

Degradation of phosphorene in air: understanding at atomic level

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Degradation of phosphorene in air: understanding at atomic level

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Abstract

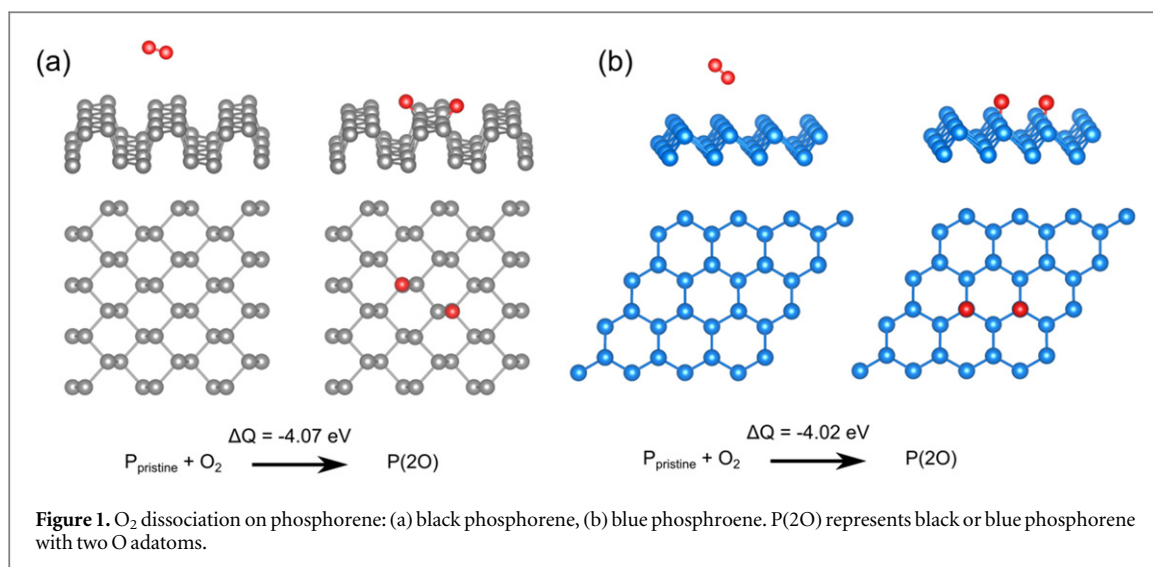
Phosphorene is a promising two-dimensional (2D) material with a direct band gap, high carrier mobility, and anisotropic electronic properties. Phosphorene-based electronic devices, however, are found to degrade upon exposure to air. In this paper, we provide an atomic level understanding of the stability of phosphorene in terms of its interaction with O₂ and H₂O. The results based on density functional theory together with first principles molecular dynamics calculations show that O₂ could spontaneously dissociate on phosphorene at room temperature. H₂O will not strongly interact with pristine phosphorene, however, an exothermic reaction could occur if phosphorene is first oxidized. The pathway of oxidation first, followed by exothermic reaction with water is the most likely route for the chemical degradation of phosphorene-based devices in air.

1. Introduction

Phosphorene is one of the group V elemental monolayers [1–4] with a direct band gap, high carrier mobility, and anisotropic electronic properties, making it a promising candidate for applications in electronics and optoelectronics [5, 6]. The chemical degradation of phosphorene upon exposure to ambient conditions, however, is a challenge to the stability and performance of phosphorene-based devices [7–11]. The presence of oxygen and humidity is suggested to be the main cause of the degradation process [12–14]. Recent experiments have also demonstrated photo-assisted degradation of phosphorene [15], which is predicted to be related to intrinsic defects [16]. Theoretically, it was reported that H₂O adsorbed on phosphorene will induce a significant distortion to its structure [8]. Contradictory results were obtained suggesting that phosphorene is stable in the presence of H₂O [17]. Despite these experimental and theoretical efforts, there are still some unanswered questions regarding the degradation of phosphorene, including (i) atomic level of understanding on the degradation process of phosphorene; (ii) the role of H₂O in the degradation process; and (3) the

environmental stability of other theoretically predicted phosphorene allotropes (e.g., blue phosphorene [18] which has not been realized in experiments).

In order to address these questions, we have performed density functional theory (DFT) calculations combined with first principles molecular dynamics (MD) simulations to investigate the interactions of O₂ and H₂O with phosphorene. In section 3.1, we focus on the interaction of O₂ with phosphorene. Since surface reaction with O₂ has been reported to be crucial in the degradation process of black phosphorene [14], we will extend the discussion to blue phosphorene. In section 3.2, the adsorption of H₂O on phosphorene allotropes is investigated in terms of adsorption configuration, binding energy, and bonding characteristics. In section 3.3, we discuss the degradation of phosphorene by calculating the relative energies along a likely interaction pathway. Our calculated results show that O₂ can spontaneously dissociate on phosphorene at room temperature. H₂O will not strongly interact with pristine phosphorene, however, an exothermic reaction could occur if phosphorene is first oxidized. Other allotropes of phosphorene, e.g. blue phosphorene are also expected to deteriorate in air.



2. Computational details

The electronic structure calculations were performed using the Vienna *ab initio* simulation package [19, 20]. The exchange-correlation was treated within the generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) [21] functional for the calculations. We also employed the DFT-D2 method of Grimme [22] to include contributions from the van der Waals (vdW) interactions. The energy of convergence was set to 1×10^{-6} eV and the residual force on each atom was smaller than $0.01 \text{ eV } \text{Å}^{-1}$ during the structural optimization. The cutoff energy for the plane-wave basis was set to 500 eV. The vacuum distance normal to the plane was larger than 30 Å to eliminate interaction between the periodic replicas. A rectangular supercell of (3×4) was used for the black phosphorene, and a parallelogram supercell of (4×4) was used for the blue phosphorene. The reciprocal space was sampled by a grid of $(2 \times 2 \times 1)$ k points in the Brillouin Zone.

First principles MD simulations were also performed to simulate the interaction processes considered. The MD simulation was based on the norm-conserving Troullier-Martins pseudopotential together with Nosé thermostat [23] as implemented in the SIESTA program package [24]. In order to minimize the constraints induced by periodicity in the slab model for MD simulations, (5×6) and (5×5) supercells were used for black and blue phosphorene, respectively. The time step was set to 1 fs, and the simulation temperature was set to 300 K. It is to be noted that most of the experiments on degradation of phosphorene were done in the air. In our MD simulations, the number density of gas molecules was about $65.8 \times 10^{25} \text{ m}^{-3}$ considering 9 O₂ molecules in a simulation cell of $(22.9 \text{ Å} \times 19.9 \text{ Å} \times 30 \text{ Å})$. Such high pressure conditions were also used for MD simulations to study oxidation of SiC [25] and graphene [26].

3. Results and discussion

Black phosphorene has a puckered surface with two sub-layers of phosphorus atoms which are arranged in a rectangular lattice. At GGA-PBE level of theory, the lattice constants along the armchair and the zigzag direction are 4.57 Å and 3.31 Å, respectively. The bond lengths are 2.22 Å and 2.25 Å. Blue phosphorene has a buckled honeycomb structure with lattice constant of 3.28 Å and bond length of 2.26 Å. Our results are in agreement with the reported lattice constants and bond lengths of black and blue phosphorene [2, 18], thereby, demonstrating the reliability of the modeling elements used in the calculations.

3.1. O₂ interacting with phosphorene

It has been established by both calculations and experiments that O₂ can easily dissociate on black phosphorene [14, 27] leading to the formation of the oxidized lattice [28]. The O₂ molecule prefers a perpendicular configuration to approach the surface of phosphorene with a distance of 2.5 Å as seen from the binding energy profile (figure S1 in the supplementary materials). Thereafter, O₂ tends to dissociate on the surface with exothermic energy (ΔQ) of -4.07 eV/O_2 molecule on black phosphorene, and -4.02 eV/O_2 molecule on blue phosphorene (figure 1). The details of calculations for ΔQ are given in table S1 in the supplementary materials. Note that the dissociation energy is calculated using the triplet state of O₂.

The calculated dissociation barrier of O₂ on phosphorene is 0.54 eV [14]. Considering that chemical reaction with an energy barrier less than 0.9 eV ($\approx 21 \text{ kcal mol}^{-1}$) from DFT calculations could occur at room temperature [29], oxidation of phosphorene is expected to occur readily at room temperature. Other external sources such as photon radiation may speed up the dissociation process. After dissociation, atomic oxygen finds the dangling position to be the

Table 1. Structural properties of atomic O adsorbed on phosphorene.

Phosphorene	Black	Blue
Bond length R_{P-O} (Å)	1.50 Å	1.50 Å
Bond angle $\angle P-O-P$ (°)	112°, 117°	123°
Bader charge, oxygen	-1.31e	-1.32e

preferred site on black phosphorene which is consistent with previous theoretical studies [14, 28, 30]. This is not the case with blue phosphorene where the preferred site is the top site (see figure S2 in the supplementary materials). The P–O bond shows similar bonding character as seen from the bond length and Bader charges [31] given in table 1. Overall, the nature of interaction of oxygen with phosphorene stems from the sp^3 bonds which leave a lone electron pair on each phosphorous atom, and the preferred binding site follows the direction of the lone electron pair on both allotropes.

The calculated results based on first principles MD simulations further affirm the dissociation of O_2 on phosphorene. Figure 2 shows time-dependent snapshots of the configurations showing interaction of oxygen with phosphorene during MD simulations. These configurations were obtained by placing a few O_2 molecules 4 Å initially above the surface at a constant temperature of 300 K. For the case of black phosphorene, some O_2 molecules will first move closer to the native phosphorus atoms, then dissociate into atomic oxygen atoms after 600 fs (see video V1 in the supplementary materials). A similar O_2 dissociation process is seen on the blue phosphorene after 1150 fs (see video V2 in the supplementary materials).

Considering the relatively high pressure conditions in our MD simulations, we have performed additional MD calculations with only one O_2 molecule in the simulation box of (22.9 Å × 19.9 Å × 85 Å) which appears to mimic number density of gas molecules of $2.5 \times 10^{25} \text{ m}^{-3}$ under standard atmospheric conditions. The results shown in figure S3, video V3 and video V4 (supplementary materials) find that dissociation of O_2 on the surface does occur under the relatively reduced pressure conditions. We may therefore conclude that both allotropes of phosphorene will go through the spontaneous oxidation process upon exposure to O_2 at room temperature due to the affinity of P and O atoms forming P=O bonds with a large exothermic energy (see figure 1).

3.2. H_2O interacting with phosphorene

Figure 3 shows the configurations of H_2O interacting with phosphorene considered for the calculations: one leg, two leg, and O closer. The configuration referred to as ‘one leg’ is the configuration in which one of the H atoms is closer to the surface, ‘two leg’ means both

H atoms are closer to the surface, and ‘O closer’ means the O atom is closer to the surface.

The calculated binding energy profiles with vdW correction using DFT-D2 method of Grimme [22] are shown in figure 4. Some of the results deduced are:

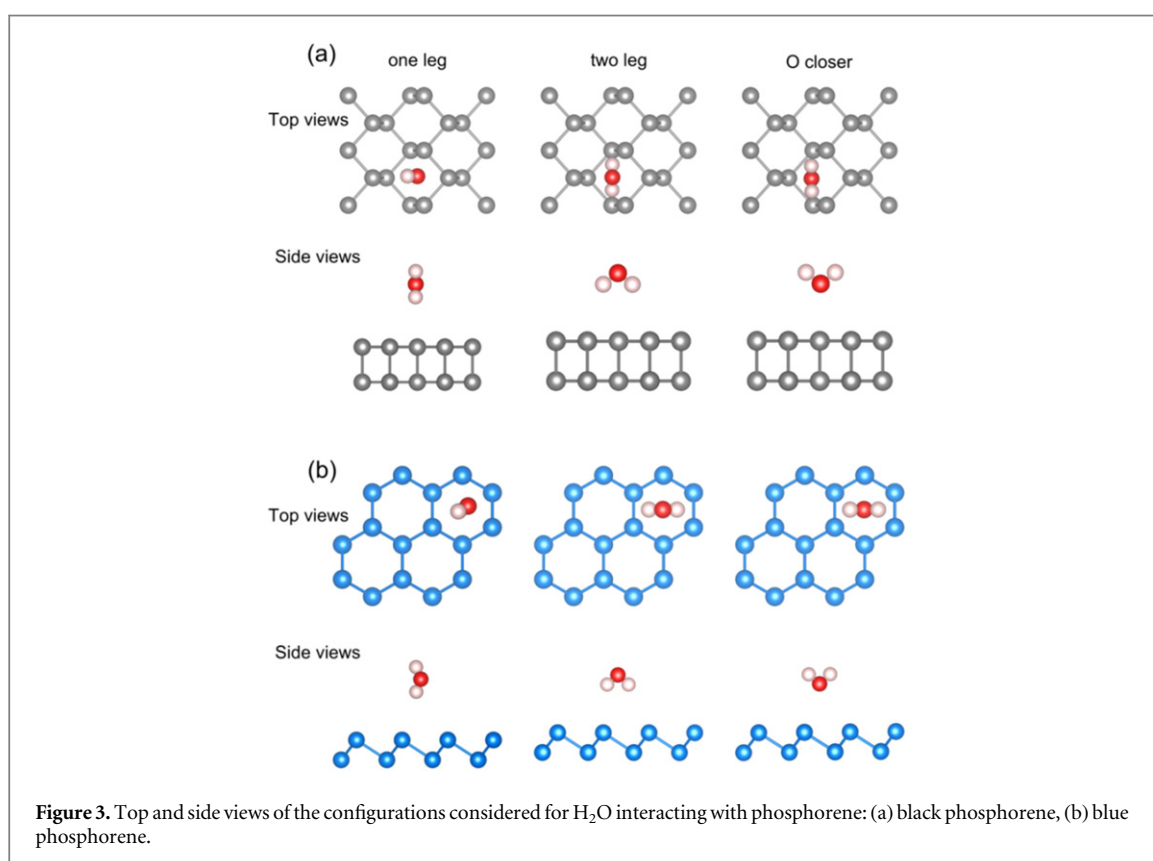
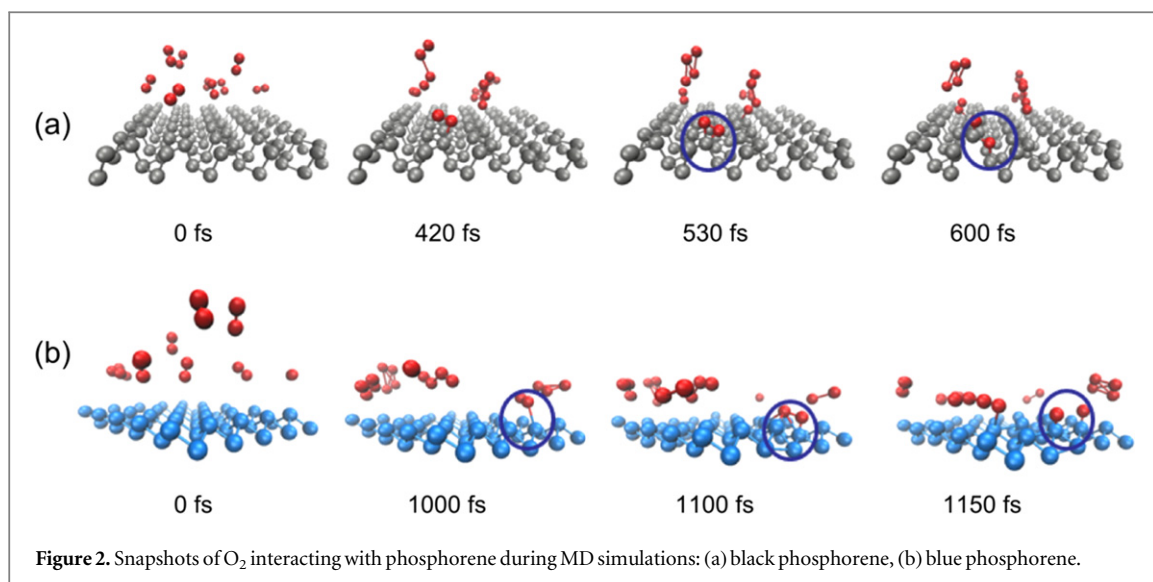
- (i) The ‘two leg’ configuration is the most stable configuration suggesting that H atoms prefer to move towards the surface. This is due to the well-known polar nature of the H_2O molecule in which H atoms tend to attract the lone electron pairs of phosphorene.
- (ii) The calculated binding energy which includes vdW correction term is about 180 and 125 meV for H_2O on the black and blue phosphorene, respectively. It is larger than that of H_2O on graphene at the same level of theory (in the range from 60 to 120 meV [32]), mainly because of the presence of the lone electron pairs on phosphorene. The attraction between H atoms and the lone electron pairs of phosphorene is clearly demonstrated by the deformation charge density plots (see figure S4 in the supplementary materials) showing the increase in the electron density in the region between H and P atoms.

In order to further examine the interaction of H_2O with phosphorene, we considered the initial configuration to consist of a ‘forced’ H_2O molecule at the interstitial site of the phosphorene lattice. If H_2O prefers to interact strongly with phosphorene, then the optimized configuration should show that H and O atoms remain in the lattice. This is not the case as H_2O moves out of the lattice to a surface site (figure S5 in the supplementary materials) without distorting the surface for both allotropes. Our first principles MD simulations up to 10 ps also find that H_2O molecules stay near the phosphorene surface without any chemical interaction within 10 ps (see video V5 in the supplementary materials). Therefore, H_2O prefers to bind to the surface through hydrogen bonds.

3.3. Stability of phosphorene in air : exposure to O_2 and H_2O

Based on the calculated results given in sections 3.1 and 3.2, we can state that the O_2 molecule could spontaneously dissociate on phosphorene at room temperature, and the H_2O molecule will not interact strongly with the pristine phosphorene.

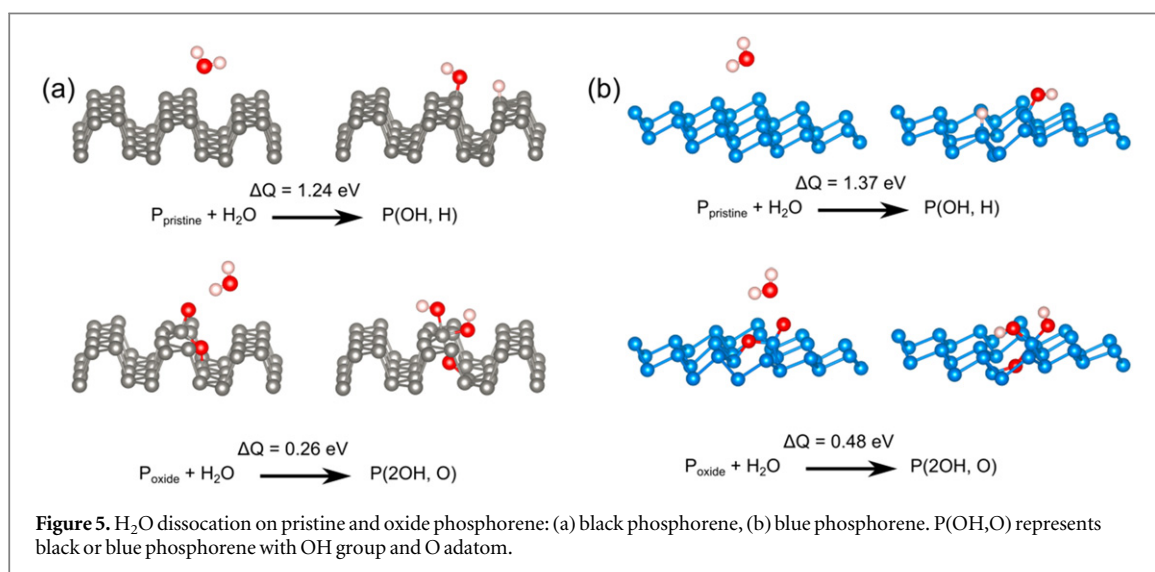
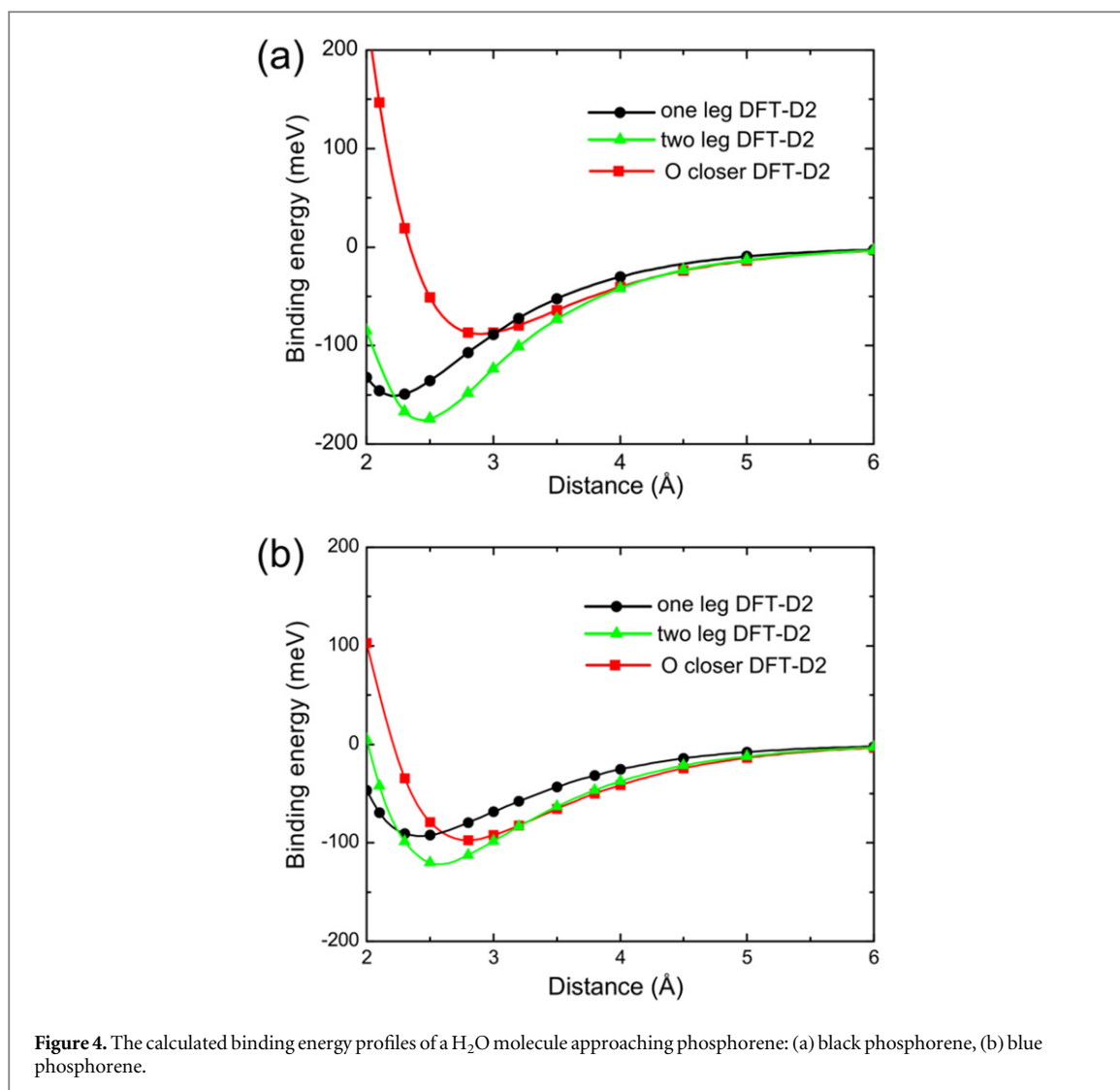
The dissociation of H_2O on pristine black and blue phosphorene is endothermic with an energy increase of 1.24 eV and 1.37 eV, respectively (figure 5). This is not the case with the oxidized phosphorene monolayers for which the endothermic energy significantly decreases to 0.26 eV and 0.48 eV, respectively. Therefore, oxidation of phosphorene may enable dissociation of H_2O on the surface. Also considering that the



phosphorous oxides (e.g., P_3O_6 , P_4O_{10}) are reactive with H_2O [33], a simple intuitive view of the degradation of phosphorene in air based on energetic considerations can be offered: first, oxidation of the two-dimensional (2D) lattice of phosphorene will occur in air; then, the oxide species will interact with H_2O .

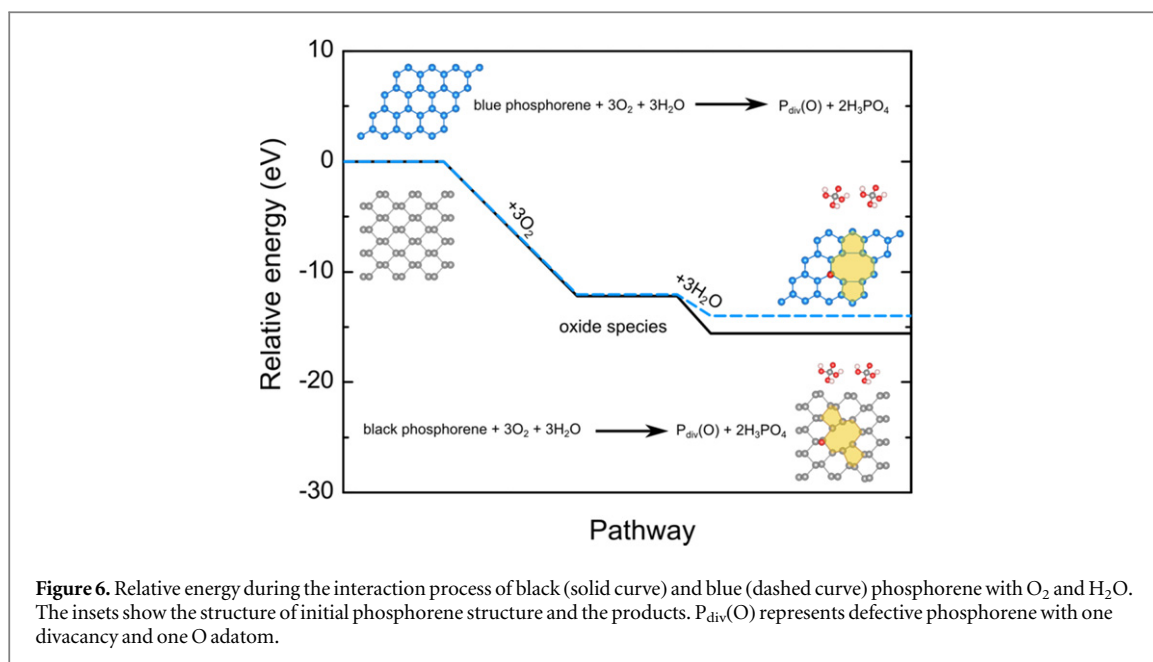
In order to validate our view of this interaction process, the relative energy of the initial and final chemical species along the pathway are calculated. The reactants are phosphorene, 3 O_2 molecules, and 3 H_2O molecules and the products are 2 phosphoric

acid and phosphorene with defects including divacancy and O adatom (figure 6). For black phosphorene, the total energy release during this process is 15.60 eV. The oxidation process is exothermic with energy release of about 12.21 eV, and the reaction of phosphorene oxide species with 3 H_2O molecule further releases 3.39 eV of energy (see tables S2 and S3 in the supplementary materials for the details of the calculations). The reaction process for blue phosphorene is also exothermic, which suggests the similarity of black and blue phases in terms of the



environmental stability. Overall, the exothermic process implies that H_2O will react with phosphorene if it is oxidized on the surface. The proposed pathway will lead to the formation of phosphoric acid and defective phosphorene. The defective phosphorene

could further be photo-oxidized [16], and then the oxide species will further react with H_2O . This reaction circle results in the fast degradation of phosphorene in air. The predicted mechanism for phosphorene is therefore different from the case of



graphene where the dangling bonds near the defect sites initiate its degradation [34].

4. Summary

In order to investigate the stability of phosphorene in air, interactions of O_2 and H_2O with phosphorene were studied by using DFT combined with first-principles MD simulations. We find that (i) O_2 will spontaneously dissociate on phosphorene at room temperature. The exposure of phosphorene to O_2 will induce its oxidation forming an oxidized phosphorene lattice; (ii) H_2O does not interact directly (chemically) with the pristine phosphorene lattice. It prefers to bind to the surface of phosphorene through hydrogen bonds; (iii) H_2O will exothermically interact with phosphorene if it has first been oxidized; (iv) other theoretically predicted 2D phosphorene allotropes, e.g. blue phosphorene, are also expected to be unstable in air.

Our calculations are supported by several experimental results; e.g. experiments have shown that fast degradation of phosphorene occurs in the presence of both O_2 and H_2O , the degradation process slows down with the exposure of phosphorene to only O_2 or H_2O [15, 35]; experiments have shown a drop of pH after water addition to phosphorene [13], which is a clear identification of the formation of phosphoric acid. Considering the rapid growth of research on 2D materials based on the group V semiconductors, our study provides an atomic scale understanding of the stability of phosphorene in air, which will aid in determining the degradation and aging effects of phosphorene-based devices.

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