*Supporting Information for*

# Doping-Stabilized Two-Dimensional Black Phosphorus

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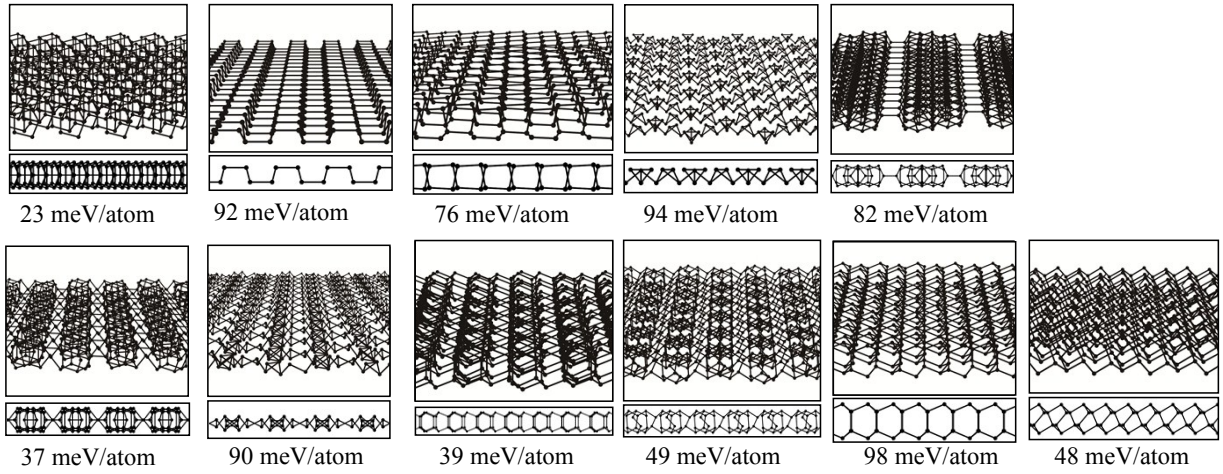


***Fig. S1***. Relaxed structures of considered low-energy monolayer phosphorus allotropes. The number below each structure is the corresponding energy with respect to the $\alpha$-P. Top is for the front view and bottom for the side view.

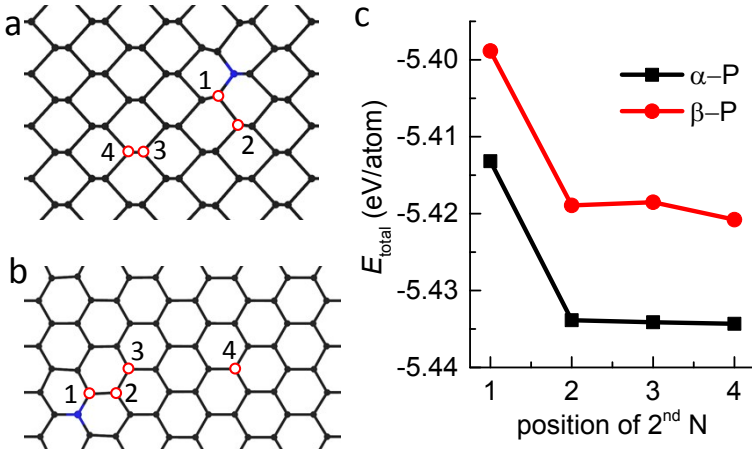


***Fig. S2***. Interaction between two substituted N atoms in 2D P. (a,b) Considered positions of the 2nd N atom relative to the 1st substituted N atom in the $\alpha$- and $\beta$-P. (c) System's total energy as a function of the position of the 2nd N atom.

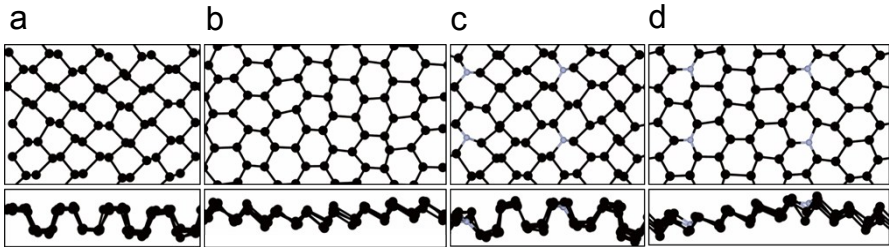


***Fig. S3***. Atomic structures of pristine and N-doped 2D P sheets after 10 ps *ab initio* molecular dynamics simulation at 1000 K. (a) and (b) show the results of pristine α-P and β-P, whereas (c) and (d) present those of N-doped α-P and β-P with 6.25% N substitution, respectively.

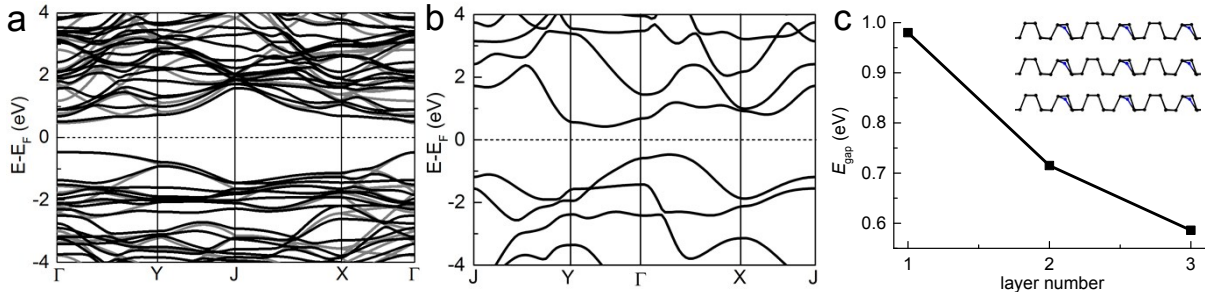


***Fig. S4***. Band structures of N-doped $\alpha$-P at doping levels of (a) 6.25% and (b) 25%, respectively. Grey lines in (a) show the bands of a pristine $\alpha$-P calculated using the same supercell as that of the N-doped one. (c) Band gap as a function of the number of layers of stacked N-doped $\alpha$-P (at a level of 6.25%). The inset presents relaxed atomic structure of a trilayer N-doped $\alpha$-P.

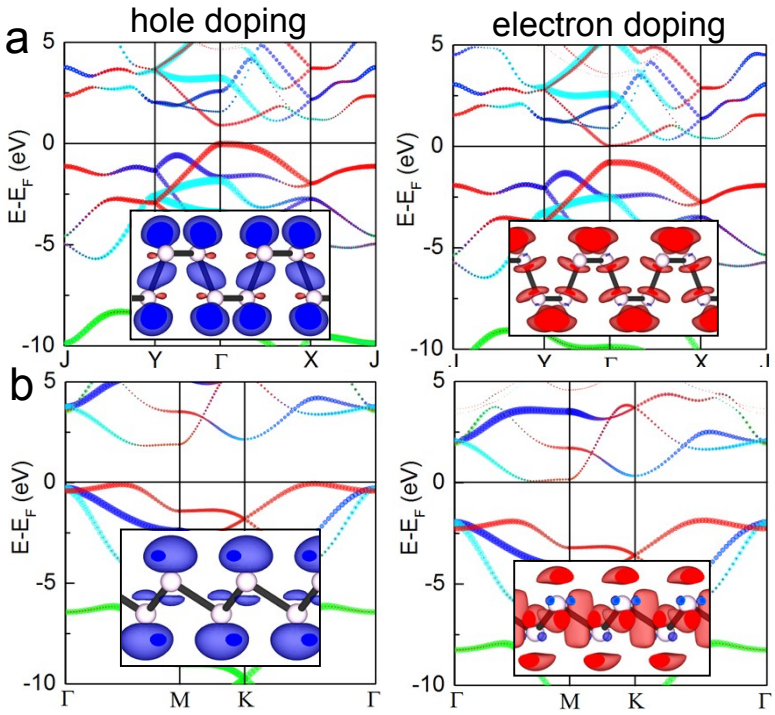


***Fig. S5***. (a) Electronic band structures of the $\alpha$-P at doping levels of (left) -2.6×10$^{13}$ cm$^{-2}$ and (right) +2.6×10$^{13}$ cm$^{-2}$, along with the isosurface plots (0.002 e/Å$^3$) of distributions of injected charge carriers. (b) The same as (a) but for the $\beta$-P. The bands derived from $p_z$, $p_x$, $p_y$ and $s$ are colored red, blue, cyan and green, respectively.