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,

\[
\begin{align*}
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{xy}
\end{bmatrix} &= \frac{1}{1-v_{xy}v_{yx}} \begin{bmatrix}
E_x & v_{yx}E_y & 0 \\
v_{xy}E_y & E_y & 0 \\
0 & 0 & G_{xy}(1-v_{xy}v_{yx})
\end{bmatrix} \begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
2\varepsilon_{xy}
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & 0 \\
C_{21} & C_{22} & 0 \\
0 & 0 & C_{66}
\end{bmatrix} \begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
2\varepsilon_{xy}
\end{bmatrix},
\end{align*}
\]

(1)

\[
E_x = \frac{C_{11}C_{22} - C_{12}C_{21}}{C_{22}}, \quad E_y = \frac{C_{11}C_{22} - C_{12}C_{21}}{C_{11}}, \quad v_{xy} = \frac{C_{21}}{C_{11}}, \quad v_{yx} = \frac{C_{12}}{C_{11}}, \quad G_{xy} = C_{66}
\]

(2)

where \( E_i = \frac{\sigma_i}{\varepsilon_i} \) (\( i = x, y \)) represents the Young’s modulus along the axis of \( i \), \( v_{ij} = -\frac{d\varepsilon_j}{d\varepsilon_i} \) 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):

\[
E_s = a_1\varepsilon_{xx}^2 + a_2\varepsilon_{yy}^2 + a_3\varepsilon_{xx}\varepsilon_{yy} + a_4\varepsilon_{xy}^2
\]

(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):

\[
C_{ij} = \frac{1}{A_0 d_0} \left( \frac{\partial E_i^2}{\partial E_j} \right) \tag{4}
\]

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):

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

The Young’s modulus along an arbitrary direction can be calculated from the formula (6):

\[
\frac{1}{E_\phi} = S_{11} \cos^4 \phi + (2S_{12} + S_{66}) \cos^2 \phi \sin^2 \phi + S_{22} \sin^4 \phi \tag{6}
\]

where \( \phi \in [0, 2\pi] \), is the angle of an arbitrary direction from +x axis, \( E_\phi \) is the Young’s modulus along \( \phi \) direction, \( S_y \) represents elastic compliance constants, which can be calculated from formula (7):

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

(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 $\gamma$-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 $\gamma$-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
