Effective Doping of Monolayer Phosphorene by Surface Adsorption of Atoms for Electronic and Spintronic Applications

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ABSTRACT
We study the effect of surface adsorption of 27 different adatoms on the electronic and magnetic properties of monolayer black phosphorus using density functional theory. Choosing a few representative elements from each group, ranging from alkali metals (group I) to halogens (group VII), we calculate the band structure, density of states, magnetic moment and effective mass for the energetically most stable location of the adatom on monolayer phosphorene. We predict that group I metals (Li, Na, K), and group III adatoms (Al, Ga, In) are effective in enhancing the n-type mobile carrier density, with group III adatoms resulting in lower effective mass of the electrons, and thus higher mobilities. Furthermore, we find that the adatoms of transition metals Ti and Fe produce a finite magnetic moment (1.87 and 2.31 μB) in monolayer phosphorene, with different band gap and electronic effective masses (and thus mobilities), which approximately differ by a factor of 10 for spin-up and spin-down electrons, opening up the possibility for exploring spintronic applications.

KEYWORDS
Adatom; Band structure; DFT; Effective mass; Phosphorene; Spintronic

1. INTRODUCTION
Thin body materials and devices are being considered as the most promising candidates for 5 nm semiconductor technology and beyond by semiconductor industry [1]. This has lead us to actively study various 2D-layered crystals, such as graphene [2], silicone [3,4], germanene [5], transition metal dichalcogenides (MoS₂, MoSe₂, WSe₂, etc.) [6], due to their excellent material properties [7–11] and reduced short-channel effects. Field effect transistors (FETs), based on graphene [12] and MoS₂ [13], have already been demonstrated with performance superior to conventional Si-based FET’s. More recently, layered black phosphorous (dubbed as phosphorene) has joined this promising family of 2D crystals. In contrast to transition metal dichalcogenides, the carrier (hole) mobility in phosphorene is quite high (~1000 cm²/V.s), which in turn gives an I_ON/I_OFF current ratio of ~10^5 at room temperature [14–17].

Phosphorene is a layered material with individual layers having a puckered structure and the layers being stacked together by a weak van der Waals interaction, allowing for mechanical exfoliation. In each layer, a phosphorous atom covalently bonds with three other atoms, forming a honeycomb structure. Semiconducting phosphorene has an intrinsic direct bandgap of ~0.31 – 1.0 eV (bulk-monomonolayer), which is inversely proportional to the number of layers [15,18]. Because of its direct bandgap at Γ point, phosphorene is a potential candidate for applications in the optoelectronic devices[14,15,19–21]. Most of the 2D materials have high electron mobility and display n-type device characteristics, while phosphorene also has a high hole mobility and FETs having both p-type and n-type characteristics have been demonstrated [14,15]. Additionally, phosphorene shows highly anisotropic behavior in effective mass and mobility, which can be controlled using appropriate uniaxial or biaxial strain [22]. Black phosphorus (BP) has also been proposed as an effective anode material for Li ion batteries [23]. Among other advantages, black phosphorous is known for its chemical inertness and superior transport properties [17,19,20,22,24–26].

For practical use of any semiconductor material in FET devices, doping is essential to enhance the carrier concentration and to control threshold voltage. Since 2D layered materials have a very high surface area, adatom adsorption can be a very effective strategy for carrier doping and band structure engineering. For example, adsorption of hydrogen/halogen, metal, and molecules in graphene can change its electronic band structure, transforming graphene, from metal to semiconductor/insulator [27–29]. Adatom adsorption in 2D transition metal dichalcogenides creates donor or acceptor levels.
in-between the valence and conduction band of the parent material, leading to electron or hole doping of wide bandgap semiconductors like MoS$_2$ [30–33]. Both experimental study and ab initio simulation of potassium adsorption in MoS$_2$ have shown to dope MoS$_2$ with n-type carriers [33,34]. Similar studies have been done for selected adatom adsorption in monolayer black phosphorous range of valences, including s and p valence metals, transition metals, and semiconductors, hydrogen, and oxygen [35–39]. Further oxidation of phosphorene has also been studied and may provide more stability and alternate route to synthesis of phosphorene [40,41].

In this article, we use ab initio spin-polarized density functional theory (DFT) calculations to systematically explore the possibility of band structure engineering and doping possibilities of monolayer black phosphorous (MBP or monolayer phosphorene) via surface adsorption of various adatoms. We consider a few representative elements from several groups in the periodic table, ranging from alkali metals (group I) to halogens (group VII) and our aim is to provide a comprehensive guideline for doping strategies of MBP via surface adsorption of adatoms. In addition, we investigate the structural and magnetic properties, and the charge transfer from the adsorbed adatom to MBP and vice versa. Five different sites are chosen for adatom adsorption, as shown in Figure 1(c,d). These are named as $T_u$ (on top of the phosphorous atom in the upper layer), $B_u$ (top of the bridge of the upper layer), $H$ (centre of the hexagon), $T_l$ (on top of the phosphorous atom in the lower layer) and finally $B_l$ (above the bridge in the lower layer). Our work broadly reaffirms the findings of [35], and extends the study to include more adatoms such as group III elements (Al, Ga, In) among others, which are the most effective electron dopants with the lowest effective mass and possibly highest electron mobility. Additionally, we also report the effective mass of spin-polarized carriers, which is useful for exploring possible usage in electronic and spintronic applications.

The paper is organized as follows: in Section 2, we present the parameters and other details of the computational method used. In Section 3, we briefly review the crystal structure and electronic properties of MBP. This is followed by systematic presentation of the results and discussion in Section 4, and finally, we summarize our findings in Section 5.

2. METHODOLOGY AND SIMULATION DETAILS

We use the spin-polarized DFT calculations, as implemented in the ATK package [42–44] for geometry relaxation, as well as the electronic and magnetic property predictions. The exchange-correlation energy is treated by the generalized gradient approximation (GGA) using the Perdew, Burke, and Ernzerhof (PBE) pseudo-

Figure 1: (a) Top view and (b) side view of monolayer black phosphorous, (c) top view and (d) side view showing the five different adatom locations: H (hexagon center), $T_u$ (top of the phosphorous atom in the upper layer), $T_l$ (top of phosphorous atom of lower layer), $B_u$ (bridge of the upper layer P–P bond) and finally $B_l$ (bridge of the bottom layer P–P bond). (e) Band structure of intrinsic MBP with dashed line showing the Fermi level, and inset displaying the symmetry points in the Brillouin zone. (f) Spin-resolved density of states (DOS) for MBP. On the right and the left hand of zero with large magnitude, is the complete DOS of MBP corresponding to ($\uparrow$-spin) and ($\downarrow$-spin) and small magnitude lines around zero represents the projected DOS of P atoms.
potential [45]. The Brillouin-zone integrations are performed with Monkhorst-Pack K-points grid with $8 \times 8 \times 1$ Brillouin-zone sampling, along with energy cut-off of 75 Hartree. We have used a double zeta polarized basis set for all the calculations performed in this work. We have used a $3 \times 3 \times 1$ simple orthorhombic phosphorene super cell (containing 36 phosphorous atoms) with a vacuum region of 10 Å along the c-axis, which is sufficient to eliminate interaction among monolayers.

The charge transfer from the adatom to the phosphorene substrate is calculated using the Mulliken charge transfer method, i.e., by calculating the difference of valence electron charge of the isolated adatom and charge of the adatom in the vicinity of phosphorene; $\rho^+ = Z_a - \rho_a$ [46]. Here, $Z_a$ indicates the valence electron charge of the isolated adatom with an appropriate sign, for example, Mg has $Z_a = -2e$ where $e \approx 1.6 \times 10^{-19}$ eV, and $\rho_a$ is the calculated electron charge on the adatom over the monolayer phosphorene layer. Thus, $\rho^+ < 0$ ($\rho^+ > 0$) implies excess electron charge transferred from (to) the adatom to (from) the phosphorene monolayer.

To establish the stability of each of the reported adatom location on phosphorene monolayer, we perform \textit{ab initio} molecular dynamics simulations using Quantum Espresso (QE) package [47]. The MBP-adatom supercell is equilibrated at 400 K temperature and the dynamics of the adatom is monitored for 1 ps. The kinetic energy cut-off of is taken to be 40 Ry. The exchange-correlation energy is treated using PBE pseudo-potential and van der Waals correction is included under Grimme-D2 approximation [48]. Ionic temperature is controlled using Anderson thermostat. We find that while all of the adatoms vibrate around their most stable locations (reported in Table 1), there is no significant shift or dislocation from the most stable location at 400 K.

Additionally, we also study the adatom mobility and diffusion kinetics on monolayer phosphorene using the nudge elastic band (NEB) approach which calculates the activation energy barriers encountered by the adatom in moving from one stable location to another. The NEB is fairly accurate approach to determine minimum energy path between initial and final positions [49,50]. For this, Broyden optimization scheme has been employed with eight intermediate images between initial and final positions to find the potential energy barrier between them. We find that for all the 27 adatoms considered by us, the minimum potential energy barrier is 0.6 eV for moving from the most stable location to the next stable location. Since the minimum potential energy barrier of 0.6 eV is much

Table 1: Adatom, its preferred adsorption site (see Figure 1(c,d)), its binding energy $^a$ (calculated using Equation (1)), vertical distance of the adatom $d$ from the upper phosphorous layer (note that $d$ is not the shortest distance from the nearest phosphorous atom), magnetic moment per adatom (in the units of Bohr magneton, $\mu_B$) in a $3 \times 3 \times 1$ supercell, electronic charge transfer and the electronic effective mass (in the units of electron rest mass, $m_e$) calculated at the $\Gamma$ point in the $\Gamma-X$ direction

| Group | Adatom | Adsorption site | $d$ (nm) | Magnetic moment on adatom ($\mu_B$) | Charge transfer (e) | Effective mass ($m_e$) |
|-------|--------|----------------|---------|----------------------------------|-------------------|---------------------|
| I     | Li     | H              | 0.146   | 0                                | 0.024             | 1.26                |
|       | Na     | H              | 0.200   | 0                                | 0.176             | 1.24                |
|       | K      | H              | 0.238   | 0                                | 0.248             | 1.27                |
|       | Ca     | H              | 0.201   | 0                                | 0.056             | 0.65                |
|       | Mg     | H              | 0.197   | 0                                | 0.170             | 0.53                |
|       | Al     | H              | 0.161   | 0                                | 0.380             | 0.37                |
|       | Ga     | H              | 0.172   | 0                                | 0.448             | 0.43                |
|       | In     | H              | 0.124   | 0                                | 0.36              | 0.43                |
|       | C      | B              | 0.129   | 0                                | 0.274             | 0.337               |
|       | Si     | B              | 0.129   | 0                                | 0.14              | 0.328               |
|       | Ge     | B              | 0.056   | 0                                | 0.028             | 0.746(1), 0.763(1)  |
| V     | N      | B              | 0.065   | 0.056                           | 0.362             |                     |
|       | As     | B              | 0.143   | 0                                | 0.036             |                     |
|       | S      | T              | 0.092   | 0                                | 0.136             | 0.696               |
|       | F      | T              | 0.153   | 0                                | 0.104             | 0.650               |
|       | Cl     | T              | 0.186   | 0.218                           | 0.206             | 0.699(1), 0.728(1)  |
|       | Br     | T              | 0.231   | 0.155                           | 0.124             | 0.715(1), 1.456(1)  |
| Nobel | Cu     | H              | 0.113   | 0                                | 0.194             | 0.838               |
| metals| Ag     | H              | 0.146   | 0                                | 0.046             | 0.494               |
|       | Au     | H              | 0.150   | 0.242                           | 0.064             | 0.502(1), 0.429(1)  |
|       | Ti     | H              | 0.150   | 1.874                           | 0.056             | 1.471(1), 0.158(1)  |
|       | Fe     | H              | 0.122   | 2.316                           | 0.006             | 2.825(1), 3.324(1)  |
| metals| Ni     | H              | 0.109   | 0                                | 0.042             | 0.765               |
|       | Pd     | H              | 0.133   | 0.522                           | 0.602             |                     |
|       | Pt     | H              | 0.121   | 0.208                           | 1.856             |                     |
|       | Sn     | H              | 0.164   | 0.092                           | 0.305             |                     |

$^a$Calculated using (i) Quantum Espresso package – PAW-PBE pseudo-potential and vdW correction; (ii) QuantumWise ATK – norm-conserving basis set with PBE and no vdW correction.
greater than the available thermal energy at room temperature (0.026 eV), this implies the stability of all considered adatoms against diffusion from their stable location.

Finally, for further confirmation of the binding energy, we redo the spin-polarized virtual crystal relaxation calculations in QE package [47] taking van der Waals forces into account. The dipole–dipole interactions have been considered in the van der Waals interactions. This was necessitated on account of the discrepancy in some of our ATK-reported binding energies, with those reported in [35,36]. For the binding energy verification in QE, we use the projector augmented wave (PAW) pseudo-potentials within the GGA-PBE approximation and the modified results of both the calculations are shown in Table 1.

3. PHOSPHORENE: CRYSTAL STRUCTURE AND ELECTRONIC PROPERTIES

BP is reported to be the most stable form among all the allotropes of phosphorus (for example, red and white phosphorous among others) under normal conditions. BP has an orthorhombic crystal structure (space group: Cmca), having eight phosphorous atoms in the unit cell [51]. Multiple layers are stacked together to form BP, although, unlike graphite, the constituent layers are not flat, but puckered in nature. Based on tight binding calculations, BP was found to be a direct bandgap semiconductor with an energy gap of ≈0.3 eV at the Z point [52], which was later confirmed via DFT calculations by Qiao et al. [18]. The authors also calculated the band structure of MBP and found it to be a direct bandgap semiconductor with an energy gap of ~1 eV at the Γ point. Our calculation yields a very similar result for pristine MBP (see Figure 1(e,f)) and this also validates the parameters chosen for simulation in this article, as described in Section 2.

4. RESULTS AND DISCUSSIONS

As shown in Figure 1, we have considered five different adatom locations – H, Tu, Tl, B, and Bl for the adatom. We start by initially placing all the adatoms studied at these five locations, and let the structure relax. The most stable configuration is determined based on maximum binding energy and is chosen for the purpose of presenting the electronic band-structure data. The binding energy is calculated according to the relation:

\[ E_{\text{binding}} = E_{\text{MBP}} + E_{\text{adatom}} - E_{\text{MBP+adatom}}, \]

where \( E_{\text{MBP}} \) is the total energy of the super cell of pristine MBP, \( E_{\text{adatom}} \) is the energy of the isolated adatom in the ground state calculated for the same super cell with the same parameters, and \( E_{\text{MBP+adatom}} \) is the total energy of the combined phosphorene–adatom system after structural relaxation. In Table 1, we have reported the maximum binding energy value among the five different adatom locations (H, Tu, Tl, B, and Bl) and presented the corresponding electronic band structure, DOS and adatom projected density of states (PDOS) results in Figures 2–4. Note that in these figures the dashed line displays the Fermi level of the MBP-adatom system and the band structure of MBP (black lines) has been shifted so as to align the conduction bands of pristine MBP and the MBP-adatom system.

Let us begin by discussing the case of alkali and alkaline earth metals. As shown in Table 1, all of them prefer H site among the five possible locations and the vertical distance (\( d \)) from the upper phosphorous layer varies depending on the size of the adatom. Smaller atoms have higher binding energies, which implies stronger binding to the underlying MBP layer. In case of alkali metals (group I), adatom adsorption leads to n-type carrier doping, because of which Fermi level shifts to the conduction band of MBP (see the case of K adsorption in Figure 2(a)). For each of the three group I adatoms studied here, MBP turns out to be electron doped, as expected, because of highly electronegative nature of alkali metal atoms. Since the electronic states of K have negligible contribution to the total density of states (DOS) near the CBM (see Figure 2(b)), the K adatom (and other alkali metals) preserves the original electronic structure of phosphorene, but shifts the Fermi level to the CBM by donating free mobile electrons, and hence enhances the electrical conductivity significantly. In case of group II, adatom adsorption yields significantly different effect. As shown in Figure 2(d), after Mg adsorption, a filled energy band is present in the band gap of MBP. Electronic states corresponding to this particular band are localized near the adatom, which is clearly visible from the PDOS plot shown in Figure 2(e). Thus, the only way these electrons can take part in electronic conduction via excitation to the conduction band of MBP. However, since the band is located ~0.7 eV away from the CBM, group II adatoms (Mg, Ca studied here) are not going to be effective as electron donors. The PDOS plots (see Figure 2(b,e)) reveal that the up- and down-spin states have mirror symmetry, which implies equal number of up- and down-spin electrons, and, accordingly, all the adsorbed atoms of group I and II are non-magnetic.

Next, we consider the group III and IV adatoms. In case of group III, all the adatoms (Al, Ga, In) are located on
Figure 2: Panels (a), (d), (g) and (j) show the band structure, panels (b), (e), (h) and (k) display the spin-polarized total (large magnitude and on right hand of zero, for ↑-spin and on left hand of zero, for ↓-spin) and projected DOS (small magnitude and on right hand of zero, for ↑-spin and on left hand of zero for ↓-spin) of MBP with selected adatoms of groups I, II, III, and IV, i.e. K, Mg, Al and Si, respectively. Panels (c), (f), (i) and (l) show the top and side views of the optimized adatom location.
Figure 3: Panels (a), (d), (g) and (j) show the band structure, panels (b), (e), (h) and (k) display the spin-polarized total (large magnitude and on right hand of zero, for $\uparrow$-spin and on left hand of zero, for $\downarrow$-spin) and projected DOS (small magnitude and on right hand of zero, for $\uparrow$-spin and on left hand of zero, for $\downarrow$-spin) of MBP with selected metallic adatoms, i.e. Au, Pd, Fe and Ti, respectively. Panels (c), (f), (i) and (l) show the top and side views of the optimized adatom location.
the H site and they have similar binding energies (see Table 1). Among the group IV adatoms, C prefers the H site, while Si and Ge are more stable on the B site and the binding energy is strongly dependent on the size of the adatom (see Table 1). Adatom–phosphorene distance \( d \) depends on the size of the corresponding adatom, as expected (see Table 1). In case of group III, as a result of adatom adsorption, the Fermi level has shifted
to the conduction band of MBP, making it a n-type semiconductor (see Figure 2(g)). On the other hand, adsorption of group IV adatoms leads to the formation of fully occupied midgap energy levels, located approximately in the middle of VBM and CBM (see Figure 2(j)). Thus, while group III adatoms are very effective for n-type carrier doping in MBP, group IV adatoms are not suitable at all for this purpose. We have not found magnetic moment on any of the adatoms of group III and IV, which is corroborated by DOS plots of spin-up and spin-down states, as illustrated in Figure 2(h,k). We emphasize here that only considering the charge transfer to determine whether an adatom adsorption leads to electron or hole doping can be misleading, as in the case of group III elements (see Table 1). In case of group III adatoms, the changes in the band structure lead to a suppression of electronic states in the valance band, and an enhancement of DOS in the conduction band (see Figure 2(h)). Also, note that group III adatoms in MBP lead to a lower effective mass of the electrons (∼0.4m_e), which implies higher mobilities and consequently excellent transport properties.

Now we consider the case of the transition metals. According to the binding energy values reported in Table 1, all of them get adsorbed preferably on the H site. Among them, only Au, Ti, and Fe are found to be magnetic (see Table 1), which is corroborated by up- and down-spin DOS, shifted with respect to each other along the energy axis (see 3(b,h,k)). Interestingly, magnitude of the bandgap for up- and down-spin electrons are different, which can be exploited for spintronic applications. Also, note that the effective electron masses for the up- and down-spin electrons in Fe and Ti differ by a factor of 10 (approximately), which will also be reflected in their respective mobilities. Each one of the adatoms gives rise to the midgap energy levels (note that the Fermi energy lies in between VBM and CBM in Figure 3(a,d,g,j)), and thus they are not effective either as n-type or as p-type dopant in MBP. We note, however, that these trap states can speed up the carrier recombination process and can be useful for devices which require fast switch-off times [53].

Finally, we describe the effect of group V, VI and VII adatoms on electronic band structure of MBP. Based on the binding energy values shown in Table 1, group V, VI and VII adatoms prefer B_h, T_1 and T_u sites, respectively. As expected, the binding energy, as well as the value of \( d \), depends on the size of the adatom. As reported in Table 1, smaller adatoms are closer to the MBP layer and bind more strongly than the larger ones. In case of group V, adatom adsorption does not dope the underlying MBP layer with n-type carriers directly (see the case of As in Figure 4(a)). However, the energy gap (indirect) between the midgap state and the CBM is very small, such that these electrons can be excited to the conduction band of MBP to increase the n-type carrier density. On the other hand, the bandgap remains unchanged by the adsorption of group VI adatoms (see the case of O in Figure 4(d)), and thus they are not effective for carrier doping in MBP. Among the group VII adatoms, while F is found to be non-magnetic, a small magnetic moment (≈ 0.15 \( \mu_B \) per adatom) is observed in case of Cl and Br. This is confirmed by the asymmetry of the DOS plots of up- and down-spin states in case of Cl adsorption, illustrated in Figure 4(g). Note that the bandgap of up- and down-spin electrons have different magnitude, which can be useful for spintronic device applications. Moreover, for group VII adatoms, the Fermi energy lies close to the valance band, which may assist in making MBP hole-doped.

Before concluding, let us compare the reported binding (or adsorption) energy in previous works [35,36] and in this work. Kulish et al. [35] did their calculations using QE, considering the PAW method with PBE as the exchange correlation functional, while ignoring dipole and van der Waals corrections. Hu et al. [36] used VASP, with PAW-PBE functional, included dipole corrections and ignored van der Waals corrections. In this paper, we have used two different methods for calculating the binding energies: (1) using norm-conserving pseudo-potential with PBE functional in ATK, ignoring van der Waals forces and (2) using PAW-PBE functional in QE, taking van der Waals forces (including dipole-dipole interactions) into account, respectively. We find that the binding energy depends significantly on the type of pseudo-potential used and whether or not the van der Waals correction is included. Furthermore, since our QE calculations use the same basis set and exchange correlation functional as in [35,36], the QE-calculated binding energies are also similar.

5. CONCLUSION

To summarize, in this article, we have systematically explored the effect of surface adsorption of 27 adatoms from different groups of the periodic table, ranging from alkali metals (group I) to halogens (group VII), on electronic, structural and magnetic properties of MBP. We find that among the adatoms considered, group I alkali metals and group III elements make MBP n-type, with the MBP-group III adatom system having lower electronic effective mass (∼0.4m_e) which should result in better mobility and transport characteristics. Group II,
REFERENCES

1. “The international technology roadmap for semiconductors (ITRS),” Semiconductor Industry Association, 2013. http://www.itrs.net/

2. A. K. Geim and K. S. Novoselov, “The rise of graphene,” Nat. Mater., Vol. 6, no. 183, pp. 183–91, 2007.

3. Z. Ni, Q. Liu, K. Tang, J. Zheng, J. Zhou, R. Qin, Z. Gao, D. Yu, and J. Lu, “Tunable bandgap in silicene and germanene,” Nano Lett., Vol. 12, no. 113, pp. 113–8, 2012.

4. P. Vogt, P. D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. L. Lay, “Silicene: Compelling experimental evidence for graphene like two-dimensional silicon,” Phys. Rev. Lett., Vol. 108, p. 155501, 2012.

5. E. Bianco, S. Butler, S. Jiang, O. D. Restrepo, W. Windl, and J. E. Goldberger, “Stability and exfoliation of germanene: A germanium graphene analogue,” ACS Nano, Vol. 7, no. 5, pp. 4414–21, 2013.

6. M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, “The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets,” Nat. Chem, Vol. 5, no. 4, pp. 263–75, 2013.

7. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, “Two-dimensional atomic crystals,” Proc. Natl. Acad. Sci. USA, Vol. 102, no. 30, pp. 10 451–3, 2005.

8. A. H. C. Neto and K. Novoselov, “New directions in science and technology: Two-dimensional crystals,” Rep. Prog. Phys., Vol. 74, no. 30, pp. 082 501–9, 2011.

9. Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” Nat. Nano, Vol. 7, pp. 699–712, 2012.

10. S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Imsach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruo, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, and J. E. Goldberger, “Progress, challenges, and opportunities in two-dimensional materials beyond graphene,” Nat. Nano, Vol. 7, no. 4, pp. 2898–2926, 2013.

11. G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S. K. Banerjee, and L. Colombo, “Electronics based on two-dimensional materials,” Nat. Nano, Vol. 9, pp. 768–79, 2014.

12. F. Schwierz, “Graphene transistors,” Nat. Nano, Vol. 5, pp. 487–96, 2010.

13. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, “Single-layer MoS2 transistors,” Nat. Nano, Vol. 6, pp. 147–50, 2011.

14. L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, “Black phosphorus field-effect transistors,” Nat. Nano, Vol. 9, pp. 372–7, 2013.

15. H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tomășneak, and P. D. Ye, “Phosphorene: An unexplored 2D semiconductor with a high hole mobility,” ACS Nano, Vol. 8, no. 4, pp. 4033–41, 2014.

16. S. P. Koenig, R. A. Doganov, H. Schmidt, A. H. Castro-Neto, and B. A. Zygelman, “Electric field effect in ultrathin black phosphorus,” Appl. Phys. Lett., Vol. 104, 2014. doi:10.1063/1.4868132.

17. W. Lu, H. Nan, J. Hong, Y. Chen, C. Zhu, Z. Liang, X. Ma, Z. Ni, C. Jing, and Z. Zhang, “Plasma-assisted fabrication of monolayer phosphorene and its raman characterization,” Nano Res., Vol. 7, no. 6, pp. 853–9, 2014.

18. J. Qiao, X. Kong, Z.-X. Hu, F. Yang, and W. Ji, “High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus,” Nat. Commun., Vol. 5, 2014. doi:10.1038/ncomms5475.

19. V. Tran, R. Soklaski, Y. Liang, and L. Yang, “Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus,” Phys. Rev. B, Vol. 89, pp. 235319–25, 2014.

20. X. Peng, Q. Wei, and A. Copple, “Strain-engineered direct-indirect band gap transition and its mechanism in two-dimensional phosphorene,” Phys. Rev. B, Vol. 90, no. 085402–11, 2014.

21. A. Rodin, A. Carvalho, and A. C. Neto, “Strain-induced gap modification in black phosphorus,” Phys. Rev. Lett., Vol. 112, p. 176801, 2014.

22. R. Fei and L. Yang, “Strain-engineering the anisotropic electrical conductance of few-layer black phosphorus,” Nano Lett., Vol. 14, no. 5, pp. 2884–9, 2014.

23. S. Zhao, W. Kangab, and J. Xue, “The potential application of phosphorene as an anode material in Li-ion batteries,” J. Mater. Chem. A, Vol. 2, no. 44, pp. 19046–52, 2014.

24. J. Dai and X. C. Zeng, “Bilayer phosphorene: Effect of stacking order on bandgap and its potential applications
in thin-film solar cells," J. Phys. Chem. C, Vol. 5, no. 7, pp. 1289–1293, 2014.
25. H. Guo, N. Lu, J. Dai, X. Wu, and X. C. Zeng, "Phosphor-ene nanoribbons, phosphorus nanotubes, and van der Waals multilayers," J. Phys. Chem. C, Vol. 118, no. 25, pp. 14051–59, 2014.
26. V. Tran and L. Yang, "Scaling laws for the band gap and optical response of phosphorene nanoribbons," Phys. Rev. B, Vol. 89, no. 24, p. 245407, 2014.
27. J. O. Sofo, A. S. Chaudhari, and G. D. Barber, "Graphene: A two-dimensional hydrocarbon," Phys. Rev. B, Vol. 75, no. 15, p. 153401, 2007.
28. H. Valencia, A. Gil, and G. Frapper, "Trends in the adsorption of 3d transition metal atoms onto graphene and nanotube surfaces: A DFT study and molecular orbital analysis," J. Phys. Chem. C, Vol. 114, no. 33, pp. 14141–53, 2010.
29. K. T. Chan, J. B. Neaton, and M. L. Cohen, "First-princi- 
pies study of metal adatom adsorption on graphene," Phys. Rev. B, Vol. 77, no. 23, p. 235430, 2008.
30. C. Ataca and S. Ciraci, "Functionalization of single-layer MoS2 honeycomb structures," J. Phys. Chem. C, Vol. 115, no. 27, pp. 13 303–11, 2011.
31. J. Chang, S. Larentis, E. Tutuc, L. F. Register, and S. K. Banerjee, "Atomicism simulation of the electronic states of adatoms in monolayer MoS2," Appl. Phys. Lett., Vol. 104, no. 14, p. 141603, 2014.
32. P. Rastogi, S. Kumar, S. Bhowmick, A. Agarwal, and Y. S. Chauhan, "Ab-initio study of doping versus adatom in monolayer MoS2," Proceeding of International Conference on Emerging Electronics, Bangalore India, 2014.
33. P. Rastogi, S. Kumar, S. Bhowmick, A. Agarwal, and Y. S. Chauhan, "Doping strategies for monolayer MoS2 via surface adsorption: A systematic study," J. Phys. Chem. C, Vol. 118, no. 51, pp. 30 309–30 314, 2014.
34. H. Fang, G. S. M. Tosun, T. C. Chang, K. Takei, J. Guo, and A. Javey, "Degenerate n-doping of few-layer transition metal dichalcogenides by potassium," Nano Lett., Vol. 13, no. 5, pp. 1991–5, 2013.
35. V. V. Kulish, O. I. Malyi, C. Persson, and P. Wu, "Adsorp-
tion of metal adatoms on single-layer phosphorene," Phys. Chem. Chem. Phys., Vol. 17, pp. 992–1000, 2015.
36. T. Hu and J. Hong, "First-principles study of metal adatom adsorption on black phosphorene," J. Phys. Chem. C, Vol. 119, no. 15, pp. 8199–8207, 2015.
37. Y. Ding and Y. Wang, "Structural, electronic, and magnetic properties of adatom adsorptions on black and blue phosphorene: A first-principles study," J. Phys. Chem. C, Vol. 119, no. 19, pp. 10 610–22, 2015.
38. X. Sui, C. Si, B. Shao, X. Zou, J. Wu, B.-L. Gu, and W. Duan, "Tunable magnetism in transition-metal-decorated phosphorene," J. Phys. Chem. C, Vol. 119, no. 18, pp. 10059–63, 2015.
39. P. Srivastava, K. P. S. S. Hembram, H. Mizuseki, K.-R. Lee, S. S. Han, and S. Kim, "Tuning the electronic and magnetic properties of phosphorene by vacancies and adatoms," J. Phys. Chem. C, Vol. 119, no. 12, pp. 6530–8, 2015.
40. A. Ziletti, A. Carvalho, P. E. Trevisanutto, D. K. Campbell, D. F. Coker, and A. H. C. Neto, "Phosphorene oxides: Bandgap engineering of phosphorene by oxidation," Phys. Rev. B, Vol. 91, no. 8, p. 085407, 2015.
41. G. Wang, R. Pandey, and S. P. Karna, "Phosphorene oxide: Stability and electronic properties of a novel two-dimensional material," Nanoscale, Vol. 7, no. 2, p. 524, 2015.
42. "Atomistix toolkit version 2014.0 QuantumWise A/S," 2015. www.quantumwise.com.
43. M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stobro, "Density-functional method for nonequilibrium electron transport," Phys. Rev. B, Vol. 65, no. 16, p. 165401, 2002.
44. J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, "The Siesta method for ab initio order-n materials simulation," J. Phys. Condens. Matter, Vol. 14, p. 2745–79, 2002.
45. J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized 
radiant approximation made simple," Phys. Rev. Lett., Vol. 77, no. 18, pp. 3865–8, 1996.
46. R. S. Mulliken, "Electronic population analysis on LCAOMO molecular wave functions. II. Overlap populations, bond orders, and covalent bond energies," J. Chem. Phys., Vol. 23, no. 10, pp. 1841–6, 1955.
47. P. Giannozzi, et al. "QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials," J. Phys. Condens. Matter, Vol. 21, no. 39, p. 395502, 2009.
48. S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," J. Comput. Chem., Vol. 27, no. 15, pp. 1787–99, 2006.
49. G. Mills and H. Jonsson, "Quantum and thermal effects in H2 dissociative adsorption: Evaluation of free energy barriers in multidimensional quantum systems," Phys. Rev. Lett., Vol. 72, no. 7, pp. 1124–7, 1994.
50. G. Henkelman and H. Jonsson, "Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points," J. Chem. Phys., Vol. 113, no. 22, pp. 9978–85, 2000.
51. W. A. Crichton, M. Mezouar, G. Monaco, and S. Falconi, "Phosphorus: New in situ powder data from large-volume apparatus," Powder Diffract., Vol. 18, no. 02, pp. 155–8, 2003.
52. Y. Takao and A. Morita, "Electronic structure of black phosphorus: Tight binding approach," Physica B+C, Vol. 105, no. 1, pp. 93–98, 1981.
53. B. G. Streetman and S. K. Banerjee, "Solid state electronic devices," in Prentice-Hall Series in Solid State Physical Electronics. New Delhi: Pearson Prentice Hall, p. 211, 2009.
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