## $\psi$ -phosphorene: a new allotrope of phosphorene

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**Mechanical properties calculation.** The orientation-dependent mechanical properties of  $\psi$ -P, such as elastic constants, Young's modulus, shear modulus, and Poisson's ratio, are calculated by our Python elastic calculation (PyGEC) package<sup>1</sup> with VASP interface. In a 2D material, the stress-strain equation is obtained from the Hooke's law [Equation S(1)] under plane-stress condition.<sup>2</sup>

We scan the energy surface of materials in the strain range -1.5%  $<^{\varepsilon}xx <$  1.5%, -

 $1.5\% < \varepsilon_{yy} < 1.5\%$  and  $-1.0\% < \varepsilon_{xy} < 1.0\%$ . The strain mesh grid is set to be  $5 \times 5 \times 5$ .

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & 0 \\ C_{12} & C_{22} & 0 \\ 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ 2\varepsilon_{xy} \end{bmatrix}$$
(1)

The orientation-dependent Young's modulus  $E(\theta)$ , Poisson's ratio  $v(\theta)$  and strain  $\varepsilon(\theta)$  under the constant stress are defined as:<sup>3</sup>

$$\begin{cases} E(\theta) = \frac{Y_{zz}}{\cos^4\theta + d_2\cos^2\theta \sin^2\theta + d_3\sin^4\theta} \\ \nu(\theta) = \frac{v_{zz}\cos^4\theta - d_1\cos^2\theta \sin^2\theta + v_{zz}\sin^4\theta}{\cos^4\theta + d_2\cos^2\theta \sin^2\theta + d_3\sin^4\theta} \\ \varepsilon(\theta) = \sigma\left(\cos^4\theta + d_2\cos^2\theta \sin^2\theta + d_3\sin^4\theta\right) (2) \end{cases}$$

where the constant stress  $\sigma = 6GPa$ ,  $d_1$ ,  $d_2$ ,  $d_3$ ,  $Y_{zz}$  and  $v_{zz}$  are elastic constant related variables.

$$v_{zz} = \frac{C_{12}}{C_{22}}$$

$$d_1 = \frac{C_{11}}{C_{22}} + 1 - \frac{C_{11}C_{22} - C_{12}^2}{C_{22}C_{66}}$$

$$d_2 = -\left(2\frac{C_{12}}{C_{22}} - \frac{C_{11}C_{22} - C_{12}^2}{C_{22}C_{66}}\right)$$

$$d_3 = \frac{C_{11}}{C_{22}}$$

$$Y_{zz} = \frac{C_{11}C_{22} - C_{12}^2}{C_{22}}$$
(3)

According to the  $E(\theta)$ ,  $v(\theta)$  and  $\varepsilon(\theta)$ , the strain matrix  $\varepsilon'(\theta)$  and lattice matrix R' can be calculated directly:

$$\begin{cases} \varepsilon'(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta\\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} 1 + \varepsilon(\theta) & 0\\ 0 & 1 - \varepsilon(\theta)\nu(\theta) \end{bmatrix} \begin{bmatrix} \cos\theta & \sin\theta\\ -\sin\theta & \cos\theta \end{bmatrix} \\ R' = R\varepsilon'(\theta) \tag{4}$$

where R is the matrix combined by origin lattice vector for unstressed structure.

The strains along different directions under a constant stress of  $\sigma$ =6.0 **GPa** can be obtained according to Equation S(2). As is shown in **Fig. S2.** A strain of 5.01% along the *x* direction and 8.26% along the *y* direction is produced under this stress. The strain difference can be explained by different values of Young's modulus. Since  $\psi$ -P has the largest Young's modulus along *x* direction, the smallest strain is obtained.

**Carrier mobility calculation.** The carrier mobility of 2D systems is defined as:<sup>4–</sup>

$$\mu_{2D} = \frac{eh^{3}E}{(2\pi)^{3}k_{B}Tm_{e}^{*}m_{d}(E_{l}^{i})^{2}}$$
(5)

where  $m_e^*$  is the carrier effective mass along the transport direction and  $m_d$  is the carrier average effective mass determined by  $m_d = \sqrt{m_x^* m_y^*}$ . The deformation potential constant of the VBM for hole along the x direction reads as  $E_l^x = \Delta E / (\Delta l_x / l_{x,0})$ , where  $\Delta E$  is the energy change of VBM under the lattice compression and stretch from the equilibrium distance  $l_{x,0}$  by a distance of  $\Delta l_x$ . The term *E* is the elastic modulus of x or y direction, which can be directly calculated by PyGEC. For y direction and CBM,  $\mu_{2D}$  can be obtained similarly.

**Absorption spectra calculation.** As for the calculation of frequency-dependent dielectric function, we first calculate the imaginary part by a summation over empty states using the equation:<sup>8</sup>

$$\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k \delta(E_{ck} - E_{vk} - \omega) \times \left\langle \mu_{ck + e_{\alpha}q} \left| \mu_{vk} \right\rangle \left\langle \mu_{ck + e_{\beta}q} \left| \mu_{vk} \right\rangle \right\rangle^*$$
(6)

where the indices c and v refer to conduction and valence band states respectively, and  $\mu_{ck}$  is the cell periodic part of the wavefunctions at the k-point

k. Then the real part of the dielectric tensor  $\varepsilon_{\alpha\beta}^{(2)}(\omega)$  is derived from the  $\varepsilon_{\alpha\beta}^{(2)}(\omega)$  by the usual Kramers-Kronig relationship. The absorption coefficient as a function of photon energy is evaluated according to the following expression:

$$\alpha(\omega) = \frac{4\pi e}{hc} \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}}$$
(7)

**Power conversion efficiency (PCE) calculation.** The upper limit of the PCE  $\eta$  is estimated in the limit of 100% external quantum efficiency (EQE)<sup>9–12</sup> with the formula given by

$$\eta = \frac{J_{sc}V_{oc}\beta_{FF}}{P_{solar}} = \frac{0.65(E_g^d - \Delta E_c - 0.3)\int_E^{\infty} \frac{P(\hbar\varpi)}{\hbar\varpi} d(\hbar\varpi)}{\int_0^{\infty} P(\hbar\varpi)d(\hbar\varpi)}$$
(8)

where the band-fill factor (FF) is assumed to be 0.65,  $P(\hbar \varpi)$  is taken to be the AM1.5 solar energy flux (expressed in Wm<sup>-2</sup>eV<sup>-1</sup>) at the photon energy  $\hbar \varpi$ , and  $E_g^d$  is the bandgap of the donor, and the  $(E_g^d - \Delta E_c - 0.3)$  term is an estimation of the maximum open circuit voltage  $V_{oc}$ . The integral in the numerator is the short circuit current  $J_{sc}$  in the limit of 100% EQE, and the integral in the denominator is the AM1.5 solar flux.

**Diffusion energy barrier calculation.** The climbing image nudged elastic band (CI-NEB) method<sup>13</sup> is used for minimum energy pathway (MEP) calculations.<sup>14,15</sup> The adsorption energy is defined as

$$E_a = E_{gas/\psi - P} - E_{gas} - E_{\psi - P} \quad (9)$$

where  $E_{gas}$ ,  $E_{gas/\psi-P}$ ,  $E_{\psi-P}$  represent the total energy of a single gas molecule, molecule adsorption on porous  $\psi$ -P, respectively.

The selectivity of  $H_2$  relative to other gas molecules through the hole of  $\psi\mbox{-}P$  can be expressed as

$$S_{H_2/gas} = \frac{r_{H_2}}{r_{gas}} = \frac{A_{H_2} exp^{[i0]} \{-E_{b,H_2}/k_B T\}}{A_{gas} exp^{[i0]} \{-E_{b,gas}/k_B T\}}$$
(10)

where r is diffusion rate, A is the diffusion prefactor, and  $E_b$  is the diffusion energy barrier.



**Fig. S1.** (a), (b) and (c) the snapshot of  $\psi$ -P's atomic configuration at 5ps with 300K, 500K and 800K, respectively.



Fig. S2 The orientation-dependent strain  $\epsilon(\theta)$  in  $\psi$ -P corresponding the constant stress  $\sigma$ =6.0 GPa.



**Fig. S3.** (a) (b) and (c) are the atom configurations of initial state (IS), the most stable state (SS) and the transition state (TS) and for H<sub>2</sub> molecule adsorption on  $\psi$ -P, respectively.



**Fig. S4.** The top view (a) and side view (b) of  $\psi$ -P on Au(110) surface. (b) Simulated STM image of  $\psi$ -P on Au(110) surface using a bias voltage of 2.5 eV.

**Table S1.** The calculated elastic constants, Young's modulus along x ( $E_x$ ) and y ( $E_y$ ) direction and Poisson's ratio along x ( $v_{xy}$ ) and y ( $v_{yx}$ ) direction of  $\psi$ -P.

Elastic constants /GPa				Young's Modulus /GPa		Poisson's ratio	
$C_{II}$ 126.55	$C_{12}$ 22.64	$C_{22}$ 76.70	$C_{66} \\ 26.74$	$E_x$ 119.87	$E_{v}$ 72.66	$v_{xy} = 0.30$	$v_{yx} = 0.18$

van der Waals (vdW) correction proposed by Grimme (DFT-D2) has been widely

**Table S3.** The calculated selectivity (S) of  $H_2$  relative to other gas molecules at room temperature (T=298K).

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**Table S2.** The layer distance and binding energy of bilayer  $\psi$ -P calculated by using DFT-D2 and optB88-vdW functional, respectively.

Functional	Layer distance/ Å	Binding energy (eV/atom)
DFT-D2	3.98	-0.04
optB88-vdW	3.95	-0.05

used to multi-layered 2D materials<sup>16–20</sup> due to its good description of long-range vdW interactions. In addition, the optB88-vdW functional has been used in phosphorene systems<sup>21–24</sup> and demonstrated to describe interlayer interaction reliably. In order to justify the use of DFT-D2 functional and check the influence of different functional on geometric structures, we calculated the interlayer distance and binding energy [ $E_{\text{bilayer}}$ - $E_{\text{single-layer}}$ )/N, N is the total number of atom] for bilayer  $\psi$ -P. As shown in **Table S2**, the differences of layer distance and binding energy calculated by DFT-D2 and optB88-vdW functional are small.

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