Effect of edge-hydrogen passivation and nanometer size on the electronic properties of phagraphene ribbons

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ABSTRACT

Based on a first-principles approach, the structures and electronic properties are investigated for both pure zigzag phagraphene nanoribbons (ZPHAGNRs) and mixture phagraphene nanoribbons (MPAHGNRs) terminated edges with hydrogen atoms or bare edges. There are many differences between bare and passivated phagraphene nanoribbons (PHAGNRs) in structure parameters after geometry optimization, although they still keep the two-dimensional plane structures. The edge states and quantum confined effect play crucial roles in the electronic properties for PHAGNRs. Our results show that ZPHAGNRs and bare MPHAGNRs are metallic, while the MPHAGNRs terminated edges with hydrogen atoms with direct band gap arise from quantum confined effect. The electronic properties of MPHAGNRs with passivated by hydrogen are further probed with the variation of width (N_M = 4–21). Our works indicate that all of the calculated H-MPHAGNRs are direct band gap, and 4-H-MPHAGNR has the largest band gap is 1.02 eV. Generally, the band gaps decreased with respect to the ribbon widths increasing. However, the variation in band gaps exhibits three distinct family behaviors. The band gap sequence is $gap_{3q} > gap_{3q+1} > gap_{3q+2}$.

1. Introduction

Carbon is one of the most attractive and versatile elements in the periodic table and forms a large number of allotropes due to its variant electron orbital characteristics. From zero-dimensional fullerene (C60) [1] to 1D nanotube [2], quasi-one dimensional graphene nanoribbon [3], 2D graphene [4], and 3D graphite, diamond as well as metallic carbon phase [5,6], all of them are a member of the carbon family and the emergence of these materials greatly promoted the development of the material science, physics, chemistry and other related disciplines.

In particular, 2D carbon allotrope graphene has been extensively studied, due to its remarkable properties, such as the ultra-high carrier mobility [7], superior thermal conductivity [8] and quantum Hall effect [9,10], which have triggered considerable interest in exploring novel 2D carbon-based nanomaterials. Therefore, a series of two-dimensional carbon materials have been investigated, some of them exist only in theory, may be not stable, such as graphyne [11–14] and penta-graphene [15,16], some have been synthesized as well, such as graphane [17,18].

Recently, a new polymorph structure of carbon, named phagraphene [19], was predicted by calculation. Distinguished with graphene hexagonal honeycomb structure, phagraphene is two-dimensional structure composed of 5–6–7 carbon rings. This planar carbon allotrope is metastable compared with graphene, but it is more favorable than other carbon allotropes proposed in previous works due to its sp²-hybridization and dense atomic packing structure [20]. As we all know, the structure of the material has important influence on its performance. Because of the structural characteristics of phagraphene, it not only shares much of same nature with graphene, such as zero-gap electronic structure, but also has some differences, like distorted Dirac cones [19], that allows it to be considered an advanced material for flexible electronic devices, transistors, solar batteries, display units and many other things. Unfortunately, a band gap will be needed, if we apply it in the field of nanoelectronics. Similar to graphene [21], an approach is to reduce the dimensionality of phagraphene from 2D to 1D by cutting phagraphene into narrow ribbons, phagraphene nanoribbons (PHAGNRs).

PHAGNRs have been preliminary studied used theoretical calculation. The calculation indicated that PHAGNRs with mixture of armchair and zigzag shaped edges are semiconducting, and that PHAGNRs with pure zigzag shaped edges are metallic. Although preliminary calculation has been completed, while a careful consideration of edge effects in nanometer sized ribbons are required to determine their bandgaps because, unlike the situation in pha-

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graphene, the bonding characteristics between atoms change abruptly at the edges. We will explore the relation between the bandgap and the geometries of PHAGNRs. In this paper, we carried out first-principles calculations to investigate the structure and electronic properties of PHAGNRs with bare edges and hydrogen passivated edges. We also obtained the size effect on nanometer scale by examining the electronic structure of PHAGNRs of different widths.

2. Calculation method and model

The calculations in this paper were performed within the framework of the density function theory (DFT) using the projector-augmented wave (PAW) method [22], as implemented in the Vienna ab-initio Simulation Package (VASP) computer code [23,24]. The electron exchange–correlation energy was treated by using the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) [25], which yielded the correct ground-state structure of the combined systems. The cutoff energy of the plane wave was adopted to be 600 eV [19]. The $2s^2 2p^2$ and $1s^1$ electrons were treated to be the valence electrons of C and H atoms, respectively. The atomic positions and lattice constants were optimized using the conjugate gradients (CG) scheme until the force components on each atom and the energy were less than 0.01 eV/Å and 1.0×10^{-5} eV, respectively. The Brillouin zone (BZ) integration is performed within a Gamma centered Monkhorst–Pack scheme using an adequate k-points for $1 \times 1 \times 25$ for geometry optimization and charge density distributions. The accurate band structure calculations are performed by using 60 k-points along high symmetry direction. A two-dimension periodic boundary condition was applied and an enough vacuum space of 18 Å along the direction of layer-to-layer was adopted to prevent interactions between two nanoribbons in nearest layer.

In our work, we first set up a model of 2D phagraphene sheet and optimized it. The calculations on band lengths and band angles are good agreement with previous reported [19] and the method used in present calculation is suitable for describing the structures and electronic properties of PHAGNRs. Next, PHAGNRs can be obtained by cutting it along different directions. There are two typical edge structures in the nanoribbons, mixture of armchair and zigzag phagraphene nanoribbons (MPHAGNRs) and zigzag pha-

graphene nanoribbons (ZPHAGNRs). However, there is no prefect armchair nanoribbons built in phagraphene because of its special structure. All these structure of PHAGNRs are composed of 5–6–7 carbon rings. For pure zigzag phagraphene nanoribbons (ZPHAGNRs) width parameter, we followed the previous convention used for graphene nanoribbons [26], is defined by the number of the zigzag chains (N_Z) across the ribbon width as shown in Fig. 1 (a). However, the MPHAGNRs is not agreement with armchair graphene nanoribbons which is classified by the number of C–C dimer lines across the ribbon width [27], we defined width parameter of MPHAGNRs by the number of carbon atoms (N_M) on pure zigzag chain (a unit cell includes only one pure zigzag chain) which is perpendicular to the one-dimensional direction as shown in Fig. 1(b). When the N_M increased one, the width of MPHAGNRs will increase a half ring. In addition, we referred to bare edges and hydrogen passivated edges ZPHAGNR with N_Z zigzag chains as bare N_Z-ZPHAGNR and N_Z-H-ZPHAGNR, respectively. Similarly, we named bare edges and hydrogen passivated edges MPHAGNR with N_M atoms number as bare N_M-MPHAGNR and N_M-H-MPHAGNR. We obtained the minimum width of ZPHAGNR and MPHAGNR are $N_Z = 4$ and $N_M = 4$, respectively. Besides, if we want to obtain pure ZPHAGNRs, the N_Z must be $3q + 1$ due to the 5–6–7 carbon rings structure of phagraphene, where q is a positive integer.

3. Results and discussions

3.1. Structures of phagraphene nanoribbons

We first optimized the typical ZPHAGNRs and MPHAGNRs with bare and hydrogen-terminated edges, named bare 6-MPHAGNR, 6-H-MPHAGNR, bare 4-ZPHAGNR and 4-H-ZPAHGNR, respectively. Fig. 2 displays the structures after geometry optimization and we defined the L_1, L_2, L_3, L_4 and d_1, d_2, d_3, d_4 representative as unit cell width and length of bare 6-MPHAGNR, 6-H-MPHAGNR, bare 4-ZPHAGNR, 4-H-ZPAHGNR, respectively.

We compared the changes of the structural parameters for bare and hydrogen-terminated edges PHAGNRs. There are many differences between bare 6-MPHAGNR and 6-H-MPHAGNR. Our results show that the bare 6-MPHAGNR has shorter average band length of edge C–C and unit cell width than that of 6-H-PHAGNR, while the average edge of C–C–C band angle and the length of unit cell
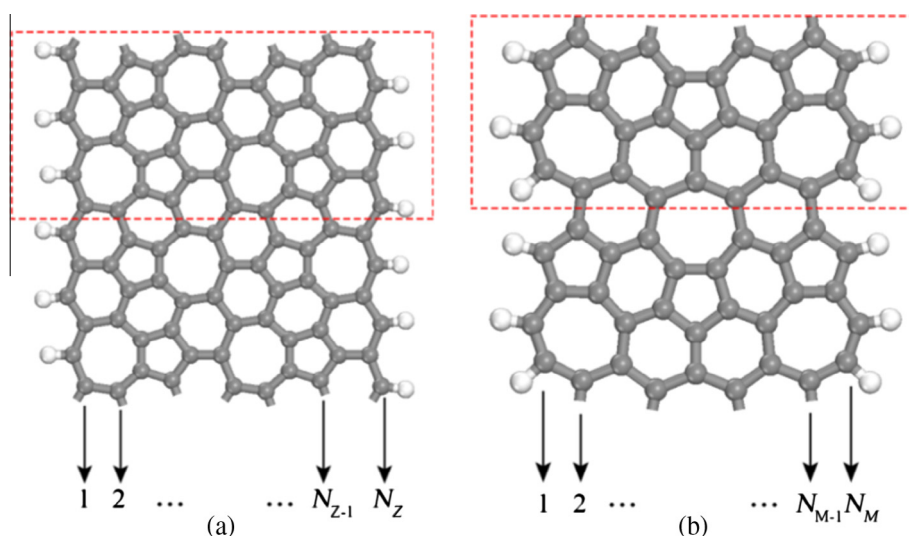

Fig. 1. The network skeleton of (a) pure zigzag phagraphene nanoribbon ($N_Z = 7$) and (b) mixture of armchair and zigzag phagraphene nanoribbon ($N_M = 9$) with H atoms terminated the edges after geometry optimization. The unit cell is indicted by the rectangles with red dashed lines. The gray and white balls represent C and H atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)