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Regulate the polarity of phosphorene's mechanical properties by oxidation

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ABSTRACT

How to effectively manipulate the mechanical properties of atomically thin materials, is critical and can enable many new types of devices for various applications, such as sensing, actuation, energy harvesting, and so on. Here, we propose and demonstrate a new way to regulate the polarity of phosphorene's mechanical properties by controlling the level of oxidation. Phosphorene and its low-level oxides are treated with *ab initio* methods in order to evaluate the influence of oxidation on the anisotropic mechanical properties of phosphorene. Our results show that the mechanical properties of phosphorene are anisotropic. For the stable configuration, the anisotropy is gradually reduced with the increase of the oxygen coverage. We have fitted the formulas of Young's (shear) modulus and Poisson's ratio of phosphorene oxide. We also investigated the mechanical properties of metastable configurations. The diagonal configuration increases the anisotropy. The horizontal configuration is very unstable and has no shear moduli. Our results demonstrate that the mechanical properties of phosphorene can be regulated by oxidation, which is useful in design of phosphorene-based mechanical and optoelectronic devices. Our general model for calculating the elastic modulus along arbitrary direction can be applied in any 2D materials.

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1. Introduction

As a new member of two-dimensional (2D) material family, phosphorene has attracted a lot of attention [1–4]. Most of 2D materials, such as graphene and transition metal dichalcogenides (TMD), are isotropic [5–7]. However, phosphorene shows anisotropy in physic properties, enabling new and promising optoelectronic applications [2,8]. The calculated Young's modulus and Poisson's ratio in the zigzag directions of phosphorene are about four times larger than those in the armchair direction [9]. Anisotropic optical response with *e-h* interactions included makes phosphorene ideal for linear optical polarizers [10]. In Ref. [11], authors have predicted exceptionally high mobility ($\sim$10,000 cm^2 -V^{-1} s^{-1}) of phosphorene which is hole-dominated and highly anisotropic. The electrical and thermal conductance exhibit strong spatial anisotropies such that their respective preferred directions of conductance are orthogonal to one another, resulting in an anisotropic thermoelectric figure of merit that is large along the armchair direction [12]. The polarity of phosphorene is attributed to its anisotropic puckered crystalline structure.

Chemisorption, doping and substrate are the effective approaches of modifying properties of materials, such as the striking graphene hydrogenation [13,14], Gd-doped monolayer MoS$_2$ [15], rare-earth metals doped ZnO [16], the interface between Gd and Monolayer MoS$_2$ [17], and so on. Oxygen chemisorption onto phosphorene can also modify its properties. On the other hand, phosphorene is very easy to be oxidized in ambient conditions [18]. Thus, oxide of phosphorene has been the subject of many studies [19–23]. When the surface of phosphorene has high oxygen coverage, it becomes an insulator [20,22]. For applications in optical and electrical devices, low-level oxidizing derivatives are desirable which will be the focus of the present study [19].

Most of previous reports [18–23] were focused on the modification of chemical or optoelectronic properties of phosphorene, but there have been few works about regulating the mechanical properties of phosphorene. However, the physical properties of 2D materials can be tuned by strain or stress. For instance, people use strain/stress to tune the band gap and thus the optoelectronic properties of 2D materials. Also, the modulation of mechanical properties can change the fundamental many-body interactions, such as exciton or trions in phosphorene, enabling new type of quantum or optoelectronics devices. In this work, we propose and develop a new way to regulate the polarity of

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phosphorene's mechanical properties by controlling the level of oxidation. Oxygen chemisorption onto phosphorene can decrease the anisotropy, which may attribute to decrease the pucker of phosphorene.

2. Computational detail

In the present work, the plane-wave method in the framework of DFT as implemented in the QUANTUM ESPRESSO code [24] is employed. General gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [25] is used for the exchange–correlation effect, and the energy cutoff of 50 Ry is chosen for electron wave function expansion. A vacuum layer thicker of more than 15 Å is included to avoid interaction between periodic layers. The *k*-point sampling is $14 \times 10 \times 1$ for the prime cell of phosphorene and an equivalent *k* point spacing is used for the supercells. The cell parameters and atomic positions are optimized simultaneously. For self-consistent field iterations, the convergence tolerance for geometry optimization is defined when the differences in total energy, the maximum ionic Hellmann-Feynman force, the stress tensor, and maximum displacement reduce to 1.0×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively.

It is well known that local density approximation (LDA) and GGA underestimate the band gap of semiconductor [26,27]. GW approximation [28] and hybrid exchange–correlation functional [29,30] can be used to remedy the shortcoming. However, the mechanical properties of LDA and GGA's results are agreement with the experimental data [31]. In present work, we have only employed GGA functional to calculate the mechanical properties of phosphorene and its oxides.

3. Results and discussion

Oxygen atom can be adopted on the different position of phosphorene. According to the results of Ref. [19], dangling configuration, which has the lowest binding energy, is the most stable in the four configurations (dangling, interstitial bridge, horizontal bridge and diagonal bridge configurations). In this work, we only focus on pure phosphorene and these four oxides configurations.

We consider first pure phosphorene (the cell including 4 atoms, 1×1) and four dangling configurations (2×1, 2×2, 3×2, 3×3 supercells). The schematic diagram of dangling configuration of oxidizing phosphorene is displayed in Fig. 1. We focus the structural information of oxygen atom and the nearest neighbor P
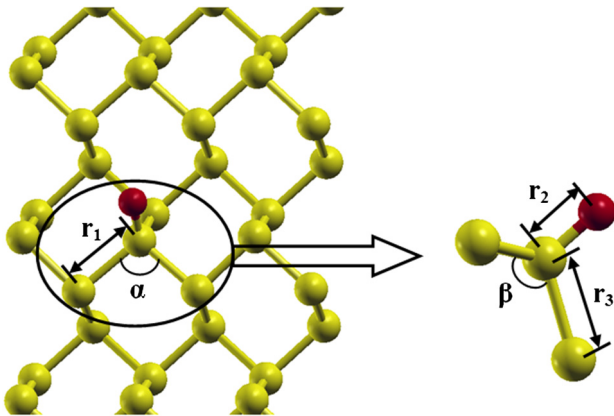
Fig. 1. The schematic diagram of dangling configuration of oxidizing phosphorene. The bond lengths of r₁, r₂, r₃ and bond angles α, β, which are the nearest neighbor of oxygen atom, are denoted.

atoms. The parameters of crystal structures, such as equivalent lattice constants *a* (zigzag direction) and *b* (armchair direction), P=P bond lengths r_1 and r_3, P=O bond length r_2, bond angle α, the angle β between P=P bond and the puckered layers of phosphorene, are presented in Table 1. For intrinsic phosphorene, we predict that the lattice constants are *a* = 3.298 Å and *b* = 4.624 Å, P=P bond lengths r_1 and r_3 are 2.220 Å and 2.258 Å, respectively, the bond angle α is 95.969°, and the angle β is 111.468°. These structural parameters of phosphorene are very good agreement with previous works [9,20].

Upon oxygen adsorption, the lattice constant increases with the increase of the oxygen coverage. In Fig. 2, it shows that the lattice constants increase almost linearly when the oxygen coverage is lower than 6.25%. And the growth rate of lattice constant *b* is about twice as much as one of lattice constant *a*. This may be attributed to the repulsive interaction between adjacent oxygen ions. Compared to intrinsic phosphorene, the bond length r_1 of oxide increases slightly, while the bond length r_2 decreases slightly. The bond angle α and the angle β increase accordingly. When the oxygen coverage is more than 6.25%, the bond length (r_1, r_2, r_3) and the bond angle (α) are almost unchanged.

Now, we focus on the mechanical properties of phosphorene and its oxides, such as elastic constants, Young's and shear moduli, and Poisson's ratios. To validate our calculations, the bulk modulus and elastic constants of bulk black phosphorus have been calculated. Including the Van der Waals correction [32,33], our result shows that the bulk modulus is 31 GPa. The experimental value is 33 GPa [34]. Our predicted elastic constants are C_{11} = 179 GPa, C_{22} = 61 GPa, C_{33} = 51 GPa. The experimental values are C_{11} = 179 GPa, C_{22} = 55 GPa, C_{33} = 54 GPa [35]. These illustrate our calculated results are in good agreement with experimental measured values.

For 2D system, Hooke's law, referred to a Cartesian coordinate system O*xy*, may be written [9,36]:

$$\begin{bmatrix} X_x \\ Y_y \\ X_y \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{61} & C_{62} & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{xy} \end{bmatrix} \tag{1}$$

where X_x, Y_y, X_y are stress components, ε_{xx}, ε_{yy}, ε_{xy} are strain components, and the C_{ij} are elastic stiffness constants. According to the symmetry, there are $C_{12} = C_{21}$; $C_{16} = C_{61}$; $C_{26} = C_{62}$. The components of strain may similarly be written in terms of the components of stress:

$$\begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{xy} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{16} \\ S_{12} & S_{22} & S_{26} \\ S_{16} & S_{26} & S_{66} \end{bmatrix} \begin{bmatrix} X_x \\ Y_y \\ X_y \end{bmatrix} \tag{2}$$

where S_{ij} are the elastic compliance constants. According to Eqs. (1) and (2), we can obtain:

$$\begin{bmatrix} S_{11} & S_{12} & S_{16} \\ S_{12} & S_{22} & S_{26} \\ S_{16} & S_{26} & S_{66} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{16} \\ C_{12} & C_{22} & C_{26} \\ C_{16} & C_{26} & C_{66} \end{bmatrix}^{-1} \tag{3}$$

It is always possible to obtain one set of quantities from Ref. [36].

S_{11} and S_{22} relate extensional stress to collinear extensional strain,

$$S_{11} = 1/E_x \tag{4}$$

$$S_{22} = 1/E_y \tag{5}$$

where E_x and E_y are the Young's moduli in the *x* and *y* directions, respectively.

S_{66} relates a shear strain to shear stress in the same plane,