

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



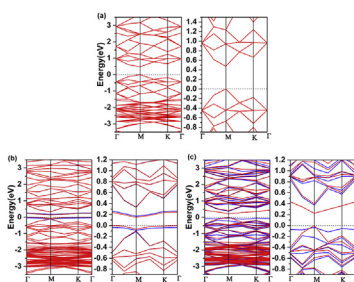
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HIGHLIGHTS

- A Jahn-Teller distortion occurs in monolayer graphyne with single vacancy.
- The spin polarization is sensitive to local geometric structure of the vacancy.
- Vacancy lying at sp^2 hybridized C site introduces weakly spin-polarized defect bands.
- A strong spin splitting occurs when the vacancy lies at sp hybridized C site.
- The magnetization is explained in terms of the valence-bond theory.

GRAPHICAL ABSTRACT



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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 [1,15,16], 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

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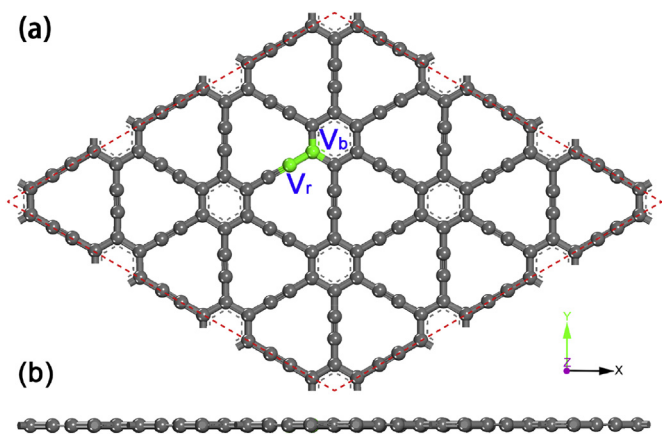


Fig. 1. The schematic structural model of monolayer graphyne with one single vacancy: (a) Top view, (b) side view. Green spheres show the inequivalent vacancy positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 sp^3 and sp^2 hybridized carbon nanomaterials, until now, studies on the effect of single vacancy on the structural, electronic and magnetic properties of graphyne are rare. In order to widely use graphyne into the field of electronic devices, a better understanding of the electronic structure and magnetic properties of the monolayer graphyne with single vacancy is essential. Here, the effect of single vacancy on the structural, electronic and magnetic properties of the monolayer graphyne is investigated by the first-principles calculations. From these results, some helpful instructions can be provided for the growth of monolayer graphyne 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 graphyne 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 $9 \times 9 \times 1$ 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 graphyne 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 graphyne with and without one single vacancy, respectively; $\mu(C)$ is the chemical potentials of the C atom using pristine graphyne as reference systems.

3. Results and discussion

For the monolayer graphyne 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 sp^2 and sp hybridized C atom in the monolayer graphyne. The calculated formation energy of the vacancy at Vr site is 9.944eV, which is 1.268eV 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 graphyne. 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 graphyne structure can be made by analyzing the contribution of each carbon bond to their cohesive energies. The calculated C–C single, C–C aromatic bond, and C–C triple bond energies in graphyne 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 triple 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 graphyne is rather high, which is larger than the experimental value of 7.0 ± 0.5 eV [44] and the previous DFT value of 7.7eV [19] for graphene. This suggests that similar to graphene, introducing of single vacancy in monolayer graphyne is energetically unfavorable.

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

$$E_c = [nE(C) - E_p]/n,$$

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 graphyne, respectively. The corresponding cohesive energy E_c is listed in Table 1. The calculated cohesive energies of graphyne and

Table 1
Cohesive energy of graphyne and graphene in units of eV/atom.

Method	Graphyne	Graphene
GGA-PBE	7.23 ^a	7.89 ^a
GGA-PBE	7.21 ^b	
GGA-PBE	7.262 ^c	7.906 ^c
GGA-PAW		8.11 ^d
GGA-PBE		8.02 ^e

^a This work.

^b Ref. [45].

^c Ref. [42].

^d Ref. [46].

^e Ref. [47].

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