Size effect on brittle and ductile fracture of two-dimensional interlinked carbon nanotube network

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\textbf{ABSTRACT}

The mechanical properties of two-dimensional (2D) interlinked carbon nanotube (CNT) network are investigated using ab initio calculation and molecular dynamics simulations (MD) with Reaxff force field. The simulation results show that bulk 2D interlinked CNT network has good mechanical properties along the axial direction which can be comparable to that of single-walled CNT and graphene, but has better ductility along the radial direction than single-walled CNT and graphene. In addition, the mechanical properties of 2D interlinked CNT network ribbon along the radial direction depend strongly on the size of the ribbon. The Young's modulus and Poisson's ratio decrease as the size increases while the fracture strain increases with the size increasing. By analyzing the atomic structural (both bond length and atomic von Mises stress) evolution of the ribbons, the mechanism of a brittle-to-ductile transition is revealed. The exploration of the mechanical properties of the 2D interlinked CNT network paves the way for application of the relevant devices that can benefit from the high Young's modulus, high tensile strength, and good ductility.

1. Introduction

CNTs have attracted great research interest for various potential applications since their discovery [1] due to their inherent outstanding mechanical, electronic, and thermal properties [2,3]. In the previously both experimental and theoretical work, it has been reported that CNTs possess extremely high axial tensile strength and Young's modulus values of about 150 GPa and 1 TPa [4–6], respectively. However, for larger-scale potential applications, the CNT networks do not exhibit expected mechanical properties because of the relatively weak van der Waals interactions between CNTs. Owing to weak interactions, individual CNTs can easily slide on each other, which results in little load transfer [7,8]. This hinders the wide range of application of CNT networks. Pressure is not only important method to study the structural and physical properties of materials, but also is an effective means to tune or modify the physical properties of materials. In order to maintain their curvature (i.e., C-C-C bond angles), small diameter CNTs have higher reactivity of surface atoms with only three bonds which are similar to the tetrahedron sp\textsuperscript{3} bonds in diamond [9]. Therefore, pressure may induce the transformations of bond state from the sp\textsuperscript{2} hybridized to sp\textsuperscript{3} bonds and produce some novel carbon based materials.

Single-walled CNTs (SWCNTs) covalent interlinking under pressure have been reported both experimentally and theoretically during the past decade. The earlier experimental studies [10] have indicated that the covalent C-C bonds interlinking between CNTs can be formed under high pressures and temperatures. In other experimental high-pressure studies, the quenchable superhard carbon phase has been synthesized by compression of CNTs under a non-hydrostatic pressure of 24 GPa [11] at room temperature. These superhard carbon allotropes have higher bulk modulus (465 GPa) than that of diamond (about 440 GPa) and high hardness (62–150 GPa) which is in the range between cubic BN (46–80 GPa) [12] and diamond (175 ± 5 GPa) [13]. These observations are supported by other obtained quenchable superhard carbon phase by compressing CNTs [14,15]. The determined bulk modulus is 447 GPa [14] and the measured hardness is 58 ± 6 GPa [15].

At the same time, variously pressure-induced 2D and 3D interlinked CNTs networks have been revealed according to the theoretical calculations. The theoretical predications of one- and two-dimensional (2D) networks of interlinked small diameter zigzag single-wall CNTs at higher external pressures are performed [16]. The small nanotubes are covalently boned to each other by sp\textsuperscript{3} hybridized carbon. However, at ambient pressure, the spontaneous cross linking is also found in the bundle of small-diameter zigzag CNTs based on density functional
theory (DFT) calculations [17]. The recent DFT calculations also find that the novel quasi-2D sheets of interlinked single-wall CNTs are formed at hydrostatic pressure [18]. The strong bonds are formed between the atoms in adjacent CNTs according to electron localization function (ELF) analysis. In addition, the transition pressure is dependent on the size and chirality of CNTs. The resulting 3D interlinked CNTs networks possess high thermodynamic stability, mechanical, and electronic properties. For example, these 3D interlinked CNTs networks can be metallic or semiconducting with wide direct/indirect gaps ranging from 0 to 3.45 eV [19,20]. Based on semi-empirical formula and DFT calculations, the Young’s modulus (about 1 TPa) and tensile strength (can be larger than 100 GPa) can be comparable to that of CNTs [19,21].

Compared to the 3D interlinked CNTs networks, the 2D interlinked CNT networks can have more potential application because of large surface area to volume ratio in nanotechnology. Recent studies have shown that 2D CNT networks with various junctions (e.g. X- and Y-junction) can find a number of applications, for example, sensors and actuators [22,23], optoelectronics [24,25], and energy devices [26,27]. The new interlinked 2D materials consisting of single-wall CNTs should have novel mechanical and electronic properties. It is therefore highly desirable to systematically investigate the mechanical properties of 2D interlinked CNT networks. However, to the best of authors’ knowledge, investigation on the mechanical properties and fracture process of 2D interlinked CNT networks has not been studied in the literature up to now.

In this work, ab initio calculations are performed to obtain robust predictions of structures and mechanical properties of the 2D interlinked CNT networks, and then we investigate the elastic properties and tensile behavior such as Young’s modulus and fracture strain using molecular dynamics (MD) simulations. Additionally, the size effect on the elastic properties and fracture strain is studied.

### 2. Simulation details

Ab initio calculations are mainly performed with the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code with atomic orbitals [28]. Some ab initio calculations are also performed using the Vienna Ab Initio Simulation Package (VASP) with projector augmented wave method [29,30] in order to obtain robust predictions and check different empirical potentials’ accuracy. In the SIESTA calculations, the double zeta plus polarization (DZP) basis set is used. The 32 × 1 × 32 grid [31] is used for k-point sampling, together with a meshcuttoff of 600 Ry for the system are used in the calculation. In the VASP calculations, the projector-augmented wave (PAW) method is used. The 1 × 1 × 16 Monkhorst Pack grid is used for k-point sampling and an energy cutoff of 850 eV is used. In both ab initio calculations, the Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) for the exchange and correlation functional is used in the calculation to account for the electron-electron interactions. To avoid interactions between species, neighboring structures are separated by more than 10 Å in the tetragonal supercells. For the bulk 2D interlinked CNT networks tension, stress-control method is performed and small stress is applied along tensile direction of the system. For the 2D interlinked CNT network ribbons tension, strain-control method is performed and the applied strain is 0.2% at each time. And then relax the geometry until the forces on each atom are less than 0.02 eV Å⁻¹.

In the MD simulations performed herein, the reactive potentials including ReaxFF [32] and AIREBO [33,34] are used to describe carbon-carbon and carbon-hydrogen interactions. Due to provide accurate descriptions of dynamic bond formation and breaking, these two potentials have been widely used in a variety of MD simulations of carbon systems and provide better representations of mechanical properties and phonon thermal transport in carbon related systems [35–38]. All MD simulations are performed using the Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [39]. All molecular systems are equilibrated at a constant pressure of 1 atm and a temperature of 300 K using NPT (constant number of particles, pressure, and temperature) for 100 ps with a time step of 0.1 fs. The temperature is controlled by employing the Nosé-Hoover thermostat [40]. The Velocity-Verlet algorithm is employed to integrate the equations of motion. And then the strain is applied along the uniaxial direction to perform uniaxial tensile tests. The applied strain rate is 0.005 ps⁻¹. The pressure component vertical to the loading direction is controlled to maintain the uniaxial tensile condition. The strain increment is applied to the structure after every 10,000 time steps with the step size of 0.1 fs. During this process, we monitored the total energy and temperature of the entire system and found that the total energy conserved very well, and the temperature remained constant with small fluctuations around 300 K, which meant that the system had reached the equilibrium state.

### 3. Results and discussions

As shown in Fig. 1a, the 2D interlinked CNT network is composed of single-walled (5,0) zigzag CNTs. The structure is optimized based on ab initio calculations. In order to determine the bonding type between CNTs, the local environment of the carbon atoms in the optimized 2D-linked (5,0) CNTs network is investigated using ab initio calculation, as shown in Fig. 1b (left). It can be seen that the bond length between CNTs in the 2D interlinked CNT network is about 1.56 Å which is comparable to that in diamond (1.55 Å calculated using ab initio calculation), indicating sp³ hybridization. In addition, the electron localization function (ELF) [41] is calculated. For comparison,
we also show the ELF plot for 2D CNT bundle where the bond length between CNT is larger than that in the 2D interlinked CNT network. The ELF plots show that the ELF is very high at the interface in the 2D interlinked CNT network, while the ELF is blank at the interface in the 2D CNT bundle, indicating that there is strong covalent bonding between the atoms on adjacent CNTs in the 2D interlinked CNT network. These results are consistent with those of interlinked (7,0) CNTs network based on ab initio calculations [16,18].

In order to verify the accuracy of empirical potentials, we first calculate the mechanical properties for single-walled (5,0) zigzag CNT using both ab initio calculations and MD simulations. The tensile strain is applied along axial direction. Fig. 2a shows the strain-stress relations. In ab initio calculations (SIESTA), the Young’s modulus is calculated from $Y = (1/V_0)(\partial^2 E/\partial \varepsilon^2)$ with a low strain (≤ 2%), where $\partial^2 E/\partial \varepsilon^2$ is the second derivative of the total energy with respect to the strain and $V_0$ is the minimum total energy volume (The thickness of the CNT is assumed to be 0.335 nm.). The calculated Young’s modulus for single-walled (5,0) zigzag CNT is 885.5 GPa along axial direction and the tensile strength is about 109.5 GPa, which are good agreement with previous theoretical results [42,43]. In MD calculation, the Young’s modulus is evaluated using the expression, $Y = \sigma/\varepsilon$ in the elastic region (the strain ≤ 5%), where $\sigma$ and $\varepsilon$ are the stress and strain, respectively. The stress is calculated in the form, 

$$\sigma = \frac{1}{V} \sum_{i,j} \left( -m_i v_i \otimes v_i + \frac{1}{2} \sum_{\rho} n_i \otimes f_j \right),$$

where $m_i$ and $v_i$ are the mass and velocity of atom $i$, $f_j$ are the forces between atoms $i$ and $j$, $n_i$ are the projection of the inter-atomic distance vectors along the tensile direction, and $V$ is the total volume. For the 2D interlinked CNT network, the total volume is obtained by adding the volume of each tube. Table 1 displays the Young’s modulus and tensile strength, and a comparison with ab initio calculations is also shown. As we can see from Table 1, the results for both Young’s modulus and tensile strength from Reaxff force field are consistent with the ab initio calculations. The tensile strength from AIREBO potential is smaller than that of ab initio calculations and AIREBO potential can also not maintain structure of 2D interlinked CNT network. Therefore, we select the Reaxff force field for the following calculations.

Table 1

<table>
<thead>
<tr>
<th>Mechanical parameters</th>
<th>Ab initio calculation</th>
<th>Reaxff force field</th>
<th>AIREBO potential</th>
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</thead>
<tbody>
<tr>
<td>Young’s modulus along axial direction</td>
<td>883.9</td>
<td>826.9</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus along radial direction</td>
<td>373.9</td>
<td>322.4</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus for (5,0) CNT (GPa)</td>
<td>885.5</td>
<td>866.1</td>
<td>871.7</td>
</tr>
<tr>
<td>Tensile strength for (5,0) CNT (GPa)</td>
<td>109.5</td>
<td>122.7</td>
<td>86.1</td>
</tr>
<tr>
<td>Fracture strain for (5,0) CNT</td>
<td>0.22</td>
<td>0.2</td>
<td>0.135</td>
</tr>
</tbody>
</table>

Base on the optimized unit cell from ab initio calculation, we construct and relax the supper cell of 2D interlinked CNT network with the size of $13.3 \times 10.3 \text{nm}^2$ with periodic boundary conditions along axial and radial directions using Reaxff force field. And then we perform displacement-control uniaxial tensile tests in the two different directions. Fig. 2b shows the strain-stress relations for 2D interlinked CNT network along two different directions. The Young’s moduli are summarized in Table 1. The results in the Fig. 2b indicate that the 2D interlinked CNT network has larger tensile strength but smaller fracture strain along axial direction than those along radial direction. The calculated Young’s modulus is 826.9 GPa and 322.4 GPa along the axial and radial direction, respectively, which are consistent with that of ab initio calculations. The Young’s modulus along the axial direction can be comparable to those of single-walled (5,0) zigzag CNT and 3D interlinked (5,0) CNTs networks [19]. In addition, the Young’s modulus along the radial direction is greatly improved since the largest value of the experimentally measured radial modulus for multi-walled CNTs is only 80.0 GPa [44,45] and the radial Young’s modulus of 3D interlinked (5,0) CNTs network is 210 GPa [19]. The calculated tensile strength is 107.7 GPa and 50.3 GPa along the axial and radial direction, respectively. Similar to the Young’s modulus, the tensile strength along axial direction can be compared to those of CNTs (100 GPa) [43], famous 2D material of graphene (107 GPa) [35], and 3D interlinked (5,0) CNTs networks (127.1 GPa) [19]. The tensile strength along radial direction also has a large increase and is approximately 10 times the yield strength of random CNT networks [46] and larger than that of 3D interlinked (5,0) CNTs networks (38.3 GPa) [19]. Furthermore, as shown in Fig. 2b, the 2D interlinked CNT network exhibits very good ductility along radial direction. It can retain the tensile stress of about 40 GPa with a large strain of 0.49 while the fracture strain along axial direction is only 0.18.

To give more insight into this phenomenon, the variation of the bond length with the strain in the axial and radial directions for 2D interlinked CNT network are studied and shown in Fig. 3. One can see that in the axial loading case, the main bond elongation is experienced by bond 1 and bond 6. In the radial loading case, the bond variation can be divided into four stages. When the strain is smaller than that of point 1 (stage I), the main bond elongation is experienced by bond 1. When the strain is larger than that of point 1 (stage II), the bond 7 suddenly becomes contracted while bonds 8, bond 9, bond 11, and

![Fig. 2. (a) Strain-Stress relations for single-walled (5,0) zigzag CNT under tensile tests in the axial directions with ab initio calculation, ReaxFF force field, and AIREBO potential. (b) Strain-Stress relations for 2D interlinked CNT network along two different directions with ReaxFF force field.](image-url)
bond 12 become elongated. When the strain is larger than that of point 2 (stage III), there is no any bond elongated further which means the deformation mechanism have changed. The deformation processes for stage III and stage IV will be investigated in detail in the following section according the structure evolution.

Hence, the above results indicate that the 2D interlinked CNT network not only maintain the excellent mechanical properties along axial direction, but also possess greatly improved mechanical properties along radial direction due to the covalent C-C bonds among the CNTs which are verified by the ELF calculation as shown in Fig. 1b.

In addition, we investigate the size effect on the mechanical properties of 2D interlinked CNT network ribbons, as shown in Fig. 4. The "n" in n-CNTs mean there are n CNTs linked along radial direction. The length along tensile direction is about 10 and 13 nm for axial and radial tension, which are similar to the bulk size of 2D interlinked CNT network. For 2D interlinked CNT network ribbons with different widths along axial direction, the edges of ribbons are terminated with hydrogen atoms to prevent the warping of the structure (as shown in Fig. 6a). It can be seen from Fig. 4a that there is little size effect on the mechanical properties of 2D interlinked CNT network ribbons along axial direction. However, significant size effects are found along radial direction in the Fig. 4b. When the width is small, 2D interlinked CNT network ribbon is brittle, when the width is increasing, 2D interlinked CNT network ribbon is becoming more ductile. The variation of fracture strain and Poisson’s ratio with the width of 2D interlinked CNT network ribbons is shown in Fig. 5a. The Poisson’s ratio for bulk 2D interlinked CNT network is 0.22 which is a little larger than that of 3D interlinked CNT network (0.21) [19]. The Poisson’s ratio decreases rapidly with the increasing of width while the fracture strain increases rapidly with the increasing of width. When the width is larger than about 4 nm, the decreasing and increasing becomes very slow. The Yong’s modulus is calculated for 2D interlinked CNT network ribbons along radial directions using the above expression, \( Y = \sigma / \varepsilon \) in the elastic region (the strain \( \leq 5\% \)). In Fig. 5b we plot the variation of Young’s modulus as a function of the size of the ribbon. It can be seen that Young’s modulus decreases with the width of the ribbon. In order to verify the results, we also calculate the Young’s modulus for the smaller size using ab initio calculations. The same variations are found for both MD results and ab initio results from both VASP and SIESTA calculations. Similar to size-dependent fracture strain, Young’s modulus also changes little when the width is larger than about 4 nm.

In order to understand detailed underlying mechanism of size effects along radial direction, two typical 2D interlinked CNT network ribbons with widths of 0.49 nm (brittle) and 1.35 nm (ductile) are further investigated. The strain-stress curves from Fig. 4b are shown in Fig. 6b again. To this end, we first calculate the variations of the bond length with the strain for the two ribbons, as shown in Fig. 6c and d. It can be obviously seen that they have different variations. For the smaller ribbon, the bond elongation or contraction is monotonous. The bond elongation is experienced by bonds 7, 8, and 9. When the strain is larger than about 0.06, the bond 7 is the mainly elongated bond. When the strain is 0.13 (critical strain), the elongated bond 7 reaches the largest value. After that, the ribbon is fractured. During the whole deformation process, the strain is mainly concentrated on bonds 7 and 8. However, for the wider ribbon, the bond variation is similar to that of bulk 2D interlinked CNT network and there are four stages during the tensile process. We will study the structural evolution in the
following section. Compared to smaller ribbon, there are more bonds experiencing elongation. For example, when the strain is smaller than 0.05, the bonds 7, 8, 9, and 11 are elongated. That is to say that there are more bonds taking part in the release of the strain energy in the width ribbon. This proves why the smaller ribbons have larger Young’s modulus since the strain energy is concentrated on fewer C-C bonds. In addition, when the strain is larger than that of point 1, except bonds 7, 8, 9, and 11, the bond 12 begins to become deformed bonds, which means that the stress is not just concentrated near bond 7. When the strain is larger than that of point 2, the length of almost all bonds begin to become contracted. When the strain is larger than that of point 3, the bond length does not change any more.

More evidence is provided by the atomic configurational evolution of these two ribbons. Figs. 7 and 8 show a series of snapshots of these two ribbons during radial deformation in tension. From Fig. 7, it can be seen that the stress of interlinked part (near bond 7) of smaller ribbon is gradually enlarged during the tensile process and the bond 7 breaks finally. The stress mainly concentrate near bond 7, which lead to a brittle fracture. This is consistent with the bond variation result as shown in Fig. 6c. For the wider ribbon, we can see from Fig. 8 that the stress mainly concentrate near bond 7 when the strain is smaller than that of point 1, as shown in Fig. 8b. When the strain is increased, some stresses transfer to the part near bond 12 which preventing bond 7 from breaking, as shown in Fig. 8c. However, when the strain is larger
than that of point 2, the plastic deformation is observed and the sliding of the one side of certain CNT happens. The graphene-like part occurs as shown with the shaded region in Fig. 8d. This is the reason that there are no bonds elongated further as shown in Fig. 3b and Fig. 6d when the strain is larger than that of point 2. With the strain increasing further, we find that the deformations have been carried mainly through the elongation of graphene-like region. Beyond this region, the ribbon has no significant change, as shown in Fig. 8e. Finally, the graphene-like region break, as shown in Fig. 8f. That is why the bonds do not change any more when the strain is larger than that of point 3. The formation of graphene-like part makes ribbon much more ductile.
4. Conclusions

In this paper, the mechanical properties of 2D interlinked CNT networks are investigated based on atomistic simulation. Compared with the ab initio calculations, Reaxff force field gives a more accurate results than AIREBO potential. As for bulk 2D interlinked CNT network, uniaxial tensile test along axial direction has good mechanical properties which can be comparable to single-walled CNT and graphene, while uniaxial tensile test along the radial direction has a very larger fracture strain compared to the axial direction. In addition, the ribbon width has a large effect on the mechanical properties of 2D interlinked CNT network ribbon along the radial direction. The fracture strain increases as the size of 2D interlinked CNT network ribbon increases while the Young's modulus and Poisson's ratio decreases with strain increases as the size of 2D interlinked CNT network ribbon along the radial direction. The fracture behaviors of carbon nanotubes: a high-pressure phase of carbon, ACS Nano 4 (2010) 3515–3521.


