



Research paper

Molecular dynamics simulations of the morphology transformations in unzipped carbon nanotubes

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ABSTRACT

Tuning the assembly of carbon nanomaterials to obtain a kaleidoscope of carbon nanostructures is very important and challenging for the development of nanotechnology. Using molecular dynamics simulations method, we studied the morphology transformations of unzipped CNTs with different unzipping patterns. By modulating the unzipping patterns, the CNTs could self-assemble forming graphene nanoribbons and carbon nanoscrolls. From the energy analysis, we find that the van der Waals interactions are responsible for the assembly of the unzipped CNTs. This unusual self-assembling method for CNTs could provide clues for further studies on the design of novel nanostructures.

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1. Introduction

Over the past decade, carbon nanomaterials such as carbon nanotubes (CNTs) [1], graphenes (GNs) [2] and fullerene (C60) [3] have been widely studied due to their remarkable mechanical, chemical and physical properties [4–6], and therefore, these carbon nanomaterials suggest extensively promising applications in sensors [7,8], separation [9,10], biological medicine [11,12], etc. However, the structural features of the carbon nanomaterials always determine their properties and the corresponding applications. Therefore, developing the preparation methods and enriching the structures of carbon nanomaterials have attracted great interests [13–15].

Up to now, new carbon nanostructures are continuously emerging, for example, carbon 'onions' [16], helical CNTs [17], carbon nanohorns [18], etc. Furthermore, enriching the carbon nanostructures through assembly of the structural motif of carbon nanomaterials (GNs, CNTs, C60) has also been proved to be a superb strategy, and a number of experiments and computational predictions have been carried out on this topic [19–23], in particular, for the assembly of GN nanoribbons (GNRs). For example, Král et al. [24] showed their computational works on the self-assembly of GNRs on nanotubes, in which the nanotubes

could induce bending, folding, sliding, and rolling of the GNRs leading to stable nanostructures of GN rings, helices, and knots.

Recently, longitudinal unzipping CNTs have been proved to be an effective method to produce high-quality and high-yield GNRs. Kosynkin et al. [25] described a simple solution-based oxidative process for producing a nearly 100% yield of nanoribbon structures by lengthwise cutting and unravelling of multi-walled carbon nanotube (MWCNT) side walls. Jiao et al. [26] also proposed an approach to making GNRs with smooth edges and controllable widths by unzipping MWCNT through plasma etching of nanotubes partly embedded in a polymer film. Apart from CNTs, the unzipping methods might also be implemented in other carbon nanomaterials, and through regulating the unzipping patterns, many other novel carbon nanostructures might be obtained. In fact, a number of computational works have successfully predicted the feasibility to produce carbon nanostructures through unzipping carbon nanomaterials, and many functionalized carbon nanostructures or nanodevices such as carbon nanocages, CNRs, GN origami have been developed [27–30]. In our previous study [31], we also proposed the self-assembly of unzipped GNs, and by modulating the unzipping patterns, many novel carbon nanostructures such as carbon nanopocket, nanoparcel, nanofunnel and nanocone were obtained.

Therefore, we considered that by unzipping CNTs, they could also self-assembly forming other carbon nanostructures. However, as far as we know, this part of investigation is still missing. Aiming to uncover the self-assembly structures of unzipped CNTs, we conducted this work. In this study, utilizing molecular dynamics (MD)

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simulations method, we studied the self-assembly and polymorphic transitions of unzipped CNTs. And by modulating the unzipping patterns, a series of scrolled carbon nanostructures were obtained. This work is hoped to stimulate further studies on the self-assembly of carbon nanomaterials and their emerging applications.

2. Simulation and method

All the MD simulations were performed using the Discover code in Materials Studio software. For the interatomic interactions, the force field of Condensed-Phase-Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) [32] was applied. This was the first ab initio force field that was parametrized and validated using condensed-phase properties in addition to various ab initio and empirical data. It has been proven to be adequate to model the properties of CNTs [33–35]. The force field was expressed as a sum of valence, cross-terms, and nonbonding interactions (Eq. (1)):

$$E_{total} = E_{valence} + E_{cross-term} + E_{nonbond} \quad (1)$$

$$E_{nonbond} = E_{vdW} + E_{Coulomb} \quad (2)$$

$$E_{vdW} = \sum l_{ij} \left[2 \left(\frac{r_0}{r_{ij}} \right)^9 - 3 \left(\frac{r_0}{r_{ij}} \right)^6 \right] \quad E_{Coulomb} = \sum_{i>j} \frac{q_i q_j}{r_{ij}} \quad (3)$$

The valence energy, $E_{valence}$, generally includes bond stretching energy, valence angle bending energy and dihedral angle torsion energy. The cross-term interacting energy, $E_{cross-term}$, accounts for the effects such as bond lengths and angles changes caused by the surrounding atoms to accurately reproduce the dynamic properties of molecules. The nonbonding interaction term (Eq. (2)), $E_{nonbond}$, accounts for the interactions between nonbonding atoms and includes the van der Waals energy, E_{vdW} , and the Coulomb electrostatic energy, $E_{Coulomb}$. Eq. (3) shows the detailed E_{vdW} and $E_{Coulomb}$. Herein, q is the atomic charge, r_{ij} is the i - j atomic separation distance, and l_{ij} is the off-diagonal parameter. These parameters are fitted from quantum mechanics calculations and implement into the Discover module of Materials Studio.

The MD simulations were performed in periodic boundary conditions in the dimensions of $500 \times 500 \times 500 \text{ \AA}^3$. The dynamic process was conducted in NVT (the volume and the temperature were constant) ensemble at 298 K. The Andersen method [36] was employed in the thermostat to control the thermodynamic temperature and generate the correct statistical ensemble. The time step during the simulation was set as 1 fs, and the data were collected every 1 ps. All the simulations were long enough to detect several cycles of thermal vibration, and the full-precision trajectory was recorded.

3. Results and discussion

Initially, a (12, 12) carbon nanotube with length of 300 Å was constructed. Like the unzipping method in experiment, in this work, a linear fissure with zigzag edges (Fig. 1a1), a spiral fissure with armchair (Fig. 1b1), and a spiral fissure with zigzag (Fig. 1c1) edges were tailored along the lengthwise direction of the CNT, respectively. After simulations, all the systems reached its equilibrium state, and the final self-assembly configurations of the tailored CNTs are shown in Fig. 1(a2, b2, c2). During our simulation, the dangling bonds in the CNT were not terminated by other atoms. However, in a real system, the carbon atoms at ends of the CNTs are unstable and always terminated by other atoms. Actually, before our study, we first simulated the self-assembly of the unzipped CNT (length 300 Å, chirality (12, 12)) with the dangling bonds at the edges terminated by hydrogen atoms. After

simulation, we found that terminating the dangling bonds had a negligible influence on the self-assembly behavior of the CNTs. Therefore, in this work, the dangling bonds at the edges of the unzipped CNT are not terminated by other atoms.

For the tailored CNT with linear fissure, it self-assembles into a double layered nanoribbon. We also simulated the self-assembly behavior of the tailored CNT with larger diameter, and found that it would unfold and form a single layered nanoribbon, i.e. GNR. However, for the unzipped CNT with spiral fissure, an unusual self-assembly behavior is observed that it self-assembles into CNS, spontaneously (Fig. 1b2 and c2). Then, why this unusual self-assembly behavior occurs? In the following, taking the unzipped CNT in Fig. 1c1 as an example, the self-assembly process and mechanism are analyzed in detail.

3.1. The mechanism for unzipping induced self-assembly of CNTs

Firstly, the driving force for the self-assembly of the unzipped CNT is illustrated. A better understanding about the driving force for the structural transition of the unzipped CNT can be obtained from energy profiles. Therefore, we calculate the evolutions of total energy, E_{total} , and vdW interaction energy, E_{vdW} , of the whole system (Fig. 1c1) versus simulation time, shown in Fig. 2. From this figure, the decreasing E_{total} indicates that the assembly of the CNT is a spontaneous process in which the system gradually reaches to a more stable state. Meanwhile, the changes of E_{total} and E_{vdW} are nearly synchronous. Thus, we suggest that the vdW interaction offers the main driving force for the assembly of the tailored CNT, and the released E_{vdW} impels the assembly of the tailored CNT. Finally, under the vdW interaction, two connected CNSs are formed gradually. We also calculated the energy profiles for the CNTs (length 300 Å, chirality (12, 12)) with the dangling bonds terminated by hydrogen atoms, and also found that vdW interaction offer the main driving force for the assembly of the unzipped CNT.

Next, in order to describe the self-assembly process in detail, Fig. 3 provides the CNT snapshots at different simulation time. According to the structural transitions, we divide the self-scrolling process into five stages: initiating stage, scrolling stage, metastable stage, re-scrolling stage and equilibrium stage.

At the initiating stage, a spiral fissure is tailored on the CNT (Fig. 3a). To some extent, this fissure could be regarded as defects existing in the CNT. They would make the CNT unstable, which results in some torsion and deformation of the CNT [37,38]. It also could increase the bond stretching, angle bending and dihedral angle torsion of the C–C bonds in the CNT. As a result, the $E_{valence}$ of bond stretching energy, angle bending energy and dihedral angle torsion energy will increase, and the increased $E_{valence}$ will further lead to the increase of E_{total} . And this also explains the increase of E_{total} at initial stage in Fig. 2. Then, under the vdW interaction, the unzipped CNT would contract from two ends to middle along the lengthwise direction of the CNT. With the simulation proceeding, the assembly process goes into the scrolling stage.

Because of the unzipping, the CNT turns to be a long spiral nanoribbon. Therefore, during the scrolling stage, the tubular structure of the CNT collapses (Fig. 3b), and three CNSs are formed in the nanoribbon. During the scrolling stage, the nanoribbon connecting the CNSs of 1 and 3 will insert into the inner cavity of these two CNSs successively. This makes the CNSs expand along its radial direction continually, and then the radius of the CNSs of 1 and 3 will increase, correspondingly. For the CNS of 2, on the left, the nanoribbon will wrap this CNS from the outboard, while on the right, the nanoribbon will insert into the inner cavity of the CNS of 2.

Then, as the scrolling of the nanoribbon, these three CNSs will get closer and closer. When all of the nanoribbon scrolls into the

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