Supporting Information

S1. Poisson's ratio for monolayer

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

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

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

The strain along θ direction corresponding to unit stress is

$$\varepsilon_{\parallel} = \vec{i}^T \varepsilon \vec{i} = [cos\theta \quad sin\theta] \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} \\ \varepsilon_{xy} & \varepsilon_{yy} \end{bmatrix} \begin{bmatrix} cos\theta \\ sin\theta \end{bmatrix}$$

$$= \frac{C_{22}cos^4\theta - (C_{12} + C_{21})cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{cos^2\theta sin^2\theta}{C_{66}}$$

$$= \frac{C_{22}cos^4\theta - 2C_{12}cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}^2} + \frac{cos^2\theta sin^2\theta}{C_{66}}$$

The strain perpendicular to θ direction corresponding to unit stress is

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

$$= \frac{-C_{21}cos^4\theta + (C_{11} + C_{22})cos^2\theta sin^2\theta - C_{12}sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{-cos^2\theta sin^2\theta}{C_{66}}$$

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

$$= \frac{\frac{-C_{21}cos^4\theta + (C_{11} + C_{22})cos^2\theta sin^2\theta - C_{12}sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{-cos^2\theta sin^2\theta}{C_{66}}}{\frac{C_{22}cos^4\theta - 2C_{12}cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}^2} + \frac{cos^2\theta sin^2\theta}{C_{66}}}$$

$$= \frac{C_{12}cos^4\theta - \left(C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}}\right)cos^2\theta sin^2\theta + C_{12}sin^4\theta}{C_{22}cos^4\theta - (2C_{12} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}})cos^2\theta sin^2\theta + C_{11}sin^4\theta}$$

In main text Equation (1),

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

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

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

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

S2. Young's modulus for monolayer

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

The strain along θ direction corresponding to unit stress is

$$\varepsilon_{\parallel} = \vec{i}^T \varepsilon \vec{i} = [cos\theta \quad sin\theta] \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} \\ \varepsilon_{xy} & \varepsilon_{yy} \end{bmatrix} \begin{bmatrix} cos\theta \\ sin\theta \end{bmatrix}$$

$$= \frac{C_{22}cos^4\theta - (C_{12} + C_{21})cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}C_{21}} + \frac{cos^2\theta sin^2\theta}{C_{66}}$$

$$= \frac{C_{22}cos^4\theta - 2C_{12}cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}^2} + \frac{cos^2\theta sin^2\theta}{C_{66}}$$

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

$$= \frac{1}{\frac{C_{22}cos^4\theta - 2C_{12}cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}^2} + \frac{cos^2\theta sin^2\theta}{C_{66}}}$$

In main text Equation (2),

$$Y_{zz} = (C_{11}C_{22} - C_{12}^2)/C_{22}$$

S3. Strain corresponding to equivalent stress 1 GPa·nm

$$\varepsilon = \frac{\sigma}{Y} = 1\ GPa \cdot nm \cdot \left(\frac{C_{22}cos^4\theta - 2C_{12}cos^2\theta sin^2\theta + C_{11}sin^4\theta}{C_{11}C_{22} - C_{12}^2} + \frac{cos^2\theta sin^2\theta}{C_{66}}\right)$$

In main text Equation (3),

$$f = 1\ GPa \cdot nm \cdot \frac{C_{22}}{C_{11}C_{22} - C_{12}^2}$$

S4. Bond lengths and angles of uniaxially-stressed phosphorene

Bond lengths and angles of deformed phosphorene under uniaxial stress σ = 0.8GPa·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 ∠ABC is the angle between bonds AB and BC. Bond lengths r_{AB}, r_{BC}, r_{CD}, bond angles ∠ABC, ∠BCD, ∠CDE and the angle between the two primitive vectors α, are shown in Figure 1 (a-c). In unstressed phosphorene, r_{AB} = r_{BC}, and ∠BCD = ∠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 θ changing from 0° to 90°, several geometric parameters show nonmonotonic behavior. For instance, ∠BCD decreases first and then increases, and so does angle α. The bond length r_{AB} and 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 σ=0.8GPa·nm. The numbers in parentheses give fractional changes of the values in each column at θ = 0° and θ = 90° with respect to the unstressed case.

θ(°)	a_1(Å)	a_2(Å)	α(°)	r_{AB}(Å)	r_{BC}(Å)	r_{CD}(Å)	$\angle ABC$(°)	$\angle BCD$(°)	$\angle CDE$(°)
Unstressed	3.300	4.623	90.00	2.222	2.222	2.259	95.93	104.14	104.14
0	3.329	4.595	90.00	2.229	2.229	2.257	96.58	103.89	103.89
	(0.9%)	(-0.6%)		(0.3%)	(0.3%)	(-0.1%)	(0.7%)	(-0.2%)	(-0.2%)
10	3.328	4.600	89.72	2.229	2.228	2.258	96.59	103.77	104.17
20	3.327	4.612	89.50	2.229	2.227	2.257	96.57	103.68	104.41
30	3.326	4.628	89.32	2.231	2.227	2.258	96.53	103.66	104.60
40	3.327	4.648	89.11	2.232	2.226	2.258	96.53	103.63	104.87
50	3.324	4.673	88.86	2.232	2.225	2.261	96.45	103.72	105.31
60	3.315	4.706	88.68	2.230	2.223	2.262	96.23	103.87	105.72
70	3.300	4.742	88.77	2.226	2.219	2.264	95.88	104.24	105.98
80	3.286	4.772	89.25	2.221	2.217	2.266	95.55	104.84	105.92
90	3.280	4.784	90.00	2.217	2.217	2.266	95.44	105.51	105.51
	(-0.6%)	(3.5%)		(-0.2%)	(-0.2%)	(0.3%)	(-0.5%)	(1.3%)	(1.3%)

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 $\varepsilon = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} \\ \varepsilon_{xy} & \varepsilon_{yy} \end{bmatrix}$

Band gap and strain has linear relationship as

$$E_g(\theta,\sigma) = E_g(\theta,0) + A\varepsilon_{xx} + B\varepsilon_{xy} + C\varepsilon_{yy} \quad \text{(S1)}$$

Here, ε_{xx}, ε_{xy}, and ε_{yy} are components of the strain tensor in non-rotated system, aligned with the lattice vectors of the 2D crystal.

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

For uniaxial stress $\sigma' = \begin{bmatrix} \sigma & 0 \\ 0 & 0 \end{bmatrix}$ along the x' axis in a system rotated counterclockwise by an angle θ w.r.t. non-rotated one, the corresponding stress tensor σ in non-rotated system is given by:

$$\sigma = R\sigma' R^T = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{xy} & \sigma_{yy} \end{bmatrix}$$

$$= \begin{bmatrix} cos\theta & -sin\theta \\ sin\theta & cos\theta \end{bmatrix} \begin{bmatrix} \sigma & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} cos\theta & sin\theta \\ -sin\theta & cos\theta \end{bmatrix}$$

$$= \begin{bmatrix} cos^2\theta & cos\theta sin\theta \\ cos\theta sin\theta & sin^2\theta \end{bmatrix} \sigma$$

In non-rotated system, the relationship between stress and strain is

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

$$\begin{cases} \varepsilon_{xx} = \dfrac{C_{22}\sigma_{xx} - C_{12}\sigma_{yy}}{C_{11}C_{22} - C_{12}^2} = \dfrac{C_{22}cos^2\theta - C_{12}sin^2\theta}{C_{11}C_{22} - C_{12}^2}\sigma \\ \varepsilon_{yy} = \dfrac{C_{11}\sigma_{yy} - C_{12}\sigma_{xx}}{C_{11}C_{22} - C_{12}^2} = \dfrac{C_{11}sin^2\theta - C_{12}cos^2\theta}{C_{11}C_{22} - C_{12}^2}\sigma \\ \varepsilon_{xy} = \dfrac{\sigma_{xy}}{2C_{66}} = \dfrac{cos\theta sin\theta}{2C_{66}}\sigma \end{cases} \quad \text{(S2)}$$

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

$$E_g(\theta,\sigma) = E_g(\theta,0) + A\frac{C_{22}cos^2\theta - C_{12}sin^2\theta}{C_{11}C_{22} - C_{12}^2}\sigma + B\frac{cos\theta sin\theta}{2C_{66}}\sigma + C\frac{C_{11}sin^2\theta - C_{12}cos^2\theta}{C_{11}C_{22} - C_{12}^2}\sigma$$

$$= E_g(\theta,0) + \left(\frac{AC_{22} - CC_{12}}{C_{11}C_{22} - C_{12}^2}cos^2\theta + \frac{B}{2C_{66}}cos\theta sin\theta + \frac{CC_{11} - AC_{12}}{C_{11}C_{22} - C_{12}^2}sin^2\theta\right)\sigma$$

$$= E_g(\theta,0) + \sigma\left(h_1cos^2\theta + h_2cos\theta sin\theta + h_3sin^2\theta\right)$$

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

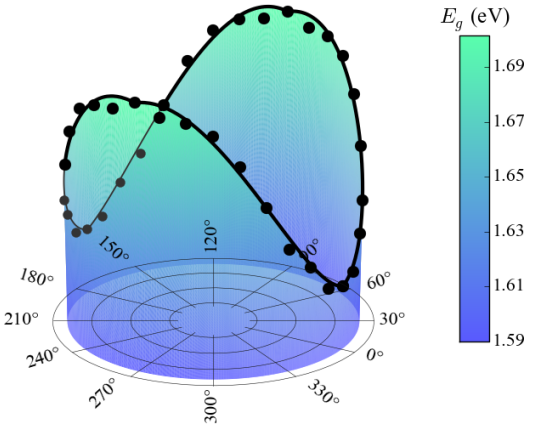

Figure S1. Computed band gap values based on HSE06 method and fitting line for monolayer phosphorene uniaxially stressed in-plane along different directions, at σ=0.8 GPa·nm. The base value of 1.60 eV represents the gap for unstrained material.

S6. Effective mass

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

$$E = ak_x^2 + bk_y^2 = ak^2cos^2\theta + bk^2sin^2\theta$$

and its second derivative is $\dfrac{\partial^2 E}{\partial k^2} = 2acos^2\theta + 2bsin^2\theta$.

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

$$m^* = \frac{\hbar^2}{\dfrac{\partial^2 E}{\partial k^2}} = \frac{\hbar^2}{2acos^2\theta + 2bsin^2\theta}$$

In the main text Equation (5), $m_{zz}^* = \dfrac{\hbar^2}{2a}, m_{ac}^* = \dfrac{\hbar^2}{2b}$.

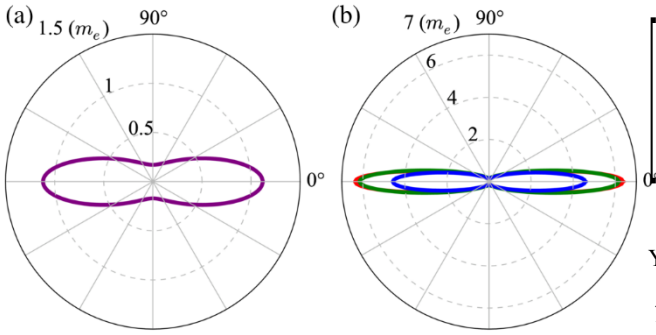

Figure S2. Effective masses based on HSE06 method of (a) electrons and (b) holes in phosphorene under uniaxial stress 0.8 GPa·nm along different directions. For electrons, the effective mass remains nearly unchanged with stress (purple line). For holes, effective mass is sensitive to stress and its direction θ, as shown for unstressed phosphorene (red), and phosphorene with stress of applied along $\theta = 0°$ (green), and $\theta = 90°$ (blue).

S7. Young's modulus for bulk

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

$$\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{bmatrix}$$

Young's modulus along zigzag direction

$$Y_{zz} = \sigma_1/\varepsilon_1$$

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

Young's modulus along armchair direction

$$Y_{ac} = \sigma_2/\varepsilon_2$$

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