The influence of silicon atom doping phagraphene nanoribbons on the electronic and magnetic properties

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A B S T R A C T

Based on a first-principles approach, the structural, electronic and magnetic properties are investigated systematically of pristine and Si-doped phagraphene nanoribbons (PHAGNRs) with different edges, including zigzag edge (ZPHAGNR) and mixed edge (MPHAGNR). The geometric structure is drastically changed when silicon atom replaces the different carbon atom on 5-6-7 rings of PHAGNRs. The calculations of formation energy show that silicon atom always prefers to substitute carbon atom at the edge position or on heptagon carbon ring both in 6-MPHAGNR and 4-ZPHAGNR. Further studies reveal that Si doping can significantly adjust electronic and magnetic properties of PHAGNRs, and the sizes of bandgaps and magnetic moments depend heavily on the doping position. Besides, doping can transfer a direct bandgap semiconductor into an indirect bandgap semiconductor for MPHAGNR, and separate the band structure near the fermi level for the ZPHAGNR. In addition, the biggest advantage for doping silicon atom in PHAGNRs is that no impurity energy levels are introduced. All these open an approach to design electronic and magnetic nanometer devices based on PHAGNRs in the future.

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1. Introduction

Graphene, a two-dimensional hexagonal network structure formed by sp^2 hybridization of carbon atoms, is considered as the promising crystalline forms of carbon and has raised tremendous attention since the mechanical exfoliation by Novoselov and Geim in 2004 [1]. Inspired by the excellent physical and chemical properties of graphene, other 2D nanomaterials have also been extensively investigated both on experiment and on theory, such as SiC [2–4], AlN [5–7], BN [8–10], borophene [11,12] and other carbon allotropes [13–20].

Phagraphene is the latest carbon allotrope to be discovered using the ab initio evolutionary algorithm USPEX [14]. This carbon material is more favorable in energy than most of the predicted 2D carbon allotropes and may be synthesized in the laboratory in the future [21,22]. Comparing the structures of graphene and phagraphene, the only difference is that phagraphene is composed of 5-6-7 carbon rings while graphene is hexagonal honeycomb structure. As we all know, properties of the material depend on the composition, structure and processing technology. Ignoring their treatment process, graphene and phagraphene have same composition, but are difference in structures, what kind of impact will be

generated? Therefore, the mysterious properties of phagraphene attract us to explore.

To date, Pereira et al. [23] have studied this 2D material by molecular dynamics simulations, and indicated that it could be a better candidate than graphene in carbon-based thermoelectric devices, due to its lower thermal conductivity. Wang et al. [14] have predicted that pristine phagraphene sheet is a zero-bandgap semiconductor and its electronic structure has distorted Dirac cones, which allows it to be considered as an advanced material for flexible electronic devices, transistors, solar batteries, and so forth. However, in terms of its application, it cannot be used in semiconductor field such as field-effect transistors (FETs) without a band gap opening. In addition, a tunable band gap is also very important. Fortunately, similar to graphene [24,25], an efficient approach is to reduce the dimensionality of phagraphene from 2D to 1D by cutting phagraphene into narrow ribbons. In the meantime, atoms doping is another powerful route to tailor the electronic properties of this material.

As is known to all, silicon (Si), an element resides in the same group of the periodic table with carbon, owns similar characters to carbon. Therefore, silicon doping in graphene structure has less destructive effect on graphene mobility, while it is the effective atom to open a band gap in graphene [26,27]. In addition, silicon is one of the most abundant elements on earth, and has been widely applied in the semiconductor, solar cells and other fields. Considering the aforementioned advantages of silicon doping in

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graphene, we are interested in exploring the characterizations of phagraphene nanoribbons (PHAGNRs) whose different carbon atoms on 5-6-7 rings are substituted by a silicon atom. Meanwhile, inspired by the magnetism of zigzag graphene nanoribbons [28–30], we also investigate the magnetism of pristine PHAGNRs and doped PHAGNRs by first-principles calculations.

2. The calculation method and model

The calculations are carried out by the framework of the density function theory (DFT) using the projector-augmented wave (PAW) method [31], as implemented in the Vienna ab initio Simulation Package (VASP) [32,33]. The electron exchange-correlation energy is described by the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) [34], which generate the correct ground-state structure of the combined systems. The plane-wave cutoff energy is chosen to be 600 eV [14]. The valence electrons of C, Si and H atoms are taken as $2s^2 2p^2$, $3s^2 3p^2$ and $1s^1$, respectively. The atomic positions and lattice constants are optimized using the conjugate gradients (CG) scheme, and the convergence threshold is set as 1.0×10^{-5} eV per electronic step in energy and 0.01 eV/Å per atom in force, respectively. Integration over the Brillouin zone is represented by a Gamma centered Monkhorst–Pack scheme using an adequate k-points for $25 \times 1 \times 1$ for geometry optimization. All structures are treated with periodic boundary conditions. The positions of all atoms in our structures are fully relaxed until they reach to ground states during the geometry optimization. The accurate band structure calculations are carried out by using 60 k-points along high symmetry direction. In order to avoid artificial inter-layer interactions between two nanoribbons, a sufficient vacuum space which is longer than 18 Å is adopted.

In our work, a model of 2D phagraphene sheet is set up and optimized, and the calculations on bond lengths and bond angles are in good agreement with previous reports [14] and the method used in present calculations is suitable. Next, PHAGNRs are obtained by cutting 2D phagraphene sheet. As shown in Fig. 1, PHAGNRs consist of 5-6-7 carbon rings with a notable space-inversion symmetry structures. Two typical phagraphene nanoribbons are investigated. One is a mixture of armchair and zigzag phagraphene nanoribbons (MPHAGNRs). Another has pure zigzag phagraphene nanoribbons (ZPHAGNRs). However, unlike graphene nanoribbons, there is no prefect armchair nanoribbons built in

phagraphene due to its special structure. In order to eliminate the dangling bonds and increase thermodynamic stability, the edges of both ribbons are passivated with hydrogen atoms. The width of MPHAGNR is defined as the number of carbon atoms (N_M) on pure zigzag chain (a unit cell has only one pure zigzag chain in all chains) which is perpendicular to the one-dimensional direction [35]. Thus we refer to a MPHAGNR with N_M carbon atoms as N_M-MPHAGNR. For ZPHAGNR's width parameter, we followed the previous convention used for graphene nanoribbons [36]. It is defined by the number of the carbon chains (N_Z) across the ribbon width. Likewise, a ZPHAGNR with Nz chains is called Nz-ZPHAGNR. Here, we take the structures with $N_M = 6$ and $N_Z = 4$ as representatives and their electronic and magnetic properties will be investigated systematically after doping Si atom in part 3. The optimized unit cell structures for (a) 6-MPHAGNR and (b) 4-ZPHAGNR are shown in Fig. 1. The S1, S2, ..., S7 and P1, P2,..., P7 represent seven different doping positions for 6-MPHAGNR and 4-ZPHAGNR. The grey and white balls represent C and H atoms, respectively.

3. Result and discussion

The band structure calculations for 6-MPHAGNR and 4-ZPHAGNR are presented in Fig. 2. The Fermi level is set to zero and indicated by the horizontal red dashed lines. We can see that 6-MPHAGNR is a direct semiconductor, because the valance band maximum (VBM) and conduction band minimum (CBM) both lie on the X point, and its bandgap is about 0.63 eV. However, 4-ZPHAGNR exhibits metallic, because the energy band passes through the fermi level.

Fig. 3 shows the total density of states (DOS) acquired from spin-polarized calculations of (a) 6-MPHAGNR and (b) 4-ZPHAGNR. The magenta and blue solid lines represent the DOS of spin up and spin down, respectively. The Fermi level is set to zero and indicated by the horizontal red dashed lines. As shown in Fig. 3, we can find that the DOS of spin up and spin down in 6-MPHAGNR is full superimposed, which indicates that 6-MPHAGNR is nonmagnetic. While the DOS of spin up and spin down in 4-ZPHAGNR is asymmetric, which reveals magnetic character of this system. Our calculated result shows that 4-ZPHAGNR has a magnetic moment of 1.01 μ_B per unit cell, which will allow us to design magnetic nanometer devices based on ZPHAGNRs. In order to gain a deep insight into the contributions of the source
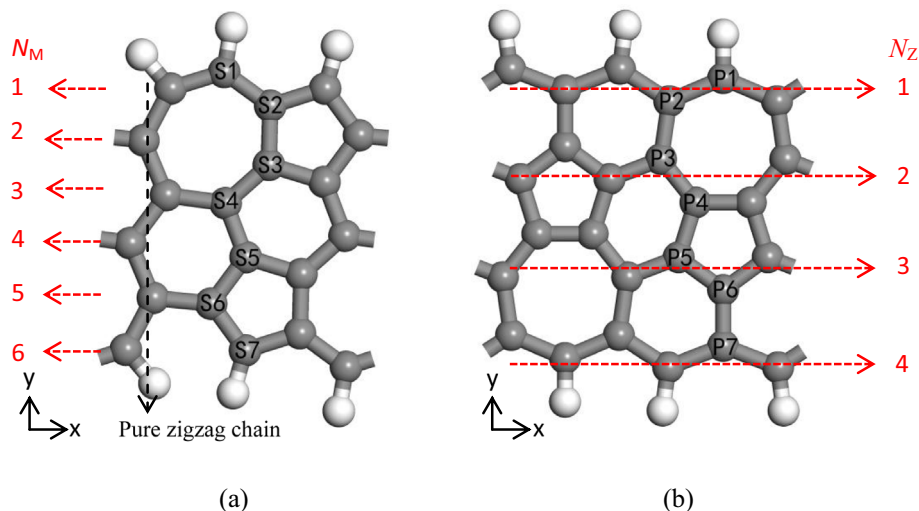

(a)   (b)

Fig. 1. The optimized unit cell structures for (a) 6-MPHAGNR and (b) 4-ZPHAGNR. S1, S2, ..., S7 and P1, P2,..., P7 represent seven different doping positions for 6-MPHAGNR and 4-ZPHAGNR. The grey and white balls represent C and H atoms, respectively.