Tuning the electronic and magnetic properties of defect blue phosphorene by the adsorption of nonmetal atoms

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Abstract. Based on the first principles of density functional theory, the adsorption of nonmetallic atoms on the surface of defective blue phosphorene was investigated. The results show that the most stable sites of different nonmetallic atoms on the defect blue phosphorene are different. The nonmetal (B, C, N, O) atoms were adsorbed on SV and SW defects blue phosphorene respectively. It was observed that B, N adsorbed SV defect blue phosphorene systems exhibited semiconducting behavior, whereas O adsorbed SV defect blue phosphorene system exhibited metallic behavior, and C adsorbed SV defect blue phosphorene system exhibited magnetic semiconducting behavior. For SW defect blue phosphorene, the results show that B, N, adsorbed SW defect blue phosphorene showed magnetic semiconductor behavior, while C, O adsorbed SW defect blue phosphorene showed semiconductor behavior.

Keywords: Blue phosphorene, Adsorption, Vacancies, Magnetism.

1. Introduction

There are several different phases of monolayer phosphorene. A stable phase is monolayer blue phosphorene, which was theoretically predicted [1] and successfully prepared, revealing that blue phosphorene is a wide band gap material with high anisotropic mobility. Like black phosphorene, it was assumed that blue phosphorene material has high carrier mobility. Interestingly, the application of nanoelectronic devices need quite adequate band gap, which makes it a good candidate for future electronic devices, especially in the photovoltaic industry. In this article, we mainly study the monolayer blue phosphorene, hoping to obtain more excellent performance by doping modification, and to provide theoretical guidance for looking for potential electric-optical and spintronic devices. Applications in spintronic devices require a high carrier mobility and dilute magnetism, for example, provided by blue phosphorene, with a carrier mobility of more than $10^3 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [2]. Previous reports have shown that doping modification [3] and heterostructure formation [4] can tune the electronic and magnetic properties of blue phosphorene. Unfortunately, neither doping sites nor bandgap widths can be manipulated very well [5]. On the one hand, experimentally have already confirmed that the molecular beam epitaxy can grow blue phosphorene on the surface of Au (111) [6], but in the synthesis of two-dimensional materials, the defect is inevitable. It cannot be denied that in the process of material transfer, the formation of defect is also expected. On the other hand, defects can be artificially generated by ionic
or electron irradiation [7] to cultivate new properties and extend their application. Defects cannot only change the electronic structure of the system but also adjust the magnetic properties of two-dimensional materials. In this paper, we systematically studied the electronic and magnetic properties of SW and SV defects in blue phosphorene as well as the adsorption of nonmetals on the defective blue phosphorene.

2. Calculation methods and model
First principles simulation was performed based on density functional theory (DFT) with Vienna Self-header Simulation Package (VASP) [8]. We use the Perdu-Burke-Enzehoff (PBE) generalized gradient approximation (GGA) [9] and Projector augmented-wave (PAW) [10] potentials to deal with the exchange correlation energy of the interacting electrons. In order to avoid interlayer interaction and simulate periodic boundary conditions, a vacuum of about 20Å is used along the Z direction. The energy cutoff value of the plane wave basis set is 500 eV. The self-consistent convergence criterion for 1x10^{-4} eV is considered. All atoms are completely relaxed until the force acting on each atom is less than 0.01eV/Å. In our work, a nonmetallic metal atom is placed on the surface of a defective blue phosphorene in a 5×5×1 supercell. The Brillouin integration is performed through Monkhorst package scheme with a 7×7×1 grid.

For the selection of adsorption sites, two kinds of adsorption sites were considered for SV defects, and five kinds of adsorption sites were considered for SW defects, as shown in Figure 1 and Figure 2, respectively. The most stable adsorption configuration is determined by the size of adsorption energy.

\[ E_{ad} = E_{total} - E_{bp} - E_{nm} \]  

Where \( E_{total} \), \( E_{bp} \), and \( E_{nm} \) is the energy of nonmetal atoms adsorbed blue phosphorene system, pristine blue phosphorene, and isolated nonmetal atoms, respectively.

3. Results and Discussion
3.1. Single vacancy defect and Stone-Wales defect
In this part, we first studied the structure of defective blue phosphorene and compared it with other literatures to ensure the correctness of our structure. After structural optimization, the buckling height is 1.24 Å and the P-P bond length is 2.26 Å with pristine blue phosphorene, consistent with previous investigations [13]. Several different configurations of defects blue phosphorene have been confirmed by previous reports. For single vacancy (SV) defect of blue phosphorene, we can produce an SV defect by removing a P atom from the original structure, as depicted in Fig. 1(a). The effects of SV defects on the geometrical, electronic and magnetic properties of blue phosphorene are studied. After relaxation, the system produces a magnetic moment of 1 \( \mu_B \), which is mainly generated by the three unsaturated suspension bonds, and the P-P bonds around the defective atoms are slightly shortened. As depicted in Fig. 1(b), SV defect blue phosphorene exhibits semi-metallic properties compared with intrinsic blue phosphorene and produces 1 \( \mu_B \) local magnetic moment. The asymmetry of energy bands also confirms the production of magnetism. We create a Stone-Wales (SW) defect by rotating a 90 angle around the center of a P-P bond. The structure is shown in Fig. 1(c). There is a specific angle between the rotating P1-P2 bond and the zigzag direction of the blue phosphorene, resulting in the irregular shape of the two five-atom rings and the two seven-atom rings of the 55-77 structure After optimization, it was found that the rotating P-P bond was shortened to 2.19 Å, and the length of other adjacent bonds was also slightly changed. As can be seen from the band structure and state density in Fig. 1(d), the SW defect is non-magnetic semiconductor with a band gap of 1.63 eV.
3.2. **B, C, N, O adsorb defective blue phosphorene**

3.2.1. **C N O adsorption of single vacancy defect blue phosphorene.** In this section, in order to study the influence of nonmetallic atoms on the SV defect blue phosphorene with electronic properties, the energy band structure, total density of states (TDOS) and projected density of states (PDOS) of the system was calculated. Firstly, two different adsorption sites were considered for the single vacancy defect blue phosphorene, as shown in Fig. 1(a). For B, O adsorption system, the most stable adsorption site is at the first position, while C, N adsorption system is at the second position. The results are shown in the Table 1. The results show that the adsorption energies are -3.26, -4.24, -5.46 and -3.75 eV, respectively. The strong interaction between N and SV defect blue phosphorene is also reflected by the distance between the adsorb atom and its nearest neighbor P atom. The distance between N atom and substrate is 1.83 Å. The maximum adsorption energy of N adsorption system may be due to the close atomic radius of N atom and P atom. As depicted in Fig. 2(a) We can clearly see that a relatively gentle magazine band appears around 1.2 and -0.6 eV, indicating a strong localization. It can also be seen that there are two sharp peaks at -0.6 and 1.2 eV for the TDOS and PDOS, indicating the p orbital interaction between P and B, exhibited in Fig. 2(e). Interestingly, B, C and N adsorption of SV defect blue phosphorene showed semiconductor characteristics, with band gaps of 1.62, 1.93 and 1.34 eV, respectively. However, the O adsorption system presents a metallic property. Magnetism is another aspect of our attention. The calculation results show that only the C adsorption defect blue phosphorene produces spin splitting, resulting in 1μB magnetic moment of the system. We calculated the magnetic moment distribution of the system. The magnetic moment mainly from the C atom is about 0.95 μB, as can be seen from Table 1. In Fig. 2(f) The two sharp peaks near the Fermi level also confirm that the magnetism comes primarily from the P orbital of the C atom, at -0.2 and 0.2eV.
Table 1. Nonmetal atoms adsorbed on single vacancy defect blue phosphorene

| Adsorption style | site | $E_{ad}$ (eV) | $d_{M-P}$ (Å) | $Q$ (e) | Total ($\mu_B$) | $M$ ($\mu_B$) | $P$ ($\mu_B$) |
|------------------|------|--------------|---------------|--------|----------------|---------------|---------------|
| B                | 1    | -3.26        | 1.92          | 1.69   | 0              | -             | -             |
| C                | 2    | -4.24        | 1.84          | 1.43   | 1              | 0.05          | 0.95          |
| N                | 2    | -5.46        | 1.83          | 1.68   | 0              | -             | -             |
| O                | 1    | -3.75        | 1.89          | 1.11   | 0              | -             | -             |

Table 2 Nonmetal atoms adsorbed on Stone–Wales defect blue phosphorene

| Adsorption style | site | $E_{ad}$ (eV) | $d_{M-P}$ (Å) | $Q$ (e) | Total ($\mu_B$) | $M$ ($\mu_B$) | $P$ ($\mu_B$) |
|------------------|------|--------------|---------------|--------|----------------|---------------|---------------|
| B                | 3    | -3.21        | 1.89          | 1.79   | 1              | 0.97          | 0.03          |
| C                | 5    | -4.81        | 1.73          | 3.63   | -              | -             | -             |
| N                | 5    | -5.76        | 1.63          | 3.80   | 1              | 0.91          | 0.09          |
| O                | 3    | -5.56        | 1.83          | 3.32   | -              | -             | -             |

Figure 2. Calculated the band structure and DOS, PDOS of 2p states for (a) B, (b) C, and (c) N, and (d) O-adsorbed single vacancy defect blue phosphorene. The vertical dashed lines represent the Fermi Energy.

3.2.2. B, C, N, O adsorbed SW defect blue phosphorene. When B, C, N, O adsorbed SW defect blue phosphorene, we found that the most stable structure of B, O adsorption was at the position 3, while the most stable configuration of C, N adsorption was at the position 5. Table 2 shows that the distance between the adsorbed atom and its nearest neighbor P atom is 1.89, 1.73, 1.63 and 1.83 Å, respectively. The close adsorption distance indicates a strong interaction force. It can also be seen from the adsorption energy that higher adsorption energy will lead to stronger adsorption system structure, and the adsorption energy is -3.21, -4.81, -5.76 and -5.56 eV, respectively. Fig. 4 shows the band structure of the adsorption system, all of which exhibit semiconductor properties and have appropriate band gaps. We found that B, N adsorbed SW defect blue phosphorene showed magnetism, which was expected by us. By analysing the magnetic moment distribution of each atom, the magnetic moment mainly came from the adsorbed atom. The magnetic moments occupied by B, N and atoms are 0.97 and 0.91 $\mu_B$, respectively. As can be seen from the TDOS and PDOS in Fig. 3(e), around the Fermi energy level, it is mainly contributed by the 2p orbital of B, which also confirms the conclusion that the magnetic moment mainly comes from the adsorbed atom.
4. Conclusion
The electronic, and magnetic properties of defect blue phosphorene with nonmetallic atom adsorption are studied in detail by first principles. It was observed that B, N, adsorbed SV defects blue phosphorene exhibited nonmagnetic semiconductor behavior, O exhibited metallic behavior, and C exhibited magnetic semiconductor behavior. B, N, adsorbed SW defect blue phosphorene exhibited magnetic semiconductor behavior, while C, O exhibited semiconductor behavior.

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References
[1] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P.D. Ye, Phosphorene: an unexplored 2D semiconductor with a high hole mobility, ACS Nano 8 (2014) 4033 - 4041.
[2] M. Sun, W. Tang, Q. Ren, S. K Wang, J.Yu, A first principles study of light non-metallic atom substituted blue phosphorene. Appl. Surf. Sci. 356 (2015) 110 – 114.
[3] R. B Pontes, R. H Miwa, A. J. R da Silva, A. Fazzio, J.E Padilha, Layer-dependent band alignment of few layers of blue phosphorus and their van der waals heterostructures with graphene. Phys. Rev. B 97 (2018) 235419.
[4] M. Sun, Y. Hao, Q. Ren, Y. Zhao, Y. Du, W. Tang, Tuning electronic and magnetic properties of blue phosphorene by doping Al, Si, as and Sb atom: a dft calculation. Solid State Commun. 242 (2016) 36 - 40.
[5] J. Lahiri, Y. Lin, P. Bozkurt, I.I Oleynik, M. Batzill, An extended defect in graphene as a metallic wire. Nat. Nanotechnol. 5 (2010) 326 – 329.
[6] H. P Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, A.V Krasheninnikov, Two-dimensional transition metal dichalcogenides under electron irradiation: defect production and doping. Phys. Rev. Lett. 109 (2012) 035503.
[7] J. Gao, J. Zhang, H. Liu, Q. Zhang, J. Zhao, Structures, mobilities, electronic and magnetic properties of point defects in silicene. Nanoscale 5 (2013) 9785 – 92.
[8] J. P Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett., 77 (1996) 3865.
[9] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method.
Phys. Rev. B, 59 (1999) 1758.

[10] Q. Wei, X. Peng. Superior mechanical flexibility of phosphorene and few-layer black phosphorus. Appl. Phys. Lett. 104 (2014) 251915.