Rational Surface Modification of Two-Dimensional Layered Black Phosphorus: Insights from First-Principles Calculations

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ABSTRACT: Surface modification of atomically thin semiconductors enables their electronic, optical, chemical, and mechanical properties to be tailored and allows these nanosheets to be processed in solutions. Here, we report first-principles density functional theory calculations, through which we show chemical functionalization of black phosphorus using phenyl, phenolate, and nitrene species, which were widely investigated for carbon-based materials. We find that covalent functionalization using nitrene-derived species introduces a strong P–N dative bond at the interface without perturbing its intrinsic electronic structure. The Lewis basic and nucleophilic P atom attacks, through a free pair of electrons, the Lewis acidic nitrene species. These results are further compared to other nitrene-derived functional groups on black phosphorus, including N-methylbenzene, N-aminobenzene, and N-nitrobenzene. We find that by tuning the charge redistribution at the interface, the work function of black phosphorus can be tuned by more than 2 eV. These results suggest valuable tunability of the electronic properties of two-dimensional layered black phosphorus by covalent functionalization for future device applications.

INTRODUCTION

Two-dimensional (2D) black phosphorus (BP),1–4 known as single-layer phosphorene, is a member of layered-material family consisting of graphene, 2D hexagonal boron nitride, and transition-metal dichalcogenides, ranging from semimetals to semiconductors and to insulators. Semiconducting BP shows a tunable direct band gap, anisotropic optical absorption, and large carrier mobility, all of which may lead to potential applications in field-effect transistors and photodetectors.4–8 However, its fast degradation upon exposure to ambient conditions, resulting from reaction with oxygen,9,10 necessitates surface functionalization and encapsulation to prepare devices with long-term stability and reliability.11–13

Chemical functionalization of atomically thin two-dimensional materials enables tunable electronic and chemical properties and also allows solution-based techniques for processing these materials. Covalent functionalization of pristine graphene and carbon nanotubes has been widely studied. The rich chemistry of carbon enables various strategies for introducing foreign groups through covalent bonds, such as using aryl radicals, cycloaddition, and nitrene addition, or mediated by surface atomic defects or impurities.14–18 By introducing these radicals onto the surface, the band gap, electronic conductivity, and solubility of graphene can be controlled.19–22 Because of the varied chemical properties resulting from different atoms exposed to the environment, surface modification through covalent bonds for BP has been challenging compared to graphene. That is, the P atoms exposed at the surface of BP have distinct chemistries with respect to C in graphene.

Covalent functionalization of exfoliated BP remains less explored, although it may be more crucial because of its fast degradation upon exposure to ambient conditions.9–12 Within the context of introducing a protective layer on BP surfaces against ambient degradation, several encapsulation techniques have been proposed, including the encapsulation of BP with transparent poly(methyl methacrylate)13 and insulating hexagonal boron nitride (h-BN).24,25 For the same purpose, using trimethylaluminum and H2O as precursors, a thin AlOx film can be deposited onto BP flakes by atomic layer deposition.26 Very recently, aryl diazonium chemistry, a widely studied chemistry for graphene, has been applied to BP and the functionalized samples have shown enhanced semiconductor performance and improved chemical stability resulting from the surface passivation.27 However, the aryl group may also introduce a flat energy band within the band gap of BP, leading to reduced hole mobility, as shown recently in first-principles calculations.28 Therefore, stable covalent functionalization of BP to modify its chemical stability and solubility without diminishing its desirable electronic properties still remains to be developed.

In this study, we report first-principles density functional theory (DFT) calculations, through which we propose alternate...
Figure 1. Electronic structure of BP with different functional groups, (a) pristine BP, (b) phenyl, (c) phenolate, and (d) nitrene as well as the optimized structures (insets). Density of states (DOS) of pristine BP (dashed curve) and projected DOS onto P atoms (solid curves) are shown for comparison. The black, white, red, blue, and purple balls denote C, H, O, N, and P atoms, respectively. The shaded areas indicate the energy window used for charge integration for the whole system. In (b) and (c), the isosurface of the charge density plot is 0.06 eV Å⁻³. Configurations of interfacial bonds formed between functional groups and BP are schematically shown next to each optimized structure.
strategies to modify the BP surface. We apply radical chemistry using three different radicals, namely, phenyl, phenolate, and nitrene, all of which have been widely explored previously for surface modification of graphene and carbon nanotubes, to functionalize BP and examine their adsorption properties and binding strength. In particular, we show that all of the three radicals can adsorb on the BP surface. Different adsorption modes, resulting from the varied electronic structure of the radicals, affect the electronic properties of BP in a significantly different way. We show that the nitrene chemistry may be a valuable strategy for BP functionalization because the interfacial binding is stable without perturbing the electronic structure of BP, resulting from a strong P−N dative bond at the interface. Meanwhile, we find that the formation of dangling bonds is the main cause for defect levels at the Fermi level in BP when using phenyl and phenolate. We further compare the results with other nitrene-derived functional groups on BP, including N-methylbenzene, N-aminobenzene, and N-nitrobenzene. We show that by tuning the polarity of the molecules the work function of BP can be tuned by more than 2 eV. These results thus suggest valuable tunability of the electronic and chemical properties of layered black phosphorus by covalent functionalization.

## RESULTS AND DISCUSSION

Figure 1 shows the projected density of states (PDOS) of BP with three different functional groups, namely, phenyl, phenolate, and nitrene species. Calculations using HSE06 hybrid functional show that the pristine BP monolayer has a band gap of 1.34 eV (Figure 1a), which agrees with reported values. The adsorptions of phenyl (Figure 1b) and phenolate (Figure 1c) introduces energy levels within the band gap of pristine BP. These localized states within the band gap are also found in a recent computational work and may lead to reduced hole mobility of BP. Partial charge density calculations within an energy window around the Fermi level have been performed to illustrate the charge distribution (insets in Figure 1). The green-shaded area in Figure 1b,c shows the energy window used for integration.

We find that the charge around Fermi Level is localized at the phosphorus at the opposite site of BP with respect to the surface being functionalized. As discussed later, this charge localization is caused by the broken P−P bond upon ligation of the phenyl (Figure 1b). Because of the same reason, that is, the newly formed P−O bond replaces previously existed P−P bond, functionalization using phenolate creates a very similar electronic structure (Figure 1c). Distinctly, when nitrene was introduced, the electronic structure of BP, particularly the band-gap and band-edge energies remain unperturbed compared to the pristine BP. We note that DFT-Perdew–Burke–Ernzerhof (PBE) calculations show the same phenomena (Figure S1). The projected DOS of the C, O, and N in the phenyl, phenolate, and nitrene in the adsorbed configurations are shown in Figure S2. The overlapping states between C (O) and P in phenyl (phenolate) at the Fermi level clearly show the orbital hybridization. We also calculated the band structure of pristine monolayer and nitrene-functionalized BP using the PBE-D3 method, as shown in Figure S3. The band structure calculations show that adsorption of nitrene on the BP surface does not perturb the intrinsic electronic structure of BP. The direct band gap at the Γ point persists. We note that the band gap is underestimated using PBE calculations compared to the Heyd–Scuseria–Ernzerhof (HSE) calculations. All of the discussion here is thus focused on the results calculated using the hybrid functional.

Table 1 shows the adsorption energies of these radicals on BP. All of the adsorbates are strongly bonded to BP, with the adsorption energy increasing from −1.0 eV for phenolate and −2.1 eV for phenyl to −3.2 eV for nitrene. Among the functional groups examined, phenyl and phenolate show similar adsorption configurations, in which the adsorption of phenyl (phenolate) lifts the first-layer P atom 0.165 Å (0.101 Å), pushes the second-layer P atom away 0.292 Å (0.181 Å), and the corresponding (broken) P−P distance is 2.96 Å (2.64 Å), which was 2.23 Å in pristine BP. By contrast, nitrene is more tightly bonded to the P atoms. The addition of nitrene pushes down the surface P atom 0.108 Å instead of pulling it outward the sheet. Displacement of the bottom-side P atom is insignificant, and at the same time, phosphorene possesses a much shorter P−P bond length (2.21 Å) compared to the other two cases.

In the following, we show the physical reason for the varied perturbation of the electronic structure caused by the different radicals. Figure 2 shows a schematic representation of the three

![Figure 2](image-url)

**Figure 2.** Structure and partial charge densities of (a) phenyl, (b) phenolate, and (c) nitrene. Black, white, red, and blue balls denote C, H, O, and N atoms, respectively. The singly occupied molecular orbital of phenyl and phenolate and highest occupied molecular orbital are shown on the right panels.
functional groups: phenyl, phenolate, and nitrene. The varied frontier orbitals, manifested by the charge density shown in Figure 2, display the difference between electronic structures of the three radicals. The phenyl and phenolate have one unpaired electron in the p orbital, which is also evidenced by the calculated density of states in Figure S4, whereas the nitrene group has two valence electrons forming a free electron pair and two remaining electrons occupying two degenerate p orbitals. This different electron distribution leads to varied adsorption configurations and energies on black phosphorus, as discussed later in the text. The density of states of these ligands is shown in the Supporting Information (Figure S4).

The varied perturbation can thus be explained on the basis of the different electronic structures of the radicals and distinct interfacial chemical bonds. Each phosphorus atom is covalently bonded to three adjacent phosphorus atoms to form a puckered honeycomb structure \(^{32,33}\) in pristine BP. By forming three bonds with each neighboring P atoms, each phosphorus atom also has a lone pair of electrons. The strong interaction between surface P and the unpaired electron in phenyl groups (P–C bond) leads to the broken P–P bond and localization of an unpaired p electron on the P atom at the bottom (Figure 1b,c). This unsaturated P atom at the bottom dominates the charge localized at the Fermi Level.

The strength of interfacial interaction does not correlate with the amplitude of perturbation of the electronic structure. Although it has the strongest interaction with the BP surface, the nitrene group has two valence electrons forming a free electron pair and two remaining electrons occupying two degenerate p orbitals. When introducing nitrene to BP, the surface P atom shared its lone pair electrons with N in nitrene (Figure 1d), forming a dative covalent bond. In other words, the Lewis basic and nucleophilic P atom at the surface attacks, through the lone pair of electrons, the Lewis acidic nitrene species. This bond is very strong and does not need to break the P–P bond, leading to very stable adsorption of nitrene (Table 1).

The nature of the dative bond is further supported by analyzing the charge transfer at the interface. Figure 3 shows the calculated charge transfer between nitrene and BP. The lone pair electrons of P are shared between P and N, leading to charge redistribution at the P–N–C atoms at the interface. The unperturbed band structure of BP upon adsorption of nitrene may suggest that nitrene-derived species could be a desirable functional group to functionalize the BP layers. This hydrophobic functionalization at the surface may help BP to resist fast degradation upon exposure to mainly water, oxygen, and light.\(^{5,10,26}\)

Next, to further tune the electronic property of BP, we have modeled functionalization of other nitrene-derived groups on phosphorene substrate, including N-methylbenzene, N-aminobenzene, as well as N-nitrobenzene, in which CH\(_3\) and NH\(_2\) are electron-donating groups, whereas NO\(_2\) is known to be an electron-withdrawing group. Because N is more electronegative than C and H, CH\(_2\)- and NH\(_2\)-substituted nitrene groups are able to release electrons to their adjacent parts, whereas N tends to withdraw electrons from ring by inductive effects. Furthermore, N in NO\(_2\)-substituted nitrene possesses a positive charge by donating partially its lone pair electrons to one of the O atoms, so it tends to withdraw electrons inside to reduce its positive charge. This charge redistribution at the interface causes a change of the surface dipole,\(^{54}\) resulting in changes of the work function of the material.\(^{34}\)

We calculated the work function of BP functionalized at only one side of the pristine BP as well as at both sides, the latter of which is helpful to reduce dipole interaction resulting from the periodic boundary condition. The calculated electrostatic potential is shown in Figure S5. Table 2 shows that among the functional groups examined, NO\(_2\)-substituted nitrene-BP shows the highest work function compared to either pristine or nitrene-BP. Instead, there is a moderate decrease in the value when nitrene-BP is decorated by NH\(_2\) which is one of the electron-donating groups. The electrostatic potential profile in Figure 4 also shows a shift of vacuum level when Fermi Level is aligned manually, indicating the strong electron-withdrawing power of NO\(_2\). Addition of CH\(_2\)- and NH\(_2\)-substituted nitrene groups results in reduced work function compared to nitrene-BP. Therefore, by introducing electron-donating and electron-withdrawing groups into the nitrene groups, we can tune the work function by 2 eV with a rather low coverage of functional groups (one group per 18 surface P atoms). We find that the work function of BP can be further modified by changing the density of the functional groups, in agreement with the literature.\(^{35}\) For example, double the coverage of the NO\(_2\)-substituted nitrene, the work function can be increased by an additional 0.7 eV (Table S1).

In addition, we calculated the charge transfer that occurs between the functional group and monolayer black phosphorus by performing Bader charge analysis,\(^{36}\) as revealed in Table 3. We find that all functional groups we have covered behave as acceptors, which withdraw electrons from BP sheet (the negative sign denotes the number of electrons that transfer from monolayer to functional groups). The changes in charge transfer upon functionalization are linearly correlated with the changes in work function.

![Figure 3. Charge transfer between the nitrene and BP. The red and blue colors indicate electron accumulation and depletion, respectively. The value of isosurface used for plotting the charged density difference is ±0.05 e Å\(^{-3}\). The charge density difference \(\Delta \rho\) is calculated as \(\Delta \rho = \rho(\text{nitrene}/\text{BP}) - \rho(\text{nitrene}) - \rho(\text{BP})\), where the \(\rho(\text{nitrene}/\text{BP})\), \(\rho(\text{nitrene})\), and \(\rho(\text{BP})\) are the charge densities of nitrene adsorption on BP, isolated nitrene, and isolated BP, respectively, with the atomic positions also fixed at the optimized adsorption configuration.](image-url)
**Figure 4.** Electrostatic potentials of BP with different functional groups at both sides, including N-methylbenzene-BP (black solid curve), N-aminobenzene-BP (blue dotted curve), and N-nitrobenzene-BP (red dotted curve). Electrostatic potentials of pristine monolayer BP (purple solid curve) and nitrene-functionalized BP (green solid curve) are shown for comparison. The black, white, red, and blue balls denote C, H, O, and N atoms, respectively.

**Table 3.** Calculated Charge Transfer (Using DFT-PBE) from BP Sheet to Each Ligand

|       | phenyl | phenolate | nitrene | -CH3 | -NH2 | -NO2 |
|-------|--------|-----------|---------|------|------|------|
| charge transfer (e-) | -1.22  | -1.13     | -1.83   | -1.83| -1.81| -1.90|

*The negative sign indicates donation of electrons from BP to the ligands.*

The tunable work function and band-edge energies are valuable for building heterostructures between BP and other two-dimensional materials as well as metal oxides. It is also desirable to tune the band edges for applications in electrocatalysis, in which the energy of the conduction and valence bands should be aligned with the electrochemical potentials of the redox reactions. In addition, functionalization of BP using the hydrophobic nitrene groups may also help to reduce contact between BP and water, and it has shown that O2 dissolved in water may cause decomposition of the BP sheets.

**CONCLUSIONS**

We have systematically investigated the adsorption of phenyl, phenolate, and nitrene on the basal plane of black phosphorus by means of DFT computations. We find that nitrene is a desirable functional group for surface modification of black phosphorus because it shows very strong thermostability and does not perturb the electronic structures due to the interfacial dative bond. In addition, functionalization of black phosphorus via nitrene-derived functional groups can be further used to tune the work function. The results reported here indicate that one can tune the substituent groups in the phenyl, phenolate, and nitrene moieties to tune the charge transfer at the interface, through which a tunable electronic structure of black phosphorus may be achieved. The great tunability of the electronic properties of black phosphorus by covalent functionalization suggests an effective way to realize its full potential in nanoelectronic and optoelectronic applications.

**COMPUTATIONAL METHODS**

DFT computations were performed using Vienna ab initio simulation package. The ion–electron interaction was described through the projector-augmented wave approach. For structural optimization, the exchange and correlation functional was represented using the Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation. The van der Waals interaction has been taken into account through Grimme’s DFT-D3 semiempirical method. To model the monolayer, we used a supercell containing 36 P atoms. The Brillouin zone was sampled using a k-point mesh of 3 × 3 × 1 for structural optimizations. A vacuum space of at least 10 Å was included in the supercell to minimize the interaction between the system and its replicas resulting from the periodic boundary condition. A 400 eV cutoff for the plane-wave basis set was adopted in all computations. The structures were relaxed until the atomic force is smaller than 0.01 eV Å⁻¹.

The optimized structures were then used for the electronic density of states calculations using the HSE06 hybrid functional. All of the calculations were performed using a Gaussian smearing with a width of 0.2 eV. We have tried to increase the cutoff energy to 500 and 600 eV for the DOS calculations with a smaller smearing width of 0.02 eV and observed no significant difference (see Figure S6). For comparison, the DFT-PBE-calculated electronic structure is shown in the Supporting Information (Figure S1). The calculated electronic structures using HSE and PBE functionals give the same trend and support the conclusion. The band gap was calculated on the basis of the eigenstates at the Γ point in the Brillouin zone of BP. The work function of pristine and functionalized BP was calculated on the basis of the difference between the Fermi Level and the vacuum level.

The adsorption energy of each configuration between the molecule and the 2D BP is defined by $E_{\text{ads}} = E_{\text{total}} - (E_{\text{BP}} + E_{\text{adsorbate}})$, where $E_{\text{total}}$, $E_{\text{BP}}$, and $E_{\text{adsorbate}}$ are the energies of functionalized 2D materials, pristine 2D materials, and the isolated functional group, respectively.
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Notes

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