

Electronic properties of phosphorene nanoribbons doped with boron, aluminum and carbon

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ABSTRACT

The doping effect of boron (B), aluminum (Al), and carbon (C) on black and blue phosphorene nanoribbons (PNRs) is investigated using density functional theory (DFT). The results show that the values of the ionization potential, electron affinity and Fermi energy for pristine black PNRs are larger than those of pristine blue PNRs. Also, the energy gap for pristine blue PNRs is slightly smaller than those of pristine black PNRs. In general, the pristine PNRs is a semiconductor with energy gap about 0.018eV. We found that the doping of PNRs with boron and carbon leading to increase in energy gap. On the other hand, the energy gap of aluminum doped PNRs are smaller than of pristine for black phosphorene while the energy gaps of aluminum doped phosphorene are larger than those of pristine for blue phosphorene. In aluminum doped phosphorene, the highest of peaks becomes less; the conduction and valence bands are less with the highest number of density of states. It is concluded that energy gap of phosphorene nanoribbon depends strongly on addition type.

KEY WORDS: Phosphorene, nanoribbons, doping, electronic structure.

1. INTRODUCTION

Graphene is a two dimensional honeycomb structure of carbon atoms has been extensively studied in the last few years because of its potential applications and exceptional mechanical and electronic properties (Geim, Novoselov, 2007; Habeeb, 2016; Ray, 2016; Fan, 2015; Jappor and Jaber, 2016; Hashmi, 2016). Graphene was at the focus for mesoscopic and nanotechnology directed by Novoselov (2004) discovered in late 2004. After the successful synthesis of graphene followed by a surge of studies novel two dimensional materials, a daunting quest was to obtain phosphorene.

Phosphorene is similar to graphene, which is a two-dimensional crystal of P atoms on a honeycomb lattice, has recently attracted intensive interest because of its electronic properties. Unlike graphene, atomic structure of phosphorene is buckled. Phosphorene is emerging as a promising 2D semiconducting material with a direct band gap. Phosphorene, a semiconducting material consisting of monolayer or multilayers of black phosphorus, has been recently attracted researchers' attentions because of its unique properties and great potentials in the field of electronics applications specifically nanodevices (Kou, 2014; Fei, 2014; Kou, 2015).

Taking into consideration the potential applications of phosphorene and the high reactivity of phosphorene, we have studied the investigation of electronic and structural properties of PNRs and the doped effect of boron and aluminum on PNRs using DFT calculations. Theoretical methods are an effective method to fine-tune the electronic and structural properties of nanostructures (Jappor, 2012; 2016; Jappor and Obaid, 2016; Habeeb, 2016) and some semiconductor (Jappor, 2011).

2. METHODS & MATERIALS

DFT calculations were performed using Gaussian 09 package (Frisch, 2009), with Perdew–Burke–Ernzerhof (PBE) functional (Perdew, 1996), at 6-311G basis set, to investigate the doping effect of B, Al and C on the electronic structure phosphorene nanoribbon (PNRs). We used two-dimensional systems consist of PNRs; blue and black. Fig.1 shows the structure of pristine PNRs that is used in the present study, one can see from the figure that the structure of blue and black contains 48 atoms of phosphorus.

3. RESULTS AND DISCUSSION

The results show a bond length for blue and black PNRs of 2.41Å, in accordance with previous results (Owens, 2015; Wang, 2015). The natural bond orbital calculations were performed to derive. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the total energy (E_{Tot}), cohesive energy (E_{coh}), energy gap (E_g), ionization potential (IP), electron affinity (EA) and Fermi energy (E_F).

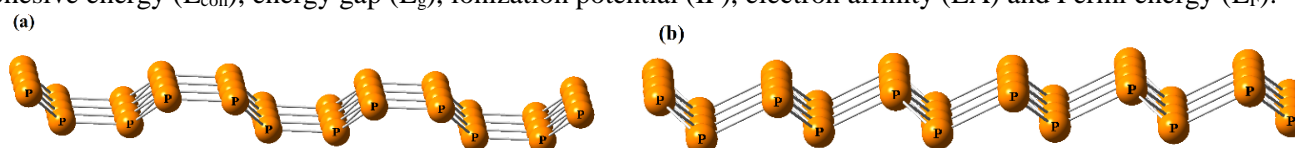


Figure.1. Phosphorene nanoribbon structures: (a) black and (b) blue.

structural and electronic properties of PNRs are listed in Table 1, it clear from the table that the energy total of PNRs black larger than PNRs blue. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that mostly acts as the electron acceptor play a significant role for molecular orbitals and the

reactant molecules in chemical reactions. It is clear from the table; there are a little difference between the HOMO and the LUMO energies PNRs black and PNRs blue. The deduced values of IP, EA are calculated by HOMO and LUMO energy, the IP, EA and Fermi energy for black PNRs are larger than blue PNRs. The energy gap plays crucial role in the properties of a solid, the E_g for black PNRs convergent with the PNRs blue.

Table.1. The structural and electronic properties of pristine PNRs

Property (eV)	Black Phosphorene	Blue Phosphorene
E_{Tot}	-445601	-4454
E_g	0.0185	0.018
IP ($= -E_{HOMO}$)	5.60	5.53
EA ($= -E_{LUMO}$)	5.58	5.51
E_F	-5.59	-5.52

Fig.2, illustrated the density of states of black and blue PNRs. According to the results of PNRs is a semiconductor, the results show a bandgap of 0.018 eV, smaller than previous results of pure phosphorene (Rodin, 2014; Zhu, 2014; Fei, 2014). In the Figure, the highest number of degenerate states in the conduction and valence bands are shown as follows: 8 and 10 for black and blue PNRs, respectively, since that all DOS there are many main peaks, there are states available for occupation at high DOS for a specific energy level and no states can be occupied at a zero-density of states for energy level.



Figure.2. DOS of pristine PNRs: (a) Black and (b) Blue. DOS spectrum (blue line), occupied orbitals (green line) and virtual orbitals (red line).

In this study, we choose three semiconducting impurities such as B, Al and C. Along with the study on the physical properties of the semiconducting impurity doped system, we also consider extra electron or hole charge doping in the impurity doped systems. Due to this extra electron or hole carrier doping, we expect that the electronic band structure can be manipulated by tuning the Fermi level. The optimized structure of B doped PNRs is shown in Fig.3, we find that the bond length between the P-B distance of 2.07Å, while the P-B-P angle is 108.68°.

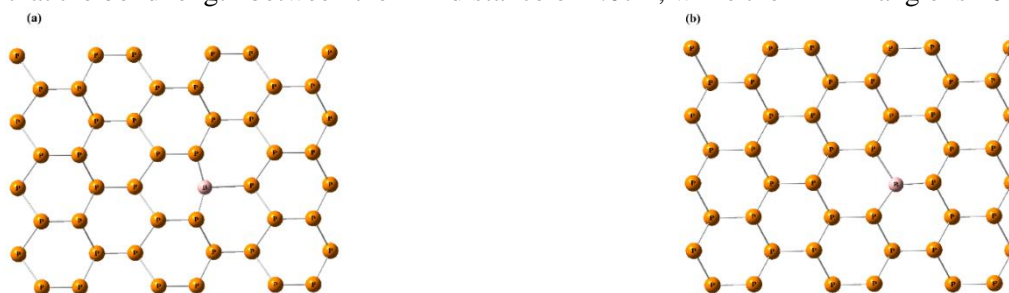


Figure.3. Boron doped PNRs structure: (a) black and (b) blue

In Table.2, we noticed that the increase of energy total of black phosphorene comparable with the boron doped blue phosphorene. The energy gap in the blue is larger than black while in the pristine PNRs energy gap convergent between the black and blue of PNRs. The ionization potential of blue little larger than those of black. On the other hand, the EA and Fermi energy of black are larger than that of blue.

Table.2. The structural and electronic properties of boron doped PNRs.

Property (eV)	Black phosphorene	Blue phosphorene
E_{Tot}	-436979	-436952
E_g	0.0187	0.101
IP ($= -E_{HOMO}$)	5.59	5.62
EA ($= -E_{LUMO}$)	5.57	5.520
E_F	-5.58	-5.57

The highest number of degenerate states in the conduction and valence bands are shown in Fig.3, which is as follows: 8for black and 10 for blue doping with the boron. This means that the energy gap in the region will be a

few from other areas, and the little density will be between the two regions 0, -2 because the energy gap is large, the doping in the blue phosphorene leading to increase in the energy gap while in black phosphorene the effect will be is very small.



Figure.4. DOS of Boron doped PNRs: (a) black and (b) blue phosphorene

The optimized structure of Al doped phosphorene is shown in Fig.5, we find that the bond length between the P-Al distance of 1.90Å, while the P-Al-P angle is 113.92°.

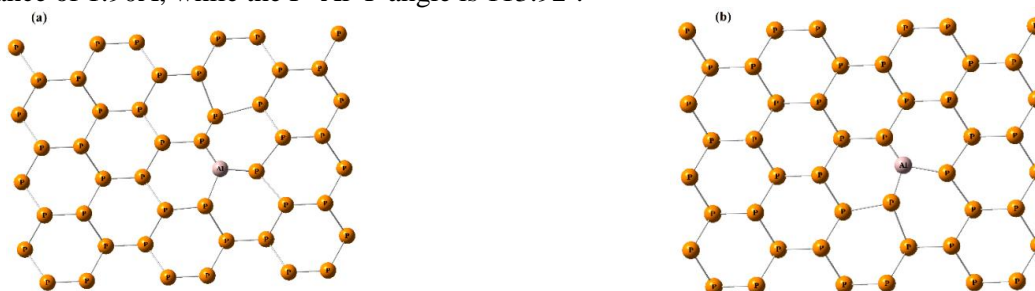


Figure.5. Aluminum doped PNRs structures : (a) black and (b) blue

We noticed in Table 3, that the energy total of black and blue phosphorene is comparable, also, ionization potential, electron affinity and Fermi energy of black PNRs are large than of that of blue phosphorene. However, the energy gap of blue phosphorene is larger than that from the black phosphorene, this behavior can be attributed to the geometry structure of black and blue phosphorene.

Table.3. The structural and electronic properties of Aluminum doped PNRs.

Property (eV)	Black phosphorene	Blue phosphorene
E_{Tot}	-442895	-442769
E_g	0.013	0.075
IP (= $-E_{HOMO}$)	5.59	5.55
EA (= $-E_{LUMO}$)	5.59	5.48
E_F	-5.59	-5.52

The highest number of degenerate states in the conduction and valence bands are shown as follows: 8 for black and blue doped with aluminum as shown in Fig.6.

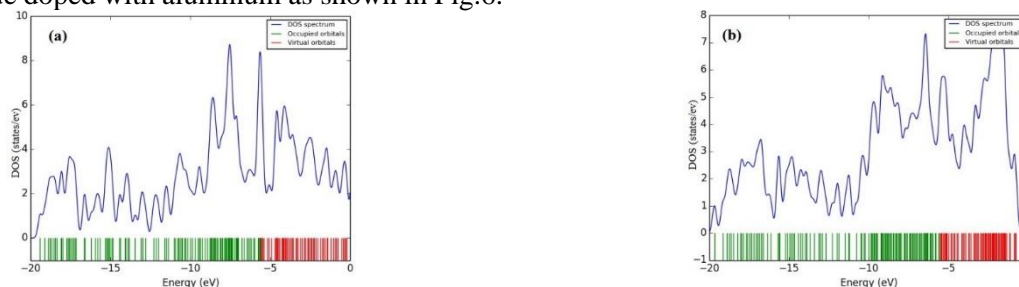


Figure.6. DOS of aluminum doped PNRs: (a) Black and (b) Blue. DOS spectrum (blue line), occupied orbitals (green line) and virtual orbitals (red line)

The optimized structure of C doped phosphorene is shown in Fig. 7, we find that bond length between the C-Al distances of 2.76Å in the phosphorene black carbon while the P-C-P angle is 107.16°, also, that bond length between the P-C distances of 2.30 Å in the phosphorene blue carbon while the P-C-P angle is 112.50°.

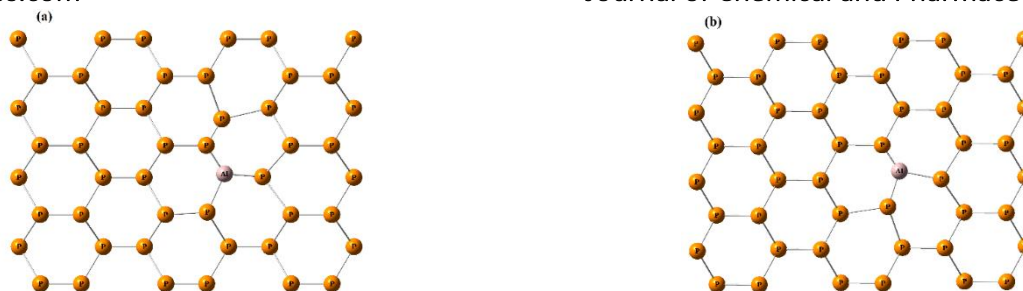


Figure.7. Carbon doped PNRs :(a) black Phosphorene and (b) blue Phosphorene

In Table.4, we noticed that of total energy of black and blue phosphorene are almost convergent, also, the ionization potential, electron affinity and Fermi energy of blue phosphorene are very large than of that of black phosphorene. However, the energy gap of blue phosphorene is larger than that from the black phosphorene, doped in carbon differs from doped in boron and aluminum.

Table.4. the structural and electronic properties of doping carbon on PNRs

Property (eV)	Black Phosphorene	Blue Phosphorene
E_{Tot}	-437343	-437265
E_g	0.06	0.09
IP ($= -E_{HOMO}$)	5.47	5.72
EA ($= -E_{LUMO}$)	5.41	5.62
E_F	-5.44	-5.67

The highest number of degenerate states in the conduction and valence bands of carbon doped phosphorene are shown as follows: 8 for black and it very highest from blue, but in the blue doped with the carbon is 7, as depicted in Fig.8.



Figure.8. DOS of carbon doped PNRs: (a) black and (b) blue

4. CONCLUSIONS

The conclusions of the current study can be summarized as following; the deduced values of the IP, EA and Fermi energy for pristine black PNRs are larger than those of pristine blue PNRs, the energy gap for pristine blue PNRs is slightly smaller than those of pristine black PNRs, according to the result, the pristine PNRs is a semiconductor with E_g ranging from (0.018 to 0.0185) eV, in addition, the energy gaps of boron doped phosphorene are larger than those of pristine, this indicates that E_g increases with the doping of boron. Also, the doping in the blue phosphorene leading to increase in the energy gap but the increasing in black phosphorene is very small. However, the ionization potential of boron doped blue phosphorene slightly larger than those of black, and the EA and Fermi energy of black are larger than that of blue phosphorene. On the other hand, the energy gaps of aluminum doped phosphorene are smaller than those of pristine for black phosphorene while the energy gaps of aluminum doped phosphorene are larger than those of pristine for blue phosphorene, also, the doping of phosphorene with carbon leading to an increase in the energy gap. Finally, DOS of carbon doped phosphorene are non-conformable with the DOS of boron and aluminum doped phosphorene.

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