Supporting Information

S1. Poisson’s ratio for monolayer

The unit stress tensor along $\theta$ direction is

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{xy} & \sigma_{yy} \end{bmatrix} = \begin{bmatrix} \cos^2\theta & \cos\theta\sin\theta \\ \cos\theta\sin\theta & \sin^2\theta \end{bmatrix}$$

The relationship between $\sigma$ and the corresponding strain tensor $\varepsilon = \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ \varepsilon_{yy} \end{bmatrix}$ can be described as the stiffness tensor $C$, and for orthogonal symmetry under plane stress conditions is

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{xy} \\ \sigma_{yy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & 0 \\ C_{21} & C_{22} & 0 \\ 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ 2\varepsilon_{yy} \end{bmatrix}$$

The unit vector along $\theta$ direction is $\vec{l} = \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix}$ and the unit vector perpendicular to it is $\vec{j} = \begin{bmatrix} -\sin\theta \\ \cos\theta \end{bmatrix}$

The strain along $\theta$ direction corresponding to unit stress is

$$\varepsilon_{\parallel} = l^T \varepsilon = [\cos\theta \sin\theta] \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ \varepsilon_{yy} \end{bmatrix} = \cos^2\theta\varepsilon_{xx} + \cos\theta\sin\theta \varepsilon_{xy} + \sin^2\theta\varepsilon_{yy}$$

$$\begin{align*}
\varepsilon_{\parallel} &= \frac{C_{22}\cos^4\theta - (C_{12} + C_{21})\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}} \\
&= \frac{C_{22}\cos^4\theta - 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}}
\end{align*}$$

The strain perpendicular to $\theta$ direction corresponding to unit stress is

$$\varepsilon_{\perp} = j^T \varepsilon = [-\sin\theta \cos\theta] \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ \varepsilon_{yy} \end{bmatrix} = -\sin\theta \cos\theta \varepsilon_{xx} - \sin^2\theta \varepsilon_{xy} - \cos\theta \sin\theta \varepsilon_{yy}$$

$$\begin{align*}
\varepsilon_{\perp} &= \frac{-C_{21}\cos^4\theta + (C_{11} + C_{22})\cos^2\theta\sin^2\theta - C_{12}\sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{-\cos^2\theta\sin^2\theta}{C_{66}} \\
&= \frac{-C_{21}\cos^4\theta + 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}}
\end{align*}$$

Poisson’s ratio $\nu = -\varepsilon_{\perp}/\varepsilon_{\parallel}$

$$\begin{align*}
\varepsilon_{\parallel} &= -\frac{C_{21}\cos^4\theta + (C_{11} + C_{22})\cos^2\theta\sin^2\theta - C_{12}\sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{-\cos^2\theta\sin^2\theta}{C_{66}} \\
&= \frac{C_{22}\cos^4\theta - 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}}
\end{align*}$$

$$\begin{align*}
\varepsilon_{\parallel} &= \frac{C_{12}\cos^4\theta - (C_{11} + C_{22} - C_{12}C_{21})\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta}{C_{22}\cos^4\theta - 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta}
\end{align*}$$

In main text Equation (1),

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

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

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

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

S2. Young’s modulus for monolayer

The unit stress tensor along $\theta$ direction

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{xy} & \sigma_{yy} \end{bmatrix} = \begin{bmatrix} \cos^2\theta & \cos\theta\sin\theta \\ \cos\theta\sin\theta & \sin^2\theta \end{bmatrix}$$

The unit vector along $\theta$ direction is $\vec{l} = \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix}$ and the unit vector perpendicular to it is $\vec{j} = \begin{bmatrix} -\sin\theta \\ \cos\theta \end{bmatrix}$

The strain along $\theta$ direction corresponding to unit stress is

$$\varepsilon_{\parallel} = l^T \varepsilon = [\cos\theta \sin\theta] \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ \varepsilon_{yy} \end{bmatrix} = \cos^2\theta\varepsilon_{xx} + \cos\theta\sin\theta \varepsilon_{xy} + \sin^2\theta\varepsilon_{yy}$$

$$\begin{align*}
\varepsilon_{\parallel} &= \frac{C_{22}\cos^4\theta - (C_{12} + C_{21})\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}} \\
&= \frac{C_{22}\cos^4\theta - 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}}
\end{align*}$$

The strain perpendicular to $\theta$ direction corresponding to unit stress is

$$\varepsilon_{\perp} = j^T \varepsilon = [-\sin\theta \cos\theta] \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \\ \varepsilon_{yy} \end{bmatrix} = -\sin\theta \cos\theta \varepsilon_{xx} - \sin^2\theta \varepsilon_{xy} - \cos\theta \sin\theta \varepsilon_{yy}$$

$$\begin{align*}
\varepsilon_{\perp} &= \frac{-C_{21}\cos^4\theta + (C_{11} + C_{22})\cos^2\theta\sin^2\theta - C_{12}\sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{-\cos^2\theta\sin^2\theta}{C_{66}} \\
&= \frac{-C_{21}\cos^4\theta + 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{\cos^2\theta\sin^2\theta}{C_{66}}
\end{align*}$$

Young’s modulus $Y = \sigma/\varepsilon_{\parallel}$

$$Y_{zz} = \frac{1}{C_{11}C_{22} - C_{12}^2/C_{22}}$$

In main text Equation (2),

$$Y_{zz} = \frac{C_{22}\cos^4\theta - 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}^2/C_{22}}$$

S3. Strain corresponding to equivalent stress 1 GPa·nm

$$\varepsilon = \frac{\sigma}{Y} = 1 \text{ GPa·nm} \cdot \left( \frac{C_{22}\cos^4\theta - 2C_{12}\cos^2\theta\sin^2\theta + C_{11}\sin^4\theta + \cos^2\theta\sin^2\theta}{C_{11}C_{22} - C_{12}^2/C_{22}} \right)$$
In main text Equation (3),

\[ f = 1 \, \text{GPa} \cdot \text{nm} \cdot \frac{C_{22}}{C_{11}C_{22} - C_{12}^2} \]

S4. Bond lengths and angles of uniaxially-stressed phosphorene

Bond lengths and angles of deformed phosphorene under uniaxial stress \( \sigma = 0.8 \, \text{GPa} \cdot \text{nm} \) along different directions are summarized in Table S1. Bonds and angles are labeled according to participating atoms. For example, \( r_{AB} \) is the bond lengths between atoms A and B, while bond angle \( \angle ABC \) is the angle between bonds AB and BC. Bond lengths \( r_{AB}, r_{BC}, r_{CD} \), bond angles \( \angle ABC, \angle BCD, \angle CDE \) and the angle between the two primitive vectors \( \alpha \), are shown in Figure 1 (a-c). In unstressed phosphorene, \( r_{AB} = r_{BC} \), and \( \angle BCD = \angle CDE \). After symmetry is broken by the application of uniaxial stress, these bonds and angles are no longer equal. Under the constant stress conditions with the angle \( \theta \) changing from 0° to 90°, several geometric parameters show nonmonotonic behavior. For instance, \( \angle BCD \) decreases first and then increases, and so does angle \( \alpha \). The bond length \( r_{AB} \) and angle \( \angle CDE \) have the opposite trend – they increase first and then decrease.

Table S1. Bond lengths and bond angles in the unstressed phosphorene and phosphorene under constant uniaxial stress \( \sigma = 0.8 \, \text{GPa} \cdot \text{nm} \). The numbers in parentheses give fractional changes of the values in each column at \( \theta = 0^\circ \) and \( \theta = 90^\circ \) with respect to the unstressed case.

<table>
<thead>
<tr>
<th>( \theta (^\circ) )</th>
<th>( a_1(\text{Å}) )</th>
<th>( a_2(\text{Å}) )</th>
<th>( \alpha (^\circ) )</th>
<th>( r_{AB}(\text{Å}) )</th>
<th>( r_{BC}(\text{Å}) )</th>
<th>( r_{CD}(\text{Å}) )</th>
<th>( \angle ABC (^\circ) )</th>
<th>( \angle BCD (^\circ) )</th>
<th>( \angle CDE (^\circ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unstressed</td>
<td>3.300</td>
<td>4.623</td>
<td>90.00</td>
<td>2.222</td>
<td>2.222</td>
<td>2.259</td>
<td>95.93</td>
<td>104.14</td>
<td>104.14</td>
</tr>
<tr>
<td>0</td>
<td>3.329</td>
<td>4.595</td>
<td>90.00</td>
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<td>2.229</td>
<td>2.257</td>
<td>95.68</td>
<td>103.89</td>
<td>103.89</td>
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<tr>
<td></td>
<td>(0.9%)</td>
<td>(-0.6%)</td>
<td>(0.3%)</td>
<td>(0.3%)</td>
<td>(-0.1%)</td>
<td>(0.7%)</td>
<td>(-0.2%)</td>
<td>(-0.2%)</td>
<td>(-0.2%)</td>
</tr>
<tr>
<td>10</td>
<td>3.328</td>
<td>4.600</td>
<td>89.72</td>
<td>2.229</td>
<td>2.228</td>
<td>2.258</td>
<td>96.59</td>
<td>103.77</td>
<td>104.17</td>
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<tr>
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<td>(-0.2%)</td>
<td>(0.3%)</td>
<td>(-0.5%)</td>
<td>(1.3%)</td>
<td>(1.3%)</td>
<td></td>
</tr>
</tbody>
</table>
S5. Band gap

The stress tensor is\[ \sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{xy} & \sigma_{yy} \end{bmatrix} \] and the strain tensor is\[ \varepsilon = \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{xy} \end{bmatrix} \] in non-rotated system, aligned with the lattice vectors of the 2D crystal.

Band gap and strain has linear relationship as\[ E_g(\theta, \sigma) = E_g(\theta, 0) + A\varepsilon_{xx} + B\varepsilon_{xy} + C\varepsilon_{yy} \] (S1)

Here, \( \varepsilon_{xx}, \varepsilon_{xy}, \) and \( \varepsilon_{yy} \) are components of the strain tensor in non-rotated system, rotated counter clockwise by an angle \( \theta \) w.r.t. non-rotated one, the corresponding stress tensor \( \tilde{\sigma} \) in non-rotated system is given by:
\[
\tilde{\sigma} = R \sigma R^T = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{xy} & \sigma_{yy} \end{bmatrix}
\]

where \( R = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \) is rotation matrix to transform from rotated to non-rotated system.

Rotation matrix to transform from rotated to non-rotated system is\[ R = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \]

In rotated system, the relationship between stress and strain is\[ \begin{cases} 
\sigma_{xx} = C_{11} \varepsilon_{xx} + C_{12} \varepsilon_{xy} \\
\sigma_{xy} = C_{12} \varepsilon_{xx} + C_{22} \varepsilon_{yy} \\
\varepsilon_{xx} = \frac{C_{22} \sigma_{xx} - C_{12} \sigma_{xy}}{C_{11} C_{22} - C_{12}^2} \\
\varepsilon_{yy} = \frac{C_{11} \sigma_{yy} - C_{12} \sigma_{xy}}{C_{11} C_{22} - C_{12}^2} \\
\varepsilon_{xy} = \frac{C_{11} \sigma_{xy}}{2 C_{66}} - \frac{C_{12} \sigma_{xy}}{2 C_{66}} \end{cases} \] (S2)

Substituting Equation (S2) into Equation (S1), we can get the band gap of phosphorene under uniaxial stress \( \sigma \) applied along arbitrary direction \( \theta \):

\[
E_g(\theta, \sigma) = E_g(\theta, 0) + \frac{C_{22} \cos^2 \theta - C_{12} \sin^2 \theta}{C_{11} C_{22} - C_{12}^2} \sigma + \frac{C_{11} \sin^2 \theta - C_{12} \cos^2 \theta}{C_{11} C_{22} - C_{12}^2} \sigma^2
\]

Three parameters \( h_1, h_2, h_3 \) can be got by fitting results from DFT calculation.

Figure S1. Computed band gap values based on HSE06 method and fitting line for monolayer phosphorene uniaxially stressed in-plane along different directions, at \( \sigma=0.8 \) GPa nm. The base value of 1.60 eV represents the gap for unstrained material.

S6. Effective mass

Based on the quadratic \( E = \frac{\hbar^2 k^2}{2m} \) dispersion relationship, the energy surface near the CBM and VBM can be described as elliptic parabolic surface equation:

\[
E = ak_x^2 + bk_y^2 \approx ak^2 \cos^2 \theta + bk^2 \sin^2 \theta
\]

and its second derivative is \( \frac{\partial^2 E}{\partial k^2} = 2ak^2 \cos \theta + 2bk^2 \sin \theta \).

The effective mass is related with the second derivative of energy:

\[
m^* = \frac{\hbar^2}{2\frac{\partial^2 E}{\partial k^2}} = \frac{\hbar^2}{2ak^2 \cos^2 \theta + 2bk^2 \sin^2 \theta}
\]

In the main text Equation (S5), \( m_{xz} = \frac{\hbar^2}{2a} m_{dc} = \frac{\hbar^2}{2b} \).
**Figure S2.** Effective masses based on HSE06 method of (a) electrons and (b) holes in phosphorene under uniaxial stress 0.8 GPa nm along different directions. For electrons, the effective mass remains nearly unchanged with stress (purple line). For holes, effective mass is sensitive to stress and its direction \( \theta \), as shown for unstressed phosphorene (red), and phosphorene with stress of applied along \( \theta = 0^\circ \) (green), and \( \theta = 90^\circ \) (blue).

### S7. Young's modulus for bulk

Bulk phosphorus is orthotropic materials, its stiffness tensor can be written as:

\[
\sigma_i = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\]

Young's modulus along zigzag direction

\[
Y_{zz} = \frac{\sigma_1}{\varepsilon_1}
\]

\[
= \frac{C_{11}C_{22}C_{33} + 2C_{12}C_{23}C_{13} - C_{22}C_{11} - C_{12}C_{22} - C_{13}C_{23}}{C_{22}C_{33} - C_{23}^2}
\]

Young's modulus along armchair direction

\[
Y_{ac} = \frac{\sigma_2}{\varepsilon_2}
\]

\[
= \frac{C_{11}C_{22}C_{33} + 2C_{12}C_{23}C_{13} - C_{22}C_{11} - C_{12}C_{22} - C_{13}C_{23}}{C_{11}C_{33} - C_{13}^2}
\]