A First Principles Study of Electric Structures of Heterostructures Built with Blue Phosphorene

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Abstract. We have built the heterostructure with 2D materials C3N and BN capping on blue phosphorene. The geometric structure and electric structure of the heterostructures have been investigated by using first-principles computations. Calculated results indicate that the strong interaction exists between the two 2D materials due to the equilibrium interlayer distances in the range of 3.31 Å and 3.30 Å. Moreover, the 2D capping layers not only protect blue phosphorene from being oxidized, but also can improve the band structure of blue phosphorene.

1. Introduction

Since Novoselov and co-workers successfully exfoliated graphene from graphite in 2004[1], two-dimensional (2D) nanomaterials have attracted extensively in the world. For example, Zhang et al. found that the N-doped graphene can be a larger adsorption energy than the pristine graphene to attract the LIPSSs[2,3]. Shao et al. investigated the defective and doped BC2N monolayers are promising as anchoring materials for Li-S batteries because defective and doped BC2N express increased binding energy and enhanced conductivity[4]. Li et al. calculated the anchoring effect of various N-doped graphene samples and only clustered pyridinic N-dopants able to strongly adsorb lithium to avoid their dissolution in the electrolyte[5].

Meanwhile, the heterostructure with two or more 2D materials stacked or stitched has attracted extensive attention and learning due to the good flexibility, electrical conductivity, high specific capacity, and excellent structural stability[6,7]. The 2D heterostructure combine the advantages of their isolated components while eliminates related shortcomings, which provides new opportunities to improve the performance of layered materials[8]. In addition, Woomer et al. found that the interlayer distance of the heterostructure of the combination of graphite and Sr2N was only 2.7 Å, smaller than the interlayer distance of sole graphite and Sr2N bilayer[9]. The similar decrease has been calculated in WS2-NbSe2/Ca2N-graphene heterostructure[10,11]. And 2D heterostructures can be easily manufactured into practically any shape to create flexible films or electrodes to meet people's needs[12,13]. The understanding of interlayer interaction and interlayer distance in heterostructures and the application of heterostructures has also aroused people's interest.

Generally, 2D heterostructures are classified into three conventional categories according to the layer spacing: type-I (2D electron gas, > 4 Å)[14], type-II (van der Waals interaction, 3-4 Å)[15-17], and type-III (2 Å < quasi-bond < 3 Å)[18], which have attracted significant attention in different kinds of fields in modern society[9,19,20]. For example, Type-I heterostructure—nitrogen-doped graphene/MoS2 with the layer spacing of 9.9 Å is conducive to ion diffusion and helps to adapt to the...
volume change during circulation[21]. Type-II heterostructures exhibit lower diffusion barrier than that of 2D monolayers, resulting in better charge and discharge performance of heterostructure as battery electrode, such as WS2/NbSe2 heterostructure[11]. Besides, the interlayer distance of the most stable MoS2/AlN(GaN) heterostructures are 2.72, 2.97 Å, respectively, and significantly improved photocatalytic performance during the photocatalysis process[22]. Heterostructures with different intercalation distances have different properties and are widely used in different fields.

Black phosphorene (Black-P) is a new and promising two-dimensional semiconductor material, which has been the focus of research activities since it was first manufactured by exfoliation in 2014 [23,24]. Some extensive studies predict that black phosphorene provides huge opportunities for high-performance energy storage [25-27]. Soon thereafter, excellent experimental work confirmed these predictions [28,29]. Recently, the blue phosphorene (BP) predicted by Zhu and Tomanek in 2014 [30] has been successfully synthesized [31]. However, the inherent nature of BP [32-35] hinder its further application. Here, we use two 2D materials, C3N[36,37] and BN[38,39] with stable chemical properties, to form heterojunctions with BP, and study the electronic structures of these heterojunctions, which can provide necessary theoretical support for the practical application of these heterojunctions.

2. COMPUTATIONAL DETAILS

All the calculations were carried out using density functional theory (DFT) based linear combination of atomic orbital method implemented in the Dmol3 package [40]. Perdew-Burke-Ernzerhof (PBE)34 functional of the generalized gradient approximation (GGA)35 was used to describe the electronic exchange-correlation energy, in conjunction with the double-numerical plus polarization (DNP) basis set. [41]. The DFT-D correction with Grimme methods was applied to accurately describe the interlayer Van der Waals (vdW) interactions. In geometry optimizations, all the atomic positions were fully relaxed until the convergence tolerance satisfies energy of 10−5 Ha, force of 0.002 Ha/Å and displacement of 0.005 Å. To ensure high-quality numerical results, we chose the real-space global orbital cutoff radius as high as 5.2 Å in all the computations. The Brillouin zone was sampled using a 4 × 4 × 1 and a 8 × 8 × 1 Monkhorst–Pack grids for the structural optimization and the electronic structure calculations, respectively. A vacuum of 25 Å between the layers was considered to safely avoid the coupling effects.

3. RESULTS AND DISCUSSION

3.1 Optimized Structure

First, the 2D structures of BN, C3N and BP are optimized and they are shown in figure 1. For h-BN, it has a hexagonal planar layered structure, the lattice parameter is 2.500 Å, the B-N bond length is 1.443 Å, and the BNB (NBN) bond angle is 120°. And for C3N, the bond lengths of C-C, C-N are 1.403 Å and 1.405 Å. While, for BP, its lattice parameter is 3.285 Å, the P-P bond length is 2.273 Å, and the PPP bond angle is 92.5°. The results coincide with previous results [32,42,43].
Afterwards, we combined the 4×4 super cells of C3N and BN and the 3×3 super cells of BP to construct the unit cells of C3N/BP and BN/BP heterojunction. The structures of heterojunctions C3N/BP and BN/BP are shown in figure 2. The balance layer spacing (d) is 3.31 Å and 3.30 Å, respectively. In order to further determine the value of d, the total energy change with d is calculated, and the result is shown in Figure 3. The result shows that d is 3.31 Å for C3N/BP and d is 3.30 Å for BN/BP. The d in C3N/BP and BN/BP is slightly longer than d in the C3N/graphene heterostructure (3.225 Å) [23], and slightly shorter than d (3.34 Å) in the C3N/phosphorene heterostructure [24], indicating that C3N and BP The interaction between C3N and phosphorene is stronger.
3.2 Electric Structure

The band structures of single layer BP, single layer C$_3$N and C$_3$N/P is shown in Figure 4. The band gap of single-layer BP is 1.92 eV, which is consistent with the result (1.95 eV) of BP[11]. The band gap of the monolayer C$_3$N is 0.48 eV, which is between 0.39 [24] and 0.67 [25] eV. When single-layer BP and C$_3$N are combined into C$_3$N/P, the band gap of C$_3$N/P is reduced to 0.28 eV, which is smaller than single-layer BP and C$_3$N. The improvement of C$_3$N/P band gap is mainly due to single-layer C$_3$N and single-layer BP synergy effect. The same situation can also be seen in single-layer BP, BN and BN/P, as shown in Figure 5. The band gap of BN is 4.55 eV. When BN covers BP, its band gap is reduced to 1.85 eV, which is mainly due to the contribution of B-2p and N-2p to the valence band.

Figure 3. The energy evolution as a function of interlayer distance between (a) BN and BP and (b) C$_3$N and BP.
Figure 4. Band structures of (a) BP, (b) C$_3$N and (c) C$_3$N/BP.
Figure 5. Band structures of (a) BP, (b) BN and (c) BN/BP.

In order to further study the electronic properties, next we calculated the density of states (DOSs) of BP and BN/BP heterostructure, as shown in figure 6. For BP, the DOSs of BP consist of P-3p and P-3s, and the P-3p state makes a major contribution to the DOS. For BN/BP heterostructure, the DOSs of BN/BP is composed of P-3p, P-3s, B-2p and N-2p. The contribution of the added DOS is mainly the orbital of B atom and the orbital of N atom. Compared with the DOS of BP, we can find that the BN capping layer can improve the electronic property of BP.
4. Conclusion

In summary, we have investigated the geometric structures and electric structures of the heterostructure built with C₃N/blue phosphorene and BN/blue phosphorene by means of the first-principles computations. The equilibrium interlayer distances of the heterostructure are 3.31 Å and 3.30 Å, indicating the strong interaction exists between the two 2D materials. The electric structures indicate that the synergy effect in the heterostructures can improve the band structure of blue phosphorene.

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