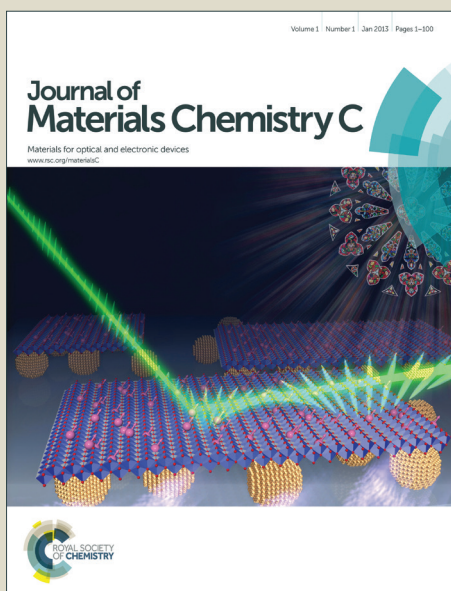


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Tunable Schottky Contacts in Hybrid Graphene/Phosphorene Nanocomposite

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Combining the electronic structures of two-dimensional monolayers in ultrathin hybrid nanocomposites is expected to display new properties beyond their single components. Here, first-principles calculations are performed to study the structural and electronic properties of hybrid graphene and phosphorene nanocomposite. Our calculations show that weak van der Waals interactions dominate between graphene and phosphorene with their intrinsic electronic properties preserved. Furthermore, we find that as the interfacial distance decreases, the Dirac point of graphene moves from the conduction band to the valence band of phosphorene in hybrid graphene and phosphorene nanocomposite, inducing a transition from n-type Schottky contact to p-type Schottky contact at the graphene/phosphorene interface.

1 Introduction

Two-dimensional (2D) ultrathin materials,^{1–5} such as graphene,^{6–8} silicene,^{9–11} hexagonal boron nitride,^{12–14} graphitic carbon nitride,^{15–17} graphitic zinc oxide^{18–20} and molybdenum disulphide,^{21–23} have received considerable interest recently owing to their outstanding properties and wide applications. Graphene,^{6–8} a 2D sp²-hybridized carbon monolayer, is known to have many remarkable properties, such as a high carrier mobility, but the absence of a bandgap limits its applications of large-off current and high on-off ratio for graphene-based electronic devices. Furthermore, intrinsic electronic properties of graphene depend sensitively on the substrates due to the graphene-substrate interactions, such as Si,^{24–26} SiO₂,^{27–29} SiC^{30–32} and metal^{33–35} surfaces. Therefore, opening a small bandgap and finding an ideal substrate for graphene always remain challenging in the experiments.

Interestingly, combining the electronic structures of these 2D materials in ultrathin van der Waals layer-by-layer heterostructures has also been widely studied experimentally and theoretically, especially, hybrid graphene-based nanocomposites, such as graphene/silicene (G/S),^{36–38} graphene/graphitic

boron nitride (G/g-BN),^{39–42} graphene/graphitic carbon nitride (G/g-C₃N₄),^{43–45} graphene/graphitic zinc oxide (G/g-ZnO),^{46–48} and graphene/molybdenum disulphide (G/MoS₂).^{49–52} These hybrid graphene-based nanocomposites show much more new properties far beyond their single components. Furthermore, most of them are ideal substrates for graphene to preserve the intrinsic electronic properties of graphene. The possibility of making 2D van der Waals heterostructures has been demonstrated experimentally for novel electronic, electrochemical, photovoltaic, photoresponsive and memory devices.^{53–56}

Recently, a new 2D material, namely, phosphorene, has been isolated in the experiments through mechanical exfoliation from bulk black phosphorus and has immediately received considerable attention.^{57–61} Phosphorene also shows some remarkable properties superior to graphene. For example, phosphorene is a direct semiconductor with a high hole mobility,⁵⁷ showing the drain current modulation up to 10⁵ in nanoelectronics.⁵⁸ Furthermore, these remarkable properties have already been used in field effect transistors⁵⁹ and thin-film solar cells.⁶⁰ Besides graphene, phosphorene is the only stable elemental 2D monolayer which can be mechanically exfoliated experimentally.⁵⁷ Therefore, introduced as an alternative to graphene, phosphorene may lead to faster semiconductor electronics in the future. Here, an interesting question arise: Whether graphene and phosphorene can form a 2D hybrid G/P nanocomposite to expect some new properties beyond pristine graphene and phosphorene monolayers?

In the present work, we design a new 2D hybrid graphene and phosphorene nanocomposite and study its electronic properties with first-principles calculations. The results show that graphene interacts overall weakly with phosphorene via van

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der Waals (vdW) interactions, thus, their intrinsic electronic properties can be preserved in hybrid graphene/phosphorene nanocomposite. Moreover, interlayer interactions in hybrid graphene/phosphorene nanocomposite can induce tunable Schottky contacts and barriers by varying the interfacial distance.

2 Theoretical Methods and Models

The lattice parameters of graphene and phosphorene calculated to setup unit cell are $a(G) = b(G) = 2.47 \text{ \AA}$,⁶¹ $a(P) = 4.62 \text{ \AA}$ and $b(P) = 3.30 \text{ \AA}$.⁶¹ We design a new 2D hybrid graphene/phosphorene nanocomposite (40 carbon atoms and 28 phosphorus atoms) as shown in Fig. 1 with a small lattice mismatch less than 2% (See the supplementary material). The vacuum space in the Z direction is about 15 Å to separate the interactions between neighboring slabs.

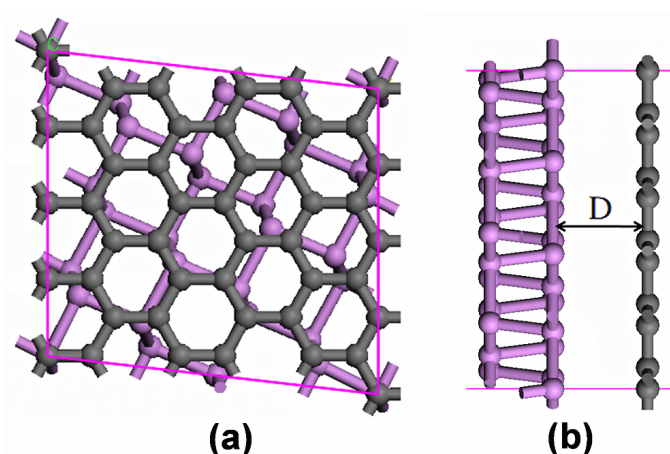


Fig. 1 (Color online) Geometric structures of hybrid graphene/phosphorene nanocomposite ((a) top and (b) side views). The gray and violet balls denote carbon and phosphorus atoms, respectively. The interfacial distance D between graphene and phosphorene is marked.

First-principles calculations are based on the density functional theory (DFT) implemented in the VASP package.⁶² The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)⁶³ with van der Waals (vdW) correction proposed by Grimme (DFT-D2)⁶⁴ is chosen due to its good description of long-range vdW interactions.^{65–75} As an benchmark, DFT-D2 calculations give a good bilayer distance of $c = 3.25 \text{ \AA}$ and binding energy of $E_b = -25 \text{ meV}$ per carbon atom for bilayer graphene, which fully agree with previous experimental^{76,77} and theoretical^{78,79} studies. Because the GGA-PBE method trends to underestimate the bandgap of semiconductors, the screened hybrid HSE06 functional⁸⁰ is

also used to check the electronic band structures. The energy cutoff is set to be 500 eV. The surface Brillouin zone is sampled with a 3×3 regular mesh and 120 (GGA-PBE) or 60 (HSE06) k points are used for calculating the tiny band gaps at the Dirac point graphene in the hybrid G/P nanocomposite supercell. All the geometry structures are fully relaxed until energy and forces are converged to 10^{-5} eV and 0.01 eV/\AA , respectively. Dipole correction is employed to cancel the errors of electrostatic potential, atomic forces and total energy, caused by periodic boundary condition.⁸¹ Charge transfer is obtained by the Bader analysis.⁸²

3 Results and Discussion

Electronic properties of pristine graphene and phosphorene monolayers in the supercells are checked first and their electronic band structures are plotted in Fig. 2a and 2b. Graphene is zero-gap, showing a linear Dirac-like dispersion relation $E(k) = \pm \hbar v_F |k|$ around the Fermi level where v_F is the Fermi velocity, and $v_F(G) \approx 10^6 \text{ m/s}$ at the Dirac point of graphene. Monolayer phosphorene is semiconducting with a direct band gap (0.85 or 1.52 eV respectively for GGA-PBE and HSE06 methods), which agrees well with previous theoretical studies.⁶¹ Furthermore, we confirm that the small lattice mismatch of about 2% for graphene and phosphorene has little effect on their electronic properties in hybrid G/P nanocomposite.

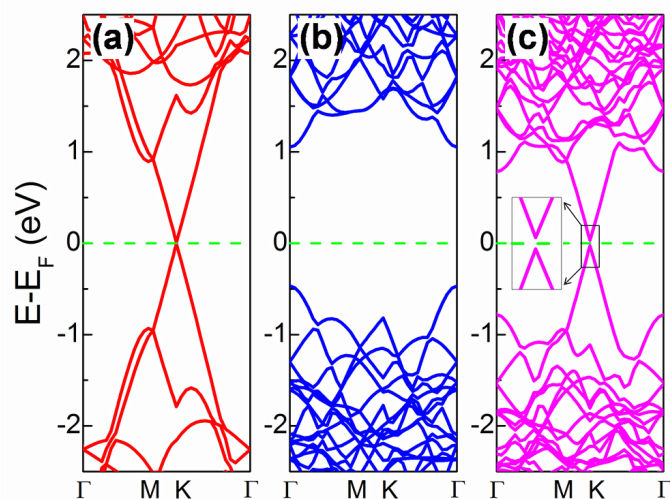


Fig. 2 (Color online) Electronic band structures (HSE06) of (a) graphene, (b) phosphorene and (c) hybrid graphene/phosphorene nanocomposite. The Fermi level is set to zero and marked by green dotted lines.

We then study the electronic structures of hybrid G/P nanocomposite. Typical vdW equilibrium spacing of about

3.43 Å with corresponding small binding energy of about -24.7 meV per atom of graphene is obtained for hybrid G/P nanocomposite, which is well comparable with recent theoretical calculations in other 2D graphene based nanocomposites, such as G/S,³⁶ G/g-BN,⁴¹ G/g-C₃N₄,⁴⁵ G/g-ZnO⁴⁶ and G/MoS₂.⁴⁹ Thus, weak vdW interactions dominate between graphene and phosphorene, suggesting that phosphorene can be used as an ideal substrate for graphene with their intrinsic electronic structures undisturbed.

Electronic band structure of hybrid G/P nanocomposite is checked with the HSE06 method as plotted in Fig. 2c. The Dirac point of graphene is still preserved in the band gap of phosphorene. The Fermi velocity at the Dirac point is almost unchanged in hybrid G/P nanocomposite compared to free-standing graphene, though small band gap (10 or 58 meV respectively for GGA-PBE and HSE06 methods) is opened at the Dirac point of graphene. Notice that induced band gaps at the Dirac point of graphene are typically sensitive and tunable to other external conditions, such as interlayer separation.³⁶ The gap values at graphene's Dirac point increase from 5 to 90 meV (GGA-PBE) as the interfacial distance decreases from 3.7 to 2.8 Å in hybrid G/P nanocomposite, showing a potential for graphene-based field effect transistors.⁴¹

Interestingly, we find that a Schottky contact can be formed between metallic graphene and semiconducting phosphorene, similar to graphene adsorption on Si²⁴⁻²⁶ and MoS₂^{51,52} substrates. Based on the Schottky-Mott model⁸³ at the metal/semiconductor interface,⁸⁴ a n-type Schottky barrier (Φ_{Bn}) is defined as the energy difference between the Fermi level (E_F) and the conduction band minimum (E_C), that is $\Phi_{Bn} = E_C - E_F$. Similarly, a p-type Schottky barrier (Φ_{Bp}) is defined as the energy difference between the Fermi level (E_F) and valence band maximum (E_V), that is $\Phi_{Bp} = E_F - E_V$. Notice that the sum of two types of Schottky barrier is approximately equal to the band gap value (E_G) of semiconductor, that is $\Phi_{Bn} + \Phi_{Bp} \approx E_G$. As shown in Fig. 3, the Dirac point of graphene moves from the conduction band to the valence band of phosphorene as the interfacial distance decreases from 4.5 to 2.8 Å, inducing a transition from n-type Schottky contact to p-type Schottky contact at the interface. The conversion of Schottky contact type in hybrid G/P nanocomposite happens when their interfacial distance increases to below 3.5 Å. Notice that it is challenging to tune the interlayer distance in the experiments, but we only demonstrate the effect of interlayer distance on the electronic structure and provide useful insight for electronic engineering of this new nanocomposite material. For example, inspired by our result, it will be interesting to see how intercalation of noble gas will modify the electronic structure of this system.

When the interfacial distance artificially increases larger than 4.5 Å, graphene's Dirac point is close to phosphorene's conduction band, forming a n-type Schottky contact with a

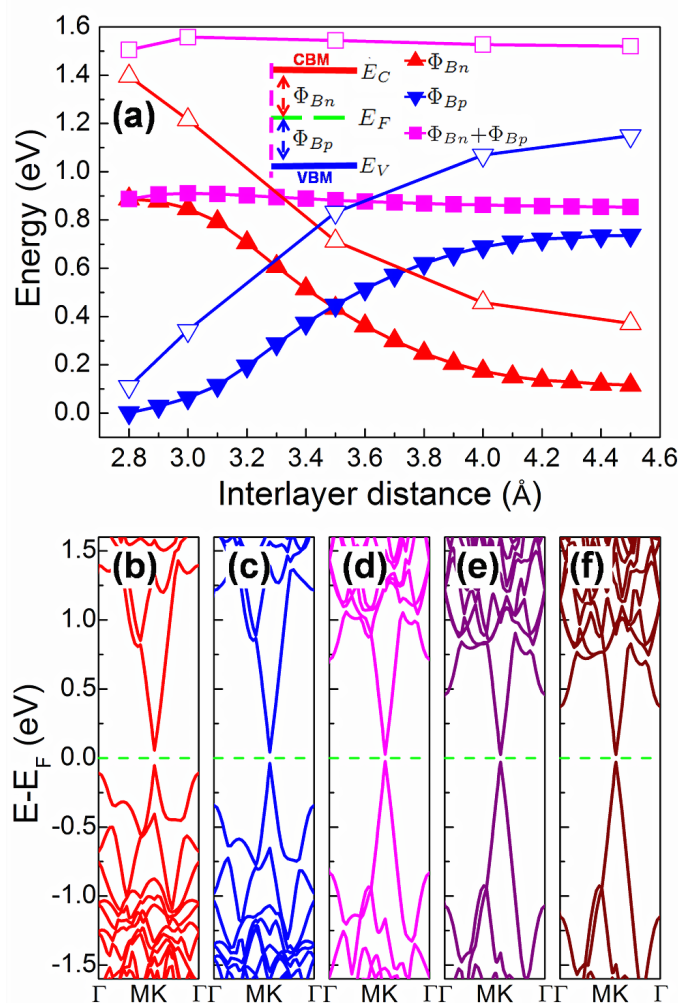


Fig. 3 (Color online) (a) Schottky barriers Φ_{Bn} , Φ_{Bp} and $\Phi_{Bn} + \Phi_{Bp}$ in hybrid graphene/phosphorene nanocomposite as a function of interfacial distance. The GGA-PBE and HSE06 methods are marked by solid and hollow points, respectively. (b-f) Electronic band structures (HSE06) of hybrid graphene/phosphorene nanocomposite at different interfacial distances $D = 2.8, 3.0, 3.5, 4.0$ and 4.5 Å. The Fermi level is set to zero and marked by green dotted lines.

small n-type Schottky barrier ($\Phi_{Bn} = 0.12$ or 0.37 eV respectively for GGA-PBE and HSE06 methods) at the interface as shown in Fig. 3f. That is because graphene's work function (4.3 eV)³⁶ is close to phosphorene's nucleophilic potential (4.1 eV), consistent with the Schottky-Mott model.⁸³

As the interfacial distance decreases from 4.5 to 3.0 Å, the effects of chemical interactions³³ and charge transfer³⁶ between graphene and phosphorene are enhanced.⁸⁴ Fig. 4 shows that XY-averaged differential charge density and electrostatic potentials at different interfacial distances $D = 4.5, 4.0, 3.5, 3.0$ and 2.8 Å in the Z direction. We find that more electrons ($0.06, 0.13, 0.21, 0.38$ and 0.56 e respectively for interfacial distances $D = 4.5, 4.0, 3.5, 3.0$ and 2.8 Å) transfer from phosphorene to graphene as their interfacial distance decreases from 4.5 to 2.8 Å (Fig. 4a), shifting down the energy level of graphene close to phosphorene's valence band as shown in Fig. 4b. Note that there is a tunneling energy barrier of electrons³⁶ at the G/P interface, which is also reduced by the interface interactions. Moreover, graphene and phosphorene have different electronegativities (carbon 2.55 and phosphorus 2.19), and graphene has a more deeper potential well than phosphorene. Thus, electrons are easily transferred from phosphorene to graphene when graphene and phosphorene are close to each other, resulting in p-type Schottky contact in hybrid G/P nanocomposite. That is why when the interfacial distance artificially decreases to 2.8 Å, graphene's Dirac point is close to phosphorene's valence band, forming a p-type Schottky contact with a negligible p-type Schottky barrier of $\Phi_{Bp} = 0.1$ eV at the interface as shown in Fig. 3c.

Notice that the Schottky contact in hybrid G/P nanocomposite is very different to traditional metal-semiconductor Schottky ones⁸³ in two important ways. One is that graphene is adsorbed physically on phosphorene in ultrathin van der Waals heterostructures without dangling bonds at the interface. Another is the Schottky contacts and barriers can be adjusted sensitively by varying the interfacial distance. Furthermore, atom doping in graphene and applying perpendicular electric fields can also be used to modify the work function of graphene⁴¹ and then to adjust the Schottky barriers in hybrid G/P nanocomposite. Most recently, tunable Schottky barriers in hybrid G/P nanocomposite with electrostatic gating have just proved theoretically⁸⁵ and experimentally.⁸⁶ But this method can mainly control the Schottky barrier height in p-type Schottky contact in hybrid G/P nanocomposite unless applying a strong electric field larger than 1.8 V/nm.⁸⁵ Thus, it is very difficult to obtain n-type Schottky contact with low Schottky barrier in hybrid G/P nanocomposite if only by applying perpendicular electric fields.^{85,86} In contrast, our proposed method by varying the interfacial distance can not only control the Schottky barriers but also the Schottky contacts (p-type and n-type) in hybrid G/P nanocomposite, and the conversion of Schottky contact type in hybrid G/P nanocompos-

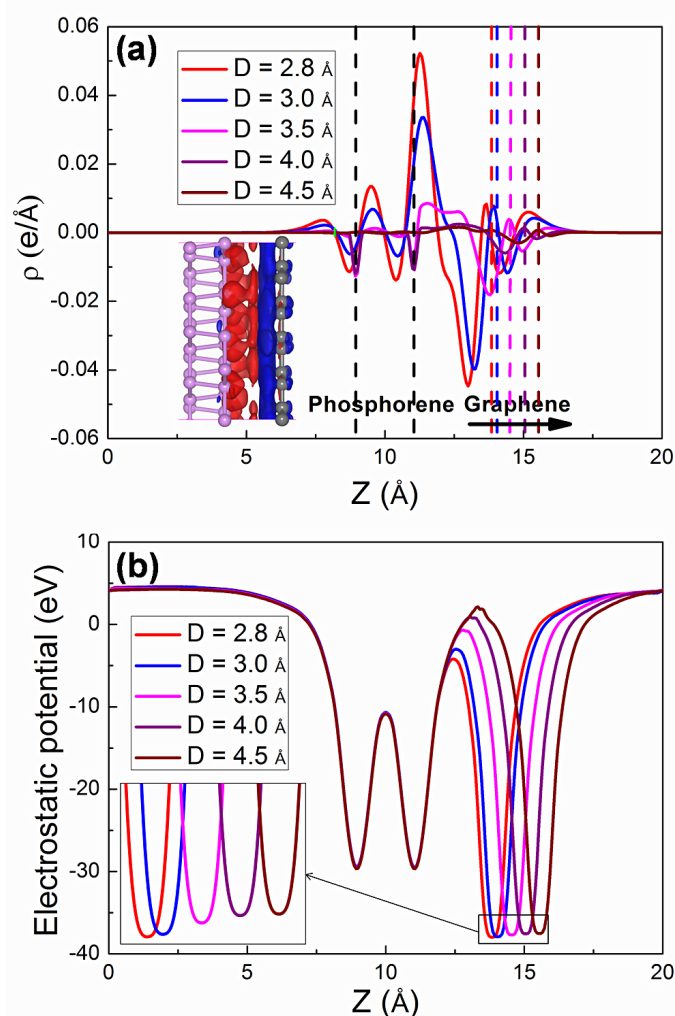


Fig. 4 (Color online) XY-averaged (a) differential charge density and (b) electrostatic potentials of hybrid graphene/phosphorene nanocomposite at different interfacial distances $D = 2.8, 3.0, 3.5, 4.0$ and 4.5 Å in the Z direction. The isosurface of differential charge density at the equilibrium distance ($D = 3.43$ Å) is shown in the inset (a). The red and blue regions indicate electron decrease and increase, respectively. Depths of potential wells of graphene are shown in the inset (b). Note that the phosphorene layer is fixed and only the graphene layer is moved away from the phosphorene layer.

ite happens when their interfacial distance varies close to the equilibrium spacing (3.43 Å). Furthermore, mixture of different methods in the further experiments will be much more easier to control tunable Schottky barriers and contacts in hybrid G/P nanocomposite, which can be used for tunable Schottky diodes in nanoelectronics.^{24–26,51,52}

4 Conclusions

In summary, we study the electronic structures of hybrid graphene/phosphorene nanocomposite with first-principles calculations. We find that phosphorene interacts weakly with graphene via weak vdW interactions to preserve their intrinsic electronic properties. Moreover, interlayer interactions can induce tunable band gaps at graphene's Dirac point, tunable Schottky contacts and barriers at the interface in hybrid graphene/phosphorene nanocomposite. With the excellent electronic properties combined beyond simplex graphene and phosphorene monolayers, 2D ultrathin hybrid graphene/phosphorene nanocomposite system is expected to be of a great potential in new electronic devices.

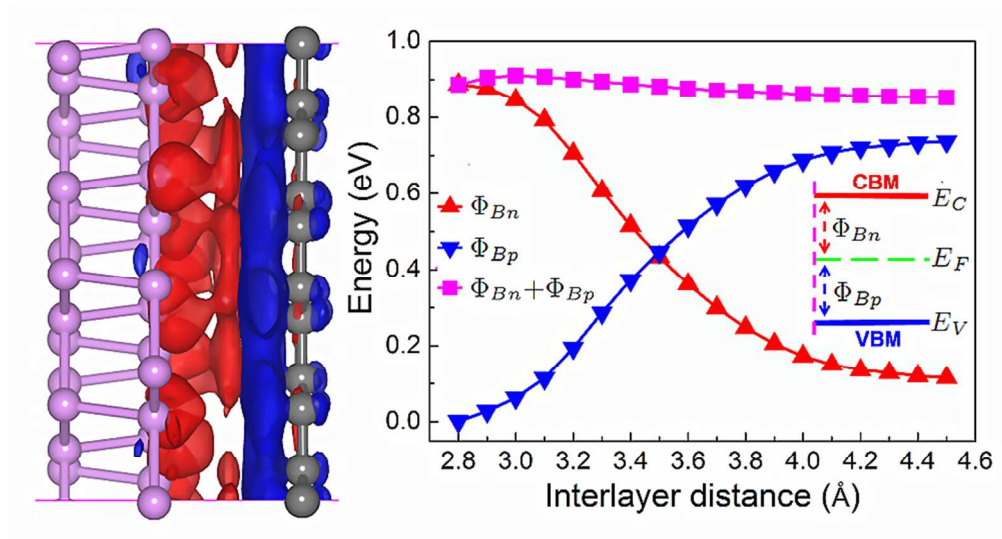
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