transformed to a 5–7–7–5 structure in stage (b).

the circumstance of axial compression at 1500 K, the zigzag nanotube deforms uniformly in the initial stage and undergoes obvious morphologic changes due to occurrence of buckling at strain $\varepsilon = 0.042$. We observe bond breakages in locally flattened areas with high curvature, leading to a 14-side vacancy on the network at the moment of $\varepsilon = 0.098$, as shown in panel (a) of figure 5. MD simulations reveal that the large vacancy defect in the SWCNT arranged in zigzag chirality is also re-mendable during the unloading process. The (17, 0) tube is found to readily recover its original elongation, resulting in reconstruction of the local structure around the 14-side hole by bond breaking, rotation and dangling bond saturation. As the strain reduces to 0.061, it is noteworthy that the 14-side vacancy is healed in the form of a SW type configuration. Again, we find that the SW transformation acts as the most effective way to release excess deformations for zigzag CNTs.

MD simulation of torsional buckling gives the critical angle as 3.98° nm^{-1} for the zigzag (17, 0) nanotube. We note that two C–C bond distances exceed the cut-off radius at the moment

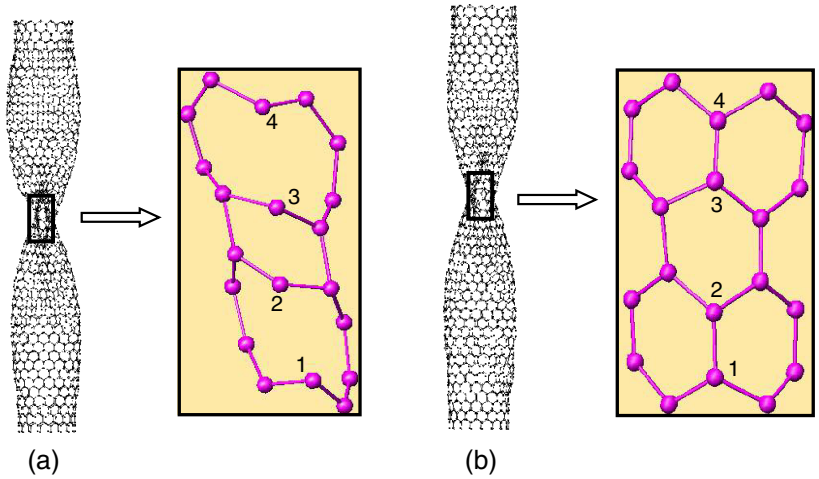

Figure 6. Self-healing of the large vacancy induced by torsional buckling during the unloading process for a (17, 0) SWCNT at 1500 K: (a) $\phi = 11.07°$ nm^{-1}; (b) $\phi = 8.52°$ nm^{-1}. (a) corresponds to the postbuckling configuration with two decagons separated by a hexagon on the wall. The defective structure is mended during the unloading process in the form of an ideal hexagonal network in stage (b).

of $\phi = 11.07°$ nm^{-1}, leading to two decagons separated by a hexagon on the wall, as shown in figure 6(a). Spontaneous healing can be observed when unloading is started after buckling. The resulting nanotube is depicted in panel (b) of figure 6, where the defective structure is mended by dangling bond saturation to construct the original hexagonal network. Unlike in the case of axial compression, no SW type transformation is found in the self-healing process, since the bond breakage pattern is different from that of the armchair SWCNT in figure 3(a).

In fact, the most likely mechanism in the self-healing process is that the stored strain energy or increased thermal activity induces surface reconstructions, thereby changing the CNT from a high-energy state to a low-energy state, which is independent of nanotube helicity. Terrones *et al* [13] observed that the presence of SW structures can result in coalescence of defective SWCNTs in both armchair and zigzag chiralities.

Taking a comparison within the different MD simulations in this paper, the SW construction is found to be energetically preferred in the self-healing processes, although there is no rigorous proof that this is universally the case. The SW transformation dominates the response of carbon nanotubes to large vacancy defects, which shows that the SW construction is very effective in releasing the excess strain. It should be mentioned that healing in carbon nanotubes is essentially stochastic due to the thermal oscillations of carbon atoms, and, therefore, the same type of vacancy defect may be mended by forming different configurations in independent simulations or experiments.

4. Conclusions

In summary, we investigate two kinds of large vacancy defect induced by compressive or torsional buckling of (10, 10) and (17, 0) SWCNTs, respectively. It is found that the defective carbon nanotube with large vacancies is re-mendable during unloading or at high temperature by spontaneously recombining dangling bonds and reducing the potential energy. We interpret the transformation of SW construction as a self-healing process, which is extremely beneficial to this nanostructure.

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