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Thermal characteristics of graphene nanoribbons endorsed by surface functionalization

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ABSTRACT

In this paper, the thermal characteristics of graphene nanoribbons with surface hydrogenation are investigated using Reverse Non-Equilibrium Molecular Dynamics (RNEMD) simulations. Thermal conductivity of graphene nanoribbons with fully hydrogenated domain (graphane) are studied by calculating the Kapitza conductance across the graphene-graphane interface. Thermal conductivity of hybrid nanoribbon is revealed to depend on the length as well as charity and initial temperature, and been systematically interpreted from the perspectives of morphology and phonon vibrational spectra. More interestingly, remarkable thermal rectification is noticed for hybrid nanoribbon with graphene-graphane interface. The thermal conductivity under heat flux from graphane to graphene is higher than that under opposite heat flux. Such thermal rectification decays with the length of nanoribbon and a critical length of 10 nm is identified for single layer nanoribbon beyond which the thermal rectification disappeared. We also studied the thermal properties of graphene nanoribbon with gradient hydrogen arrangement at the surface. Gradient hydrogenation can provide graphene nanoribbon with similar thermal rectification while eliminating the dependency on chirality and length. The proposed gradient hydrogenation can be used for length-insensitive thermal diode with practical application. Our work reveals detailed thermal characteristics of hydrogenated graphene nanoribbons, and provides a possible design of carbon-based thermal diodes.

1. Introduction

As a 2D plate-like material gifted with exceptional properties in terms of chemical [1,2], thermal [3], electrical [4,5], mechanical [6] and optical [7] characteristics, graphene has attracted tremendous research attention over the last few decades [8,9]. Graphene is also a good conductor of electricity with zero band gap [10], and has remarkable electron mobility compared to silicon [11]. What's more, the outstanding thermal property of graphene is also of important practical significance in many potential applications. Thus, graphene has been acknowledged as a promising candidate for developing the next-generation semiconductor material. Recently, experimental investigations found that pristine graphene had excellent thermal conductivity of 2500–5000W/mK [3,12,13]. The anisotropy of thermal conductivity in finite graphene nanoribbons caused by the edge effect has been reported by the molecular dynamic (MD) simulations [14–16], while the anisotropy of thermal conductivity becomes negligible when the graphene nanoribbon has an infinite size [17]. Sophisticated manipulation of the outstanding thermal characteristics is crucial to the practical application of 2D nanomaterials [18].

With the advancement in the synthesis and assembly of 2D nanomaterials [19], 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 [20–23]. Hydrogenation has been widely accepted as an efficient way to manipulate the electronic [24], magnetic [25], mechanical [26–28] as well as the thermal properties [29,30] of graphene. The enhanced properties provided by hydrogenation are reported to be tunable by changing the hydrogen coverage and distribution [31–35]. Thermal conductivity of graphene is found to deteriorate with the increase of randomly hydrogen coverage. It declines rapidly with the coverage from 0% to 30%, and then becomes

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insensitive with further increasing coverage [29]. For graphene with fully hydrogenated domain, the interfaces between graphene and graphane shows an attractive role in the thermal transport, and play an important role in developing graphene-graphane-based electronic devices [36]. It can reduce the thermal conductivity of composites due to interface phonon scattering. However, the detailed thermal properties of hydrogenated interface in hybrid graphene-graphane nanoribbon still remain unclear. In this paper, we systematically investigate the thermal transport across hydrogenated interface using the Reverse Non-Equilibrium Molecular Dynamics (RNEMD) simulations [37]. The dependencies of interface conductance on chirality, simulation length and initial temperature are considered. Length-sensitive thermal rectification caused by hydrogenated interface in graphene nanoribbons is revealed. We also proposed a length-insensitive thermal diode by doping graphene surface with gradient hydrogenation.

2. Methodology

Reverse Non-Equilibrium Molecular Dynamics (RNEMD) simulations are performed for the thermal properties of graphene nanoribbon using LAMMPS package [38]. The interaction between carbon atoms is described by the Adaptive Intermolecular Reactive Empirical Bond Order potential (AIREBO) [39], which has been widely adopted for studying the thermal and mechanical properties of carbon-based nanomaterials [40–42], including hydrogenated graphene [43]. The key idea of the RNEMD method is to apply a heat flux across the nanoribbon and obtain the temperature profile along the direction of heat transfer to determine the temperature gradient.

Fig. 1 shows the geometry of the RNEMD simulation for zigzag- and armchair-oriented graphene nanoribbons with surface hydrogenation. Periodic boundary conditions are employed along the length (parallel to the heat flux) as well as the width direction (perpendicular to the heat flux). The thickness of the nanoribbon is assumed to be 0.34 nm as suggested [44]. All the nanoribbons are fully relaxed at a given initial temperature until the systems reach equilibrium before applying a heat flux. We divide the simulated graphene ribbon into many narrow slabs equally, which are approximately 0.4 nm width perpendicular to the heat flux. The heat flux is introduced by continuously exchanging the kinetic energy between the hottest atoms from a cold slab, located at the both ends of the nanoribbon, with the coldest atoms from the hot slab, located at the middle of nanoribbon, under NVE ensemble. The heat flux q can be written as

$$q = \frac{1}{2tA}\sum_{transfer}\frac{1}{2}\left(m_h v_h^2 - m_c v_c^2\right) \tag{1}$$

where t is the total simulation time, A is the cross-sectional area perpendicular to the heat flux, m_h, m_c and v_h, v_c refer to the mass and velocity of the hottest atom in cold slab and the coldest atom in hot slab, respectively. The procedure of kinetic energy transferring is repeated every 50 time steps with a time step of 0.0002 fs The heat flux from cold slab to hot slab reaches a dynamic steady state after 100000 simulation time steps and a temperature gradient appears in the nanoribbon. To obtain the temperature profile along nanoribbon, the temperature in each divided slab can be calculated by

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

Then the temperature gradient $\frac{dT}{dx}$ can be calculated by linear fitting of the temperature variation in each slab. The thermal conductivity can further be determined by Fourier laws

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

By repeating the procedure of kinetic energy transfer, a linear response of temperature variation appears in pure graphene nanoribbons [37]. In the case of nanoribbons with hydrogenated interface, a sudden jump of temperature ΔT arises at the graphene-graphane interface, as shown in Fig. 2*b*. The thermal property of the interface between graphene and hydrogenated graphene (graphane) is evaluated by the Kapitza conductance G, which is defined as

$$G = \frac{q}{\Delta T} \tag{4}$$

For graphene nanoribbons with fully hydrogenated domains, the graphene-graphane interfaces are placed in the middle of the cold and hot slab. Across the interface, a sharp change from 0 to 100% in the hydrogenation ratio can be noticed.

3. Results and discussion

We first calculate the thermal conductivity of pristine graphene by RNEMD simulation to verify the reliability of our computational models. The typical temperature profile calculated for pure

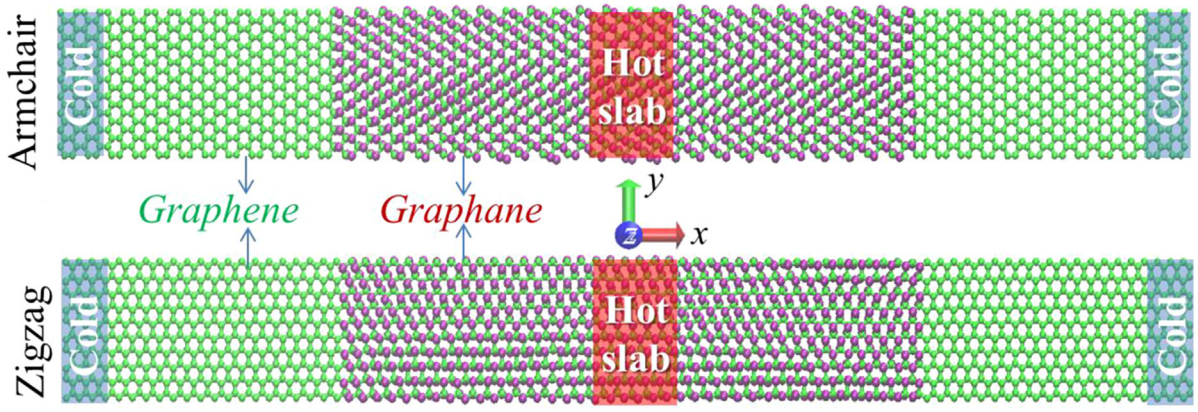

Fig. 1. Geometry of the RNEMD simulation for zigzag- and armchair-oriented graphene nanoribbons. The cold slabs are placed at the ends of the simulation cell, while the hot slab is located in the middle of the cell. Hydrogen atoms are colored in purple while the carbon atoms are colored in green. (A colour version of this figure can be viewed online.)