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Tuning the electronic and magnetic properties of graphyne by hydrogenation

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ABSTRACT

First-principles calculations are performed to study the electronic and magnetic properties of graphyne by chemisorption of hydrogen atoms. The results show that it is possible to tailor the magnetism of selected graphyne regions. More importantly, the spin-polarized state essentially localized on the unhydrogenated carbon atoms can extend more than 31.81 Å away from the hydrogen atoms. When the carbon atoms are hydrogenated in an alternating manner in hexagonal C rings, the strong σ-bonds are formed between C and H atoms, at the same time, the sp C atoms become the sp2 C atoms and the sp2 C atoms turn to be sp3 C atoms, leaving the electrons localized and unpaired in the unhydrogenated C atoms and with the maximum magnetic moment of 1.59 μ_B. In the case of the bilayer graphyne, the magnetic moment mainly distributes on the top layer, while the bottom layer has almost no influence on the magnetic moment distribution. The hydrogenated bilayer graphyne can show semiconductive, metallic or half-metal characters depending on the stack style and adsorption structure. These findings may provide a new route for exploring magnetic semiconductors experimentally and theoretically.

1. Introduction

The main goal of spintronics is to find ways to manipulate and use electronic spin as a degree of freedom, just as electronic charge used in silicon-based electronics. One of the key steps to achieve the goal is the development of new semiconductor materials that show ferromagnetism and maintain their ferromagnetic behavior at room temperature. The ferromagnetic semiconductor materials have been prepared by the method of doping and adsorption in the last couple of years, such as gallium arsenide, ZnO, and MoS_2 doped by transition-metals [1–6]. However, it is a great challenge to control the interface of the ferromagnetic semiconductor materials due to these materials having extremely high doping levels. Hence, up to date, it is highly desirable to fabricate ferromagnetic lower-doped semiconductor materials for designing novel storage devices based on ferromagnetic semiconductors.

Previous theoretical works have revealed that hydrogen adsorption is an effective approach to modify the electronic properties and induce magnetic moments in nonmagnetic materials. The graphane, fully hydrogenated graphene and successfully synthesized in experiment [7], is a semiconductor with large band gap. However, graphone, half-hydrogenated graphene, becomes magnetic semiconductor with an indirect small band gap [8,9], which indicates that hydrogen adsorption can tailor the electronic and magnetic properties of graphene. Recently, experimental results have verified that the adsorption of a single hydrogen atom on graphene induces a magnetic moment characterized by a ~20–millielectron volt spin-split state at the Fermi energy [10]. From a theoretical point of view, one of the carbon allotropes named graphyne, first predicted by Baughman et al. [11] offers more freedom for hydrogen adsorption, mostly because it is a new form of carbon sheet that consists of sp and sp2 carbon atoms. Graphyne is mainly divided into three categories–α graphyne, β graphyne and γ graphyne, depending on the various arrangements of acetylenic linkages and percentage of the inserted acetylenic linkages (—C≡C—) [12–17]. A large number of studies are focused on γ-graphyne over the last two decades [16,18–24], because it is the lowest energy member among the three types of graphyne with a small direct

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band gap of 0.44 eV [24], 0.46 eV [25], or 0.53 eV [13] at the Γ point, which makes it to be one of the suitable candidates for experimental preparation of room temperature field effect transistors. Previous studies have reported that the stability of the fluorographynes increases with the F/C ratio, and the fluorinated derivatives became wide-band-gap semiconductors [26]. However, as far as we know, there has been rare study about the magnetic characters of hydrogenated graphyne so far. Therefore, it is necessary to perform a systematic study of magnetic characters of hydrogenated graphyne.

Although much knowledge has been gained about graphyne, many questions are still worth discussing. (1) Graphene sheet is known to be nonmagnetic metal. Atomic H chemisorbs on the carbon atoms of graphene changing the initial sp2 hybridization to essentially sp3 and effectively inducing magnetic moments in graphene [10]. Due to graphyne including sp and sp2 carbon atoms, can atomic H chemisorbed on top of sp and sp2 carbon atoms induce magnetic moments? Well, if this could be, how the magnetic moment distributes in the monolayer graphyne? (2) With the progress in the study of the monolayer graphyne, much less attention has been devoted to bilayer graphyne. Is hydrogenated bilayer graphyne still a semiconductor? Do the underlying graphyne layers influence the magnetic moment distribution? These problems have inspired us to investigate the electronic and magnetic properties of hydrogenated monolayer and bilayer graphyne systematically, which is a crucial step in gauging the potential applications of graphyne in spintronics. Our investigation may provide useful information regarding spintronics.

2. Computational method

The first-principles calculations are based on spin polarized density functional theory (DFT) with a generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) [27] form implemented in the Vienna ab initio simulation package (VASP) code [28–30]. We construct 3×3 supercell consisting of 108 carbon atoms in order to get lower-doped semiconductor materials as shown in Fig. 1. A kinetic energy cutoff of 500 eV is selected for the plane wave expansion and high precision calculation. The Monkhorst-Pack k-point sampling $5 \times 5 \times 1$ is used for the Brillouin zone integration. A vacuum space of 20 Å is introduced to avoid interactions between images. All the structures are fully optimized with respect to the ionic positions until the forces on all atoms are less than 0.01 eV/Å. The optimized lattice constant of graphyne is a = b = 6.89 Å, which is in good agreement with the previous theoretical values of 6.89 Å [21] and 6.86 Å [13,31]. The electronic structure calculations indicate that graphyne has a direct band gap of about 0.456 eV, also in good agreement with the results of other DFT calculations [13,31,33], which confirms the accuracy of our calculation and the validity of the above-mentioned strategy in describing the graphyne and related parameters. In order to clarify the magnetic moment distribution and the magnetic coupling, we choose the larger supercell up to 5×5 with one or more sp2 carbon atoms are hydrogenated. To find the stable stack of bilayer graphyne, we take into account the interlayer vdW forces used a non-local vdW density functional in the form of Becke88 optimization (optB88) [34], which has been verified to give a reasonable description for various systems including graphene/metal interfaces [35]. We optimize the interlayer distance *d*, adopting the following method: We first investigate the optimal relative in-plane position by shifting the upper layer in the primitive cell at first with a fixed layer distance, and then we relax and optimize the layer distance with the optimized relative in-plane position.

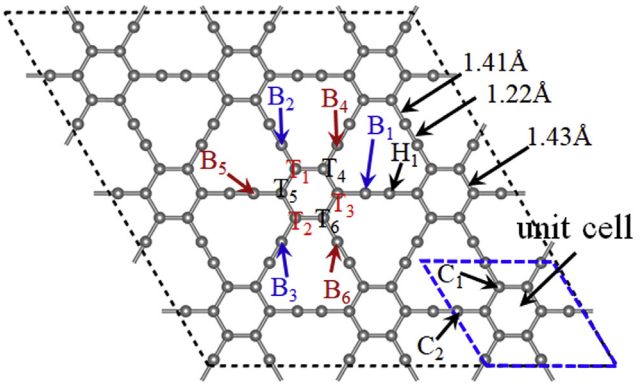

Fig. 1. The optimized atomic structures of unit cell and 4×4 supercell of monolayer graphyne.

3. Results and discussion

3.1. The structure, electronic and magnetic properties of the monolayer graphyne adsorbed by H atoms

Different from graphene, graphyne possesses two types of carbon atoms (sp2 and sp): The sp2 hybridized C atom is labelled C_1, which construct the carbon hexagon by C=C joining. Another type of C atom is labelled C_2, which is sp hybridized C atoms by C≡C connecting as shown in Fig. 1. Hence, considering the geometry properties of the monolayer graphyne, there exist the following two possible adsorption sites: on top of C_1 (T) and on top of C_2 (B) as shown in Fig. 1. Hydrogen atoms placed on the monolayer graphyne one by one, are marked positions T_i (i = 1–6) and B_j (j = 1–6), respectively. We first relaxed the geometric structures of hydrogenated graphyne named nHT-graphyne (n is the number of the adsorbed hydrogen atoms), in which only C_1 atoms are hydrogenated. Then, the geometric structures of hydrogenated graphyne named nHB-graphyne, in which only C_2 atoms are hydrogenated, are also considered. To answer which of the above two geometric structures of graphyne is more stable, we should calculate the average adsorption energies of the hydrogenated graphyne. Here the average adsorption energy is defined as

$$E_{ad} = -(E(nH/graphyne) - E(graphyne) - nE(H))/n \quad (1)$$

where E(nH/graphyne) is the total energy of the graphyne with *n* H atoms, E(graphyne) is the energy of the pristine graphyne, E(H) is the energy of an isolated H atom, *n* is the number of the H atoms. Fig. 2 displays the average adsorption energies, the relaxed bond lengths of C—H, the magnetic moment of nHT-graphyne and nHB-graphyne, respectively. Note that when the number of hydrogen atoms adsorbed in an alternating manner increases to three, the other hydrogen atoms can be adsorbed on the same side or the opposite side. When the number of the adsorbed hydrogen atoms is less than 3, the C—H bond length, the adsorption energy and the magnetic moment have the same rule in the same side and the opposite side. As shown in Fig. 2(a), the adsorption energies in nHT-graphyne slightly reduce with increasing the number of the hydrogen atoms when the number of hydrogen atoms is less than 3. When the adsorbed hydrogen atoms are more than 3, the adsorption energies of hydrogen atoms adsorbed on the opposite side are larger than those on the same side. Moreover, the adsorption energy is continuously increased with the increasing of the number of the hydrogen atoms. However, the C—H bond length first increases as the number of hydrogen atoms increasing from 1 to 3 then decreases as the number of hydrogen atoms increasing from 4 to 6 as shown in Fig. 2(b). This behavior is closely related to