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Single-atom vacancy induced changes in electronic and magnetic properties of graphyne

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ABSTRACT

Density functional theory calculations were carried out to investigate how single-atom vacancies affect the electronic and magnetic properties of three types of graphyne model systems. Our simulations demonstrate that a single-atom vacancy can lead to an in-plane structural rearrangement, which plays an important role in tuning the electronic structures. A dispersionless spin-polarized band was observed around the fermi level, inducing strong magnetism in the three graphyne models. The single-atom vacancy can induce a 1.1–1.3 μ_B magnetic moment into αGy and βGy, while this value increases significantly to about 1.8μ_B for γGy. This single-atom vacancy technique is a promising method of manipulating the electronic and magnetic properties of graphyne.

1. Introduction

In most cases, magnetism is observed in materials containing metals with partially occupied *d* or *f* shells. A challenge to the existing theoretical understanding of magnetic interaction mechanisms is that ferromagnetism has been observed in materials containing only *sp*-bonded materials. The observation of unconventional magnetism in carbon-based materials has attracted interest in metal-free magnetic materials because of their technological advantages [1,2]. Since graphene was first observed experimentally [3], it has shown fascinating properties that have made it a hot research topic over the last decade. Extensive theoretical and experimental efforts have been undertaken to study its potential applications after it has been properly functionalized via chemical or mechanical methods [4–6]. As is well-known, ideal graphene is semi-metallic and non-magnetic. However, imperfections or defects are always inevitable during material production, and these have a strong influence on the electronic, optical, thermal, and mechanical properties of graphene [7]. Defects or impurities are crucial in determining the properties of materials. A chemical or structural defect such as dislocation, vacancy, and impurity atom can induce a magnetic moment [8,9]. The simplest point defect, a single-atom vacancy, undergoes a Jahn-Teller distortion, which leads to the saturation of two of the three dangling bonds in the missing atom; one dangling bond always remains, resulting in magnetism [10]. Considering that single-atom vacancies can be introduced by ion irradiation [11], it may be possible to manipulate the magnetic properties of graphene.

Scientists are working to discover and synthesize new carbon materials other than graphite, carbon nanotubes, and graphene in order to obtain unique physical, mechanical, and electrical properties [12,13]. A new kind of carbon allotrope called graphyne was theoretically identified and has gained recent attention; in this material, an acetylenic linkage (−C≡C−) is inserted between two bonded carbons of graphene [14,15]. Graphyne was predicted by Baughman et al. in 1987 [16] as a two-dimensional single-atom-thick carbon layer that has a variety of fascinating properties including good chemical stability, large surface area, and excellent electronic conductivity induced by −C≡C− bonds [17–19]. The fascinating electronic properties could allow graphyne to have potential in some applications, and recent theoretical studies have shed light on its potential [20]. For instance, −C≡C− can increase the Li storage capability and greatly reduce the Li diffusion barrier, thus graphyne can improve the performance of Li ion batteries [21]. Graphyne has abundant positively charged sites, which can enhance the oxygen reduction reaction, thus improving the performance of fuel cells [22,23]. The pores in graphyne would make it an ideal candidate material for water desalination as well [24]. Recently, Li et al. experimentally obtained a large-area graphdiyne

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sheet [25,26], which opened up a new research field in carbon materials Although perfect graphyne has not yet been experimentally synthesized in significant quantities, recent achievements in obtaining some finite building blocks or cutouts have encouraged continued efforts to fabricate more extended structures [27,28].

As with graphene, graphyne materials can be functionalized to present the desired properties, the techniques for which have been extensively explored for graphene. Metal-decorated graphyne was predicted as a promising H_2 storage [29] or magnetic storage material [30]. Hydrogen and oxygen adsorption have been theoretically predicted to open the band gap of graphyne, which may be tunable by means of adsorbate coverage [31,32]. Cutting 2D graphyne films into 1D nanoribbons can induce a tunable band gap depending on the width of the nanoribbons [33].

In previous work, we focused on graphyne functionalization using density functional theory (DFT) calculations. When two-dimensional graphyne sheets are rolled into one-dimensional seamless graphyne nanotubes, we found that the band gap shows an oscillatory dependence on tube size [34,35]. Atomic oxygen bound to the carbon atom of graphyne can form a stable oxide that converts graphyne into a semiconductor [32]. The position of the dopant (B, N, or O) was found to play an important role in tuning the electronic structure of graphynes [36]. One study explored how the vacancy defects affect the properties of graphyne [37]. Herein, density functional theory (DFT) calculations were performed to clarify the effects of single-atom vacancies in α-graphyne (αGy), β-graphyne (βGy), and γ-graphyne (γGy). The presence of $-C\equiv C-$ in graphyne leads to the coexistence of *sp*-hybridized and sp^2-hybridized carbons (Fig. 1). In this paper, a single *sp* or sp^2 carbon atom was removed to simulate the single-atom vacancy. The corresponding properties of electron density, spin density, and band structure were thus obtained after a full relaxation. We found that the single-atom vacancy is an efficient approach to induce magnetism in graphyne, especially γGy.

2. Computational method

In this work, DFT calculations were performed using the Vienna ab initio simulation package (VASP) computer code [38]. The spin-polarized generalized gradient approximation (GGA) method of Perdew, Burke, and Ernzerhof (PBE) [39] was used to deal with the exchange-correlation functional with the projector-augmented wave (PAW) method [40]. The cutoff energy was set to 400 eV. First, the unit cell of each graphyne model (showed as dashed line in Fig. 1) was fully relaxed until none of the residual forces acting on any atom exceeded 0.001 eV/Å with a 11 × 11 × 1 k-point grid; the lattice constants for αGy, βGy, and γGy were thus computed to be 6.97, 9.46, and 6.89 Å, respectively. The optimized structures were used to calculate electronic band structures. For band structure calculations, a finer 50 × 50 × 1 k-point grid was chosen along the $\Gamma-K-M-\Gamma$ direction; the corresponding band structures are shown in Fig. 2. It is clear that αGy and βGy have a zero band gap, whereas γGy is a semiconductor having a band gap (E_g) of 0.48 eV. Our results are in good agreement with earlier reports [29,32,41,42]. We built a 2 × 2 × 1 supercell to introduce single-carbon vacancy defects to avoid the interactions between adjacent defects. As pictured in Fig. 2, one C1 (*sp* carbon) or C2 (sp^2 carbon) atom was removed to simulate the initial structure of single-atom vacancy, thus the defect concentration was 3.12%, 1.39%, and 2.08% for αGy, βGy, and γGy, respectively. Then, structural optimization and the electronic property calculations were performed at the same level with a 7 × 7 × 1 k-point grid. During all calculations, a 20 Å vacuum space along the perpendicular direction was imposed to avoid interlayer interactions.

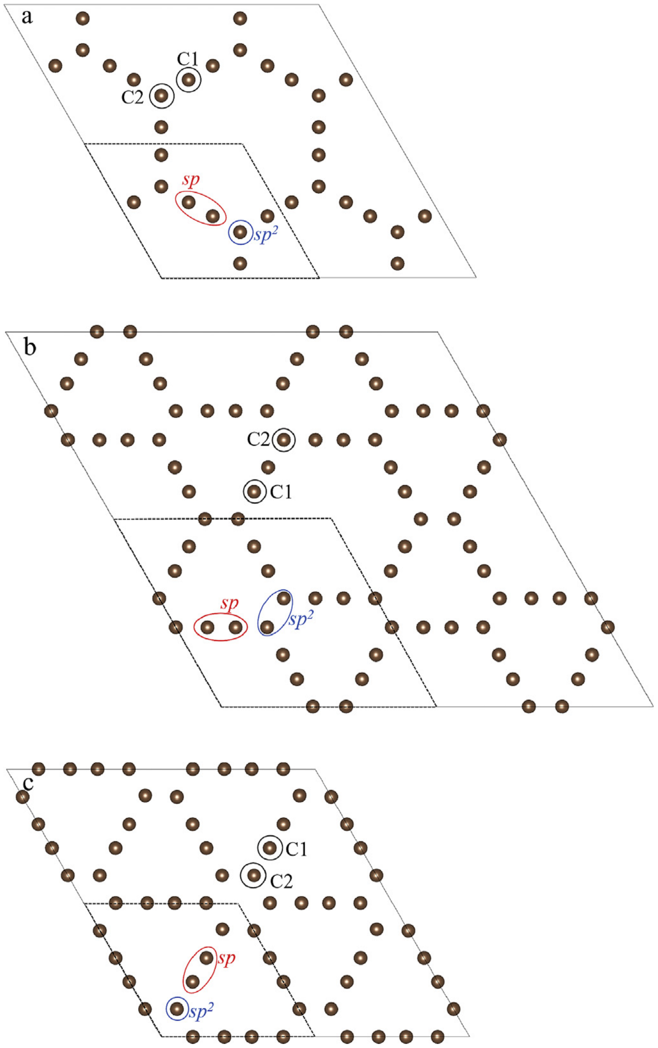

Fig. 1. Scheme of (a) αGy, (b) βGy and (c) γGy (dashed line stands for unit cell). (A colour version of this figure can be viewed online.)

3. Results and discussion

Due to the equivalence of all carbon atoms, there is only one approach to introduce a single-atom vacancy into pristine graphene. However, owing to the hybrid network of *sp* and sp^2 carbon in graphyne, there are two inequivalent sites, C1 (*sp* carbon) or C2 (sp^2 carbon) as shown in Fig. 1, can be removed to produce the single-atom vacancy. αGy has one C1 (C2) atom that can be removed in 2 × 2 × 1 supercell, and it is denoted hereafter as v1-αGy (v2-αGy). Similar notation is used for the cases of βGy and γGy. After removing one C1 atom, two sigma electrons from the adjacent *sp* and sp^2 carbon atoms and two *p* electrons from the adjacent *sp* carbon atoms are exposed, while the removal of the C2 atom leads to the exposure of three sigma electrons. Therefore, the remaining part will certainly undergo structural rearrangement, including changes in the electron configurations. All optimized structures of single-atom vacancy graphyne after full structural relaxation are shown in Fig. 3, and the corresponding electron densities are provided in Fig. 4. We clearly demonstrated an in-plane reorganization of other C atoms in all studied systems. In v1-αGy, removing one C1 causes two rings to combine into a larger pore, as shown in Fig. 3 (a). There is no electron density between the two carbon-chain with a distance of 4.23 Å, as shown in Fig. 4 (a). For v2-αGy