Optimal water adsorption on phosphorene

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ABSTRACT

Water adsorption on phosphorene has fundamental importance to device development from black phosphorus, but the stable adsorption configuration remains in confusion. Here we explore the water adsorption configurations on phosphorene through comprehensive first principle calculations. It is found that water takes an optimal adsorption configuration on phosphorene with one of the hydrogen atoms pointing to the surface of phosphorene. This optimal adsorption configuration is significantly more stable than all the configurations reported previously for the strongest van de Walls interaction between the adsorbed water and the phosphorene compared to other adsorption configurations. It is also shown that water serves as an acceptor in the optimal adsorption configuration, clarifying the confusing results from less stable configurations.

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1. Introduction

Phosphorene [1], monolayer exfoliated from layered black phosphorus, is a novel two-dimensional (2D) material. The structure of phosphorene is significantly different from 2D materials like graphene [2], hexagonal boron nitride (h-BN) [3] and molybdenum disulfide (MoS_2) [4]. The phosphorous atoms in phosphorene are arranged hexagonally, but the surface of phosphorene is puckered, and the puckered surface is different from silicene [5]. Previous studies show that phosphorene has a lot of extraordinary properties. Phosphorene is an intrinsic p-type semiconductor[1] with a direct band gap of 1.0 eV, a high hole field-effect mobility of 286 $cm^2/(V \cdot s)$, and an on/off ratio up to 10^4. Due to its unique puckered crystal structure, the electronic, optical, thermal and mechanical properties of phosphorene are anisotropic [6–11]. Phosphorene has superior mechanical flexibility that can sustain tensile strain up to 27% and 30% in the zigzag and armchair directions, respectively [12], and exhibits a negative Poisson's ratio [13]. Besides, molecule dynamics simulations show that the disruption of proteins caused by phosphorene is much smaller than that by graphene [14]. Although phosphorene has so many extraordinary properties, it is fatal that phosphorene is not stable in atmosphere. Once a time, high-quality STM images display that black phosphorous is etched under the condition of oxygen and water [15]. Recently,

phosphorene can be produced by liquid exfoliation method [16,17], indicating excellent water stability. It has been shown that the phosphorene breaks apart due to the high enough oxygen concentration that result in a large stress in phosphorene [18]; NO_2 and O_2 have a strong interaction with phosphorene [19]; water would not strongly interact with pristine phosphorene unless the phosphorene was first oxidized [20]; water has nearly the same adsorption energy at the vacancy site as that at the perfect one [21]. All these results indicate that phosphorene is not chemically sensitive to water. So far, several possible water absorption configurations on phosphorene have been reported. Wang et al. [20] showed that water prefers binding to phosphorene with both hydrogen atoms close to the surface of phosphorene, while in the most stable configuration reported by Cai et al. [19] and Kistanov et al. [21]. The oxygen atom of water is closer to the surface of phosphorene than the hydrogen atoms. It is more important that water adsorption configuration always determines the electron depletion of the phosphorene crystal, or whether the water molecule acts as an accepter or a donor. In this work, we systematically studied the water adsorption on different sites of phosphorene. It is shown that water prefers to adsorb on phosphorene with one of the hydrogen atoms pointing to the surface of phosphorene, which is similar to the global minimum configuration on graphene [22,23] but distinctively different from water adsorption on metals [24,25]. Our analyses of charge transfer and the work function show that water serves as an acceptor.

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2. Theoretical methods

The first-principle calculations are performed within the framework of density-functional theory as encoded in Vienna Ab-initio Simulation Package code [26–28]. The projector-augmented wave method for the core region and the Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation potential [29] were employed. The relaxed lattice constant of the phosphorene unit cell is a = 4.621 Å and b = 3.299 Å along armchair and zigzag orientations, respectively, based on a $10 \times 14 \times 1$ Monkhorst-Pack (MP) grid for k-point sampling. The kinetic energy cutoff of the plane-wave expansion was set to be 500 eV. A vacuum space of 15 Å was set between two layers to avoid the interactions between them. The geometry was fully relaxed with the conjugate gradient method until the force on each atom was less than 0.01 eV/Å and a total energy convergence of 10^{-5} eV. We employed the DFT-D2 method of Grimme [30] and the Becke88 [31] optimization functional to include contributions from the vdW interactions. The charge transfer in this work was estimated by Bader charge analysis [32].

Water adsorption on phosphorene was modeled using the repeated slab geometry employing a (3×4) unit cell and a $5 \times 5 \times 1$ MP k-point mesh. We also considered a (4×5) unit cell with a $4 \times 5 \times 1$ MP k-point mesh. The isolated water molecule was modeled in a unit cell of $20 \times 20 \times 20$ Å^3, with an $11 \times 11 \times 11$ MP k-point mesh. For calculating work function, the vacuum space is not less than 30 Å with a $10 \times 10 \times 1$ MP k-point mesh.

3. Results and discussion

The study begins from phosphorene. The relaxed structure of phosphorene is shown in Fig. 1. There are four phosphorus atoms in the unit cell, and we number them from 1 to 4, as shown in Fig. 1b.

In Fig. 2, we show water adsorbed on four different adsorption sites of phosphorene. The four adsorption sites are chose that water adsorbed near the phosphorus atoms numbered from 1 to 4. There are three main possible orientations for the adsorbed water on
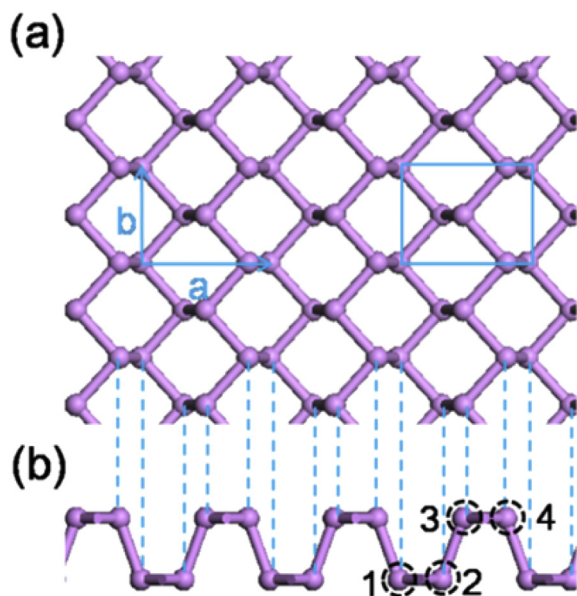

Fig. 1. Top (a) and side (b) views of phosphorene. The blue rectangle in (a) shows the unit cell of the periodic structure. The four dashed black circles in (b) show the four phosphorus atoms in the unit cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

phosphorene, one-leg-down (A), two-legs-down (B) and oxygen-closer (C). The van der Waals (vdW) interactions between water and phosphorene are considered by the DFT-D2 method and the optB88-vdW method. It can be seen that the adsorption configurations (Fig. 2, Fig. S1) are similar on different adsorption sites except for the oxygen closer configurations in Fig. S1-c3a and c3b that can only be obtained by the optB88-vdW method.

The adsorption energy can be estimated as:

$$E_{ad} = E_{PW} - E_P - E_W, \tag{1}$$

where E_{PW}, E_P and E_W are the energies of phosphorene with the adsorbed water, the pristine phosphorene and the isolated water molecule, respectively. The adsorption energies of the water adsorption on different sites of phosphorene are presented in Table 1. Although the adsorption energy is different under different vdW descriptions, the configuration of one-leg-down is invariably the optimal configuration. Due to the unique puckered crystal structure of phosphorene, the phosphorous atoms in the unit cell are not equivalent. As a result, the stable configuration is different on different adsorption sites even for the same orientation. As shown in Table 1, the results calculated by the DFT-D2 method show that the configuration of one-leg-down is invariably the most stable configuration, independent of adsorption sites. For results calculated by the optB88-vdW method, the one-leg-down adsorption configuration is still the most stable configuration. Detailed results show that when water adsorbed near sites 3 and 4, the oxygen-closer configuration (C-a) is slightly more stable than the one-leg-down configuration. However, the adsorption energy of the configuration C-a is about 20 meV high than the one-leg-down configuration adsorbed near sites 1 and 2. In terms of energy conversion, 20 meV is equivalent to a temperature difference of about 232 K, illustrating that the one-leg-down configuration is much more stable. The adsorption energies shows that the interaction between the adsorbed water and phosphorene is physisorption, in accordance with the results that a large energy barrier is existed from physisorption of water on phosphorene to chemisorption [20]. Besides, we compared the adsorption energies of the (4×5) unit cell and the (3×4) unit cell. Previous researches showed that the supercell size affected the adsorption energies not much [33,34]. As shown in Table S1, the differences of the adsorption energies between the two unit cells are small, in agreement with previous results.

We also consider the dipole correction to the adsorption energy. The results in Table 2 show that the adsorption energies change not much when taking the dipole correction into consideration, and the optimal water adsorption configuration remains unchanged. Consequently, the dipole correction is neglected in the following calculations.

The distances between the oxygen atom and the hydrogen atom (L_{H-O}), the bond angles of H–O–H (θ) of an isolated water molecule and the adsorbed water molecule are showed in Table 3. For an isolated water molecule, L_{H-O} and θ are 0.972 Å and 104.54° by the DFT-D2 method, respectively; while 0.973 Å and 105.41° by the optB88-vdW method, respectively. When a water molecule adsorbed on phosphorene, the bond length and bond angle of the water molecule is changed. For the results calculated by DFT-D2 method, the bond length of adsorbed water is changed less than 0.066 Å, while the bond angle is changed less than ±1.01°. By contrast, the bond length is changed less than ±0.079 Å and the bond angle is changed less than ±0.80° for the optB88-vdW method. The changes in bond length and bond angle by different vdW methods are similar, both showing that the phosphorene substrate has little influence on the adsorbed water.

The influence of phosphorene to the adsorbed water can be