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Theoretical study of core/shell composite structure made by carbon nanoring and aluminum nanowire

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ABSTRACT

Molecular dynamics (MD) simulations have been performed to investigate the interaction between the carbon nanorings (CNRs) and Al nanowires (NWs). Our results show that the NW can activate, guide and stabilize the self-assembly of the CNR to form a double-deck helix, as a result of the combined action of the van der Waals interaction and the offset face-to-face π-π stacking interaction. The cross section of the NWs has a negligible effect on the helix-forming process, whereas the size (diameter and length) of the CNRs should meet some required conditions to guarantee the helical configuration. It is worth noting that the helical conformation for the hydrogen-terminated CNRs is energetically more stable than scroll or stacking. Furthermore, we also study how the surface roughness affects the self-assembly of the CNRs.

INTRODUCTION

Carbon nanotubes (CNTs) have exhibited distinctive electrical properties, thermal conductivity[1] and outstanding mechanical strength[2] because of their unique structures. These remarkable properties have made them promising candidates for potential applications in nanosized electronical and mechanical devices, particularly for the fabrication of novel structural CNTs-based composites[3]. The functional "CNTs-based composites" have stimulated great interest due to the eminent prospects and opportunities in hydrogen storage, sensors, nanodevices, heterogeneous catalysis[4], electromagnetic wave absorption, as well as biomolecular and drug delivery in the field of biology[5, 6]. The "CNTs-based composites" can be fabricated with methods such as the encapsulation of foreign fillers in the CNTs, and the wrapping of polymers on the outside wall of the CNTs[7-10]. Generally, CNTs can deform their idealized cylindrical geometry to various cross-sectional shapes[12], including oval, peanut, trigon and ribbon shapes, as a result of the Van der Waals interaction[13] between CNTs and substrate. Moreover, both theoretical and experimental results demonstrated that the CNTs' superior properties can be affected by the deformation and defects of the CNTs[14, 15]. Yan and his coworkers[16] reported the radical collapse and self-scroll of the CNT induced by Cu NW, resulting in the coaxial core-shell composite nanostructure. This core-shell composite structure has two advantages. On one hand, the inner NW tremendously alters the properties of the pristine tube[17]. On the other hand, the inner NW is surrounded by the carbon shell, which can be regarded as a natural layer protecting against oxidation and shape fragmentation[18]. This phenomenon inspires us to imagine what would happen between the super-short carbon nanorings and NWs. The super-short carbon nanorings can also be regarded as enclosed and rolled narrow graphene nanoribbons (GNRs)[19]. The CNRs with a large diameter tend to be thermodynamics unstable and undergo collapse[20], which makes the wrapping of the CNR around the NWs possibly. Actually, the lengths of CNRs along the axial direction are proved to be difficult to realize controllable synthesis[21]. Recently, Sun et al. developed a facile method to fabricate CNRs, which adopted the catalytic growth in the confined space of the two-dimensional interlayer galleries in a layered double hydroxide (LDH) host, controlling in situ growth of the CNR to limit the length down to the molecular scale of ~1 nm[19]. Therefore, building an explicit model on the interaction between CNR and NW is necessary and urgent.

In this study, we perform molecular dynamics simulations on CNRs and Al NWs to reveal how the CNR interact with the Al NWs and what is the final shape of the CNR adhering on the Al NWs. In addition, we also explore many complicated factors which may influence the final configuration of the CNRs. This work is not only vital to the better understanding of the self-assembling process but also significant for the fabrication of novel CNTs-based composite structures. In this paper, we just simulated the physical interaction between the CNR and NW, dominated by the van der wall interaction, without considering the chemical bonding. An exhaustive follow-up study is also needed to clarify the chemical interactions.

COMPUTATIONAL METHODS

In this work, the atomistic interaction is described by the force field of condensed-phased optimized molecular potentials for atomistic simulation studies (COMPASS)[22]. It is a an ab initio force field that has been parametrized and validated using condensed-phase properties in addition to various ab initio calculations and experimental data. It has been proven to be applicable in the prediction of properties of CNTs[23]. The molecular dynamics simulations are carried out under a constant volume and constant temperature (NVT) ensemble with temperature of 298 K. The Nose method in the thermostat is employed to control the thermodynamic temperature, which can be kept constant by allowing the system to exchange energy with a "heating bath", and generate the correct statistical ensemble. The time step is chosen to be 1.0 fs, and data are collected in intervals of 1.0 ps. Then the full-precision trajectory is recorded for further analysis. Herein, we prepared the simulation models consisting of the Al NWs and CNRs. All Al NWs are fixed as rigid structures, the axes of which are positioned in the (0 0 1) direction. The CNRs are super-short CNTs with a length down to the molecular scale. Initially, all CNRs are placed in the middle of the Al NWs, with the separation of 5 Å. Each of the CNR-NW system is sufficiently relaxed to achieve an equilibrium state.

RESULTS AND DISCUSSION

Fig. 1 shows the representative snapshots of CNR (80, 80) with the length of 24.60 Å spontaneously wrapping on the Al NW in a spiral manner. In Fig. 1(a), the axe of the CNR is perpendicular to that of the Al NW in the initial stage. As the simulation starts, the CNR with a diameter of 108.48 Å tends to be thermodynamically unstable, resulting in the discontinuous ripples and wrinkles[24] in the circumference. Directed by the Van der Waals interaction[13], the CNR approaches the Al NW rapidly and subsequently deform its circle to a pear shape. When the simulation time is up to 30 ps, the opposite walls of the CNR adhere to each other, and collapse to be inverted “T” shape on the Al NW. As the simulation continuous, the inverted “T” shape experiences successive collapse to form a linked double graphitic nanoribbon. Simultaneously, the axes of the CNR and Al NW begin to offset and the flatten nanoribbon shows a double-walled helix wrapping on the Al NW with a certain pitch. In Fig. 1(b), the axes of the CNR and the Al NW are parallel to each other at the beginning. Due to the Van der Waals interaction, the CNR stretches its conventional circular configuration to an oval, then collapses to a “△” shape, and eventually becomes a linked double graphitic nanoribbon, accompanied by the bending and rolling of the CNR to form a helix. Our results show that no matter whether the axe of CNR is perpendicular, parallel or offset to that of the Al NW in the initial stage, a perfect helix would be obtained. This spiral configuration is quite similar to the self-winding of helices in plant tendrils shown in Fig. 1(c). The tendrils often twist into a helix or curl into spirals around a tree trunk[25], which makes the climbing plant soak up maximum sunshine and grow strong in the minimum space. This similarity of the structures gives some enlightenment on the wide potential application of the “CNRs-NWs” system.

To reveal these two helix-forming processes, we plot the curves of the total potential energy (E_p) in Fig. 1(d). The total potential energy has a significant downward trend during the first 120 ps, suggesting that the two collapse and helix-forming processes are spontaneous. With decreasing energy, these two CNR-NW systems increase contact areas and gradually reach more stable states.

Finally, after 100 ps, the energy reaches its minimum and subsequently remains at the minimum value with some minor fluctuations, indicating that the whole system reaches its equilibrium.

The geometric characteristics of the CNR-NW system can be indicated by the concentration distribution profiles. Taking the CNR-NW system with parallel axes originally as an example, Fig. 2 shows the concentration profiles of the core/shell composite structure in the X and Y directions. The pick details are labeled in Fig. 2. On one hand, the distance between the NW and the CNR layer is about 3.0 Å, which is very close to the scale of the chemical bonding. This short-haul distance also indicates that the interaction between the collapsed CNR and the NW is very strong. On the other hand, the separation between the two layers of the collapsed graphene nanoribbon is exactly close to 3.5 Å, which is in good agreement with the wall thickness of the multiwall CNTs (3.4Å) and also in accordance with the parallel stacking distance of the offset face-to-face π-π stacking interaction.

It is essential to answer why the CNR collapses to the Al NW spontaneously and sticks on the NW in a spiral form. Theoretically, the collapse and helix-forming process is attributed to the competition between the van der Waals interaction energy and the bending strain energy of the CNR[16]. The bending strain energy of the CNR always tends to keep the intrinsic circular form and provide an energy barrier to structure transition[26]. When the Al NW approaches, the attractive van der Waals force can help the CNR overpass the energy barrier to collapse, and undergo self-assembly[27]. As illustrated in Fig. 3, the negative ΔE_{vdW}, indicating an attractive force, has decreased dramatically and finally reaches the lowest energy state. It is worth mentioning that the evolution of the ΔE_{vdW} and the potential energy E_P are nearly synchronous during the whole helix-forming process. The van der Waals energy has partially converted into the internal energy, which drive the geometry deformation of CNR, and partially transformed to kinetic energy, which sustains the structure transition. As a result, the van der Waals interaction between the CNR and Al NW plays a dominant role in driving the self-assembly of the CNR-NW system. The other force, the offset face-to-face π-π stacking interaction[28] between the CNR and the SWCNT, also plays a significant role in the self-assembly. We speculate that the π-π stacking interactions can provide two key elements for the formation of double-deck helix, one is an energetic contribution that stems from the stacking itself, and such a contribution can thermodynamically drive the collapse process; the other is specific directionality and orientation provided by the specific pattern of stacking[29]. Therefore, in the CNR-NW system, a parallel displaced π-stacking should be the major organization of π-π interactions displacement, which makes the CNR follow a double-deck form adhering on the NW.

The collapse and self-assembly process might be affected by complicated factors. It is of paramount importance to investigate the influence of these factors in order to control the helix-forming process. Among these factors, the size effect could be a dominant one. Herein, three prime aspects are summarized: the cross section of the Al NWs, the diameter and the length of the CNR. Firstly, we simulate the CNRs (60, 60) with the same length of 24.60 Å adhering on the Al NWs with various radii, to study the size effect of the Al NWs. Fig. 4 shows the final helical nanostructures of the CNRs wrapping on the Al NWs with different diameters, such as 9.1, 18.1, 21.8, 30.9 Å. It is obvious that a perfect double-walled helix around the Al NW is obtained after the collapse of the CNR, which is independent of the size for the circle Al NWs. As expected, the rectangular can also help the CNR overcome the energy barrier to form a helix. Therefore, we can control the cross section of the Al NWs to obtain some different core-shell structures. To further investigate the diameter effect of the CNRs, we select the CNRs with different diameters adhering on the Al NWs with the diameter of 17.2 Å. We choose some Al NWs with same length of 81 Å, and set the lengths of all CNRs to be 24.60 Å. As summarized in Fig. 5, the CNR (8, 8) with a diameter of 10.85 Å can maintain its original circle after the MD simulations, implying that the van der Waals energy cannot overcome the energy required for the fully mechanical deformation of the CNR. It can be concluded that there exists a critical diameter of the armchair CNRs with estimated value of 12.20 Å, beyond which the CNRs can collapse and stick on the Al NWs in a spiral manner. The final structures of the armchair CNR (60, 60) with various lengths wrapping around the Al NWs are shown in Fig. 6, in which the length of the Al NW is set to 81 Å. It can be seen that the final core/shell composite structure can be directly affected by the length of the CNRs. If the length of the CNRs is smaller than 36.89 Å, a perfect helix around the NW can be obtained, whereas if the length of the CNRs is larger than 36.89 Å, the CNRs cannot allow the axe to offset, resulting in the knot or scroll rather than a helical confirmation. Hence, whether or not a CNR can transform to a helical conformation would rely on the diameter and length of the CNRs, instead of the cross section of the Al NWs.

In the above discussion, we focused mainly on the size effect of the CNRs and Al NWs on the helix-forming process. Next, we are devoted to studying how the CNRs interact with different NWs, such as Si, Cu, and Ni. We set all CNRs (60, 60) with the same length of 24.60 Å and all NWs with similar cross section and length. The Al, Cu, and Ni NWs are prepared in face-centered cubic (FCC) crystal structure, while the Si NW is diamond structure. The axes of the NWs are all oriented in the (0 0 1) direction. The cross sections of Al, Cu, and Ni have the same atomic arrangement, yielding the diameters of 17.2, 15.3 and 15.0 Å. The circular Si NW has the similar diameter of 16.3 Å. Fig. 7(a) illustrates that CNRs can spontaneously wrap on these metallic NWs in a spiral manner, proving that such self-assembly of CNRs on NWs is a universal but fascinating phenomenon. The interaction energy between the CNR and NWs can be reflected by the adsorption energy (E_{ads}), which can be calculated from the following equation[30]: $E_{ads} = E_{total} - (E_{CNR} + E_{NW})$. Where E_{total} represents the total potential energy of the whole system, E_{CNR} and E_{NW} are the intrinsic energy of the isolate structure. As shown in Fig. 7(b), the sequence of the adsorption energy (E_{ads}) is shown as follows: Ni > Cu > Al > Si. As we know, the metallic character of Ni is stronger than Cu, and Si is nonmetal. Therefore, we can conclude that the adsorption energy is related to the metallic character of the NWs. The adsorption energy increases with the increasing metallic character, which might be ascribed to the increase of the van der Waals interaction. In addition, the structures of the NWs also affect the adsorption energy. In Fig. 7(b), we can find that the FCC close-packed structures of Al, Cu, and Ni NW have an evident stronger attraction than the diamond structure of Si.

The above-mentioned CNRs are not hydrogen-terminated, and the attractive forces between the adjacent edges of the CNRs are large[31]. In this section, we will study the interaction between the Al NW and CNR (60, 60) with the dangling σ-orbitals on carbon atoms saturated by hydrogen atoms. Interestingly, after repeated simulation on the same CNR-NW system, we obtain two different final structure of the saturated CNR: the helix (Fig. 8(a)) and the scroll (Fig. 8(b)). To quantitatively compare the difference of the two configurations, the curve of potential energy (E_p) is plotted in Fig. 8(c). When each CNR-NW system is sufficiently relaxed, the energy of the system reaches the minimum, achieving an equilibrium state. Obviously, the potential energy of the helical configuration is lower than that of the scrolling one, indicating the helix is more stable. This unique wrapping of the CNR on the Al NW arouses our interest to investigate other metal i.e. Ni. We select the Ni NW because of its strong metallic character. Under the strong van der Waals interaction, the saturated CNR can convert into three configurations: the helix (Fig. 8(d)), the scroll (Fig.8(e)) and the stacking (Fig. 8(f)). It is speculated that the stacking is attributed to the strong van der Waals force, which leads to the rapid collapse of the enclosed graphene nanoribbon. Meanwhile, the potential energy (E_p) of these three systems is also summarized in Fig. 8(g). Similarly, it can be seen that the helix has the lowest energy, suggesting that the scroll and the stacking are the metastable states in CNR-Ni systems. The mentioned discoveries are of great importance in the better understanding the interaction of the CNT-NW systems.

Now we will clarify how the surface roughness affects the self-assembly of the CNR. The upper surface of the designed systems, consisting of Al (0 1 0) lattice plane with a thickness of 24.5 Å, are changed into some morphologies with different surface roughness. Fig. 9 shows the final configuration of the CNR collapsing on different surface morphology. In Fig. 9(a) and 9(b), due to the surface roughness is small, the CNRs collapsing on the Al surface have no difference with that on the natural smooth Al surface. In Fig. 9(c), the graphene nanoribbon produces a slight twist with the increase of the surface roughness. Fig. 9(d)-(f) show that as the surface roughness increases continuously, the final configuration of the CNR changes with the morphology of the Al surface. To understand the effect of roughness on the adsorption of the CNR, we compare the adsorption energy between the CNR an Al surface in the systems. As shown in Fig. 9(g), the adsorption energy of the system (f) is highest, indicating the strongest attraction between the CNR and the surface. The lowest adsorption energy of the system (b) illustrates poor adsorption ability. The system (c), (d) and (e) have the similar adsorption energy due to the slight difference in the roughness. The dotted line in Fig. 9(g) represents the adsorption energy between the CNR and the smooth Al surface, with the value of 2.43 Mcal/mol. It is indicated that the roughness of the surface weakens the adsorption ability of the CNR. Therefore, we can conclude that the morphology of the surface has a remarkable impact on the collapse of the CNR.

CONCLUSION

In summary, we have used MD method to simulate the interaction between the CNR and metallic NW. It is found that the CNRs can spontaneously wrap on the Al NWs in a spiral manner, forming a double-deck helix. The decrease of the potential energy in the CNR-NW systems indicates that the helix-forming processes are spontaneous. The Van der Waals interaction between NWs and CNRs is found to be dominant in driving the CNRs to collapse and self-assembly around the NWs. The double-deck form of the nanoribbon is attributed to the offset face-to-face π-π stacking interaction between the two adjacent layers of the CNRs. It can be found that the diameter and length of the CNRs should meet some required condition to guarantee the helical configuration. Our results also indicate that the saturated CNRs modified with –H show different configuration adhering on the NWs, of which the helix is the minimum energy state. In addition, the surface roughness of the NW has a remarkable impact on the collapse of the CNR.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

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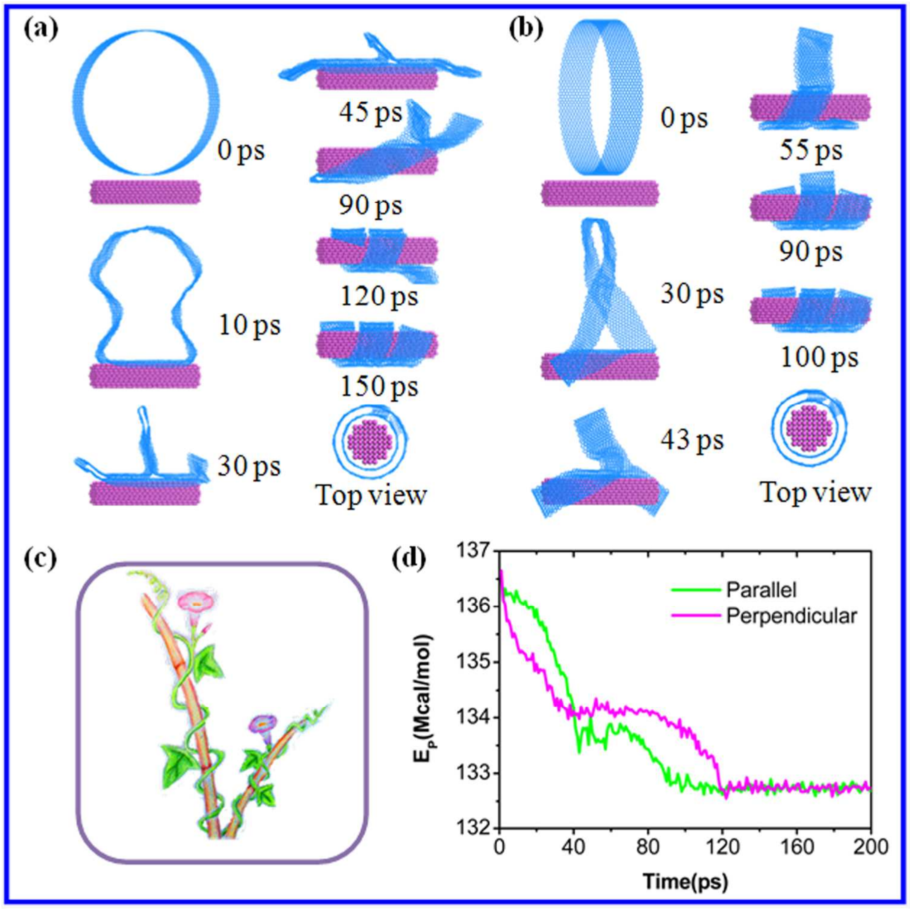

Fig.1 Typical collapse snapshots of the CNR (80, 80) with diameter of 108.48 Å on the Al NW with same diameter of 17.2 Å in a spiral manner. The length of the Al NW is 81 Å and the one of the CNR is 24.60 Å. (a) the perpendicular axes. (b) the parallel axes. (c) Sketch of the self-winding of helices in plant tendrils. (d) Total potential energy (E_P) of these two CNR-NW systems as a function of time.

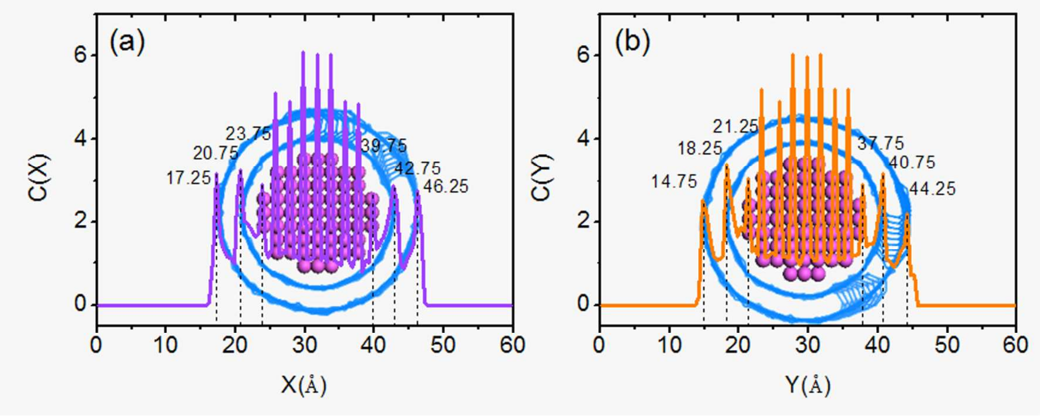

Fig. 2 Concentration distribution profiles of the core/shell composite structure from the CNR and NW with parallel axes in the X-direction (a) and in the Y-direction (b).

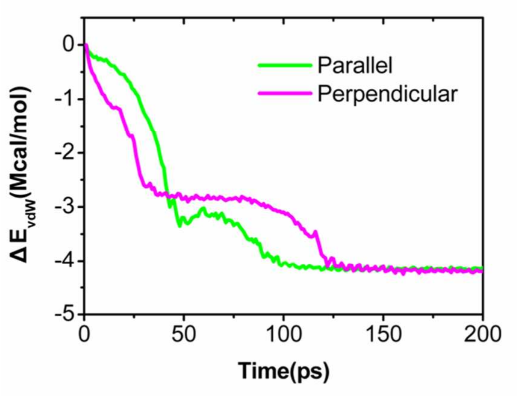

Fig.3 The evolution of Van der Waals interaction energy (ΔE_{vdW}) between the CNR and NW as a function of time.

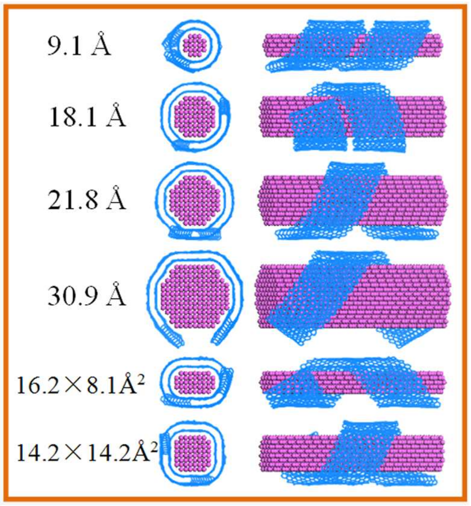

Fig.4 The final helical nanostructures of the CNRs (60, 60) wrapping on the Al NWs with different cross sections. The length of the CNRs (60, 60) is 24.60 Å and the length of the Al NWs is 81 Å.

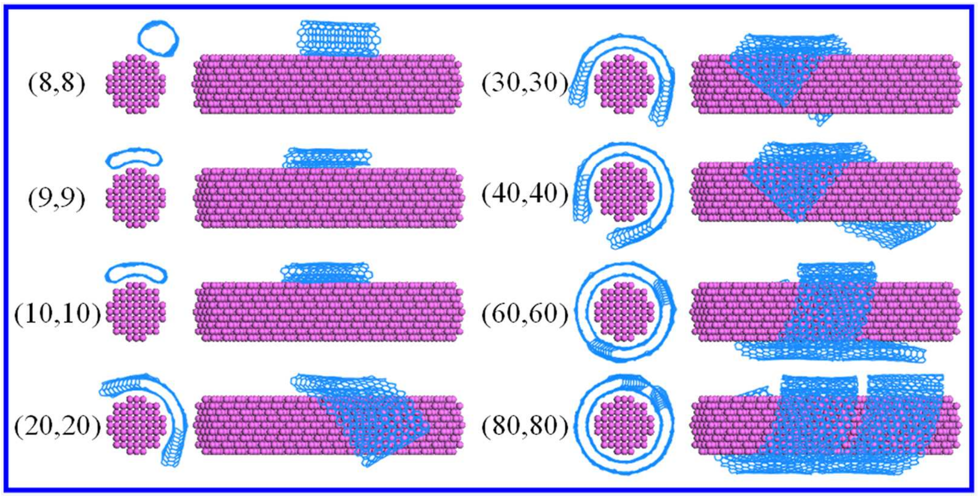

Fig.5 The helical wrapping of CNRs with different diameters around the Al NW with same diameter of 17.2 Å. The length of the CNRs is 24.60 Å and the one of the Al NWs is 81 Å.

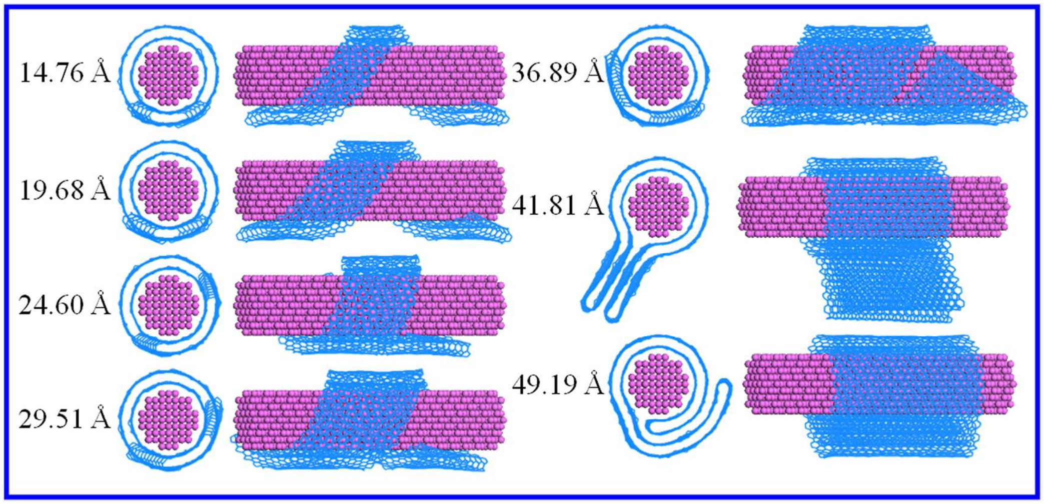

Fig.6 The self-assembly of CNRs (60, 60) with different lengths around the Al NWs with same diameter of 17.2 Å.

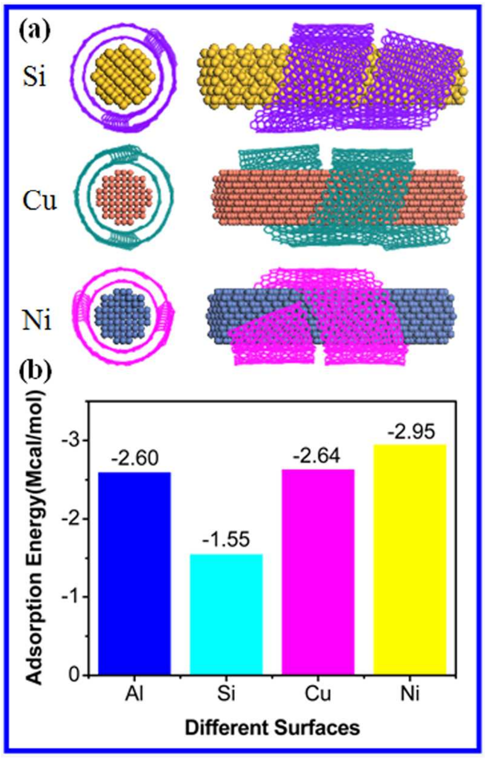

Fig.7 (a) The spontaneously wrapping of CNRs (60, 60) on different metallic NWs in a spiral manner. (b) The corresponding adsorption energy between the CNR and NW.

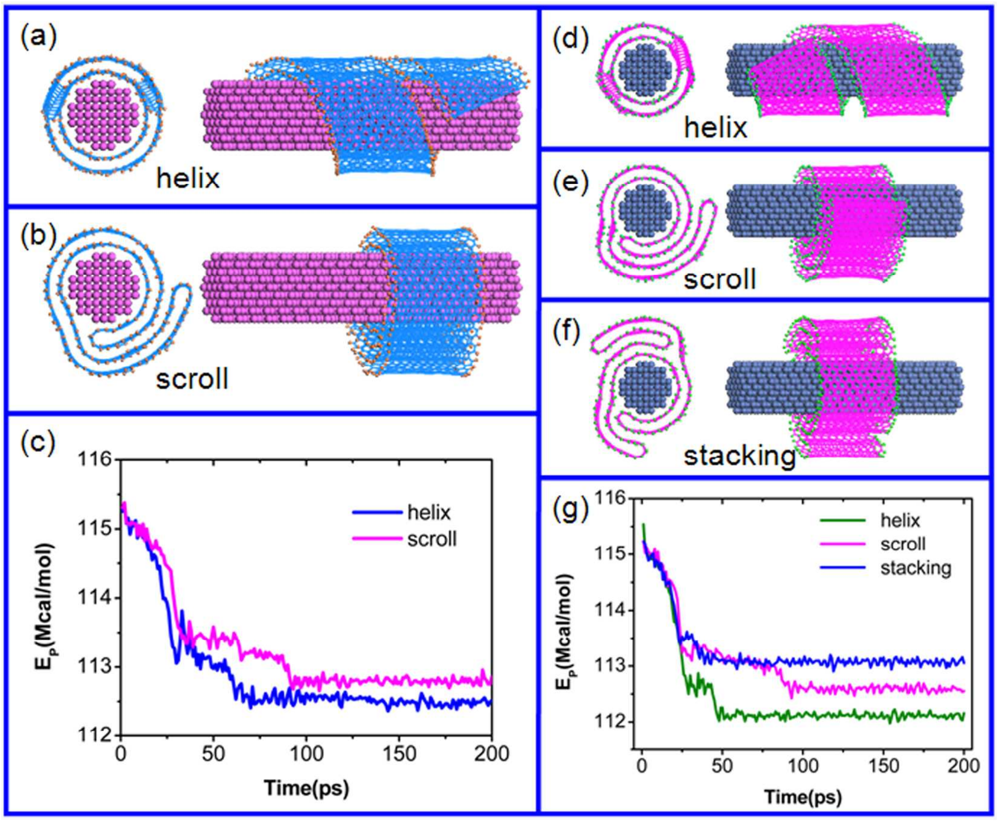

Fig.8 The final configuration of the CNR (60, 60) wrapping on the Al NW. (a) helix (b) scroll (c) the total potential energy (E_P) of the CNR-Al systems as a function of time. The final configuration of the CNR wrapping on the Ni NW. (d) helix (e) scroll (f) stacking (g) the total potential energy (E_P) of the CNR-Ni systems as a function of time. All CNRs are terminated with hydrogen atoms.

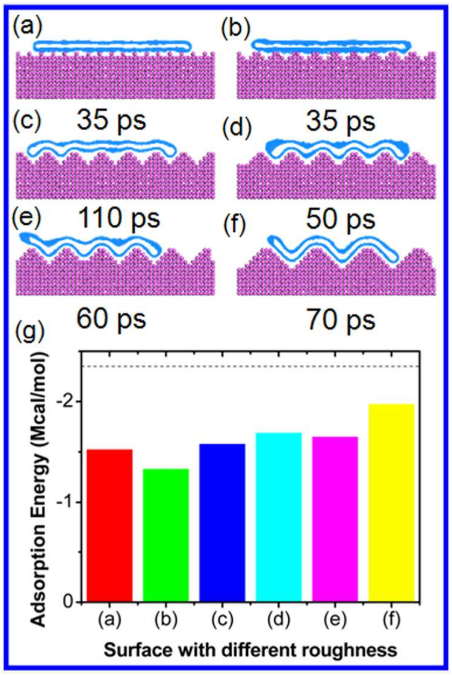

Fig. 9 (a)-(f) The final configuration of CNR (60, 60) adhering on the Al surfaces with different roughness. (g) The corresponding adsorption energy between the CNR and different surfaces.

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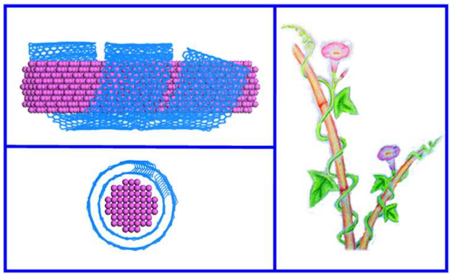

The super-short carbon nanoring can spontaneously wrap on the Al NW to form a double-deck form a double-deck helix.