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Thermal characteristics of graphene nanosheet with graphane domains of varying morphologies

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ABSTRACT

In this paper, thermal characteristics of graphene nanosheet embedded with graphane quantum dots (QDs) are investigated using Non-Equilibrium Molecular Dynamics (NEMD) method. Thermal conductivity of nanoribbon is demonstrated to be tunable by manipulating the geometrical characteristics of graphane QDs without changing the amount of hydrogenation. Graphane QDs of larger circumferences cause more deterioration in heat transfer due to the scattering of phonons occurred at the graphene-graphane interface. As a result, nanoribbon with graphane QDs possesses higher thermal conductivity than that with random hydrogenation of same amount. Under fixed circumferences, the length-to-width ratio of QD is revealed to be the most important causes of deterioration in thermal conductivity. Graphane QDs of high length-to-width ratio have smaller deterioration effect on thermal conductivity. Combing the effect of circumference and length-to-width ratio, the thermal difference between nanoribbons with graphane QDs of different shapes can be sufficiently interpreted. The demonstrated mechanism can be applied for the optimization of nanodevices fabricated from hydrogen functionalized graphene.

1. Introduction

Graphene is a 2D plate-like material gifted with exceptional properties in terms of chemical [1,2], electrical [3], mechanical [4] and optical characteristics [5], which has attracted tremendous research attention over the last few decades [6,7]. Meanwhile, graphene has been well known for its outstanding thermal property with fundamental and significant applications [8,9]. As the development of nanoelectronic devices, requirements for efficient heat dissipation of nanodevices are raised to ensure the performance and lifetime. Graphene has great applications in thermal management of nanoelectronic devices due to its fascinating thermal characteristics [10–12]. Experimental investigations found that pristine graphene had excellent thermal conductivity of 2500–5000 W/mK [13–15]. Thermal conductivity of finite graphene nanoribbons has been reported to be anisotropic caused by the edge effect by the molecular dynamic (MD) simulations [16–18], while the anisotropy of thermal conductivity becomes negligible when the graphene nanoribbon has an infinite size [19].

With the advancement in the synthesis and assembly of 2D nanomaterials [20], graphene can be effectively modified via surface functionalization, in which the carbon atoms are converted from sp^2 to sp^3 hybrids to bond with the adatoms [21–24]. It is both important and necessary to manipulate the thermal characteristics in the practical application of 2D nanomaterials. Hydrogenation has been widely accepted as an efficient way to manipulate the electronic [25], magnetic [26], mechanical [27–29] as well as the thermal properties [30,31] of graphene. Thermal conductivity of graphene has been reported to deteriorate with the increase of randomly hydrogen coverage from 0% to 30%, and then becomes insensitive with further increasing hydrogenation [30]. For graphene with fully hydrogenated domain (graphane domain), the interfaces between graphene and graphane shows an attractive role in the thermal transport, which can reduce the thermal conductivity of composites due to interface phonon scattering [30,32]. Remarkable thermal rectification is reported in hybrid nanoribbon with graphene-graphane interface [33]. Recently, the production of mosaic graphene is achieved by patterning the doped atoms on graphene surface [34], and in-plane heterostruc-

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ture of graphene with controlled and patterned hydrogenation distributions has also been created experimentally [35], which shed light on the fact that graphane quantum dots of specific geometrical shapes are practical via specific experimental procedures. The effects of graphane quantum dots on the mechanical properties and failure process of graphene sheets have been reported [36]. However, the detailed effect on the thermal properties of graphene nanosheet introduced by graphane quantum dots on the surface has not been fully revealed yet. In this paper, the thermal conductivity of graphene nanosheet embedded with graphane quantum dots are systematically investigated. By calculating the temperature profiles of graphene nanosheets with various graphane QDs, the difference in their heat conductivity can be revealed conveniently by comparing the heat flux across the nanosheet under fixed temperature interval. Thus the method of Non-Equilibrium Molecular Dynamics (NEMD) simulations [37,38], which has been widely used for simulating the thermal characteristics of nanomaterials, is adopted in this paper. Our results show that the thermal conductivity of graphene nanosheet can be effectively manipulated by doping graphane QDs of varying geometrical characteristics: circumferences and length-to-width ratio.

2. Methods and model

In our simulations, non-equilibrium molecular dynamics (NEMD) method are performed for the thermal properties of graphene nanosheet using LAMMPS package [39]. The interactions of C—C bonds and C—H bonds are described by the Adaptive Intermolecular Reactive Empirical Bond Order potential (AIREBO) [40], which has been widely adopted for the thermal and mechanical properties of carbon-based nanomaterials [41–43]. The key idea of the NEMD method is to impose a temperature gradient along the direction of heat transfer and calculate the heat flux across the graphene nanosheet.

Fig. 1a and b shows the atomistic structure of graphene nanosheet embedded with graphane QD and random hydrogenation, respectively. All the graphene nanosheet in our simulations have the same length ($X = 40$ nm), width ($Y = 10$ nm) as well as the hydrogenation percentage ($H = 5\%$). The overall simulation length $X = 40$ nm includes the fixed boundary, hot and cold slabs and free region. The thickness of the graphene nanosheet is assumed to be 0.34 nm as suggested [44]. The graphane QD is placed in the middle of the graphene nanosheet. Periodic boundary condition is employed along y-direction (width) while the atoms at both ends of the graphene nanosheet (5 Å width in X direction) are fixed after fully relaxation to keep simulation system from drifting and oscillating. With these constraints in place, all the graphene nanosheet are fully relaxed at room temperature (300 K) coupled with Nosé–Hoover temperature thermostat (NVT ensemble) for 3×10^6 time steps for equilibrium.

Then the heat flux transports is applied from hot slab and cold slab (2 nm width in X direction) along x-direction for stabilized temperature profile. The average temperature of atoms in hot and cold Nosé–Hoover reservoirs (as shown in Fig. 1) are set to be $T_{hot} = 320$ K and $T_{cold} = 280$ K, respectively. A dynamic steady state of heat flux along the graphene nanosheet can be reached after a simulation period of 0.2 ns. To obtain the temperature profile along graphene during simulation, we divide the graphene ribbon into many narrow slabs equally, which are approximately 2 nm width in X direction. The temperature in each divided slab can be calculated by [38]

$$T_{slab} = \frac{2}{3Mk_B}\sum_j \frac{p_j^2}{2m_j} \tag{1}$$

where M is the number of atoms in the slab, m_j and p_j represent the mass and momentum of the atom j respectively, and k_B is the Boltzmann constant. Then the temperature profile along graphene nanosheet can be established by the calculating the temperature in each slab. The temperature gradient $\frac{dT}{dx}$ can be calculated by linear fitting of the temperature variation in each slab.

The heat flux J is defined as the energy transported along the simulation system per unit cross-sectional area and unit time, which can be given as [45]

$$J = \frac{1}{V}\left[\sum_i^N \varepsilon_i v_i + \frac{1}{2}\sum_{ij;j\neq j}^N (F_{ij}\cdot v_i) r_{ji} + \frac{1}{6}\sum_{jik;i\neq j\neq k}^N (F_{ijk}\cdot v_i)(r_{ji}+r_{ik})\right] \tag{2}$$

where the subscripts i, j, k denote the three different atoms. ε_i and v_i are the energy and velocity of atom i, respectively. Vector r_{ij} represents the interatomic distance between atoms i and j, and F_{ij} and F_{ijk} represent the two-body and three-body force, respectively. V is the volume of the studied system.

The thermal conductivity of graphene nanosheet can be determined by Fourier laws

$$k = J\left(\frac{dT}{dx}\right)^{-1} \tag{3}$$

where J is heat flux, and $\frac{dT}{dx}$ is the temperature gradient.

In this work, the time step is 0.1 fs and each calculation contains 2.8×10^7 time steps which giving a total simulation time of 2.8 ns. The initial relaxation under 300 K takes 0.3 ns, the temperature gradient typically stabilize at 0.5 ns, and the time average of heat flux is performed from 0.5 ns to 2.8 ns after the system reached the non-equilibrium steady state.

3. Dependence of thermal properties on circumference of graphene QD

We first calculate the thermal conductivity of armchair and zigzag oriented pristine graphene nanosheet with a length of 40 nm and a width of 10 nm by NEMD simulation to verify the reliability of our model. The typical temperature profile in pristine graphene nanosheet is plotted in Fig. 1. In order to average the heat flux J at each time step, we accumulate the heat flux J over simulation time to calculate the total energy transported across the pristine graphene nanosheet per unit cross-sectional area. As the Fig. 1d shown, the total energy increases linearly with the simulation time, which suggests a steady and time-independent heat flux J. Therefore the averaged heat flux J can be obtained by the slope of the curve in Fig. 1d. In this paper, the temperature interval between hot and cold slabs is fixed at 40 K in each simulation. Although the temperature profiles of different simulation systems have different shapes, the thermal conductivity can still be compared by the heat flux transported from heat slab to cold slab under fixed temperature interval. More heat flux transported implies better capability of heat conduction, corresponding to a higher thermal conductivity. The absolute value of thermal conductivity obtained may be not precise enough, however, the qualitative variation relationship can be effectively revealed from the perspective of the heat flux. The calculated thermal conductivities along armchair and zigzag direction are calculated to be 165 W/mK and 179 W/mK, which are in good agreement with the reported simulation results of about 170 W/mK using the AIREBO potential [46]. It can be noticed that the simulated thermal conductivity along zigzag direction is larger than that along armchair direction. The dependency of thermal conductivity on chirality is consistent with the reported results [16–18]. What's more, the experimental thermal conductivity of graphene is about 2500–5000 W/mK [13,15,47]. Such difference between experimental and simulated