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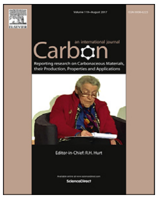

On the influence of junction structures on the mechanical and thermal properties of carbon honeycombs

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ABSTRACT

Carbon honeycomb is a 3-dimensional carbon allotrope experimentally discovered recently, but its lattice structure has not been well identified. In this paper, we perform density-functional theory (DFT) calculations to examine the stability of carbon honeycombs with different configurations (chirality and sidewall width). We find that graphene nanoribbons with both zigzag edges and armchair edges can form stable carbon honeycombs if sp^3 carbon-carbon bonding is formed in the junction. We further study the mechanical properties and the thermal conductivity of carbon honeycombs with different chirality and the sidewall widths using both DFT calculations and molecular dynamics simulations. All these stable carbon honeycombs exhibit superior mechanical properties (large strength and ductility) and high thermal conductivity (larger than 100 W/m K) with a density as low as 0.5 g/cm^3. Light-weight carbon honeycombs could be promising functional materials for many engineering applications.

1. Introduction

Lightweight materials with exceptional physical properties are highly desirable for many engineering applications. For example, lightweight materials with high mechanical strength can be utilized in spacecraft and skyscrapers, while those with high thermal conductivity can find their applications as heat sink materials for power electronics and high performance heat exchangers. In the past few decades, the research on various kinds of carbon allotropes, from bulk diamond and graphite to low-dimensional fullerene, carbon nanotube (CNT) and graphene, has stimulated remarkable progress in fundamental material sciences [1]. A few carbon allotropes, especially the low-dimensional graphene and CNT, possess high mechanical strength [2] and high thermal conductivity [3]. Using low-dimensional carbon materials as building blocks to construct three-dimensional (3-D) structures provides a promising routine to achieve multifunctional lightweight materials with strong strength and high thermal conductivity.

Very recently, carbon honeycombs, another 3-D carbon allotrope, has been experimentally synthesized by depositing vacuum-sublimated graphite [4], and immediately became a research focus [5–9]. Indeed long before the successful synthesis of carbon honeycombs, a few hypothesized structures, which were sometimes called carbon foams, had been proposed [10–17]. However, the stability of these hypothesized 3-D carbon structures is seldom examined. While most of these hypothesized 3-D structures can be regarded as armchair graphene nanoribbons connected through sp^3 bonding [12,14], our recent first-principles density functional theory (DFT) calculations has revealed that stable carbon honeycombs can also be formed by connecting zigzag graphene nanoribbons if sp^3 carbon-carbon bonds are formed at the junction region [18]. Furthermore, DFT calculations and molecular dynamics simulations showed that the carbon honeycombs made of zigzag graphene nanoribbons possess appealing specific strength (25 GPa cm^3/g), which is much larger than any reported three-dimensional materials, and high thermal conductivity (>100 W/mK). These exceptional properties are due to the covalent nature of C–C bonding in carbon honeycombs. The large specific strength and high thermal conductivity make carbon honeycombs excellent

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lightweight multifunctional materials for various applications.

Considering that carbon honeycombs can be made up of graphene nanoribbons with different chirality along their edges, it is hence of great relevance to explore how different structures in the junction of carbon honeycomb influence their stability, mechanical and thermal properties. In this paper, we perform DFT calculations to understand the stability and to predict mechanical strength of carbon honeycombs with different chirality and honeycomb sidewall (nanoribbon) width, and molecular dynamics simulations to study their thermal conductivity.

2. Simulation method

The essential step to realize a carbon honeycomb is to form a stable junction by connecting three graphene ribbons along their edges with appropriate bonding. How to connect them coherently is the key to maintain the extraordinary properties of graphene in 3-D carbon honeycombs. With a junction formed, nanoribbons with different widths can be connected to form carbon honeycombs with irregular hexagons. For simplicity, in this work we analyze only the carbon honeycombs with periodic structure along the junction, as shown in Fig. 1(a). In the previous report [18], we investigated two types of junctions, one formed with the zigzag edges of graphene ribbons and the other along the armchair edges of graphene ribbons. The atomic details of the junctions and the graphene nanoribbons connected are presented in Fig. 1(b, c). We termed the former as 5-5-8 junction since it is composed of an array of defective units, and each containing two 5-rings and one 8-ring, and the latter is called 6-6-6 junction as there are two coplanar 6-atom rings and one non-coplanar 6-atom ring in one period of the junction. Now we consider five carbon honeycombs which are constructed by the two kinds of junctions (5-5-8 and 6-6-6) and shifted defect arrangement along the two edges of a graphene nanoribbon, as shown in Fig. 1(d–h). Three-dimensional views of these honeycombs are also presented in Supplementary Fig. S1. In these structures, carbon atoms are in pink if they are in the junction lines, while other atoms are colored in cyan and silver colors. For brevity, we refer the five types of graphene nanoribbons studied in this paper, which are shown in Fig. 1(d–h), as ZZ1, ZZ2, ZZ3, AC1 and AC2 carbon honeycombs. Here the graphene nanoribbons of both ZZ1 and ZZ2 honeycombs only include odd number of hexagonal carbon rings and those of ZZ3 honeycombs have even number of hexagonal carbon rings. The difference between ZZ1 and ZZ2 carbon honeycombs is that the nanoribbons in ZZ1 honeycombs are asymmetric with respect to the center line of nanoribbons, while those in ZZ2 honeycombs are symmetric. For armchair-type of carbon honeycombs, the width of graphene nanoribbons in AC1 carbon honeycombs has to be roughly $n\sqrt{3}a_0$, where n is an integral number and a_0 is carbon-carbon bond length, while that in AC2 carbon honeycomb is $\left(n+\frac{1}{2}\right)\sqrt{3}a_0$.

We perform DFT calculations using VASP package [19,20] to examine the stability of the carbon honeycombs with different lattice structures including both chirality and sidewall width and to study their mechanical properties. The DFT calculations are based on the projector augmented wave (PAW) pseudopotentials [21] and the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional [22] with a kinetic-energy cutoff for the plane-wave basis set of 520 eV. To find the possible atomic structures of carbon honeycombs, we first construct the primitive unit cells (See Fig. 1(a)) of different carbon honeycombs by connecting together the corresponding graphene nanoribbons, as shown in Fig. 1(d–h), to form the honeycomb structure based on the equilibrium lattice parameter of graphene. The primitive unit cells of all the structures studied here are then relaxed in the DFT calculations using a conjugate gradient (CG) algorithm until the atomic forces are converged to 10^{-5} eV/Å and the total energy is minimized. To study the stability of these relaxed carbon honeycombs, we calculate their phonon dispersion curves using the Phonopy package [23], which is based on the supercell method. In the supercell method, the atoms in the supercell which contains several primitive unit cells of carbon honeycomb, are displaced by ±0.01 Å along the Cartesian directions, then the interatomic forces exerting on the atoms in the supercell are recorded. The second-order harmonic force constants are extracted through the finite difference scheme, so that the dynamical matrices of the lattice are constructed with the extracted force constants and phonon dispersion relation is calculated by diagonalizing the dynamical matrices [24].

With the relaxed crystal structures of these carbon honeycombs, we then compute their strain–stress curves, from which the mechanical strength and failure strain can be determined, through DFT calculations. While the engineering stress σ, evaluated using the cross-section of the material before deformation, is frequently used to describe the mechanical state of materials, it would underestimate the true stress σ' for materials with large deformation, such as carbon honeycombs. Therefore, we report the true stress of carbon honeycombs in this work. To conveniently obtain the stress and strain along principal axes, we convert the primitive unit cells of the relaxed carbon honeycombs to the conventional ones, as illustrated by the green rectangle in Fig. 1(a). In the following DFT calculations, we start from the unstrained honeycombs, and apply the quasi-static displacement-controlled deformation by imposing the deformation with a small strain increment. Once being stretched to a specific strain, the carbon honeycomb is then relaxed to achieve both zero stress along the directions perpendicular to the straining one and small atomic forces (less than 0.01 eV/ Å). As we calculate the stress based on the relaxed configuration of the simulation box, the obtained stress along the stretching direction is regarded as true stress. The results presented are calculated using the minimal conventional cells with periodic boundary conditions, and the calculated results are consistent with those using larger supercells, as demonstrated in Supplementary Fig. S2, where an AC1 carbon honeycomb with a sidewall width of 5.2 Å is examined as an example.

Many simulation techniques have been employed to study the thermal transport in solid crystals. While the first-principles-based Boltzmann transport equation approach have been successfully applied to predict the thermal conductivity of quite a few bulk [25,26] and two-dimensional crystalline materials [27–29], significant computational burden make it inapplicable for materials with complicated crystal structures, like carbon honeycombs. To avoid the computational challenges, we study the thermal conductivity of different stable carbon honeycombs using classical equilibrium molecular dynamics (MD) simulations, which are conducted via a well-tested software package LAMMPS [30]. The modified reactive empirical bond order (REBO) potential [31], whose parameters are optimized to predict the thermal conductivity of graphene and carbon nanotubes, are used to describe the interatomic interactions between carbon atoms. The thermal conductivity of graphene from our MD simulations is very close to that from the first-principles-based Boltzmann transport equation calculations where the quantum effects [29] are fully taken into account (within 15%), as well as the measured data [24]. In the MD simulations, the position and velocity of each atom in the simulation system are determined by numerically integrating the Newton's law of motion of atoms using the velocity Verlet algorithm with a time step of 0.5 fs. The