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Influence of Temperature and Species in the Feedstock on the Growth of Single-Wall Carbon Nanotubes *

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A molecular dynamics simulation method is used to study the growth of narrow single-wall carbon nanotubes. It is found that the growth temperature and the species of small carbon clusters in the feedstock are important for the quality of the nanotubes grown. There is a temperature range of 1000−1500 K in which the narrow armchair single-wall carbon nanotubes can grow rapidly via adduction of C_2 dimers, even without the existence of catalysts. The narrow zigzag tubes cannot keep open-ended growth. If the feedstock consists of various species of carbon clusters, the tubes cannot keep open-ended growth. At higher temperatures, the narrow nanotubes close rapidly in the noncatalytic environment, and the products grown are fullerene-like capsules.

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To fulfil the technological promises of carbon nanotubes, for instance applications in novel nanoscale materials and electronic device structures,[1−5] one should have successful ways to control the quality of the nanotubes grown. However, the growth of carbon nanotubes cannot be directly observed and the underlying microscopic mechanisms are still far from settled. Molecular dynamics simulations (MDSs) may provide important insight into the microscopic growth processes. Extensive MDSs have been performed for the growth of both single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs).[6−10] While the MDS results indicate that SWCNTs with a diameter less than ∼3 nm cannot keep growing in the typical arc discharged growth condition at 3000−4000 K, narrow SWCNTs can be well formed in metal–catalytic growth environments at a temperature of ∼1000 K. Considering possible contamination for the narrow SWCNTs grown in a metal catalyst environment, it is worthwhile searching for an alternative growth method for the narrow SWCNTs in an environment without the existence of catalysts.

The study of the closure time of the open tips of SWCNTs (Ref. 11) shows that the closure time can be expressed as an Arrhenius form. From these results, it is obvious that the narrow SWCNTs may keep open-ended growth at lower temperatures under a noncatalytic growth environment. In the present work, extensive MDSs on SWCNT growth, via collisional adduction of small carbon clusters onto the tips of open-ended SWCNTs, have been performed in the temperature range of 1000−3300 K using a Langevin MDS scheme.[12,13] The potential used to calculate the interatomic forces was a realistic multibody potential developed by Brenner.[14] The details of the simulation method have been reported elsewhere.[15] The narrow SWCNTs examined were a model (5,5) armchair tube and a model (9,0) zigzag tube. Each tube had one of its tips capped with a hemisphere of C_{60}, while the other tip was opened. Small carbon clusters, C_2, C_3, C_6 and C were simulated to collide onto the open tip area at thermal velocities. The incident energies of the clusters were randomly selected in the range from 0.1 to 0.5 eV. Following the kinetic collision, the complex of the tube and the adatoms was annealed at a designated temperature to see the growth process. Fig. 1 shows the growth of a (5,5) armchair SWCNT through capturing and incorporating C_2 dimers, which collide onto the open tip area. The direction of the molecular axis of each incident C_2 dimer and the collision point were randomly selected. The only constraint added to the selection of the collision point was that the dimer could be captured on the tube tip upon the collision. Considering the growth of SWCNTs in a gas phase collision environment, the C_2 dimers in the feedstock should not be crowded. Therefore, in the simulation, the C_2 dimers collide onto the tip area one by one. The distance between the collision points of two consecutive collisions was larger than 2 Å.

In Fig. 1, the atoms of the C_2 dimers are represented by grey balls, while the larger solid balls and the larger open balls are the carbon atoms on the tube tip, which are most likely to be involved in the growth process. Fig. 1(a) shows that C_2 is captured by an atom on the tip of the tube upon a collision. When this tube–adatoms complex is annealed at 1000 K for 12 ps, the dangling atom of the dimer joins up with the larger solid ball, forming a hexagon, and the dimer is

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thereby assembled properly into the tube network, as shown in Fig. 1(d). Fig. 1(b) depicts a subsequent collision, showing another C_2 being captured on the tip. Annealing the complex shown in Fig. 1(b) at 1000 K for 40 ps, the dangling atom of the C_2 joins up with the larger solid ball forming a hexagon, and the C_2 is also assembled into the network, as shown in Fig. 1(e). Similarly, Fig. 1(c) shows the third collision of C_2 onto the open tip area, and Fig. 1(f) depicts the dangling atom of the C_2 joining with the solid ball to form a new hexagon after annealing at 1000 K for 20 ps. From this figure, it is obvious that the growth of the (5,5) tube via incorporation of C_2 dimers has a very clear feature. The C_2 dimers are firstly adsorbed on the open tip and then are incorporated into the six-numbered rings (6NRs) during annealing at 1000 K for a few tens of ps. The dangling atoms of the dimers preferentially join up with the larger solid balls (atoms) to form 6NRs, rather than joining up with the larger open balls (atoms) to form five-numbered rings (5NRs) or four-numbered rings (4NRs). It is easy to understand this feature, since forming 6NRs is energetically more favorable than forming 5NRs or 4NRs. We have simulated 100 events of these kinds of collisions and annealing runs in a temperature range of 1000−1500 K. We find that 97 events have the same growth mode as that shown in Fig. 1. Since SWCNTs should remain open during growth,[16] and the growth mode shown in Fig. 1 keeps the tip of the tube opened, it indicates that the narrow armchair SWCNTs can grow continuously in the environment without the existence of catalysts. In this temperature range, the tube growth proceeds in a very simple mode, in which the adatoms just join with atoms on the tube tip to reduce the number of dangling bonds through the formation of 6NRs. There is no bond breaking or reforming process. The adsorbed C_2 dimer is self-assembled into the network of the armchair tube. However, when the temperature is higher than 2500 K, bond breaking and reforming can appear in a timescale of a few ps. This reconstruction can result in pentagons. Adjacent pentagons cause the tube closure, and thereby stop the growth of the SWCNTs. Using other species, e.g., C_3, C_6 or C, we find that the narrow armchair tube cannot keep growth in an open-ended mode.

Fig. 2(a) shows a branch-shape complex formed by six C_3 trimers, six C_2 dimers and five C_6 clusters colliding on a model (5,5) armchair tube. In order to get the adsorbed branches to be incorporated into the tube segment, the complex is annealed at 3000 K for 50 ps, and then is annealed at 3300 K for 40 ps. Upon these annealing runs, we obtain a cluster, as shown in Fig. 2(b). Then this cluster is annealed at 3000 K for 50 ps and is followed by a long time annealing at 2000 K for 500 ps to obtain a fullerene-like capsule, as shown in Fig. 2(c). From this figure, it is obvious that when the feedstock consists of various cluster species, the SWCNTs cannot keep open-ended growth in the noncatalytic environment. The higher temperature needed to incorporate the adsorbed atoms is likely to form higher fullerene-like products.

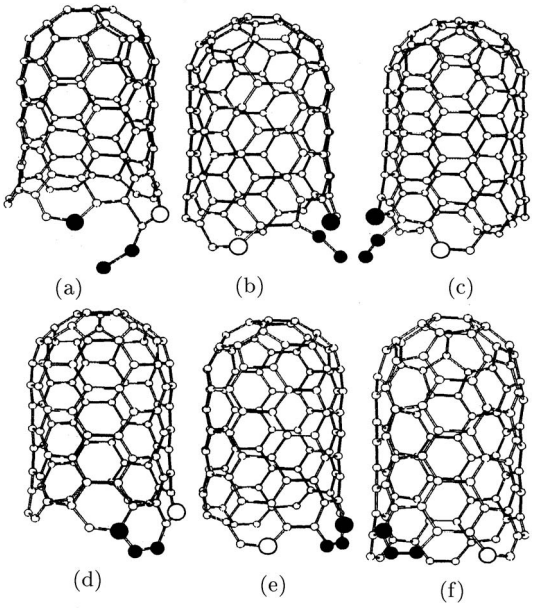


Fig. 1. Growth of a (5,5) armchair SWCNT at 1000 K through the assembly of C_2 dimers which collide at thermal velocity onto the open end of the tube in random collisional directions.

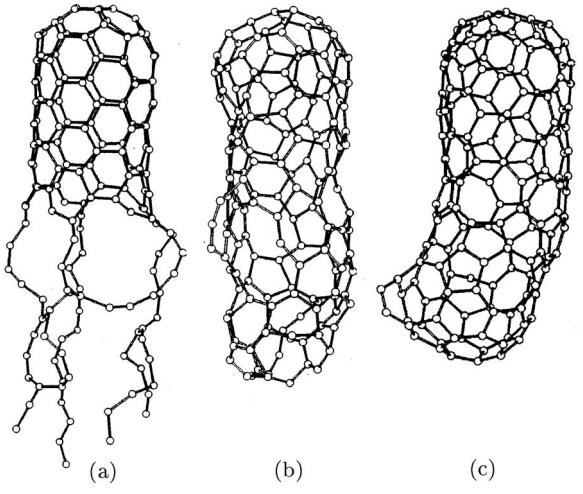


Fig. 2. Growth of a (5,5) armchair tube via deposition of different cluster species onto the open end of the tube. (a) C_2, C_3, and C_6 clusters consecutively deposited on the tip area to form a branch shape complex. (b) The complex is annealed at 3000 K and 3300 K to have the branches to be incorporated into the network. (c) The fullerene-like cluster formed in a long time annealing at 2000 K.

Fig. 3 shows the simulated growth process of a (9,0) zigzag SWCNT via capturing and incorporating C_3 trimers, which are represented by the grey balls. Fig. 3(a) shows C_3 is captured on the tube tip upon the collision. Annealing the tube–adatoms

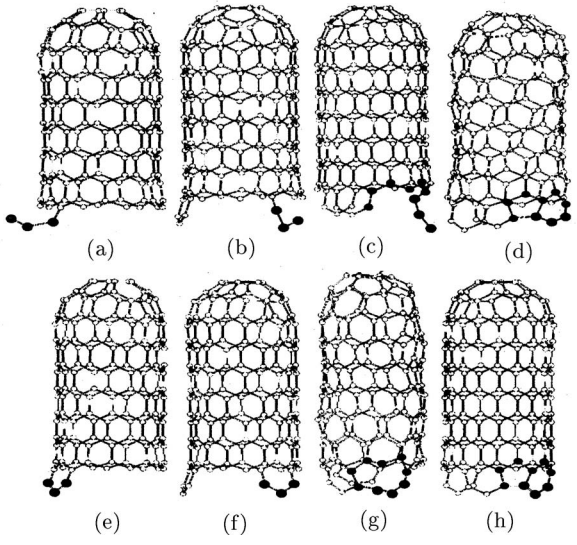


Fig. 3. Growth of a (9,0) SWCNT at 1300−1500 K through incorporation of C_3 trimers which collide at thermal velocity onto the open end of the tube in random collisional directions, showing a pentagon formed on the tip by consecutive collision and annealing runs.

complex at 1300 K for 80 ps, the C_3 trimer is properly assembled into the hexagonal network of the zigzag tube, as shown in Fig. 3(e). Fig. 3(b) depicts a tube–adatoms complex formed by a subsequent C_3 collision, while Fig. 3(f) shows the product formed by annealing the complex at 1400 K for 100 ps to have the C_3 perfectly assembled into the network of the tube. However, when another C_3 collides onto the tube tip, we obtain a complex as shown in Fig. 3(c). Annealing the complex at 1400 K for 12 ps, the dangling atom of C_3 joins up with an atom that was just assembled into the network in the previous collision and annealing run, forming a larger nine-numbered ring (9NR), as shown in Fig. 3(g). After further annealing the product, shown in Fig. 3(g), at 1500 K for 80 ps, two of the atoms in the 9NR join up with each other forming a 6NR–5NR pair, as shown in Fig. 3(d). In order to see the 6NR–5NR pair more clearly, the tube shown in Fig. 3(d) was cooled from 1500 K to 300 K, obtaining smoother tube, as shown in Fig. 3(h). The formed pentagon (5NR) makes the tube tip start to curve inward. Subsequent deposition of C_3 on the tip area will initiate the tip closure. From this figure, it is obvious that the narrow zigzag tube does not keep growing continuously although some of the deposited C_3 trimers can be properly assembled into the network of the tube. Using other species as the incident cluster, the tip of the zigzag tube is closed more rapidly upon continuous deposition of the clusters. Therefore, the narrow zigzag SWCNTs cannot grow in the open-ended mode in the noncatalytic environment. From the present work, it is seen that there is a temperature range of 1000−1500 K, in which narrow armchair SWCNTs can grow rapidly via adduction of C_2 dimers in an environment without the existence of catalysts. If one can pursue a mass selection method to choose C_2 dimers from the gas phase feedstock as the deposition species, then a rapid growth of high quality narrow armchair SWCNTs in a pure carbon environment is possible. However, the growth rate may be lower than that obtainable under the metal–catalytic condition. This problem may be solved through optimizing the density of the feedstock.

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