Effect of single vacancy on the structural, electronic structure and magnetic properties of monolayer graphyne by first-principles

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Abstract

The effect of single vacancy on the structural, electronic and magnetic properties of monolayer graphyne is investigated by the first-principles calculations. The calculated results reveal that single vacancy can result in the spin polarization in monolayer graphyne and the spin polarization is sensitive to local geometric structure of the vacancy. In the case of monolayer graphyne with one single vacancy at the sp$^2$ hybridized C site, the vacancy introduces rather weakly spin-polarized, flat bands in the band gap. Due to the localization nature of the defect-induced bands, the magnetic moment is mainly localized at the vacancy site. As for the monolayer graphyne with one single vacancy at the sp hybridized C site, one defect-induced state which is highly split appears in the band gap. The spin-up band of the defect-induced state is highly dispersive and shows considerable delocalization, suggesting that the magnetic moment is dispersed around the vacancy site. The above magnetization in monolayer graphyne with one single vacancy is possibly explained in terms of the valence-bond theory.

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1. Introduction

Graphyne, as presented in Fig. 1, a novel allotropic form of carbon, is a one-atom-thick layer of carbon sheet [1–6]. The presence of the sp hybridized C atoms in graphyne endows this new carbon sheet with outstanding properties, including excellent electronic conductivity [7–9], good chemical stability [10–12] and unique optical properties [13,14]. Especially, compared with graphene, graphyne is a direct-band-gap semiconductor with a band gap of 0.52eV [11,15,16], which is superior to the zero band gap graphene in the application of nanoelectronics and spintronic devices.

Defects and impurities are crucial to the properties of materials. Previous studies have shown that during the growth process and
under ion irradiation, introducing defects is an efficient way to functionalize carbon nanomaterials [17–32]. In particular, various studies have revealed that the vacancy defects can modify the electronic properties of carbon nanomaterials [17,19,22,27–31], such as the electron conductivity and spin-polarization of graphene. For example, Deng et al. [22] reported that the vacancy mainly works as a source of electronic scattering and modifies electronic transmission in the metallic graphene systems. Yuan et al. [29] demonstrated that the formation of impurity band in graphene is the main factor determining electrical and optical properties at intermediate impurity concentrations. These interesting electronic properties are of great importance in the application of functionalize carbon nanomaterials in spintronic devices.

Compared with the advances on the sp³ and sp² hybridized carbon nanomaterials, until now, studies on the effect of single vacancy on the structural, electronic and magnetic properties of graphene are rare. In order to widely use graphene into the field of electronic devices, a better understanding of the electronic structure and magnetic properties of the monolayer graphene with single vacancy is essential. Here, the effect of single vacancy on the structural, electronic and magnetic properties of the monolayer graphene is investigated by the first-principles calculations. From these results, some helpful instructions can be provided for the growth of monolayer graphene with single vacancy in the application of the spintronic devices.

2. Computational details

As shown in Fig. 1, a 3 × 3 supercell containing 108 atoms is built to model the monolayer graphene with one single vacancy. This model corresponds to about 0.926 at% vacancy defect. To avoid the interaction between adjacent images, a vacuum region up to 30 Å is set along the z-direction.

All of the calculations are performed by using the plane-wave total energy calculation method based on the density functional theory (DFT) as implemented in the CASTEP package [33]. The Vanderbilt ultra-soft pseudo-potential [34] is used to describe the core electrons. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof parameterization [35] is performed for the exchange-correlation energy of interacting electrons. A cutoff energy of 680 eV is set for the plane wave basis and a 9 × 9 × 1 Monkhorst-Pack k-point mesh [36] is used for the Brillouin zone integration. The convergence tolerance of each calculation is set as 1 × 10⁻⁶ eV/atom. For each calculation, the spin-polarized calculations are adopted to properly describe the electronic structure and magnetic properties of monolayer graphene with one single vacancy.

The vacancy formation energy $E_f$ [18,37–41] was calculated as

$$E_f = E_v - E_p + \mu(C),$$

where $E_v$ and $E_p$ are the total energies of the monolayer graphene with and without one single vacancy, respectively; $\mu(C)$ is the chemical potentials of the C atom using pristine graphene as reference systems.

3. Results and discussion

For the monolayer graphene with one C atom removed, there are two inequivalent vacancy positions which are denoted as Vb and Vr, as shown in Fig. 1. That is, the Vb and Vr sites represent, respectively, the sp³ and sp hybridized C atom in the monolayer graphene. The calculated formation energy of the vacancy at Vr site is 9.944 eV, which is 1.268 eV smaller than that at Vb site. This indicates that the vacancy prefers to occupy the Vr site and distribution of vacancy at Vr site is more energetically favorable. The above site preference can be attributed to the different binding features of the C atoms in graphene. When one C atom is removed from the Vb site, it needs breaking two C–C aromatic bonds together with one C–C single bond. However, one C–C triple bond together with one C–C single bond will be broken in order to form the vacancy at Vr site. Previous studies [42,43] reported that the cohesion energetics of a new graphene structure can be made by analyzing the contribution of each bond to their cohesive energies. The calculated C–C single, C–C aromatic bond, and C–C triple bond energies in graphene is 4.520, 6.735 and 8.762 eV [42], respectively. Because the energy of breaking of two C–C aromatic bonds (13.470 eV) is larger than that of breaking of one C–C single bond (8.762 eV), therefore the vacancy prefers to occupy the Vr site.

On the other hand, it is evident that the formation energy of vacancy in monolayer graphene is rather high, which is larger than the experimental value of 7.0 ± 0.5 eV [44] and the previous DFT value of 7.7 eV [19] for graphene. This suggests that similar to graphene, introducing of single vacancy in monolayer graphene is energetically unfavorable.

To further clarify the stability of monolayer graphene, we calculate the cohesive energy $E_c$ defined as

$$E_c = \frac{|nE(C) - E_p|}{n},$$

where $E(C)$, $n$, and $E_p$ represent the energy of isolated C atoms, number of C atoms in a supercell, and total energy of the monolayer graphene, respectively. The corresponding cohesive energy $E_c$ is listed in Table 1. The calculated cohesive energies of graphene and

<table>
<thead>
<tr>
<th>Method</th>
<th>Graphyne</th>
<th>Graphene</th>
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<tbody>
<tr>
<td>GGA-PBE</td>
<td>7.23</td>
<td>8.02</td>
</tr>
<tr>
<td>GGA-PBE</td>
<td>7.21</td>
<td>8.02</td>
</tr>
<tr>
<td>GGA-PBE</td>
<td>7.262</td>
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<td>GGA-PBE</td>
<td>8.11</td>
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<tr>
<td>GGA-PBE</td>
<td>8.02</td>
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This work.

References:
[18,37–41]: Cited references.
[42]: Ref. [42].
[45]: Ref. [45].
graphene are 7.23 and 7.89 eV/atom, respectively, which is consistent with previous reported values [42,45–47] for graphyne and graphene. Note that the cohesive energy of graphyne is smaller than that of graphene, which indicates that graphyne possesses lower stability than graphene. Interestingly, recently Li et al. [48] successfully fabricated the graphyne family (e.g., graphdiyne) on the surface of Cu foil via a cross-coupling reaction.

Next, the geometrical properties of monolayer graphyne with one single vacancy are evaluated. As shown in Fig. 2, when one C atom is removed from the monolayer graphyne, the geometric structure of monolayer graphyne remains planar. However, the bond lengths and bond angles around the vacancy exhibit significant changes. For the monolayer graphyne with one single vacancy at Vb site (Fig. 2a and b), the vacancy does undergo a Jahn-Teller distortion after relaxation, since two of the C atoms nearby the vacancy (labeled as Cb1 and Cb2) move closer, forming a covalent bond between Cb1 and Cb2 atoms and the Cb2 atom has a 0.275 Å in-plane displacement from Cb3 atom. In detail, the distance between Cb1 and Cb2 atoms alters from 2.452 Å to 1.492 Å after relaxation. This distance is in comparison with the standard C–C single bond length of 1.407 Å in graphyne. Meanwhile, the electron density difference seen in Fig. 2c demonstrates clearly the increase in density between Cb1 and Cb2 atoms, further indicating the formation of a covalent bond between Cb1 and Cb2 atoms. Furthermore, due to the Jahn-Teller distortion induced by the reconstruction of Cb1 and Cb2 atoms, one corresponding angle is increased from Fig. 2.

(a) and (b) geometrical structure of the monolayer graphyne with one single vacancy at Vb site, (a) before relaxation, (b) after relaxation; Also, the corresponding electron density difference is presented in (c). While (d) and (e) geometrical structure of the monolayer graphyne with one single vacancy at Vr site, (d) before relaxation, (e) after relaxation; Also, the corresponding electron density difference is presented in (f).
90.203° to 103.592°, the other two angles are decreased respectively from 120° to 110.106° and 149.797°–146.302°.

For the case of the monolayer graphyne with one single vacancy at Vr site (Fig. 2d and e), a Jahn–Teller distortion also occurs, which gives rise to the in-plane displacement of other C atoms in the graphyne monolayer. The distance between Cr1 and Cr2 atoms is decreased from 2.628 Å to 1.498 Å after relaxation. The bond length of 1.498 Å is in fact close to the bond length of C–C single bond length, suggesting that a covalent bond between Cr1 and Cr2 atoms has been formed. This result is further confirmed by the increased electron density difference between Cr1 and Cr2 atoms shown in Fig. 2f. In addition, the bond length of the Cr2–Cr4 bond is increased from 1.407 to 1.500 Å, and the aromatic bonds of Cr1–Cr3 and Cr1–Cr5 around the vacancy changes from 1.424 to 1.493 and 1.489 Å, respectively. The in-plane displacement of C atoms around the vacancy also results in corresponding bond angles alternations. As can be seen in Fig. 2d and e, one bond angles is decreased from 120° to 108.392°, the other two are respectively increased from 120° to 125.057° and 126.551°.

Fig. 3 presents the band structure (BS) and density of states (DOS) of the monolayer graphyne with one single vacancy. For easy comparison, the BS and DOS of the pristine monolayer graphyne are first presented in Fig. 3a. It is evident that the pristine monolayer graphyne has a direct band gap of 0.474 eV, which is in good accordance with previously reported results [1,15,16]. In particular, the pristine monolayer graphyne displays symmetrical spin-up and spin-down bands, which suggests that the pristine monolayer graphyne is a nonmagnetic semiconductor. However, a spontaneous magnetization is induced by the vacancy as shown in Fig. 3b and c. Note that the spin polarization is sensitive to local geometric structure of the vacancy. In the case of monolayer graphyne with one single vacancy at Vb site (Fig. 3b), except for the two defect-induced states all other electron bands in the whole energy scale are fully spin degenerate. Particularly, the spin splitting of the
defect-induced states is rather weak. For the defect-induced state which lies at the top of valence band (VB), the splitting energy between the spin-up and spin-down bands at the M point is merely 19 meV. As for the defect-induced state which locates in the band gap, the splitting energy is as small as 20 meV. Moreover, the spin-polarized defect-induced states are almost dispersionless in the whole first Brillouin zone, which indicates that the corresponding electron state is heavily localized. Therefore, the magnetic moment is mainly localized at the vacancy site, which is further confirmed by the spin density distribution presented in Fig. 4a).

By analysis of the DOS plotted in Fig. 3b, it can be seen that the defect states located in the band gap region exhibits a weak spin-split, indicating the existence of local magnetic moments. Interestingly, both the spin-up band and spin-down band show semi-conducting behaviors. The band gaps for the spin-up and spin-down ones are 0.445 and 0.434 eV, respectively, which are smaller than that of pristine graphyne (0.474 eV). Besides the above mentioned perturbation to the BS and DOS, the whole BS and DOS move towards low energy after introducing one single vacancy at the Vb site.

Turning to the electronic structure of monolayer graphyne with one single vacancy at the Vr site presented in Fig. 3c, it is observed that the net spin is mainly localized at the Cb3 atom. In detail, the splitting energy between the occupied and unoccupied band is as large as 0.259 eV. This suggests that a strong magnetization exists in the monolayer graphyne with one single vacancy at the Vb site. In particular, the spin-up band of the defect-induced state is fully occupied and the spin-down band is left unoccupied. As for the monolayer graphyne with one single vacancy at the Vr site, the Cr1 atom now has one sp2 dangling bond and the Cr2 atom holds three sp dangling bonds. Since the formation of a covalent bond between Cr1 and Cr2 atoms merely gives rise to the saturation of Cr1 atom, the other two sp dangling bonds of Cr2 is still unsaturated. Therefore, the Cr2 atom provides the main contribution to the magnetic moment of the vacancy defect at the Vr site. On the other hand, when the monolayer graphyne with one single vacancy is neutral, the two remaining unsaturated sp dangling bonds of Cr2 atom interacts with each other to lower the total energy of the whole system. In this case, because the -Cr4-Cr2-Cr1-chain structure, the interaction between the dangling bonds results in hybrid orbital splitting. Therefore, the magnetic moment is dispersed around the vacancy site.

4. Conclusions

In conclusion, the effect of single vacancy on the structural, electronic and magnetic properties of the monolayer graphyne is investigated by the first-principles calculations. It is observed that the vacancy prefers to sit at the sp-hybridized C atom in chains and has little effect on the geometrical structure of the monolayer graphyne. The large value of vacancy formation energy suggests that introducing of single vacancy in monolayer graphyne is energetically unfavorable. Particularly, the single vacancy can break the degeneracy of the spin polarization of pristine monolayer graphyne. In the case of monolayer graphyne with one single vacancy at
Vb site, the electronic structure calculation results reveal two weakly spin-polarized defect-induced states. Since the defect-induced states are almost dispersionless in the whole first Brillouin zone, the magnetic moment is mainly localized at the vacancy site. As for the monolayer graphyne with one single vacancy at Vr site, one defect-induced state which is highly split appears in the band gap. The spin-up band of the defect-induced state is highly dispersive and shows considerable delocalization, suggesting that the magnetic moment is dispersed around the vacancy site. The above magnetization in monolayer graphyne with one single vacancy can be attributed to the unpaired magnetic electrons.

Acknowledgments

This work is supported by National Natural Science Foundation of China (61306009), the Science and Technology Star Project of Shaanxi Province (2013KJXX-24) and the NWU Graduate Innovation and Creativity Funds (YZZ13112).

References