The optical properties and structural stability calculation of blue phosphorus and ZnO van der Waal heterostructure

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Abstract. In this work, the van der Waal heterostructures (vdWHs) based on blue phosphorus (blue-P) and ZnO were investigated in terms of structural stability and optical properties. Two vdWHs, that are (4,6)-tetraogonal-ZnO/blue-P (46tet-ZnO/blue-P) and hexagonal-ZnO/blue-P (hex-ZnO/blue-P), were investigated using the density functional theory (DFT). The vdW interaction between the 2D material layers was included in term of vdW-DF level. The calculation shows the energy gaps of 46tet-ZnO/blue-P and hex-ZnO/blue-P are 0.4 eV and 1.2 eV, respectively. Both 46tet-ZnO/blue-P and hex-ZnO/blue-P was found to have indirect bandgap and type-II band alignment, which are useful for charge separation in photo-energy conversion devices. In addition, the binding energy extracted indicates that 46tet-ZnO/blueP and hex-ZnO/blue-P have higher level of structural stabilities than that of their parents in isolated monolayer structures. Consequently, these suggest that the considered vdWHs are synthesizable and are potential candidates for implementation in optoelectronics applications.

1. Introduction
Two dimensional (2D) materials have drawn a lot of attention due to their outstanding properties on top of their bulk counterpart. Since the discovery of the graphene, many 2D materials have been synthesized such as BN, MoS2, and ZnO [1]. Recently, 2D blue phosphorus (blue-P) was successfully fabricated [2], and expected to have some superior electrical properties, e.g. high hole mobility [3]. Nevertheless, blue-P has poor structural stability under the presence of water and oxygen molecules. Blue-P was suggested to get interfaced with hexagonal ZnO (hex-ZnO) monolayer to improve their strength against structural volatility as the ZnO has somewhat strong structural stability [4]. This blue-P/hex-ZnO heterostructure is called van der Waals heterostructures (vdWHs) because strong in-plane covalent bonds greatly help stabilizing the 2D layer, whereas the relatively weaker vdW interlayer coupling is just enough to hold 2D layers together [5]. Thus, the individual band structure of each 2D materials are preserved, which allow the use of 2D electronic structure of the vdWHs in bulk scale. The ZnO monolayer can have both the hex-ZnO and tetragonal (tet-ZnO) phases, with comparable structural stabilities [6]. Since tet-ZnO and hex-ZnO have different band structures, the coupling with blue-P to form blue-P/ZnO vdWHs may result in band structure modification. Therefore, in this work, both hex-ZnO and tet-ZnO interfacing with blue-P in 2D vdW heterostructures were investigated, emphasizing on how distinct phases of the ZnO affect the blue-P/ZnO vdWHs’ band structure.
2. Materials and methods

To investigate the 2D vdWH of 46tet-ZnO/blue-P and hex-ZnO/blue-P, the electronic structures calculations were performed using density functional theory (DFT). The DFT calculation were carried out using the Quantum Espresso package [7] with the plane wave basis set and norm-conserving pseudopotential. The generalized gradient approximation (GGA) in PBE version was employed for electron exchange and correlation functionals. A k-point grid of 8x8x1 was used for the Brillouin zone integrations and the kinetic energy cutoff was set at 80 Ry. For the atomic structures modelling, the (4,6)-tetragonal ZnO (46tet-ZnO), the hex-ZnO, and the blue-P were composed of 4, 2, and 2 atoms per unit cell, respectively. The pseudopotential calculation included valence electrons from orbitals {2s,2p} of O atom, {3p, 3d, 4s} of Zn atom, and {3p} of P atom. The calculated unit cells of 46tet-ZnO, the hex-ZnO, and the blue-P can be represented as those enclosed in the black dash boundaries as shown in figure 1. Structure relaxation was performed using PBE functional, and equilibrium position was assumed when the force acting on each atom being less than 0.01 eV/Å in magnitude. The vdWHs of 46tet-ZnO/blue-P and hex-ZnO/blue-P were modelled as structures shown in figure 2. As seen, the unit cells of 46tet-ZnO/blue-P and hex-ZnO/blue-P contain a total of 8 and 4 atoms, respectively. For the interfacial properties calculation, each 2D layer/structure of the 46tet-ZnO, hex-ZnO, and blue-P were firstly optimized. Next, the supercells of 46tet-ZnO/blue-P and hex-ZnO/blue-P were formed. For the 46tet-ZnO/blue-P, the blue-P unit cell was firstly constructed in rectangular shape that contains of 4 atoms as enclosed in orange boundary in figure 1(c), before interfacing with the 46tet-ZnO unit cell. Since the GGA neglects the long rang or non-local correlation that typically originate the vdW force, van der Waals interaction were then included via vdW-DF level [8] in accounting for interlayer interaction between the ZnO and blue-P layer. The 20 Å of vacuum were added onto the normal direction of the layer to eliminate interactions arisen from the periodic images.

3. Results and discussion

From the calculation, the relaxed structure of 46tet-ZnO, hex-ZnO, and blue-P monolayer can be shown as in figure 1. The calculated lattice constants are $a_1(h_1) = 3.055 (6.075)$ Å for 46tet-ZnO, $a_2 = 3.273$ Å for hex-ZnO, and $a_3 = 3.367$ Å for blue-P. As seen, the hex-ZnO and blue-P lattice parameters agree well with literatures [9]-[10]. Then, vdWHs were constructed by planar interfacing of 46tet-ZnO with blue-P and hex-ZnO with blue-P. For 46tet-ZnO/blue-P, the unit cell of blue-P was mapped into a rectangle unit cell with $a_3' = 3.366$ Å and $b_3' = 5.828$ Å, which is displayed as the orange rectangle in figure 1(c). The most stable 46tet-ZnO/blue-P and hex-ZnO/blue-P heterostructures were shown in figure 2(a) and (b), respectively. Note that, in 46tet-ZnO/blue-P, the oxygen atoms of 46tet-ZnO layer slightly move out of plane, see figure 2(a, right), because of lattice mismatches in the heterostructure [11]. The interlayer distance $d$ of 46tet-ZnO/blue-P and hex-ZnO/blue-P were 2.915 Å and 2.861 Å, which are consistent with the those found in other vdWHs [12, 13]. The averaged bond length of Zn-O and P-P in the heterostructures were almost unchanged compared with the bond length in the isolated monolayer. This means that the in-plane stability of each materials maintain and confirms that 46tet-ZnO/blue-P and hex-ZnO/blue-P are van der Waals heterostructures [14].

![Figure 1](image1.png)

**Figure 1.** The monolayer structures of (a) 46tet-ZnO, (b) hex-ZnO/blue-P, and (c) tetragonal-ZnO/blue-P. Red, purple, and yellow spheres are for O, Zn, and P, respectively.
For the binding energy $E_b$ of the heterostructures, we defined $E_b = E[46tet(hex)-ZnO/blue-P] - E[46tet(hex)-ZnO] - E[blue-P]$, where $E[46tet(hex)-ZnO/blue-P]$, $E[46tet(hex)-ZnO]$, and $E[blue-P]$ are the energies of the considered compounds. From the calculation, it was found that $E_b = -2.41$ eV and $-2.48$ eV per formula unit for 46tet-ZnO/blue-P and hex-ZnO/blue-P, respectively. This suggests 46tet-ZnO/blue-P and hex-ZnO/blue-P are more structurally stable than their standalone monolayers. Then, the band structure of 46tet-ZnO, hex-ZnO, blue-P, were calculated and displayed in figure 3. Both tet46-ZnO and hex-ZnO have a direct bandgap of 0.9 eV and 1.7 eV, respectively, but the blue-P shows an indirect bandgap of 1.9 eV. As seen, valence band maximum (VBM) and conduction band minimum (CBM) of 46tet- and hex-ZnO locate at Γ point, while the blue-P has the VBM located between K point and Γ point and the CBM located between Γ point and M point. For the heterostructures, both 46tet-ZnO/blue-P and hex-ZnO/blue-P have indirect bandgaps as show in figure 4. The energy gap of 46tet-ZnO/blue-P is 0.4 eV with the CBM located between X and M points, and the VBM located at Γ point. Note that the VBM of the 46tet-ZnO/blue-P was resembled as VBM of the 46tet-ZnO but the CBM of the 46tet-ZnO/blue-P was resembled as CBM of the blue-P. This means that the band alignment of 46tet-ZnO/blue-P can be categorized as type-II because the CBM and VBM of 46tet-ZnO is higher than those of the blue-P in the heterostructure [15]. On the other hand, the energy gap of hex-ZnO/blue-P is 1.2 eV with CBM located between Γ and M points and VBM located at Γ point. This implies CBM and VBM of hex-ZnO/blue-P are contributed from both blue-P and hex-ZnO, similar to the case of 46tet-ZnO/blue-P. The band alignment of hex-ZnO/blue-P can also be categorized as type-II. From the results, 46tet-ZnO/blue-P and hex-ZnO/blue-P clearly established themselves as vdW heterostructures because their band structures preserve the characteristic of CBM from blue-P and the characteristic of VBM from ZnO band structure [16]. The lower bandgap of 46tet-ZnO/blue-P compared with hex-ZnO/blue-P could be accounted from the lower bandgap of 46tet-ZnO compared with hex-ZnO. This also indicates that the bandgap of ZnO/blue-P heterostructure could be modified by the bandgap of ZnO monolayer, which will be useful in band alignment engineering.
4. Conclusion

The DFT calculation of the heterostructures showed that the energy gap of 46tet-ZnO/blue-P is lower than the energy gap of hex-ZnO/blue-P and both have an indirect bandgap. When comparing with the energy gap of their 2D material composition, these heterostructures energy gaps are lower. The calculated binding energies also ensured that their structural stability be improved from the isolated 2D materials layer and their structural stabilities are comparable. The band alignment of 46tet-ZnO/blue-P and hex-ZnO/blue-P heterostructure established that they have type-II band alignment, which can be implemented in the solar cell application. Moreover, the knowledge of that the individual ZnO layer could be used to predict the changing of the blue-P/ZnO bandgap in accordance with the changing of the ZnO bandgap, which will be useful in the band engineering and optoelectronic application.

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