Supplementary Information

δ-phosphorene: a two dimensional material with high negative Poisson's ratio Haidi Wang,¹ Xingxing Li,^{1,2} Pai Li,¹ and Jinlong Yang^{1,2*}

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Equation S1:

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

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

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

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

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

Equation S2:

The strained structures are obtained by the following equation.

$$\begin{cases} \varepsilon(\theta) = \sigma \left(\cos^4 \theta + d_2 \cos^2 \theta \sin^2 \theta + d_3 \sin^4 \theta \right) \\ \varepsilon'(\theta) = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} 1 + \varepsilon(\theta) & 0 \\ 0 & 1 - \varepsilon(\theta)\nu(\theta) \end{bmatrix} \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \\ R' = R\varepsilon'(\theta) \end{cases}$$

where σ is the constant stress applied along the different directions (θ). According to the $E(\theta)$, $\mathbf{v}(\theta)$ and $\mathbf{\varepsilon}(\theta)$, the strain matrix $\varepsilon'(\theta)$ and lattice matrix R' can be calculated.



Fig. S1. Phonon bands of δ -P at different uniaxial strains.



Fig. S2. The wireframe sketch of δ -P (right panel), BP (left panel), and locally enlarged structure δ -P (bottom panel).



Fig. S3. Four stacking structures of double-layered δ -P. (a, b, c and d) Top views (upper panel) and side views (lower panel) of AA-, AB'-, AC-, AB-stacking, respectively.

In Fig. S3, a 2×2 supercell is adopted for the top and side views. AB-stacking is the most favorable configuration for double-layered δ -P, being 16.7, 13.6 and 26.8 meV per atom lower than that of AA-, AB'-, and AC-stacking, respectively.

Fig. S4. (a) The band structure, dash-dotted line indicates the Fermi level. (b) The charge density corresponding to the valance band (yellow) and conduction band (red). (c) The total and projected DOS of primitive δ -P.

In Fig. S4, the band structure and associated density of states (DOS) for primitive δ -P is shown. Consistent with previous study,¹ our results suggest that δ -P is a direct-gap semiconductor with a band gap of 0.50 eV, with the valence band maximum (VBM) and conduction band minimum (CBM) all located at Γ point. Meanwhile, both states are mainly contributed by 3*p* orbitals of P atoms. To better understand the electronic structure of δ -P, we also calculated the charge density of valence and conduction bands. As plotted in Fig. S4(b), a noticeable overlap can be found along the *x* direction for valence band, while along the *y* direction for conduction band respectively. This will result in different response of valance and conduction bands under external stress as we discussed later.

Fig. S5 (a) Band structure of δ -P under a stress of σ = 7.0 GPa in various directions. (b) Band gaps and spline fitting curve. (c) A color map of direct semiconductor (D) to indirect semiconductor (I) transition, and semiconductor to metal (M) transition tunable by changing the applied stress direction.

In Fig. S5, electronic structure of δ -P in response to external tensile stress is presented. Under a small uniaxial stress of σ =1.0 GPa, the band gap of δ -P changes little. To adapt the different electronic device applications, a wide band gap engineering is desired. So we try to use a relatively large stress of σ =7.0 GPa. Such a stress is realizable, since a previous study² showed that a maximum stress of about 14 GPa is accessible for graphene. As is shown in Fig. S5(a), by gradually changing the stress direction, the VBM position moves up firstly when the stress direction angle is smaller than 40°, then it declines, while the CBM presents an opposite change. To gain a full knowledge of band gap variation, we plot the band gap vs. angle relationship in Fig. S5(b). It's obvious that the band gap strongly depends on the applied stress direction, which further

demonstrates the strong anisotropy of δ -P. In detail, the band gap ranges from 0.0 to 0.467 eV with a maximum band gap along the *y* direction and a zero band gap around θ =45°, becoming metallic. As a consequence, four band gap valleys are obtained. The calculations show that a semiconductormetal (M) transition can be observed by only changing the stress direction, and a direct semiconductor (D) to indirect semiconductor (I) transition can also be realized. A schematic light disk in Fig. S5 (c) clearly illustrate a 'MID' loop formed when the stress direction scans from 0° to 360°. It should be pointed out that these are DFT results, and the predictions are only qualitative.

Table S1. The calculated elastic stiffness constants for mono-layered δ -P from PyGEC.

unit	elastic stiffness constants				
	C ₁₁	C ₂₂	C ₆₆	C ₁₂	
GPa	88.64	149.21	24.50	-23.71	

In a 2D system, the stress calculated from the DFT has to be modified to avoid the force being averaged over the entire simulation cell including the vacuum slab³. In order to compare Young's modulus among different layered-structures, the length along z direction is rescaled by αh , where *h* is mean interlayer distance and α denotes the number of layer.

System	Stacking order	Lattice constants/Å		لم ر م	$\Delta E/m a V/atom$	
		а	b	H/A		
Mono	А	5.50	5.40	/	0.00	
Double	AB	5.49	5.40	5.09	-49.5	
Triple	ABA	5.48	5.40	5.10	-66.8	
Quadruple	ABAB	5.47	5.40	5.19	-75.4	
Bulk	AB	5.46	5.39	5.11	-101.4	

Table S2. The calculated lattice constants a and b, mean interlayer distance h, and bonding energies ΔE of layered and bulk structure for δ -P.

Table S3. The calculated elastic stiffness constants for bulk δ -P.

unit	elastic stiffness constants								
	C ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₁₂	C ₁₃	C ₂₃
GPa	95.76	151.82	65.06	25.32	24.58	27.77	-17.09	14.77	11.82

References

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