Influence of Solid Surface and Functional Group on the Collapse of Carbon Nanotubes

Jie Xie, Qingzhong Xue,* Huijuan Chen, Dan Xia, Cheng Lv, and Ming Ma

College of Physics Science and Technology, China University of Petroleum, Dongying, Shandong 257061, People's Republic of China

Received: November 8, 2009; Revised Manuscript Received: December 18, 2009

Using molecular dynamics (MD) simulations, we focus on the influences of different solid surfaces and functional groups on the collapse of single-walled nanotubes (SWNTs). The results show that the SWNTs can fully collapse on Fe, Ni, and graphite surfaces, which may attribute to the strong metallicity of these surfaces, but partially collapse on the Si surface, and the deformation of SWNTs with different diameters on the Si surface is in line with previous investigations. Besides, with increasing oxygen concentration, the deformation degree of SWNTs on Fe, FeO, and Fe₂O₃ surfaces decreases, which demonstrates that the deformation of SWNTs is mainly caused by the interaction between the SWNT and the metal atoms. Take −NH₂-modified SWNT as an example. It is found that the modification coverage required for avoiding the collapse of the SWNTs varies for different surfaces. The interaction energies between Fe, Ni, graphite, and Si surfaces and −NH₂-modified SWNTs linearly decrease with increasing functional group coverage. For four kinds of functional groups, −NH₂ and −COOH have similar and better ability to avoid the collapse of the SWNTs; −CH₃ has a worse ability; and the ability of −OH is the worst.

1. Introduction

Carbon nanotubes (CNTs) are hollow cylindrical structures made of networks of carbon atoms. They display a fascinating variety of new physical and chemical properties ranging from ultrahigh-strength mechanical property, to thermal conductivity, to electronic property, to optical property, and to acting as catalyst supports. However, CNTs with localized kinks and bends, as well as minor radial deformations, have been observed. Chopra et al. also reported the existence of multi-shelled CNTs whose overall geometry differs radically from that of a straight, hollow cylinder. Their observation revealed that CNTs had suffered complete collapse along their length. Both experimental and theoretical studies have demonstrated that CNTs, especially for the intrinsic CNTs with large diameters, can be easily deformed and collapsed under certain external forces, such as van der Waals force, electron beam pressure, and hydrostatic pressure. Lourie et al. reported their experimental observations of various deformation and fracture modes under compression of single multiwalled CNTs, which are obtained as a result of embedment within a polymeric film. Theoretical studies also show that the collapse of CNTs can be governed by the number of walls, the radius of the innermost wall, the diameter of single-walled carbon nanotubes (SWNTs), and the chirality, etc. Previously, our group has studied the radial collapse of SWNTs on the Cu₂O surface using molecular dynamics (MD) simulations. It is found that, when the diameter of CNTs exceeds a threshold (10 Å), the CNTs approach the Cu₂O surface and collapse spontaneously by the van der Waals force between the CNTs and the Cu₂O surface. The CNT collapse on the Cu₂O surface is not dependent on the chirality, length, placement, and boundary saturation. We also demonstrated a novel method to produce core/shell composite nanowires (NWs) by self-scrolling CNTs onto copper NWs via forced-field-based MD simulations. Here, we will focus on the influences of the solid surfaces and functional groups on the collapse of SWNTs using MD simulations.

2. Experimental Section

Molecular mechanics (MM) and MD simulations have been carried out using a commercial software package called Materials Studio (MS) developed by Accelrys Software, Inc. All MD simulations are performed in the NVT ensemble, and a fixed time step size of 1 fs is used in all cases. The Andersen thermostat method is employed to control the system at the temperature of 300 K, and the interactions are determined within a cutoff distance of 9.5 Å. MM simulations are performed to find the thermal stable morphology and achieve a conformation with minimum potential energy for all SWNTs. Initially, all of the SWNTs were put onto the solid surfaces with a distance of 3 Å so that SWNTs can approach the surfaces quickly. All of the systems were simulated long enough to achieve an equilibrium state.

The primary goal of simulations of the systems containing a large number of particles is generally to obtain the systems’ bulk properties which are mainly decided by the location of atomic nuclei. If a reasonable, physically based approximation of the potential (force-field), which can be used to generate a set of system configurations that are statistically consistent with a fully quantum mechanical description, can be gained, we could have a good insight into the behavior of a system. As stated above, the force-field is one of the most essential concepts. The force-field we use here is the COMPASS force-field. It is a parametrized, tested, and validated first ab initio force-field, which enables an accurate prediction of various gas-phase and condensed-phase properties of most of the common organic and inorganic materials. A brief overview of the force-field is given in the following.

* Corresponding author. E-mail: xueqingzhong@tsinghua.org.cn.

10.1021/jp910630w © 2010 American Chemical Society
Published on Web 01/15/2010
In general, the total potential energy of a molecular system includes the following terms

\[ E_{\text{total}} = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{nonbond}} \]  

(1)

\[ E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{UB}} \]  

(2)

\[ E_{\text{cross-term}} = E_{\text{bond-bond}} + E_{\text{angle-angle}} + E_{\text{bond-angle}} + E_{\text{end bond-torsion}} + E_{\text{middle bond-torsion}} + E_{\text{angle-torsion}} + E_{\text{angle-angle-torsion}} \]  

(3)

\[ E_{\text{nonbond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{H-bond}} \]  

(4)

The valence energy generally includes a bond stretching term, \( E_{\text{bond}} \), a two-bond angle term, \( E_{\text{angle}} \), a dihedral bond-torsion term, \( E_{\text{torsion}} \), an inversion (or an out-of-plane interaction) term, \( E_{\text{oop}} \), and a Urey-Bradlay term (involves interactions between two atoms bonded to a common atom), \( E_{\text{UB}} \).

The cross-term interacting energy, \( E_{\text{cross-term}} \), accounts for the effects such as bond length and angle changes caused by the surrounding atoms and generally includes: stretch-stretch interactions between two adjacent bonds, \( E_{\text{bond-bond}} \), bend-bend interactions between two valence angles associated with a common vertex atom, \( E_{\text{angle-angle}} \), stretch-torsion interactions between a two-bond angle and one of its bonds, \( E_{\text{bond-angle}} \), stretch-torsion interactions between a dihedral angle and one of its end bonds, \( E_{\text{end bond-torsion}} \), stretch-torsion interactions between a dihedral angle and its middle bond, \( E_{\text{middle bond-torsion}} \), bend-torsion interactions between a dihedral angle and one of its valence angles, \( E_{\text{angle-torsion}} \), and bend-bend-torsion interactions between a dihedral angle and its two valence angles, \( E_{\text{angle-angle-torsion}} \).

The nonbond interaction term, \( E_{\text{nonbond}} \), accounts for the interactions between nonbonded atoms and includes the van der Waals energy, \( E_{\text{vdW}} \), the Coulomb electrostatic energy, \( E_{\text{Coulomb}} \), and the hydrogen bond energy, \( E_{\text{H-bond}} \).

The COMPASS force-field uses different expressions for various components of the potential energy as follows.
where \( q \) is the atomic charge; \( \varepsilon \) is the dielectric constant; and \( r_{ij} \) is the \( i-j \) atomic separation distance. \( b \) and \( b' \) are the lengths of two adjacent bonds; \( \theta \) is the two-bond angle; \( \phi \) is the dihedral torsion angle; and \( \chi \) is the out-of-plane angle. \( b_0, k_i (i = 2-4), \theta_0, H_i (i = 2-4), \phi_i (i = 1-3), V_i (i = 1-3), F_{b0}, b'_0, F_{bb'}, b'_0, F_{bb'}, F_{b00}, F_{b0}, F_{b00}, V_i (i = 1-3), F_{b00}, K_{b00}, A_0, \) and \( B_0 \) are fitted from quantum mechanics calculations and are implemented into the Discover module of MS.

The surfaces here, including Fe, Ni, graphite, Si, FeO, and Fe\(_2\)O\(_3\) surfaces, are used for providing SWNTs an external force. We set all the surfaces with similar size and thickness to avoid their influence. The information of all surfaces is listed in Table 2.

### Table 2: Geometric Sizes of Intrinsic SWNT (14, 14) for Both the Initial and Final States on the Fe Surface

<table>
<thead>
<tr>
<th>SWNT (14, 14)</th>
<th>( \Delta x ) (Å)</th>
<th>( \Delta y ) (Å)</th>
<th>( \Delta z ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial (0 ps)</td>
<td>37.0</td>
<td>18.3</td>
<td>18.3</td>
</tr>
<tr>
<td>final (100 ps)</td>
<td>36.5</td>
<td>27.1</td>
<td>3.6</td>
</tr>
<tr>
<td>deformation (Å)</td>
<td>-0.5</td>
<td>8.8</td>
<td>-14.7</td>
</tr>
</tbody>
</table>
Figure 4. (a) Final configurations of SWNTs with different functional coverage on Fe, Ni, graphite, and Si surfaces. (b) Adsorption energies between SWNTs with different functional coverage and Fe, Ni, graphite, and Si surfaces.
1, and the roughness influence on the collapse of SWNTs is neglected since the roughness of all surfaces is not obvious at all. When we built FeO and Fe$_2$O$_3$ surfaces, we first applied the force-field type to each atom in the surfaces, then deleted the covalent bonds between the Fe atoms and oxygen atoms. SWNT (14, 14) was built by MS, and the unsaturated boundary C--C bond length was 1.42 Å, and the C--H bond length was 1.14 Å. The hydrogen atoms had charges of $+0.1268$ e, and the carbon atoms connecting hydrogen atoms had charges of $-0.1268$ e; thus, the neutrally charged SWNTs were constructed.

### 3. Results and Discussion

MD simulations are conducted to investigate the dynamic behaviors of the SWNTs on Fe, Ni, graphite, and Si surfaces. Figure 1(a) shows the final configurations of SWNTs on Fe, Ni, graphite, and Si surfaces. For Ni, Fe, and graphite surfaces, the SWNTs on them have dynamic behavior similar to the collapsing process described in previous studies.$^8$ The SWNT rapidly transforms into linked double graphitic layers parallel to the plane like a ribbon on top of them. However, SWNT does not fully collapse on the Si surface at all. In the initial stage, the cross section of the SWNT (14, 14) stretches from a circle (0 ps) to an oval (13 ps) along the normal direction of the plane to try to contact the Si surface. Then, the cross section of the SWNT gradually transforms into an oval along the plane and behaves stably in the shape as shown in Figure 1(a). SWNTs with different radii were also put on the Si surfaces to estimate the radius influence. From Figure 1(b), it is found that, with increasing SWNT radius, the deformation degree of SWNTs becomes higher, which is well in line with the previous study.$^7$

Peak details of the concentration profile$^9$ are listed in the Table 2 to specifically reflect the geometric deformation of the SWNT on the Fe surface. We can find that $\Delta x$ and $\Delta z$ of the initial SWNT are approximately equal, which indicates that the circular tube of the SWNT (14, 14) is about 18.3 Å in diameter. $\Delta x = 37.0$ Å and $\Delta z = 36.5$ Å denote a slight deformation (0.5 Å) in length between the initial and final SWNT. The size of the SWNT increases by 8.8 Å along the $y$-axis and decreases by 14.7 Å along the $z$-axis, which means that the SWNT (14, 14) fully collapsed and covered on the Fe surface just like a 36.5 $\times$ 27.1 $\times$ 3.6 Å$^3$ ribbon.

The adsorption energy ($E_{\text{ads}}$) is estimated from the energy difference between the total energy ($E_{\text{total}}$) and the energies of the surface ($E_{\text{surface}}$) and the intrinsic SWNT ($E_{\text{SWNT}}$) as the following equation: $E_{\text{ads}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{SWNT}}).$ As shown in Figure 2(a), we can find that the adsorption energies between SWNTs and the surfaces are as follows: $E_{\text{ads-Fe}} > E_{\text{ads-Ni}} > E_{\text{ads-graphite}} > E_{\text{ads-Si}}$ ($E_{\text{ads-Fe}}$ denotes the adsorption energy between the SWNT and the Fe surface, same for others). Since the metallicity of Fe is better than that of Ni, graphite also has good metallicity, and Si belongs to the nonmetal, we generally conclude that this maybe has some relation with the metallicity of the surfaces. From Figure 2(b), it is observed that, for surfaces of Fe, Ni, graphite, and Si, the sizes of SWNTs along the $z$-axis are basically the same, which means that once the SWNTs fully collapse on the surfaces the change of surfaces does not influence the fully collapsed SWNTs’ final structures a lot. However, some surfaces such as the Si surface can not induce the full collapse of the SWNTs because of weaker attractive force.

For FeO, Fe$_2$O$_3$, and Fe surfaces, as shown in Figure 3(a), we can find that SWNTs do not fully collapse on FeO and Fe$_2$O$_3$ surfaces but fully collapse on the Fe surface easily. Figure 3(b) and (c) show the interaction energies between the SWNTs and three surfaces and the sizes of the final SWNTs along the $z$-axis. It is found that, with increasing oxygen concentration, the interactions between the SWNTs and the surfaces decrease, and the sizes of the final SWNTs along the $z$-axis increase. Deleting the oxygen atoms or Fe atoms in the FeO surface at the equilibrium state, we calculate the adsorption energies between the rest of the atoms and the SWNT. The results show that, though the number of Fe atoms and oxygen atoms is equal, the interaction between Fe atoms and SWNT ($-808.9$ Kcal/mol) is much stronger than the interaction between oxygen atoms and the SWNT ($-191.4$ Kcal/mol), which well indicates that the adsorption energy between the surface and the SWNT is mainly from the interaction between the SWNT and the metal atoms.

Using the Dmol$^3$ module of MS, we have performed DFT calculations for the Fe$^{2+}$--SWNT and O$^{2-}$--SWNT systems. After structure optimization, the multiplet charge analysis indicates that Fe is distributed with 0.451 eV and O is distributed with $-0.547$ eV. Obviously, the charge transfer of the Fe atom is more than that of the O atom, which further proves that the Fe atom bonds more strongly with SWNT than the O atom.

Previously, we have reported that the structural stability of the cylindrical SWNT on the aluminum surface can be improved through the surface modification method.$^{30}$ The stability of SWNTs can be enhanced by increasing the modification coverage. When the modification coverage exceeds certain coverage, the modified SWNTs can basically maintain the cylindrical structure in our described systems. Using the same way, the chemical modification of the SWNTs has been performed by randomly attaching functional groups to the surface of the SWNTs through chemical covalent bonding. By changing the $-\text{NH}_2$ functional group coverage on SWNTs, the systemic study has been carried out to observe the dynamic behavior of the modified SWNTs on Fe, Ni, graphite, and Si surfaces. The final configurations of the $-\text{NH}_2$-modified SWNTs with different modification amounts on different surfaces are shown in Figure 4(a). It is observed that, for Fe, Ni, graphite, and Si surfaces, when the modification coverage gets to $\sim3.4\%$, $3.3\%$, $2.4\%$, and $2.4\%$, respectively, the cylindrical structures of SWNTs can be basically maintained. The interaction energies between the modified SWNTs and different surfaces are calculated to estimate the modification influence. As shown in Figure 4(b), on all surfaces, the interaction energies linearly decrease with increasing functional coverage. The order of the energy change is as follows: Fe $>$ Ni $>$ graphite $>$ Si. These may be because the functional groups destabilize the $\pi-\pi$ stacking of the linked collapsed CNT layers. The local tetrahedrons in the SWNTs provide the additional structure strength to the cylindrical structures, or the increment of the functional coverage increases the distance between the SWNTs and the surfaces and thus weakens the influence of the external force on SWNTs.$^{30}$

### Table 3: Geometric Sizes of the Final State of $-\text{NH}_2$-Modified SWNT (14, 14) Whose Structures Are Basically Maintained on Fe, Ni, Graphite, and Si Surfaces

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Coverage</th>
<th>First Peak (Å)</th>
<th>Last Peak (Å)</th>
<th>$\Delta z$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>4.3%</td>
<td>22.2</td>
<td>37.3</td>
<td>15.1</td>
</tr>
<tr>
<td>Ni</td>
<td>4.8%</td>
<td>22.2</td>
<td>35.2</td>
<td>13.0</td>
</tr>
<tr>
<td>Ni</td>
<td>4.8%</td>
<td>21.4</td>
<td>38.4</td>
<td>17.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>3.3%</td>
<td>21.8</td>
<td>38.6</td>
<td>16.8</td>
</tr>
<tr>
<td>Si</td>
<td>2.4%</td>
<td>21.2</td>
<td>40.2</td>
<td>19.0</td>
</tr>
<tr>
<td>Si</td>
<td>2.9%</td>
<td>21.4</td>
<td>39.4</td>
<td>18.0</td>
</tr>
<tr>
<td>Si</td>
<td>2.9%</td>
<td>21.4</td>
<td>37.9</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Figure 5. (a) Final configurations of SWNTs with different functional groups (–OH, –CH$_3$, –NH$_2$, –COOH) on the Ni surface. (b) Adsorption energies between SWNTs with different functional groups (–OH, –CH$_3$, –NH$_2$, –COOH) and the Ni surface.
We calculate the $z$ sizes of the SWNTs whose structures are basically maintained. From Table 3, though we can find that their sizes along the $z$-axis decrease compared with the initial $z$ size of SWNT (18.3 Å), the maximum size difference is 5.3 Å on the Fe surface, and the minimum size difference is 0.3 Å on the Si surface reflecting the strong geometric stability of these SWNTs. The reason for this may be the strongest interaction between the SWNT and the Fe surface and the weakest interaction between the SWNT and the Si surface.

Modifying the surface of CNTs with chemical groups is an efficient way for their utilization in different applications, such as fabrication of the soluble CNTs. CNTs can be modified by various kinds of groups such as methyl, amidogen, hydroxyl, carboxyl, and phenyl, etc. Here, we select four kinds of small functional groups, methyl, amidogen, hydroxyl, and carboxyl, to study their different influences on the SWNTs with different functional groups avoiding their collapse on the Ni surface. From the energy file, we can clearly observe four kinds of functional groups' ability of avoiding collapse of SWNTs. From Figure 5(b), it is found that if we increase the same amount of functional groups the energy variations are different. The energies of $\text{NH}_2$ and $\text{COOH}$ change more than those of $\text{CH}_3$ and $\text{OH}$, and compared to the other three groups, the energy change of $\text{OH}$ is the smallest. Thus, we can generally conclude that for four kinds of functional groups $\text{NH}_2$ and $\text{COOH}$ have similar and better ability to avoid collapse of SWNT; $\text{CH}_3$ has a worse ability; and the ability of $\text{OH}$ is the worst.

From the energy file, we can clearly observe four kinds of functional groups' ability of avoiding collapse of SWNTs. From Figure 5(b), it is found that if we increase the same amount of functional groups the energy variations are different. The energies of $\text{NH}_2$ and $\text{COOH}$ change more than those of $\text{CH}_3$ and $\text{OH}$, and compared to the other three groups, the energy change of $\text{OH}$ is the smallest. Thus, we can generally conclude that for four kinds of functional groups $\text{NH}_2$ and $\text{COOH}$ have similar and better ability to avoid collapse of SWNT; $\text{CH}_3$ has a worse ability; and the ability of $\text{OH}$ is the worst.

4. Conclusions

In summary, MD simulations were conducted to study the behaviors of the SWNTs (14, 14) on different solid surfaces, including Fe, Ni, graphite, Si, FeO, and Fe$_2$O$_3$ surfaces, and the influence of functional groups. The results show that the SWNTs can fully collapse on Fe, Ni, and graphite surfaces, which may attribute to the strong metallicity of these solid surfaces, but partially collapse on the Si surface. The deformation of SWNTs with different diameters on the Si surface is in line with previous investigations. Besides, with increasing oxygen concentration, the deformation degree of SWNTs on Fe, FeO, and Fe$_2$O$_3$ surfaces decreases, which demonstrates that the deformation of SWNTs is mainly caused by the interaction between the SWNT and the metal atoms. Take $\text{NH}_2$-modified SWNT as an example. It is found that the modification coverage required for avoiding the collapse of the SWNTs varies for different surfaces. For Fe, Ni, graphite, and Si surfaces, when the $\text{NH}_2$ modification coverage gets to $\sim4.3\%$, 3.3%, 2.4%, and 2.4%, respectively, the cylindrical structures of SWNTs can be basically maintained. The interaction energies between Fe, Ni, graphite, Si surfaces, and $\text{NH}_2$-modified SWNTs linearly decrease with increasing functional group coverage. For four kinds of functional groups, $\text{NH}_2$ and $\text{COOH}$ have similar and better ability to avoid the collapse of the SWNTs; $\text{CH}_3$ has a worse ability; and the ability of $\text{OH}$ is the worst.

Acknowledgment. This work is supported by the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (708061), Natural Science Foundation of China (10974258), Program for New Century Excellent Talents in University (NCET-08-0844), and Scientific Research Innovation Foundation of Graduate School of China University of Petroleum.

References and Notes


JP910630W