Mechanical Behaviors of Carbon Nanoscrolls

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Theoretical analysis and molecular dynamics simulations are presented to study the mechanical behaviors of Carbon nanoscrolls (CNSs). The study shows that a graphene sheet can rapidly self-scroll onto a carbon nanotube. The van der Waals interaction between the graphene sheet and the nanotube is the driving force of self-assembly process. During self-assembly process, the van der Waals energy of the system is partially balanced with the bending energy of the graphene walls and partially converted to the kinetic energy of the CNS. If a new graphene sheet is attached to the nanoscroll with end to end joint, the new graphene will self-assemble into the CNS and the spontaneously formed CNSs will rotate around the nanotube. If a new graphene sheet is attached the CNS with lap joint, the new graphene sheet will self-scroll onto the CNS and the spontaneously formed CNSs will oscillate around the nanotube with high frequency.

Keywords: CNS, Graphene, Self-Assembly.

1. INTRODUCTION

In the last few years carbon-based nanomaterials such as carbon nanotubes (CNTs), graphene (GN) and carbon nanoscrolls (CNSs) have attracted enormous attention owing to their unique properties and promising applications. Particularly CNSs, which is a spirally wrapped 2D GN sheet onto a 1D tubular structure, intrigue more and more researchers. Besides some properties distinct from those of GN and CNT, the CNS is also expected to have some excellent properties, such as high carrier mobility and high mechanical strength. Because of its open topology, the interlayer spaces of CNS can be easily intercalated. Therefore CNS facilitates chemical doping,¹ hydrogen storage² and nanoactuator in nanomechanical devices.³ The core size of the CNS can be adjusted and used as a tunable matter-delivery channels, such as tunable water and ion channels, nanofluidic devices, and nanofilters.⁴

The existing several CNS chemical fabrication methods^{5–7} are difficult to produce high-purity and high-quality CNS. With the development of technology of graphene,^{8,9} the tailoring of GN sheets with nanoscale precision in a vacuum has been successfully achieved.¹⁰ How to fabricate CNS from GN sheets directly is focused on by researchers. Recently Xie et al.¹¹ reported a simple and effective way of fabricating high-quality CNSs, using isopropyl alcohol solution to roll up monolayer GN predefined on SiO₂/Si substrates and integrated it into devices.

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This fabrication process is sensitive to the contamination of GN. Xia et al.¹² has given a simple way of synthesizing CNT/CNS core/shell nanostructures by GN sheet's spontaneous rolling onto CNT. When the CNS radius is large enough, they can form a stable core/shell structure, the chirality of the CNT and GN sheet does not affect the self-scrolling process. Zhang and Li¹³ also found the spontaneous process is reversible with the assistant of applied dc/ac electric field. Jiang et al.¹⁴ study interaction between the graphene nanoribbon (GNR) and single-wall carbon nanotube (SWNT) and they found the GNR enters the SWCNT spontaneously to display a helical configuration which is quite similar the chloroplast in the spirgyra cell. A DNA-like double helix would be formed inside the SWCNT with the encapsulation of two GNRs. Li et al.¹⁵ study the self-assembly of GN and metallic particle and got similar results. Patra et al.¹⁶ found nanotubes can induce bending, folding, sliding and rolling of the nanostructures in vacuum and in the presence of solvent, leading to stable GN rings, helices, and knots. These works not only give a simple way for fabricating high-quality CNSs, but also open new and exciting possibilities for the fabrication of metal/carbon core/shell composite nanostructures through the self-scrolling of GN. However, GN will produce out-of-plane fluctuations with ripples under thermodynamic perturbation. This fluctuation will make GN self-bend, twist, scroll along the contour length direction at a high aspect ratio.¹⁷ So there will be problems with CNT-activated method when fabricating large CNSs. But in many applications, especially CNT/CNS core/shell

composite and nanoactuator devices, CNSs of large diameters are needed. How to fabricate large CNSs is the key for these applications.

In the present work using molecular dynamics (MD) simulations we suggest a simple method for synthesizing large CNT/CNS core/shell composite nanostructures by self-scrolling up several GN sheets onto a single walled CNT. As the first step, the self-scrolling of one or two GN sheets onto a single walled CNT was simulated using MD and analyzed based on the energy principle. For a fixed (8, 8) CNT with given axial length, we study the effects of the length of a single GN sheet on the self-scrolling process. We demonstrate that if the length of the GN sheet is not too long, the GN sheet can scroll completely onto the CNT and form a stable CNT/CNS nanocomposite structure. We present a formula to calculate the equilibrium positions of the atoms for the system of the CNT/CNSs at finite temperature. The theoretical prediction is in good agreement with MD simulation. The CNSs can rotate or oscillate around the CNT after finishing self-scrolling process. We investigate the self-assembly process of the second GN sheet onto the existed CNT/CNSs and show clearly that these self-scrolling process are wonderful and very rich.

2. SELF-ASSEMBLY OF CARBON NANOSCROLL INITIATED BY A CARBON NANOTUBE

2.1. Molecular Dynamics Simulation

The self-scrolling of a GN sheet on CNT was simulated using MD under isothermy condition. We choose an (8, 8) CNT with a length of 51.65 Å and a GN sheet with a width of 32.66 Å and different lengths (121.6 Å, 415.457 Å, 714.26 Å, 1314.92 Å etc.). And the GN sheet is placed above the CNT at a distance of 5 Å. The CNT is fixed in all simulations. Then the single GN sheet is attracted by the CNT due to van der Waals interaction and starts to scroll onto the CNT. The thermodynamic temperature of the simulation system is kept 300 K during simulations.

When the radius of CNT is larger than a threshold of about 5 Å and the length of GN sheet is not so long, the GN sheet can fully self-scroll onto the CNT forming a stable core/shell composite nanostructure. This result is similar to that of Ref. [12]. We found that the structure of the CNT/CNS core/shell nanocomposite is not the same as the truncated Archimedean-type spiral structure of CNS_{1,18} but more similar to the coaxial cylindrical shells (with cross section of concentric circles) structure of multivalled carbon nanotubes (MWCNTs) with a small part of transition regions between adjacent layers (see Fig. 1).

The theoretical prediction based on multiple coaxial cylindrical shells of MWCNTs agrees well with the MD simulation for the structure of CNT/CNSs within the regions $0 \leq \theta < \theta_i$, where θ is the circular angle of i th

Fig. 1. The schematic of the equilibrium state of the CNT/CNSs. The transition regions between adjacent layers can be described by an angle $\Theta = 2\pi - \theta_i$. The blue discrete points denote the equilibrium positions of the carbon atoms in the MD simulation result. The continuous lines are the theoretic predictions of Eqs. (1) and (5). (a) A GN sheet with length $L = 121.77$ Å rolling onto the (8, 8) CNT. (b) A GN sheet with length $L = 261.24$ Å rolling onto the (15, 15) CNT.

layer, measured from the initial point of the i th layer, θ_i is the transition angle (see Fig. 1). Therefore, each layer of the CNSs consists of two parts: the first part can be described as a truncated concentric cylindrical shell; the second part can be described the truncated Archimedean-type spiral structure. We have the following formula,

$$r = \begin{cases} r_i & 0 \leq \theta \leq \theta_i \\ r_i + \frac{h_i}{2\pi - \theta_i}(\theta - \theta_i) & \theta_i < \theta \leq 2\pi \end{cases} \quad (1)$$

2.2. Analytic Method

The total potential energy of the MWCNTs consists of the bending energy of all layers and the interaction energy of adjacent layers, which can be expressed as

$$E_i = L \left[\sum_{0 \leq i \leq N} \frac{\pi D}{r_i} + \frac{1}{2} \sum_{i \neq j} V(r_i, r_j) \right] \quad (2)$$

$$V(r, R)$$

$$= 3\pi\theta\epsilon\sigma^2 \left[\frac{21}{32} \left(\frac{\sigma}{R} \right)^{10} \left(\frac{R}{r} \right)^{11} M_{11} \left(\frac{R}{r} \right) - \left(\frac{\sigma}{R} \right)^4 \left(\frac{R}{r} \right)^5 M_5 \left(\frac{R}{r} \right) \right] \cdot 2\pi r \quad (3)$$

$$M_n(x) = \int_0^\pi d\phi \frac{1}{(1+x^2-2x\cos\phi)^{n/2}} \quad (4)$$

where $D = 1.331$ eV is the bending modulus, r_i is the radius of the i th cylindrical shell, $V(r_i, r_j)$ is the interlayer interaction between the i th and j th cylindrical shells, $\theta = 0.38 \text{ \AA}^{-2}$ is the surface density of carbon atoms, $\sigma = 3.4 \text{ \AA}$ and $\epsilon = 2.84$ meV are the LJ parameters.¹⁹

Using the principle of minimum potential energy, the radius of each layer of the MWCNTs can be obtained by solving the following N equations:

$$-\frac{\pi D}{r_i^2} + \sum_{j \neq i} \frac{\partial V(r_i, r_j)}{\partial r_i} = 0 \quad (1 \leq i \leq N) \quad (5)$$

It's found that the prediction of Eq. (5) is in accordance with the MD simulations for the CNT/CNSs nanostructure within the regions $0 \leq \theta < \theta_c$ as shown in Figure 1. The interlayer spaces are about $3.4\text{--}3.5 \text{ \AA}$, which is in good agreement with Ref. [12].

So the CNT inside the CNSs has great effect on the CNT/CNSs nanostructure. The van der Waals interaction between the CNT and CNSs plays an important role.

2.3. The Effect of GN Sheet Length

The present MD simulation clearly shows that the CNS will continually rotate around the CNT with high speed after the GN sheet wraps completely onto the CNT. The van der Waals interaction between the GN sheet and the CNT is the driving force of the self-assembly process. During the self-assembly process, the van der Waals energy of the system is partially balanced with the bending energy of the CNS and partially converted into the kinetic energy of the CNS. The circumferential velocity of the CNS increases as the drop of total potential energy increases and can reach about one tenth order of the root mean square speed of thermodynamics at 300 K.

Figure 2(a) shows a typical result of MD simulation for the CNT/CNS nanostructure with $L = 100 \text{ \AA}$. The GN sheet fully rolling onto the CNT forms a stable CNT/CNS core/shell composite nanostructure.

If the length of the GN sheet is large enough, the left part of the GN sheet spontaneously wraps onto the CNT and forms a single layer CNS like a tadpole-type head with a long tail (the right part of the GN). The long tail can not scroll further and vibrates strongly out-of plane like an ocean wave, as shown in Figure 2(b) in which $L = 400 \text{ \AA}$.

Fig. 2. (a) The GN sheet with length about $100 \text{ \AA}$ can fully roll onto the (8, 8) CNT. (b) The GN sheet with length about $400 \text{ \AA}$ after finishing self-assembly process looks like a tadpole-type head with a long tail hanging on the CNT. (c) The GN sheet with length about $700 \text{ \AA}$ clamping the CNT, and swinging like a sheet hanging on a clothes-pole. (d) The GN with length of about $1300 \text{ \AA}$ detaching from the CNT.

The simulation result for $L = 700 \text{ \AA}$ is shown in Figure 2(c). Due to the length L is too long, the fluctuation of thermodynamic non-equilibrium is remarkable, the knot between the CNT and the tadpole-type head of CNS is broken. The horizontal component of the attract force acting on the left end of the CNS from the right part of the GN is larger than the horizontal component of the attract force from the CNT. Therefore the left end of the GN slides along the planar sheet of the GN and form a knotted GN surrounding the CNT inside.

For a GN sheet with a given width, the amplitude of the out-of-plane vibration (ripples) increases with the increase of its aspect ratio.¹⁷

2.4. Two Type of Structures of Double GN Sheets and CNT

After the first GN sheet scrolls completely onto the CNT, a new GN sheet is put on the place closely near the

CNT/CNT core/shell structure. The second GN sheet has the same width as that of the first GN sheet.

If the new GN sheet is attached to the existed CNT/CNS with end to end joint, the new GN sheet will self-assemble into the CNS and the spontaneously formed CNSs will rotate with a high speed around the CNT. A typical result is shown in Figure 3(a) in which $L = 198.8 \text{ \AA}$. The new GN seems only to create new layers and to form large size of CNS.

If the new GN sheet is attached the CNS with lap joint, it will self-scroll onto the existed CNS and the spontaneously formed CNSs will oscillate around the CNT with a high frequency. Figure 3(b) is a typical result with $L_1 = 122.77 \text{ \AA}$ and $L_2 = 244.77 \text{ \AA}$. The length of the second GN sheet is about twice of the length of the first GN sheet. The new GN sheet is placed on the right side of the CNS with a distance about $5 \text{ \AA}$. The new GN sheet is attached the existed CNS with lap joint and penetrates into the existed CNS to form the first layer of the spontaneously formed CNSs instead the original first layer. Then the original first layer climbs along the new first layer until catching the end of the first layer. After the new GN sheet wraps completely onto the CNS, the spontaneously formed CNSs oscillates around the CNT with low frequency.

If the new GN sheet is placed symmetrically above the CNT/CNS, the left and right wings of the new GN will

Fig. 3. (a) The second GN sheet with length $L = 198.8 \text{ \AA}$ is attached to the existed CNT/CNS with end to end joint and formed a new CNT/CNSs with four layers. (b) The new GN sheet with length to be twice of the first GN sheet, is attached the existed CNS with lap joint and penetrates into the existed CNS. (c) The new GN sheet is placed symmetrically on the top of the CNT/CNS to form a sandwich of GN sheets. The original CNS is exfoliated from the CNT and becomes the core gripper of the sandwich of the GN sheets.

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wrap the CNS and attract the end of the CNS, which results in the CNS exfoliation from CNT to form a sandwich of GN sheets as shown in Figure 3(c).

3. CONCLUSIONS

In summary, we have used MD simulations to study the self-scrolling process of one and two GN sheets onto a single walled CNT. When the second GN sheet scrolling onto the CNT, there exist two useful stable structures: one is a new CNT/CNSs composite nanostructure with end to end joint between the first and second GN sheets; another is a serial CNS sheets with lap joint between the first and second GN sheets. When more sheets self-assembly on a CNT, the structure will be a hybrid structure of these two types. Besides the two types of core/shell composite nanostructure, there are various interesting shapes of composite nanostructure which need to be investigate further.

4. EXPERIMENTAL DETAILS

All the MD simulations are implemented with a free boundary condition at 300 K using LAMMPS. A constant temperature ensemble (NVT) is used in our simulations with Nose-Hoover thermostats. The carbon atoms at boundaries are saturated by hydrogen atoms. The interactions between C-C, C-H, and H-H atoms are characterized by a second generation reactive empirical bond-order potential (AIREBO) with 6–12 Lennard-Jones correction at long distance. AIREBO potential has been shown to accurately capture the bond-bond interaction between hydrocarbon atoms as well as bond breaking and bond reforming. The velocity-verlet algorithm is used to solve the equations of motion. A time step of 0.5 fs is used in all simulations and data is collected at an interval of 50 fs. The trajectory is then recorded and the results are analyzed with assistant of the VMD visualization package.

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References and Notes

1. S. F. Braga, V. R. Coluci, S. B. Legoas, R. Giro, D. S. Galvão, and R. H. Baughman, *Nano Lett.* 4, 881 (2004).
2. S. F. Braga, V. R. Coluci, R. H. Baughman, and D. S. Galvão, *Chem. Phys. Lett.* 441, 78 (2007).
3. X. Shi, Y. Cheng, N. M. Pugno, and H. Gao, *Appl. Phys. Lett.* 96, 053115 (2010).
4. X. Shi, Y. Cheng, N. M. Pugno, and H. Gao, *Small, Weinheim an Der Bergstrasse, Germany* 6, 739 (2010).
5. R. Bacon, *J. Appl. Phys.* 31, 283 (1960).
6. L. M. Viculis, J. J. Mack, and R. B. Kaner, *Science New York, N.Y.* 299, 1361 (2003).

7. M. Savoskin, V. Mochalin, A. Yaroshenko, N. Lazareva, T. Konstantinova, I. Barsukov, and I. Prokofiev, *Carbon* 45, 2797 (2007).
8. A. Dimiev, D. V. Kosynkin, A. Sinitskii, A. Slesarev, Z. Sun, and J. M. Tour, *Science* 331, 1168 (2011).
9. S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Özyilmaz, J.-H. Ahn, B. H. Hong, and S. Iijima, *Nat. Nanotechnol.* 5, 574 (2010).
10. L. Tapasztó, G. Dobrik, P. Lambin, and L. P. Biró, *Nat. Nanotechnol.* 3, 397 (2008).
11. X. Xie, L. Ju, X. Feng, Y. Sun, R. Zhou, K. Liu, S. Fan, Q. Li, and K. Jiang, *Nano Lett.* 9, 2565 (2009).
12. D. Xia, Q. Xue, J. Xie, H. Chen, C. Lv, F. Besenbacher, and M. Dong, *Small Weinheim an Der Bergstrasse, Germany* 6, 2010 (2010).
13. Z. Zhang and T. Li, *Appl. Phys. Lett.* 97, 081909 (2010).
14. Y. Jiang, H. Li, Y. Li, H. Yu, K. M. Liew, Y. He, and X. Liu, *ACS Nano* 5, 2126 (2011).
15. Y. F. Li, H. Q. Yu, H. Li, C. G. An, K. Zhang, K. M. Liew, and X. F. Liu, *The Journal of Physical Chemistry C* 115, 6229 (2011).
16. N. Patra, Y. Song, and P. Král, *ACS Nano* 5, 1798 (2011).
17. Z. Xu and M. J. Buehler, *ACS Nano* 4, 3869 (2010).
18. X. Shi, N. M. Pugno, Y. Cheng, and H. Gao, *Appl. Phys. Lett.* 95, 163113 (2009).
19. S. J. Stuart, A. B. Tutein, and J. A. Harrison, *The Journal of Chemical Physics* 112, 6472 (2000).

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