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Geometry, stability and thermal transport of hydrogenated graphene nanoquilts

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ABSTRACT

Geometry, stability, and thermal transport of graphene nanoquilts folded by hydrogenation are studied using molecular dynamics simulations. The hydrogenated graphene nanoquilts show increased thermodynamic stability and better transport properties than folded graphene structures without hydrogenation. For the two-fold graphene nanoquilt, both geometry and thermal conductivity are very sensitive to the adsorbed hydrogen chains, which is interpreted by the red-shift of PDOS. For the multi-fold nanoquilts, their thermal conductivities can be tuned from 100% to 15% of pristine graphene, by varying the periodic number or length. Our results demonstrated that the hydrogenated graphene nanoquilts are quite suitable to be thermal management devices.

1. Introduction

Graphene is a superior material for electronics and phononics [1–4] because of super high electron mobility [5] and thermal conductivity [6]. Various functionalizations [7–10] are used to tune physical properties of graphene in order to achieve desired devices. Folding [10–12] is considered as an effective way of functionalization. Although graphene is very hard in the planar direction, it can be easily warped in the out-of-plane direction. Folding can drastically change the physical properties of graphene [10–15]. For example, the Fermi velocity in the graphene is reduced by folding [13]; an armchair nanoribbon changes from semiconducting to metallic after folding [14]; the thermal conductivities of graphene decrease as folding occurs [15]. Based on these folded graphene structures, some devices have been proposed, such as resistors [16], diverters [16], and conductance modulators [17], etc.

Experimentally, folded graphene can be obtained by random ultrasonic stimulation [18] or patterned etched trenches [19] i.e., by external mechanical forces. However, the geometries of these folded structures are not able to be easily controlled [18,19] and they are not stable at high temperatures, especially for multi-folded graphene [15]. The former studies indicated that the physical properties of folded graphene are very sensitive to their geometries [10–15]. Therefore, another more effective way should be found to precisely fold graphene. In fact, advances in microscopy technologies have provided an exciting opportunity to manipulate graphene morphologies by chemical functionalization [20,21]. A recent study shows that graphene can be folded by hydrogenation with different folding angles [21,22]. These hydrogen folded structures are more suited for thermal devices, however, to our best knowledge thermal transport in these folded graphene, especially in the multi-folded graphene, has been reported scarcely.

In this paper, we study thermal transport properties of two-fold and multi-fold graphene by applying classical molecular dynamics methods. Because graphene can be folded like a quilt by hydrogenation, as shown in Fig. 1(b) and (d), we call these folded graphene nanoquilts. The geometric evolution from pristine graphene to a two-fold nanoquilt is discussed at first. The thermal conductivities decrease rapidly with hydrogenation, ultimately to about 30% of pristine graphene. The tuning range of thermal conductivities is much larger than the case of folded graphene without hydrogenation. On the basis of the two-fold nanoquilt, thermal transports in multi-fold nanoquilts are studied. The multi-fold nanoquilts exhibit excellent thermal stability at high temperatures, and their thermal conductivities can be well modulated by periodic number and periodic length. We find that, after pristine graphene is folded into a multi-fold structure, its thermal conductivity can at most be reduced to 15%. These findings are very useful for the applications of graphene in thermal devices.

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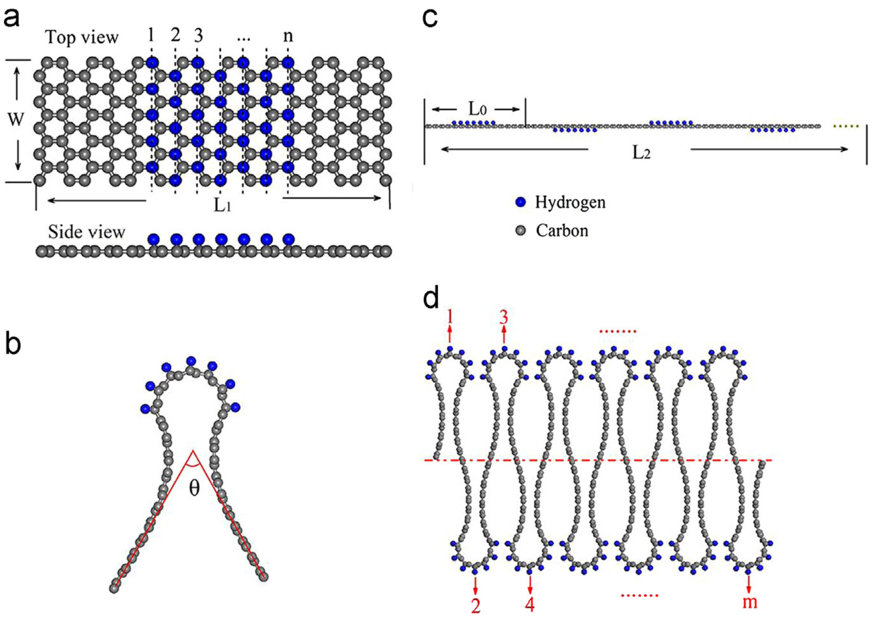

Fig. 1. (Color online) (a) Schematic view of an armchair-edge graphene nanoribbon adsorbing n hydrogen chains. L_1 and W represent the length and width of nanoribbon, respectively. Top panel is the top view while the bottom panel is the side view. (b) Optimized structure of (a), a two-fold nanoquilt with a bending angle θ. (c) Schematic view of a periodic hydrogenated graphene nanoribbon in units of (a). L_2 is the length of the nanoribbon and L_0 is the periodic length. (d) Optimized structure of (c), a multi-fold nanoquilts of m period.

2. Simulation method and model

Fig. 1(a) shows a graphene nanoribbon with length L_1 and width W, where n hydrogen chains are adsorbed on the middle of top surface. The optimized structure can be seen in Fig. 1(b), showing the graphene nanoribbon being folded by hydrogenation. θ is used to represent the folding degree defined as the angle between two-side straight ribbons. The folding process likes a quilt being folded into two layers, so we call it a two-fold nanoquilt. Based on Fig. 1(a), a periodic two-surface hydrogenated graphene nanoribbon is shown in Fig. 1(c), in which L_0 represents the periodic length and L_2 is the total length. Fig. 1(d) is the optimized structure, i.e., it forms a multi-fold graphene nanoribbon with a periodic number m, which is called multi-fold nanoquilts.

In our simulations, the *LAMMPS* package [23] with the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [24] is adopted. Periodic boundary conditions are applied only to the direction perpendicular to the functionalized rows and other two directions are set free. Then atomic positions are relaxed to obtain minimum energy configuration using the conjugate gradient algorithm. After relaxation, we extend the relaxed structure to the desired hydrogenated graphene nanoribbons. That is, we prepared the folded graphene nanoribbons by C–H chemical bonding effects.

In the non-equilibrium molecular dynamics simulation (NEMD), the AIREBO potential is still adopted. On each hydrogenated graphene nanoribbon, fixed boundary conditions are implemented with the atoms at the left and right ends are fixed at their equilibrium positions. Next to the boundaries, the adjacent two cells of atoms are coupled to Nosé–Hoover thermostats [25,26] with temperatures 320 K and 280 K, respectively. That is, the average temperature is 300 K with a temperature difference 20 K. From Fourier's law, the thermal conductivity K is defined as

$$K = -\frac{J}{\nabla T \cdot S}, \tag{1}$$

where ∇T is the temperature gradient in structure, J is the heat flux from the heat bath to the system, which can be obtained via calculating the heat baths power. $S = W \times H$ is the cross-sectional area, W is the width and H is the thickness of graphene nanoribbons, which we have chosen as H=0.144 nm. In order to focus on the hydrogenation and deformation effect on phonons transport in nanoribbons, we keep the cross section area as a constant. With a time step of 0.5 fs, the graphene ribbon is first relaxed to the equilibrium states at 300 K for up to 500 ps under the canonical ensemble (NVT). Next, a temperature gradient is achieved by thermostat bath. After reaching the non-equilibrium steady state, 100 ps been used to calculate the thermal conductivity. In addition, the adopted AIREBO potential included the LJ term [24], which can be used to describe the *van der Waals forces* between ribbon parts after deformation, as shown in Fig. 1(b) and (d).

To understand the underlying mechanisms of phonon transport in hydrogenated graphene, the phonon density of states (PDOS) has been calculated. The PDOS is calculated from the Fourier transform of the velocity autocorrelation function [26,27]:

$$\mathrm{PDOS}(\omega) = \frac{1}{\sqrt{2\pi}}\int e^{-i\omega t}\left\langle \sum_{j=1}^{N} v_j(t)v_j(0)\right\rangle dt \tag{2}$$

where $v_j(0)$ is the average velocity vector of a particle j at initial time, $v_j(t)$ is its velocity at time t, and ω is the vibration wavenumber.

3. Results and discussion

In Fig. 2(a), the geometric evolution of two-folded graphene nanoquilts by hydrogenation is shown. The size of the graphene nanoribbon we considered is L_1=6.3 nm and W=2.21 nm with armchair edge. The nanoribbon will be bended gradually as hydrogen chains are adsorbed on the middle. This is because the hydrogenation of graphene leads to a transformation of sp2 to sp3 and then causes a local distortion. The more chains, the more the bending deformation accumulates. Fig. 2(a) displays the relation between the bending angle θ and the number n of adsorbed hydrogen chains. As the number n increases from 1 to 9, the