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Molecular dynamics simulation of the effect of oxygen-containing functional groups on the thermal conductivity of reduced graphene oxide

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ABSTRACT

Models of reduced graphene oxide (RGO) with different numbers of layers and simulation sizes were established and molecular dynamics simulations were performed to study the influence of oxygen-containing functional groups on the thermal conductivity (TC) of RGO. The results show that the TCs of both monolayer RGO (MRGO) and bilayer RGO (BRGO) increase with the increasing simulation length; under the same simulation size, the TC of BRGO is always lower than that of the MRGO. With the increasing content of functional groups, TCs of both MRGO and BRGO increase firstly and then decline. For MRGO, the optimum content occurs at about 2%. The phonon resonant frequency of MRGO with content of functional groups lower than 2% remains constant, and shifts to a lower frequency when the content of functional groups is higher than 2%; this confirms the effects of functional groups and wrinkling structure with ripples on the phonon scattering. For BRGO, the optimum content occurs at about 1%, which is lower than that for MRGO, since the interlayer distance of BRGO increases linearly with the increasing content of functional groups. Moreover, the changing trends of interaction energy and interlayer thermal resistance of BRGO are consistent with the TC change of BRGO.

1. Introduction

As a two-dimensional monolayer of sp^2 bonded carbon atoms arranged in honeycomb lattices [1], graphene possesses many fascinating properties such as giant electron mobility [2], extremely high electrical conductivity [3], and very high thermal conductivity (TC) of 5000 $W{\cdot}m^{-1}{\cdot}K^{-1}$ [4]. Due to its superior thermal property, graphene can be applied to improve thermal conductivity of polymer composites [5], which can be widely used in plastic heat exchanger [6,7] and thermal interfacial materials [8]. Several methods including micromechanical exfoliation of graphite [1], epitaxial growth [9], reduction/exfoliation of graphene oxide (GO) [10] and chemical vapor deposition (CVD) [11], have been reported to obtain individual graphene. Among these fabrication approaches, only the reduction/exfoliation of GO can produce graphene in a large scale. However, Cecilia et al. [12] reported that the reduced graphene oxide (RGO) contains residual oxygen-containing functional groups that are sp^3 bonded to the carbon atoms in the basal plane; the small amount of sp^3 bonds disrupt the transport of carriers in sp^2 carbon-carbon (C—C) network, limiting the electron mobility and conductivity of RGO atomic thin films.

Recently, studies of the influence of oxygen-containing functional groups on the properties of RGO have attracted much attention. Bagri et al. [13] employed molecular dynamics (MD) simulation methods to study the evaluation of the atomistic structure of RGO, and elucidated the evaluation of oxygen-containing functional groups, such as carbonyl (—COOH) and ether groups (—O—), which hinder the complete reduction of RGO. Wang et al. [14] found that the functional groups, the hydroxyl (—OH) and carboxyl groups, might bend the single-layered graphene sheet and the resonant frequency shift of such a graphene resonator reaches 67–135% of that of a non-functionalized graphene resonator; this provides an important guide to the design of single-layered RGO nanomechanical resonator with variable frequency in the terahertz range. Aref et al. [15] used reverse non-equilibrium molecular dynamics (RNEMD) simulation methods to study the influence of alkyl functional groups on the TC of GO nanosheets, and found that the TC of GO reduces after alkylation and decreases with an increase in the chain length of functional groups. Song et al. [16] reported that the annealing temperature greatly influences the

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oxygen content of RGO, and therefore influences the TC of RGO flakes, which reaches its highest value at 1200 °C with 4.1% oxygen content. The presence of sp^3 bonds disrupts the conjugated sp^2 network of the pristine graphene, which leads to a high resistant channel, and hence decreases the TC of RGO.

To further explore the influence of oxygen-containing functional groups on the TC of RGO, the thermal and physical properties of RGO with different numbers of functional groups were analyzed through RNEMD simulations in this paper. In detail, the monolayer RGO (MRGO) model was firstly established with content of functional groups changing from 0% to 5% and simulation length changing from 5 nm to 15 nm. Then the influences of modification degree and simulation size were systematically investigated by analyzing TC, temperature distribution, configuration, and phonon vibrational density of states (VDOS) of MRGO after equilibration. Furthermore, to explore the interfacial interaction between different layers of multilayer RGO, the bilayer RGO (BRGO) model with two-layer structure was established, and the interfacial properties between two layers of BRGO, such as the interlayer distance (d_{int}), interaction energy (E_{int}) and interlayer thermal resistance (R_{int}), were calculated, which is very important for the experimental research and industrial applications of RGO.

2. Modeling and simulation methods

2.1. Molecular models of RGO

In this work, the MRGO and BRGO models were created by the Accelrys Materials Studio 7.0 software. The condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field [17], which has been parameterized to study many common organic and inorganic molecules, was used to establish the initial molecular configurations.

As observed in XPS spectrum of RGO [16,18,19], the functional groups on RGO films are mainly —OH, —COOH and —O— groups, and the number ratio of these groups is about 4:3:2. In the simulations of this work, the functional groups were assumed to be randomly dispersed on the surface of RGO films. Geometry optimization (less than 5000 steps) was performed followed by 500 ps NVT (constant number of particles, volume and temperature) MD simulation at 298 K and 1 atm with a time step of 1 fs to reach an equilibrium condition. A Nose/Hoover thermostat was implemented for temperature control [20]. Then the obtained equilibrated systems were taken as the initial configurations to calculate the TCs of MRGO and BRGO. Fig. 1 shows two examples of initial configurations of MRGO and BRGO, which contain 5 wt% functional groups (MRGO-5% and BRGO-5%).

2.2. Calculation of thermal conductivity

Thermal conductivity can be predicted either by equilibrium or non-equilibrium molecular dynamics. In the equilibrium molecular dynamics (EMD) approach, the system remains at equilibrium condition, and the Green-Kubo relations [21] are mainly used to calculate the transfer coefficients. But, in the non-equilibrium molecular dynamics (NEMD) approach, a driving force or field is applied and the resulting flux is measured [22]. To calculate the TC values easily, Muller-Plathe's [23] proposed a simple and rapid converging RNEMD method. The RNEMD simulation applies the reversed process of NEMD, which means that a heat flux is imposed and a temperature field is calculated as a result. Aref et al. [15] has employed this RNEMD approach to calculate the TC of GO nanosheets with alkyl functional groups on the surface. Pei et al. [24] also employed this RNEMD method to investigate the TC of hydrogenated graphene.

In our simulation, the RNEMD simulation based on Muller-Plathe's method was performed by LAMMPS. The bonding interaction of C—C rings was described by the adaptive intermolecular reactive empirical bond order (AIREBO) potential [25], which has been widely adopted for the study of carbon-based materials [24,26,27]. And the third-generation Charge-Optimized Many-Body (COMB3) potential [28] was applied to the simulation of oxygen-containing functional groups and their interaction with the carbon atoms of C—C rings. Moreover, the velocity Verlet algorithm was used to integrate the motive equation and periodic boundary condition (PBC) was applied in all the three directions (x, y, z). The simulation box dimensions of 5 nm-long, 10 nm-long and 15 nm-long MRGO are around 50 Å×50 Å×10 Å, 100 Å×50 Å×10 Å and 150 Å×50 Å×10 Å, respectively; the dimensions of 5 nm-long, 10 nm-long and 15 nm-long BRGO are around 50 Å×50 Å×20 Å, 100 Å×50 Å×20 Å and 150 Å×50 Å×20 Å, respectively. As shown in Fig. 2(a), the whole unit cell was divided into N slabs along the x-axis. In the RNEMD simulations, the hot and cold slabs were located at the middle and the two ends of RGO, respectively. The heat flux along the x-direction, J_x, was generated by exchanging the atomic kinetic energy between the hottest atom in the cold

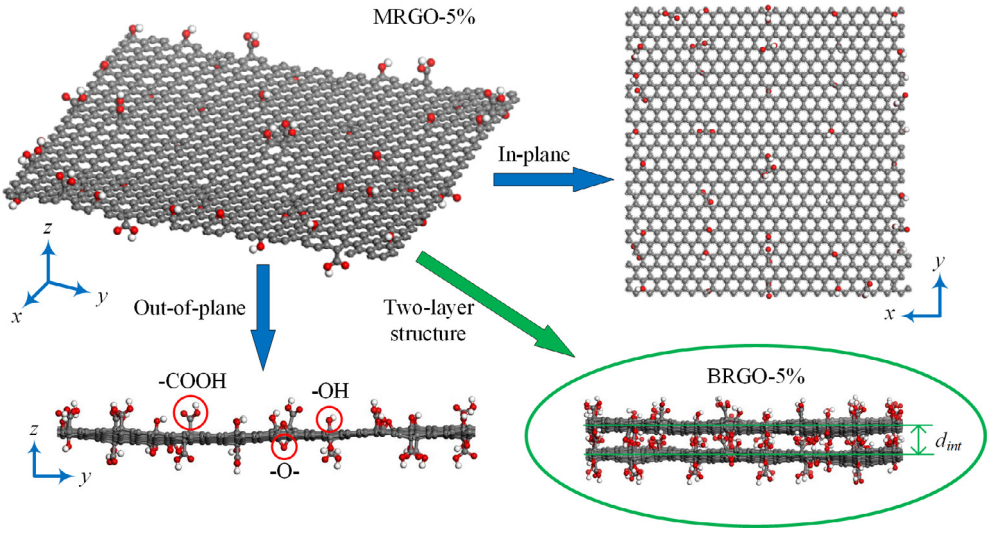

Fig. 1. Molecular models of MRGO-5% and BRGO-5%, in which d_{int} is the average interfacial distance between two layers of BRGO. Carbon, hydrogen and oxygen atoms are represented by gray, white and red particles, respectively.