Supplementary Material for

Two-dimensional Phosphorus Carbide as Promising Anode Materials for Lithium-ion Batteries

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1. *Kinetic and thermal stability calculation*

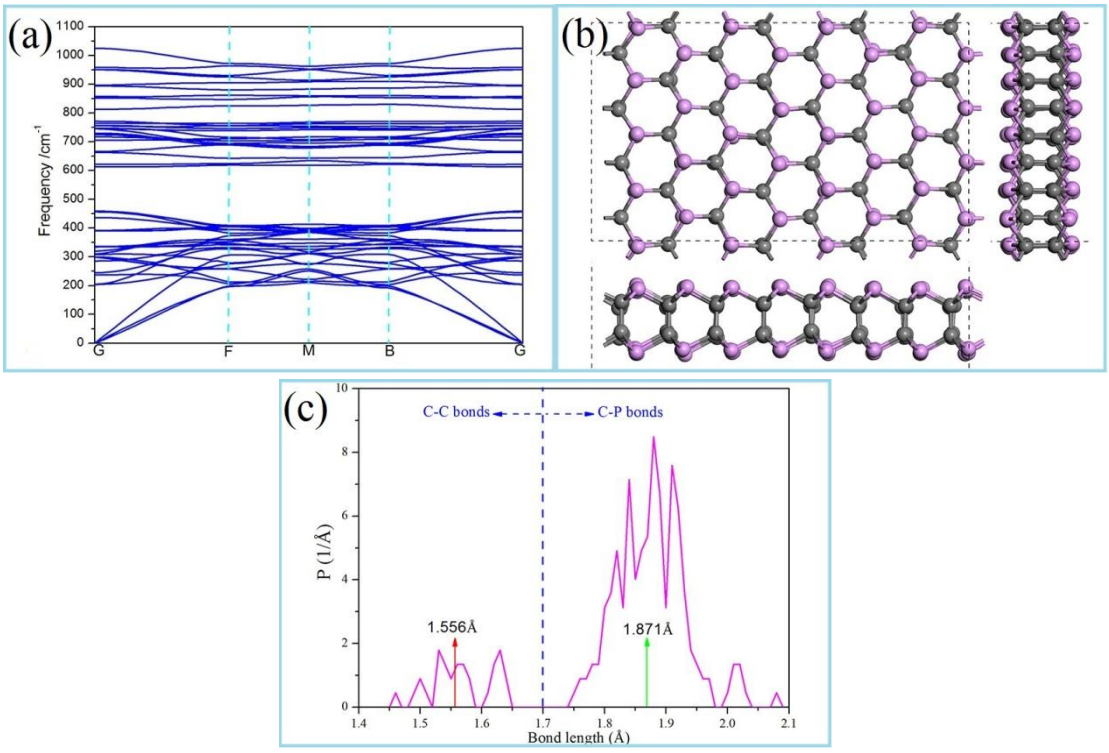


Figure s1. (a) The phonon dispersion curves of monolayer γ-PC. **(b)** Top and side

views of AIMD simulations for monolayer γ-PC at T=500K. **(c)** The distribution of bond length after AIMD simulation. The red and green arrows stand for the C-C and C-P bond length at T=0K, respectively.

2. *Mechanical properties calculation*

The calculations of mechanical properties of monolayer γ-PC are listed as follows. For 2D materials, the elastic constants and moduli can be calculated from Hooke's law under plane-stress condition,[1, 2]

$$\begin{bmatrix}\sigma_{xx}\\ \sigma_{yy}\\ \sigma_{xy}\end{bmatrix}=\frac{1}{1-\nu_{xy}\nu_{yx}}\begin{bmatrix}E_x & \nu_{yx}E_x & 0\\ \nu_{xy}E_y & E_y & 0\\ 0 & 0 & G_{xy}\left(1-\nu_{xy}\nu_{yx}\right)\end{bmatrix}\begin{bmatrix}\varepsilon_{xx}\\ \varepsilon_{yy}\\ 2\varepsilon_{xy}\end{bmatrix}=\begin{bmatrix}C_{11} & C_{12} & 0\\ C_{21} & C_{22} & 0\\ 0 & 0 & C_{66}\end{bmatrix}\begin{bmatrix}\varepsilon_{xx}\\ \varepsilon_{yy}\\ 2\varepsilon_{xy}\end{bmatrix} \quad (1)$$

$$E_x=\frac{C_{11}C_{22}-C_{12}C_{21}}{C_{22}},\ E_y=\frac{C_{11}C_{22}-C_{12}C_{21}}{C_{11}},\ \nu_{xy}=\frac{C_{21}}{C_{22}},\ \nu_{yx}=\frac{C_{12}}{C_{11}},\ G_{xy}=C_{66} \quad (2)$$

where $E_i=\frac{\sigma_i}{\varepsilon_i}$ $(i=x,y)$ represents the Young's modulus along the axis of i, $\nu_{ij}=-\frac{d\varepsilon_j}{d\varepsilon_i}$ is the Poisson's ratio with tensile strain applied in the direction i and the response strain in the direction j.

The relationship between the strain energy and the applied strains can be expressed as formula (3):

$$E_s=a_1\varepsilon_{xx}^2+a_2\varepsilon_{yy}^2+a_3\varepsilon_{xx}\varepsilon_{yy}+a_4\varepsilon_{xy}^2 \quad (3)$$

Where $E_s=E(\varepsilon)-E_0$ is the strain energy calculated from the energy difference between strained and no strained structures.

The elastic stiffness constants can be calculated with equation (4):

$$C_{ij} = \frac{1}{A_0 d_0}\left(\frac{\partial E_s^2}{\partial \varepsilon_i \partial \varepsilon_j}\right) \tag{4}$$

where $i, j = xx, yy, xy$, A_0 is the area of the structure in xy plane and d_0 is the effective thickness of the structure.

From formula (3) and (4), we derive the Young's moduli, shear moduli and Poisson's ratios for the structures as a function of a_i as formula (5):

$$E_x = \frac{4a_1a_2 - a_3^2}{2a_2A_0d_0},\ E_y = \frac{4a_1a_2 - a_3^2}{2a_1A_0d_0},\ G_{xy} = \frac{2a_4}{A_0d_0},\ v_{xy} = \frac{a_3}{2a_2},\ v_{yx} = \frac{a_3}{2a_1} \tag{5}$$

The Young's modulus along an arbitrary direction can be calculated from the formula (6)[2]:

$$\frac{1}{E_\varphi} = S_{11}\cos^4\varphi + \left(2S_{12} + S_{66}\right)\cos^2\varphi\sin^2\varphi + S_{22}\sin^4\varphi \tag{6}$$

where $\varphi \in [0, 2\pi]$, is the angle of an arbitrary direction from +x axis, E_φ is the Young's modulus along φ direction, S_{ij} represents elastic compliance constants, which can be calculated from formula (7):

$$S_{11} = \frac{C_{22}}{C_{11}C_{22} - C_{12}^2},\ S_{22} = \frac{C_{11}}{C_{11}C_{22} - C_{12}^2},\ S_{12} = \frac{-C_{12}}{C_{11}C_{22} - C_{12}^2},\ S_{66} = \frac{1}{C_{66}} \tag{7}$$

(i) We calculated the Young's modulus, shear modulus and Poisson's ratios firstly. The strain along armchair or zigzag direction ranged from -0.02 to 0.02 with an increasing step of 0.005. Then, the corresponding energy changes were collected and plotted in figure s3 (a). Through quadric surface fitting the strain-energy curved surface, the

coefficients a_1, a_2, a_3 in formula (3) can be determined. a_4 can be calculated by parabolic fitting the energy&shear strains points plotted in figure s3 (b). From formula (5), the Young's modulus, shear modulus and Poisson's ratios can be determined.

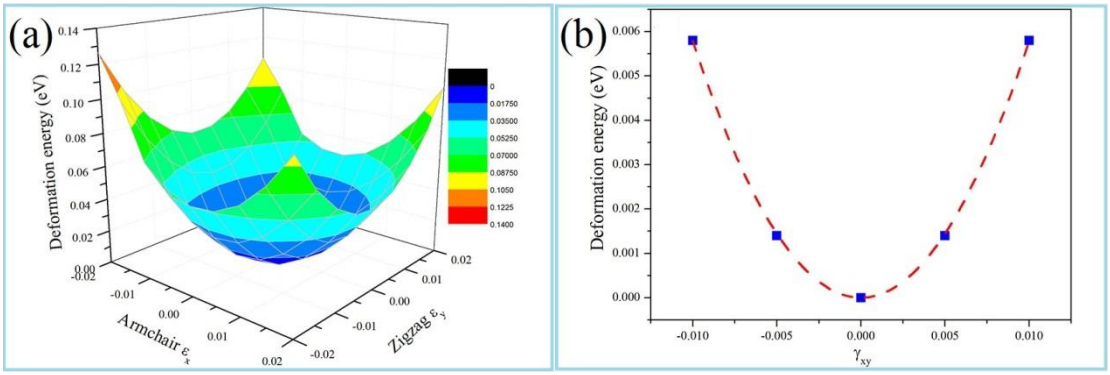


Figure s2. (a) The three-dimensional energy curved surface with corresponding strains. **(b)** The energy difference between the relaxed and shear strained monolayer γ-PC.

(ii) Through formula (3), (4) and (7), we can get the elastic compliance constants S_{ij} and then put them into the formula (6) to gain the relationship between Young's modulus and directions.

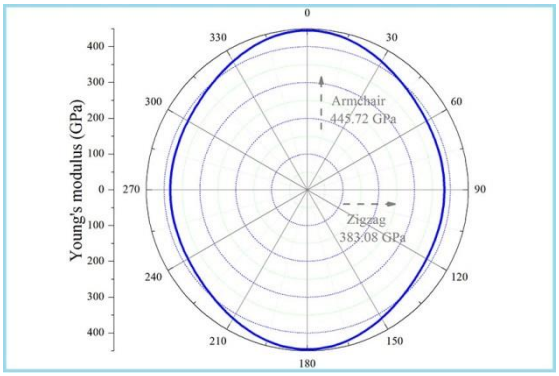


Figure s3. The direction dependence of Young's modulus for monolayer γ-PC.

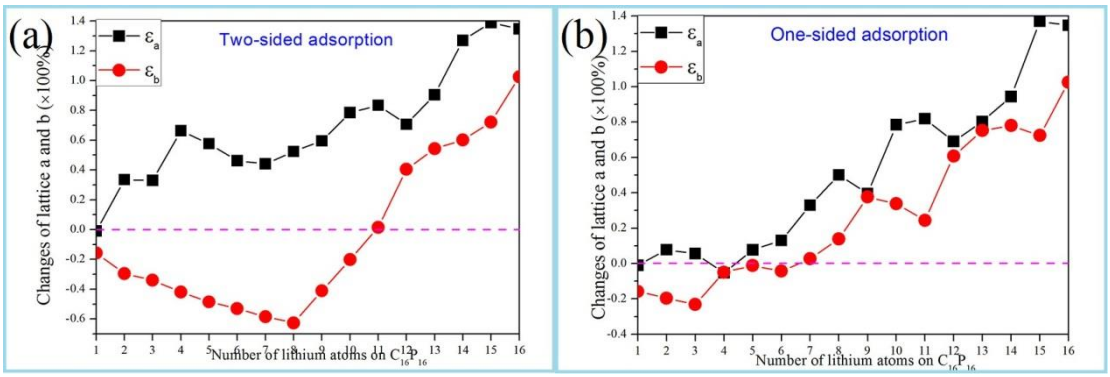


Figure s4. The lattice changes of the lithiation $P_{16}C_{16}$ for **(a)** two-sided adsorption and **(b)** one-sided adsorption with corresponding numbers of adsorbed Li atoms.

3. *Conductivity calculation*

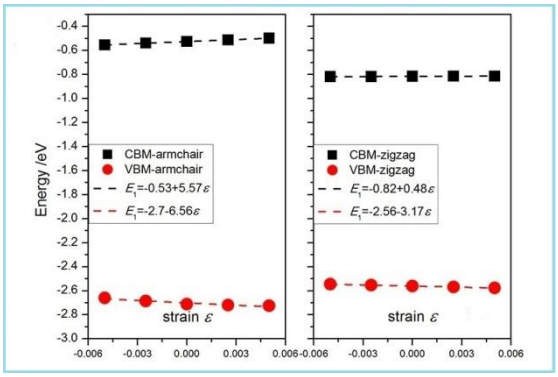


Figure s5. Energy shift of CBM and VBM for monolayer γ-PC with respect to the lattice dilation and compression along the zigzag and armchair directions, respectively.

4. *Capacity calculation*

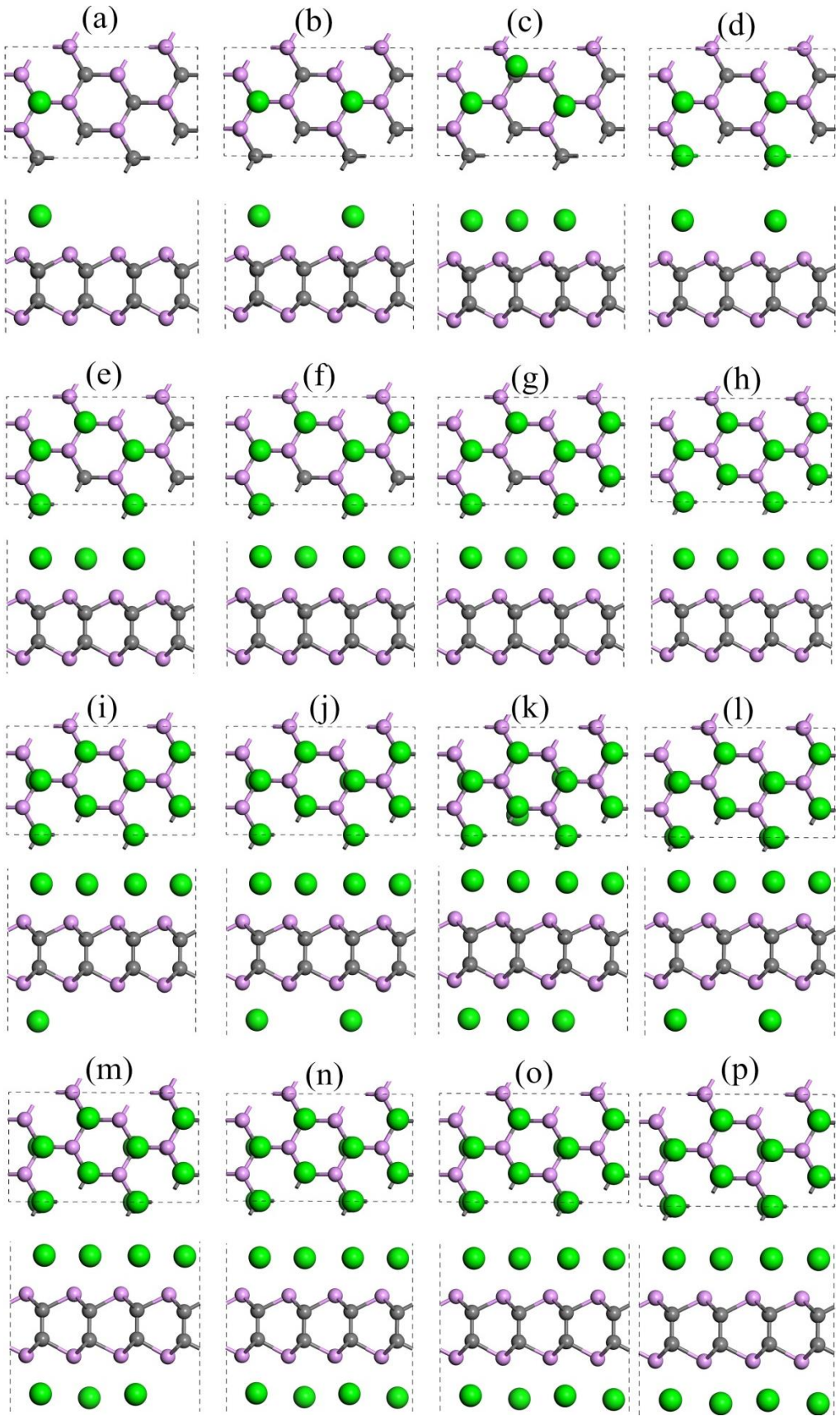


Figure s6. Top and side views of the most stable structures at different x values of

$P_{16}C_{16}Li_x$, the x values are 1, 2, 3…16 for **(a)**, **(b)**, **(c)**….**(p)**, respectively. Noted that, the Li adsorption starts from one-sided filling (a~h) to two-sided storing (i~p).

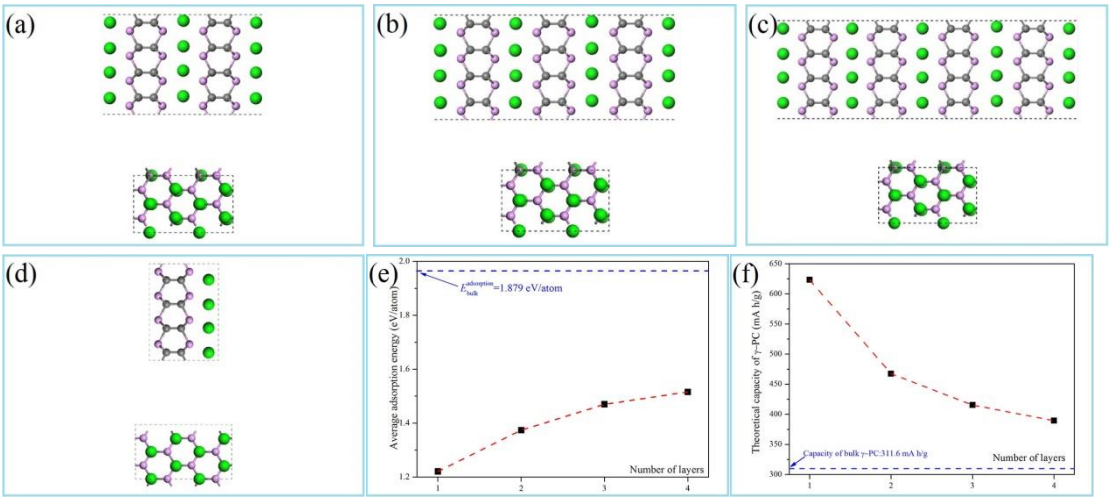
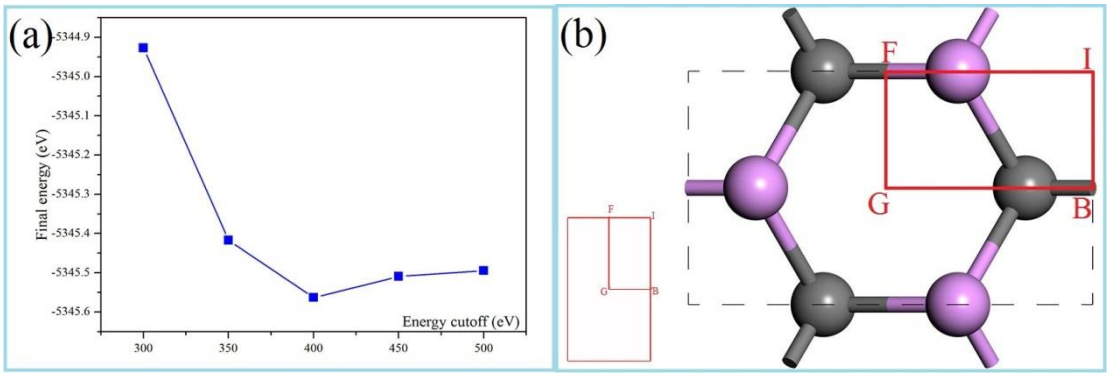


Figure s7. Side and top views of fully adsorbing for Li onto **(a)** two-layers, **(b)** three layers, **(c)** four layers and **(d)** bulk γ-PC in AA stacking with corresponding **(e)** average adsorption energy and **(f)** capacity.

5. *Setting of calculation*



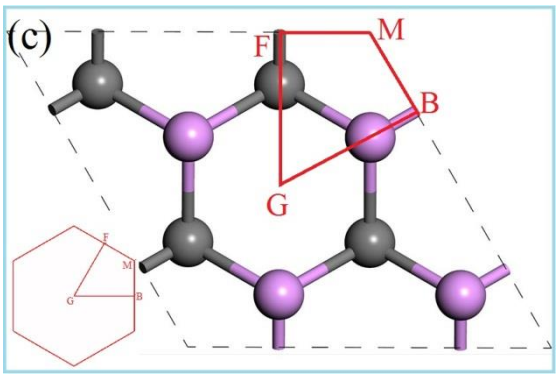


Figure s8. **(a)** The total energy of $P_{16}C_{16}$ at different cutoff energy when Monkhorst-Pack K-point mesh is set as 3×4×1. The integration path in Brillouin zone used for **(b)** electronic structure calculations and **(c)** phonon dispersion calculations.

References

1. Zhou, J.; Huang, R., Internal lattice relaxation of single-layer graphene under in-plane deformation. *J. Mech. Phys. Solids* 2008, 56, 1609-1623.

2. Wei, Q.; Peng, X., Superior mechanical flexibility of phosphorene and few-layer black phosphorus. *Appl. Phys. Lett.* 2014, 104, 372-98.