

The Role of Stone-Wales Mechanism in Self-assembly Mechanism of Annealed Carbon Peapod System

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Abstract

Double-walled carbon nanotube (DWCNT) can be synthesized by annealing carbon peapod at high temperature (at least 1000 °C) [1]. Carbon peapod is a hybrid nanostructure created by inserting fullerenes (buckyballs) into carbon nanotube. In this work, we use molecular dynamics simulations to perform the annealing process of carbon peapod into DWCNT. Due to very high annealing temperature (3500 K), there is a stage during the annealing process where the structure collapsed involving few hundreds atoms. However the nanostructure is able to self-repair itself and eventually formed a double-walled carbon nanotube. We found out that self-assembly during the annealing process is largely driven by Stone-Wales mechanisms.

Methodology

Molecular dynamics is performed with LAMMPS [2]. Adaptive intermolecular reactive empirical bond-order (AIREBO) potential [3] is employed in our simulations. AIREBO potential is defined as

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{kijl}^{TORSION} \right]$$

First term is the REBO [4] potential that describes the covalent bonds in hydrocarbon systems. Second term describes the van der Waals interaction which is similar to Lennard-Jones potential. The third term is the torsional term (disabled in this study) that describes the dihedral 4-body configuration in hydrocarbon systems. We build our carbon nanotube (12, 12) of length 137.73 Å with VMD [5] and insert it with 13 C₆₀ fullerenes. CNT (12, 12) has a diameter of 16.27 Å which allows the C₆₀ molecules to have some space to move along the radial plane (x-y plane). Periodic boundary condition is set along the CNT tubular axis (z-axis) where the length of the simulation box size is calculated such that the outer CNT represents a CNT with infinite length. We then anneal the system at 3500 K for 100 ns with a time step of 0.5 fs. The simulation took about 2 weeks to complete on a computer cluster with 48 Intel Xeon CPU connected with InfiniBand.

Carbon Peapod to DWCNT

Experimental work [1] showed that it is possible to synthesize a DWCNT by annealing a carbon peapod. Studies have shown that the required mechanism is the coalescences of C₆₀ molecules to form an encapsulated CNT with both ends capped. The dimension of the outer CNT also determine the diameter of the inner CNT. Using the methodology mentioned above, we are able to simulate the annealing process of a carbon peapod into DWCNT. The annealing process starts with the carbon peapod being equilibrated at 300 K for 100 ps. The temperature is then increased to 3500 K in 175 ps. The carbon peapod was then heated at constant temperature of 3500 K for 100 ns. At the final stage, the annealed system was cooled down to 300 K in 175 ps and further equilibrated for 100 ps.

We have chosen 5 simulation frames to show the different stages of the annealing process in our work. Fig. 1(a) shows the configuration of a carbon peapod at room temperature. The C₆₀ molecules can move freely within the outer CNT along the z-axis. Once the temperature is increased to 3500 K and maintain so for 5 ns, we can observe all 13 C₆₀ molecules are joined together to form a CNT. In Fig. 1(b), the CNT is shaped like an elongated peanut which means that the coalescences of the C₆₀ molecules is not thorough. This is particularly visible at both ends where they still looked like balls and are barely bonded at one end. Fig. 1(c) shows an unexpected defect which is most likely due to the high annealing temperature resulting in unstable structure. In Fig. 1(d), we can see that the inner CNT is repaired through self-assembly. At this stage, the repair is almost completed as the open(hollow) end observed in Fig. 1(c) is closed and only a few bonds remained between inner CNT and outer CNT. Fig. 1(e) shows the final result of the annealing simulations. At room temperature, a stable DWCNT is obtained with a high quality inner CNT which is capped at both ends.

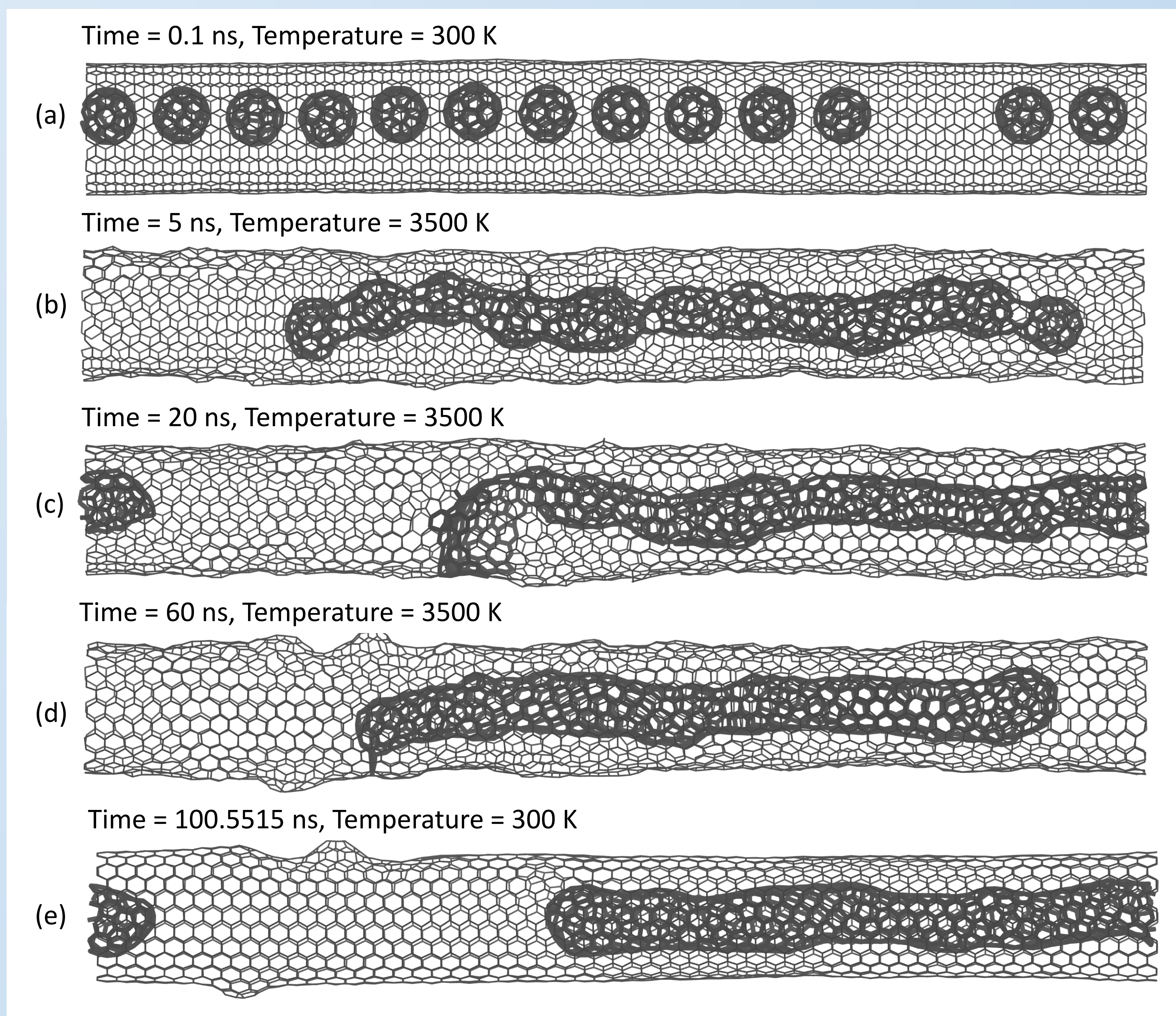


Figure 1 Annealing process of 13 C₆₀@CNT (12, 12) shown in chronological order. (a) The studied carbon peapod structure is shown here. 13 C₆₀ molecules are roaming freely within the CNT when it is at room temperature (300 K). (b) The carbon peapod has been annealed for 5 ns at 3500 K. All 13 C₆₀ molecules are fused to form a crudely shaped CNT. (c) Defect due to the collapsed structure is observable here. The inner CNT is found to have bonded with the outer CNT and has an open end. Please refer to the presenter for an interactive 3d illustration of the defect. (d) The inner CNT has recovered almost completely through self-assembly. (e) A DWCNT without major defect is observed. This is also the final simulation frame.

Stone-Wales Defects

Stone-Wales defects is a type of crystallographic defects where two π-bonded carbon atoms in a four-hexagon molecule rotated by 90° and form two pentagon-heptagon pairs rather than four hexagon pairs. There are a few types of Stone-Wales rotations and all rotations involves changes of hexagons rings into heptagon/pentagons rings and vice versa. Stone-Wales defects are observed in graphene, carbon nanotubes and similar carbon structures.

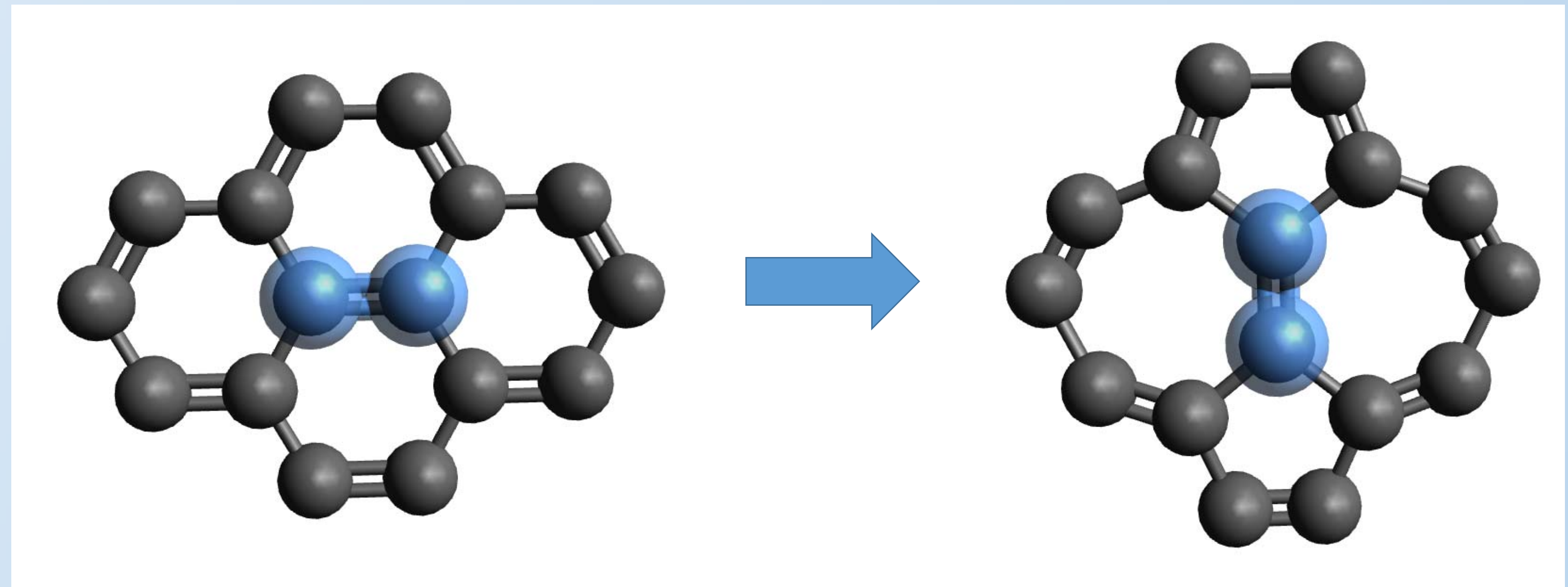


Figure 2 Stone-Wales defect is shown here with the two highlighted carbon atoms being rotated by 90°. The rearrangement is associated with changes of many properties in graphene and carbon nanotubes.

Self-assembly Mechanism

After defect was formed at 15 ns mark, the structure goes through a self-assembly process that restructures itself into a DWCNT with inner CNT capped on both ends. We found that the self-assembly involves Stone-Wales rotations which allow pentagon/heptagon rings to rotate and change the topology near the edge of the defect. Due to their respective Gaussian curvatures, the pentagon/heptagon rings rotations give rise to the change of topology in the structure where the uncapped end of the inner CNT closes up and also detached itself from the outer CNT.

We can observe the role of Stone-Wales rotations in the self-assembly process in this particular series of atomic rearrangement shown in Fig. 3. If we look at the atomic rearrangement from topological point of view involving just the 10 labelled carbon atoms in Fig. 3(a), the initial net Gaussian curvature is negative contributed by the heptagon ring. After going through rearrangement of the carbon atoms, we ended up getting hexagon/hexagon pair in Fig. 3(d) which produces net zero Gaussian curvature. The increment of Gaussian curvature is required for the structure to close up according to Euler's characteristic. We can also observe that the total atoms at the open edge are reduced from 7 in Fig. 3(a) (atom 1-7) to 4 atoms in Fig. 3(b) (atom 1, 5-7). This indicates that less atoms are contributing to the defect after the self-assembly process.

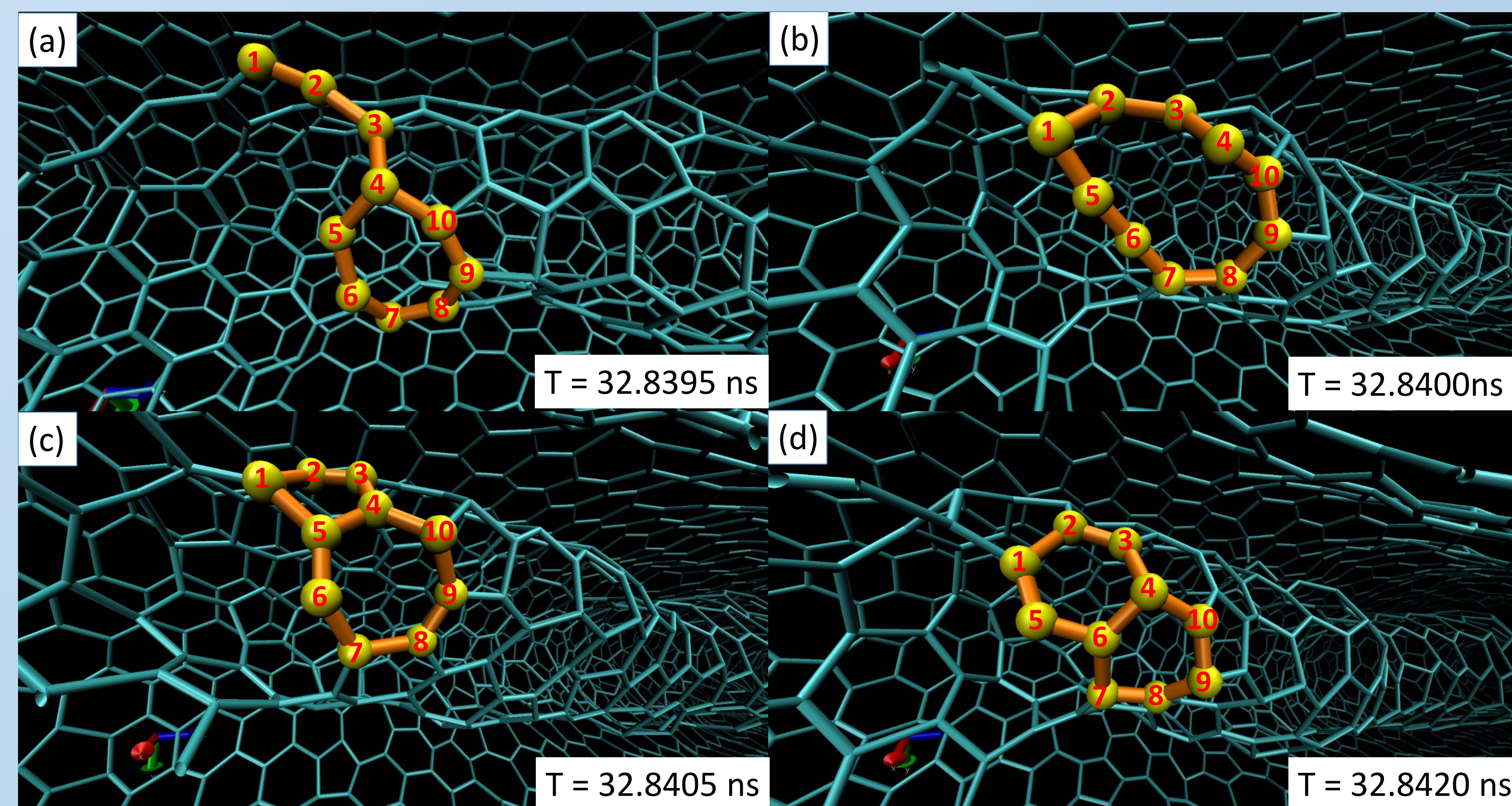


Figure 3 Self-assembly driven by Stone-Wales mechanism is shown here through a series of atomic rearrangement. (a) Heptagon ring is highlighted together with three atoms at the edge of the open “wound” of the inner CNT. (b) The ten atoms formed a temporary decagon ring. (c) The decagon ring is then reduced to pentagon/heptagon pair. (d) Heptagon/pentagon pair changed to hexagon/hexagon pair due to Stone-Wales rotation.

Conclusions

Carbon peapod collapsed when undergoes annealing at very high temperature (3500 K). The defect has made an initially encapsulated inner CNT being open at one end and bonded to the outer CNT. However self-assembly driven by Stone-Wales mechanism is shown to have “sew” up the open part of the inner CNT and detached itself from the outer CNT. In this particular self-assembly example shown above, the heptagon ring and the three carbon atoms at the boundary formed a decagon which is then reduced to a pentagon/heptagon pair. Finally, the heptagon-pentagon pair changes to a more stable hexagon-hexagon pair through Stone-Wales rotation.

References

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