Influence of Defects on the Mechanical Performances of Super Carbon Nanotube

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Abstract: Although nanotechnology processes greatly in recent years, defects are still unavoidable in the production of CNTs and relevant structures, which remarkably reduce their theoretical high-performance. In this study, the influence of defects on the mechanical and fracture performances of SCNT, a CNT-based honeycomb structure, are investigated via molecular dynamics simulations. Defects are revealed to reduce the bearing capacities of SCNTs and the reducing degree significantly relies on both the defect position and the SCNT structure. Defects also modify the cracking path of SCNTs and slow down the fracture propagation, especially for zigzag SCNT. Essentially, defects bring force concentration near the defective area, resulting in the local early fracture. Yet the force concentration degrees of the armchair and zigzag SCNTs are affected by different mechanisms. The force concentration degree of armchair SCNT is displacement-controlled, but that of zigzag SCNT is determined by the force redistribution. The underlying reason for controlling the influence of defect is found to be the force transfer mode of the armchair and zigzag SCNT. With the fact that defects widely exit in the CNT-based networks, this investigation could provide valuable information for the practical applications of CNT-based structures.

1. Introductions

With a variety of excellent properties and promising potentials, CNT has received much attention in recent decades. One of the amazing features of CNTs is their ultra-high Young’s modulus, which can be as high as 1 TPa, according to the theoretical predictions [1]. However, such superior mechanical performances can be greatly affected by the existence of defects [2, 3], which are common and unavoidable in the production of CNTs. Vacancy defects and Stone-Wales (SW) defects are two major types of defects for CNT, which have been observed in the experiments [4]. Some other topological defects, such as helical defects [5], were also explored in terms of the newly appearing synthetic technology.

Many studies have been conducted to identify the influence of defects on the performances of CNT. For example, Hao and coworkers [6] reported that Young’s modulus of the defective graphene slightly depends on the concentration of monatomic vacancies and SW dislocations, whereas the thermal conductivity is much more sensitive to defects. Electrically, structural defects greatly affect the electrical transport properties of graphene nanostructures. According to the study of Vicarelli [7], it is
useful to control the defects of graphene to optimize the electrical performance of graphene-based nano-devices.

In addition, some investigations presented the contributions of defects on various applications of CNTs or graphene, such as catalytic activities and composite performance. Yang and coworkers [8] reported that the existence of SW defects results in better synergistic performances of CNT/graphene polymer nanocomposite by increasing the interfacial interaction energy. Besides, graphene clusters with the specific defects show electro-catalytic capability for oxygen reduction reactions, which facilitates the efficiency of fuel cells [9].

In recent years, CNTs have been applied as building blocks to fabricate a variety of 2D or 3D structures and networks. In the fabrication process, invalid connections between individual CNTs may exist, which should also be regarded as a certain kind of defect. Such defects would have a dominant influence on the various properties of CNT-based networks. Moreover, these defects are no doubt wildly existed in the production of CNT-based structures, due to the limitation of current technology. Therefore, it is necessary to explore the influence of connecting defects on the CNT-based networks.

In this study, a CNT-based hierarchical honeycomb structure, super carbon nanotube (SCNT), is investigated. As a typical CNT-based network, it is believed that the defect effect on SCNTs could provide valuable references for other CNT-based architectures. The defect effect on SCNTs will be discussed in terms of the defect position and different SCNT structures.

2. Methodology
In this study, armchair SCNT [6,6]@(6,6) and zigzag SCNT [10,0]@(6,6), are chosen to represent two typical chirality structures of SCNT, which are illustrated on the left of Figure 1 (a) and (b). In order to simplify the discussion, the CNTs with approximate length are used to fabricate the armchair and zigzag SCNTs. Based on the structure illustrated in the figures, CNTs in the armchair and zigzag SCNT structures can be divided into two groups according to the different positions. Therefore, defects are set according to the position for each SCNT model (Figure 1 (a) and (b)): diagonal-CNT defect (D-defect) and vertical-CNT defect (V-defect) for zigzag SCNT, as well as the diagonal-CNT defect (D-defect) and horizontal-CNT defect (H-defect) for armchair SCNT.

To obtain the defective SCNT models, a group of atoms at the corresponding CNT components are deleted. A proper area is chosen after a series of tests to ensure that the edge of the defective area will not be too close and will not affect the stress states of other arm tubes. After the construction of SCNT models, an energy minimization process is performed to obtain equilibrium structures. Then tensile displacements are applied along the axial direction, with one side moving at a constant rate and the
other side being constrained (Figure 2). Loading rate is set as 0.1 Å/ps, referring to the previous MD simulations about CNTs or CNT-based networks \[5, 10-13\].

According to Newton’s third law, the resultant force along the tensile direction can be obtained from the summary of the counterforce at the end of the SCNT. In order to reduce the effect of thermal fluctuation, the temperature of the simulating system is kept at 0.5 K by utilizing the Nosé-Hoover extended ensemble \[14, 15\]. Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential \[16\] is adopted to describe the interactions between carbon atoms, which has been widely applied for carbon-based materials \[17-19\]. MD simulations in this study are carried out through LAMMPS open source code \[20\].

![Figure 2. Tensile loading mode of SCNT.](image)

3. Results and discussions

3.1. Defects reduce the bearing capacities of SCNTs

Tensile force-strain curves of defective models are plotted in Figure 3 (a) and (b) for armchair and zigzag SCNT, respectively. Corresponding defect-free SCNTs are also analyzed as the reference group. The specific values and percentages can be known from Table 1 and Table 2.

![Figure 3. Force-strain curves of defective SCNTs compared with defect-free SCNTs. (a) Zigzag SCNT [10,0]@(6,6). (b) Armchair SCNT [6,6]@(6,6).](image)

From the curves, it can be seen that defects generally bring reductions of bearing capacities for armchair and zigzag SCNTs and the corresponding degrees are significantly related to the location of the defect. For zigzag SCNT (Table 1), the reductions of the bearing capacities caused by D-defect and V-defect is 8.5% and 26.1%, respectively. The latter value is three times as large as the former one. For the armchair SCNT [6,6]@(6,6) (Table 2), the occurrence of D-defect leads to 12% reduction of the ultimate values of bearing capacities, while H-defect has almost no effect on the tensile curve.
Table 1. Bearing capacities of zigzag SCNTs [10,0]@(6,6) with and without defects.

| Models   | Ultimate force (eV/Å) | Percentage |
|----------|-----------------------|------------|
| Non-defect | 788.64                | 100%       |
| D-defect  | 721.61                | 91.5%      |
| V-defect  | 582.80                | 73.9%      |

Table 2. Bearing capacities of armchair SCNTs [6,6]@(6,6) with and without defects.

| Models   | Ultimate force (eV/Å) | Percentage |
|----------|-----------------------|------------|
| Non-defect | 671.63                | 100%       |
| D-defect  | 595.74                | 88.7%      |
| H-defect  | 669.12                | 99.6%      |

3.2. Defects modify the cracking performances of SCNTs

Opposite to the reductions of bearing capacities, it should be noted that the fracture processes of SCNTs extend due to the defects, especially for zigzag SCNTs. We determine the ranges from the initial breaking of CNT to the state with 80% drop of the ultimate force, which are listed in Table 1 and Table 2 for armchair and zigzag SCNT, respectively. For zigzag SCNT, the length of fracture stage has more than 200% and 300% increments with the existence of D-defect and V-defect defects, which means the fracture propagation of zigzag SCNTs greatly slow down when defects exist. However, the extension of fracture stage is not remarkable for armchair SCNT.

Table 3. Lengths of fracture stage for zigzag SCNT [10,0]@(6,6).

| Models   | Crack strain | Length of fracture stage |
|----------|--------------|--------------------------|
| Non-defect | 44.1%        | 0.9%                     |
| D-defect  | 41.2%        | 3.8%                     |
| V-defect  | 34.2%        | 4.2%                     |

Table 4. Lengths of fracture stage for armchair SCNT [6,6]@(6,6).

| Models   | Crack strain | Length of fracture stage |
|----------|--------------|--------------------------|
| Non-defect | 31.3%        | 2.9%                     |
| D-defect  | 26.9%        | 3.9%                     |
| H-defect  | 31.1%        | 3.1%                     |

This difference may be related to the different fracture features of the defect-free models for armchair and zigzag SCNTs. Due to the different structures, zigzag SCNTs present brittle-material behaviors but armchair SCNTs are more like ductile materials, which has been reported by Qin [17]. Therefore, armchair SCNT generally has longer fracture process than zigzag SCNT. The reason for different lengths of fracture stage can be obtained from the corresponding snapshots of the armchair
and zigzag SCNT, which are illustrated in Figures 4 (a). The fracture of zigzag SCNT happens suddenly and the CNTs of the same layer break simultaneously. Nevertheless, in armchair SCNT, the crack propagates along the diagonal section with CNTs breaking one by one.

In Figure 4 (b) and (c), the cracking paths of zigzag and armchair SCNTs are presented. On the whole, the cracking paths of both armchair and zigzag SCNT do not change a lot with the existence of defects. However, there appear several local turns at the cracking paths. It is known that crack propagation is often related to the fracture energy. Based on the theory of fracture mechanics, a previous study of 2D honeycomb structures has concluded that the structure with diagonal cracking paths experience slower fracture due to larger fracture energy required for the same crack length [21]. That may be the reason for the slower fracture processes of both armchair and zigzag SCNT. Note that the length increases of fracture length generally correspond to the number of the local turns at the cracking paths. V-defect of zigzag SCNT and D-defect of armchair SCNT bring more zigzag turns along crack propagation, so they possess longer fracture process. Besides, changing from the brittle fracture to gradually crack propagation, the extension of fracture process of zigzag SCNT is more remarkable.

3.3. Different fracture mechanisms of the armchair and zigzag SCNTs induced by defects
The reductions of bearing capacities induced by defects are essentially due to the uneven distribution of forces. For both zigzag and armchair SCNTs, the internal forces of some specific components are much greater than others, which can be seen from the snapshots of MD simulations (Figure 5). This phenomenon can be regarded as the force concentration, which leads to early failure at the local area.
Under this circumstance, the internal forces of most CNT components are lower than the critical values of fracture, resulting in the lower bearing capacities of defective SCNTs. However, the force concentration degrees of the armchair and zigzag SCNTs are determined by distinct mechanisms. It is the local displacement that controls the force concentration degree of defective armchair SCNT, while different force distribution modes result in various force concentration degrees of defective zigzag SCNT.

![Figure 5. Atomistic stress distributions of defective SCNTs. (a) Zigzag SCNT [10,0]@(6,6) with V-defect and D-defect. (b) Armchair SCNT [6,6]@(6,0) with D-defect and H-defect.](image)

From the snapshots of defective armchair SCNT in Figure 5 (a), great local displacements can be observed at the defective area of D-defect model. Due to the existence of the D-defect, the components at the nearby area move remarkably as the loading increases, especially for the CNTs along the same chain. Such movements result in shear deformation at the nearby junctions. In this way, four nearest CNT components have larger internal forces than others, especially at the junction area (pointed by black arrows). However, there is no displacement of any CNT components in H-defect model and the internal forces are still uniformly distributed. As a result, the bearing capacity of armchair SCNT with D-defect reduces remarkably, but there is no reduction of bearing capacity for H-defect model.

For zigzag SCNT, however, both D-defect and H-defect models possess no displacement at the defective area, but the force distributions vary as the change of defect position. In both two models (Figure 5(b)), two CNT components possess larger internal forces, but the layout is symmetrical in V-defect model and is staggered in D-defect model. Such different modes of distribution lead to different force concentration degrees, which can be seen from the color of the internal force in two models. Apparently, the red-colored area of the D-defect model is larger and darker than that of the V-defect model, indicating the greater force concentration.

3.4. Force transfer modes of the armchair and zigzag SCNTs control the influence of defect
In fact, the essential reason controlling the influence of defect is the force transfer mode of the armchair and zigzag SCNTs. By doing the static force analysis, we can determine the internal forces in these two structures, which are illustrated in Figure 6. In zigzag SCNTs (Figure 6 (a)), the internal forces of longitudinal CNTs are double of those of the diagonal CNTs. In armchair SCNT (Figure 6 (b)), transverse CNTs subject no force in the loading direction and diagonal CNTs are the major force-bearing components. In this way, the force transfer mode of the armchair and zigzag SCNT can be identified. In zigzag SCNTs, the external loads are regarded as being transferred by two
interconnected zigzag paths, which separate at the diagonal components and merge at the longitudinal components. The force bearing mode of armchair SCNT is just like the CNT bundle. The parallel chains comprised by diagonal CNT are relatively independent in the force transfer process, while the transverse CNT only play a connection role.

Figure 6. Different force transferring paths along the tensile direction in two SCNT structures (a) Zigzag SCNT [10,0]@(6,6). (b) Armchair SCNT [6,6]@(6,6).

With the interconnected force transfer mode, the V-defect of zigzag SCNT cuts both two load transfer paths, whereas D-defect only interdicts one path. Hence, more internal forces released when defects are at the longitudinal CNTs, causing more decrease of the bearing capacities. In armchair SCNT, only D-defect could affect the real force transfer path and the breaking of transverse CNT has no effect on the major force transfer path. Accordingly, the H-defect brings no difference for bearing capacities, while D-defect leads to a remarkable reduction. It can be concluded that a defect at a more crucial position of force transfer causes greater reductions of bearing capacity.

4. Concluding remarks
By considering typical defect positions in different SCNT structures, the influence of defects on the bearing capacity of SCNT structures are investigated. According to the discussions, some conclusions are obtained as follows.

The existence of the single defect reduces the bearing capacities of SCNTs for 0% ~ 25% with major dependency on SCNT structure and defect position. Defects also affect the fracture performance of SCNTs, increasing the number of local turns along the crack propagation paths. Essentially, defect brings force concentration and local early fracture, resulting in the reductions of bearing capacities. The force concentration degrees of the armchair and zigzag SCNTs are affected by different mechanisms. Local displacement near defective area controls the force concentration degrees of armchair SCNTs, while that of zigzag SCNTs is determined by the specific force concentration modes. The underlying mechanism of determining the influence of defects on SCNTs structures is revealed to be the force transfer modes of the armchair and zigzag SCNTs.
With the fact that defects are widely existed in the CNT-based networks, understanding the defect effect is of great value for the practical applications of CNT-based networks.

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