**ψ-phosphorene: a new allotrope of phosphorene**

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**Mechanical properties calculation.** The orientation-dependent mechanical properties of ψ-P, such as elastic constants, Young’s modulus, shear modulus, and Poisson’s ratio, are calculated by our Python elastic calculation (PyGEC) package1 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.2

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 $\nu(\theta)$ and strain $\varepsilon(\theta)$ under the constant stress are defined as:3

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

(2)

where the constant stress $\sigma = 6 GPa$, $d_1$, $d_2$, $d_3$, $Y_{zz}$ and $v_{zz}$ are elastic constant related variables.
\[
\begin{align*}
  v_{zz} &= \frac{C_{12}}{C_{22}} \\
  d_1 &= \frac{C_{11}}{C_{22}} + 1 - \frac{C_{11}C_{22} - C_{12}^2}{C_{22}C_{66}} \\
  d_2 &= -\left(2\frac{C_{12}}{C_{22}} - \frac{C_{11}C_{22} - C_{12}^2}{C_{22}C_{66}}\right) \\
  d_3 &= \frac{C_{11}}{C_{22}} \\
  Y_{zz} &= \frac{C_{11}C_{22} - C_{12}^2}{C_{22}}
\end{align*}
\] (3)

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

\[
\left\{\begin{array}{c}
  \varepsilon'(\theta) = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \left[ 1 + \varepsilon(\theta) \begin{bmatrix} 0 & 0 \\ 0 & 1 - \nu(\theta)\varepsilon(\theta) \end{bmatrix} \right] \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \\
  R' = Re^\prime(\theta)
\end{array}\right.
\] (4)

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

The strains along different directions under a constant stress of \(\sigma=6.0\ \text{GPa}\) 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:\(^4-7\)

\[
\mu_{2D} = \frac{e\hbar^3E}{(2\pi)^3k_BTm^*_e m_d(E)}
\] (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 \(E^x_1 = \Delta E/(\Delta l_x/l_{x,0})\), 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:

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

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

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

Power conversion efficiency (PCE) calculation. The upper limit of the PCE $\eta$ is estimated in the limit of 100% external quantum efficiency (EQE)$^{9-12}$ with the formula given by

$$
\eta = \frac{J_{sc} V_{oc} \beta_{FF}}{P_{solar}} = \frac{0.65(E_{d} - \Delta E_{c} - 0.3) \int_{E} P(h\omega)d(h\omega)}{\int_{0}^{\infty} P(h\omega)d(h\omega)} \tag{8}
$$

where the band-fill factor (FF) is assumed to be 0.65, $P(h\omega)$ is taken to be the AM1.5 solar energy flux (expressed in Wm$^{-2}$eV$^{-1}$) at the photon energy $h\omega$, and $E_{d}$ is the bandgap of the donor, and the $(E_{d} - \Delta E_{c} - 0.3)$ 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$^{13}$ is used for minimum energy pathway (MEP) calculations.$^{14,15}$ The adsorption energy is defined as

$$
E_a = E_{gas/\psi - P} - E_{gas} - E_{\psi - P} \tag{9}
$$

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 ψ-P can be expressed as

$$S_{\text{H}_2/\text{gas}} = \frac{r_{H_2}}{r_{\text{gas}}} = \frac{A_{H_2}}{A_{\text{gas}}} \exp\left\{-\frac{E_{b,H_2}}{k_B T}\right\} \frac{\exp\left\{-\frac{E_{b,\text{gas}}}{k_B T}\right\}}{\exp\left\{-\frac{E_{b,\text{gas}}}{k_B T}\right\}}$$

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

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig_s1.png}
\caption{(a), (b) and (c) the snapshot of ψ-P’s atomic configuration at 5ps with 300K, 500K and 800K, respectively.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig_s2.png}
\caption{Fig. S2 The orientation-dependent strain $\varepsilon(θ)$ in ψ-P corresponding the constant stress $σ=6.0$ GPa.}
\end{figure}
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\textsubscript{2} molecule adsorption on ψ-P, respectively.

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

<table>
<thead>
<tr>
<th>Elastic constants /GPa</th>
<th>Young’s Modulus /GPa</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>$C_{12}$</td>
<td>$C_{22}$</td>
</tr>
<tr>
<td>126.55</td>
<td>22.64</td>
<td>76.70</td>
</tr>
</tbody>
</table>

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

Table S3. The calculated selectivity (S) of H\textsubscript{2} relative to other gas molecules at room temperature (T=298K).

<table>
<thead>
<tr>
<th>Membranes</th>
<th>$S$(H\textsubscript{2}/CH\textsubscript{4})</th>
<th>$S$(H\textsubscript{2}/CO\textsubscript{2})</th>
<th>$S$(H\textsubscript{2}/N\textsubscript{2})</th>
<th>$S$(H\textsubscript{2}/CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ψ-P</td>
<td>10</td>
<td>15</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>Silica</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Graphene</td>
<td>10</td>
<td>19</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Hydrogenated</td>
<td>10</td>
<td>15</td>
<td>12</td>
<td>11</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Functional</th>
<th>Layer distance/Å</th>
<th>Binding energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-D2</td>
<td>3.98</td>
<td>-0.04</td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>3.95</td>
<td>-0.05</td>
</tr>
</tbody>
</table>
used to multi-layered 2D materials due to its good description of long-range vdW interactions. In addition, the optB88-vdW functional has been used in phosphorene systems 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 \( \frac{E_{\text{bilayer}} - E_{\text{single-layer}}}{N} \), \( N \) is the total number of atom for bilayer \( \psi\text{-P} \). As shown in Table S2, the differences of layer distance and binding energy calculated by DFT-D2 and optB88-vdW functional are small.

References