Supporting Information

Assembling Phosphorene Flexagons for 2D Electron-density-guided Nanopatterning and Nanofabrication

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(Dated: May 12, 2017)

Brief computational setup

We perform first-principles density-functional theory (DFT) calculations with the projector-augmented wave (PAW) method as implemented in the Vienna *Ab initio* Simulation Package (VASP). In our DFT calculations, periodic boundary conditions are enforced with a vacuum region of 15 Å along the out-of-plane direction for all 2D models used in this work. A planewave kinetic energy cutoff of 500 eV is employed, and for geometry optimization, the semi-local approximation to the exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE) is used. To achieve a higher precision in our electronic band structure calculations, we have adopted the HSE06 hybrid DFT functional instead. A Γ-centered **k**-point grid of a reciprocal space sampling distance of 0.2 Å^{-1} and 0.15 Å^{-1} are used for all geometry optimization and electronic band structure calculations, respectively. All geometries are relaxed until the forces do not vary more than and 0.02 eVÅ^{-1}.

TABLE S1. The calculated elastic stiffness constants (in GPa) of selected phosphorene flexagons.

Structure	C_{11}	C_{12}	C_{22}	C_{44}	Born-Huang criteria
he-2F-*t*	17.10	-1.33	61.75	16.03	◯
he-3F-*t*	27.08	12.25			◯
he-4F-*t*	63.29	-7.42		5.74	◯
ho-6F-*t*	27.71	18.51			◯
α-P	24.31	17.48	103.95	22.65	◯

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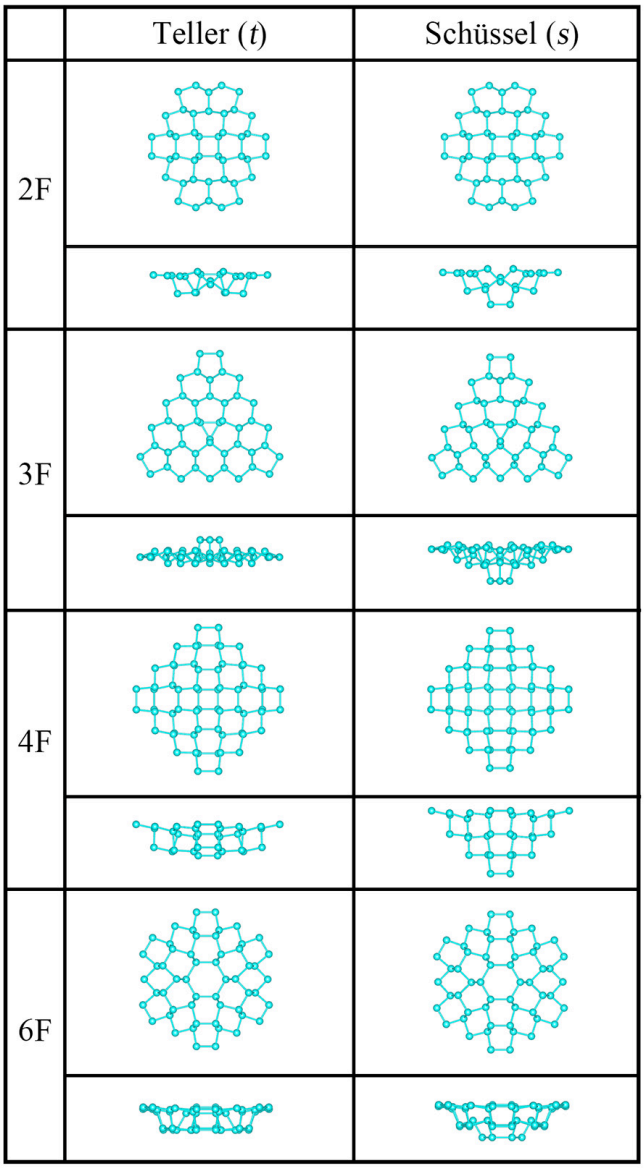

FIG. S1. (Color online) Atomic structure of unit phosphorene nanoflakes with different symmetry (2-, 3-, 4-, and 6-fold) and shape (flat- (t) and bowl-shaped (s)), which used to build phosphorene flexagons.

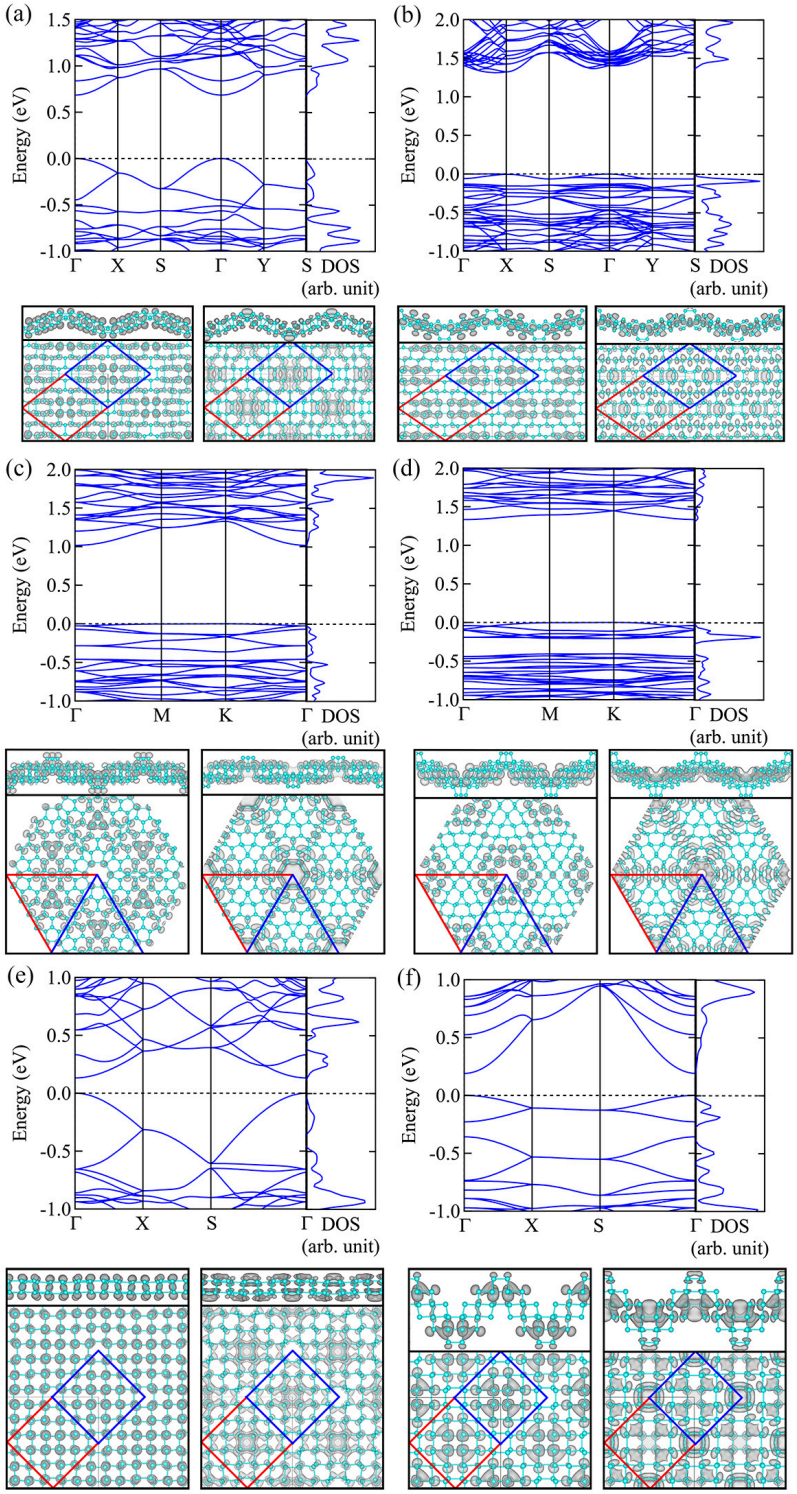

FIG. S2. (Color online) Calculated band structures, density-of-states, and partial electron densities at valence band edge (bottom-left) and conduction band edge (bottom-right) of *he*-flexagons; (a) *he*-2F-*t*, (b) *he*-2F-*s*, (c) *he*-3F-*t*, (d) *he*-3F-*s*, (e) *he*-4F-*t*, and (f) *he*-4F-*s*. Red and blue lines are to show different vertical arrangement of adjacent flakes.

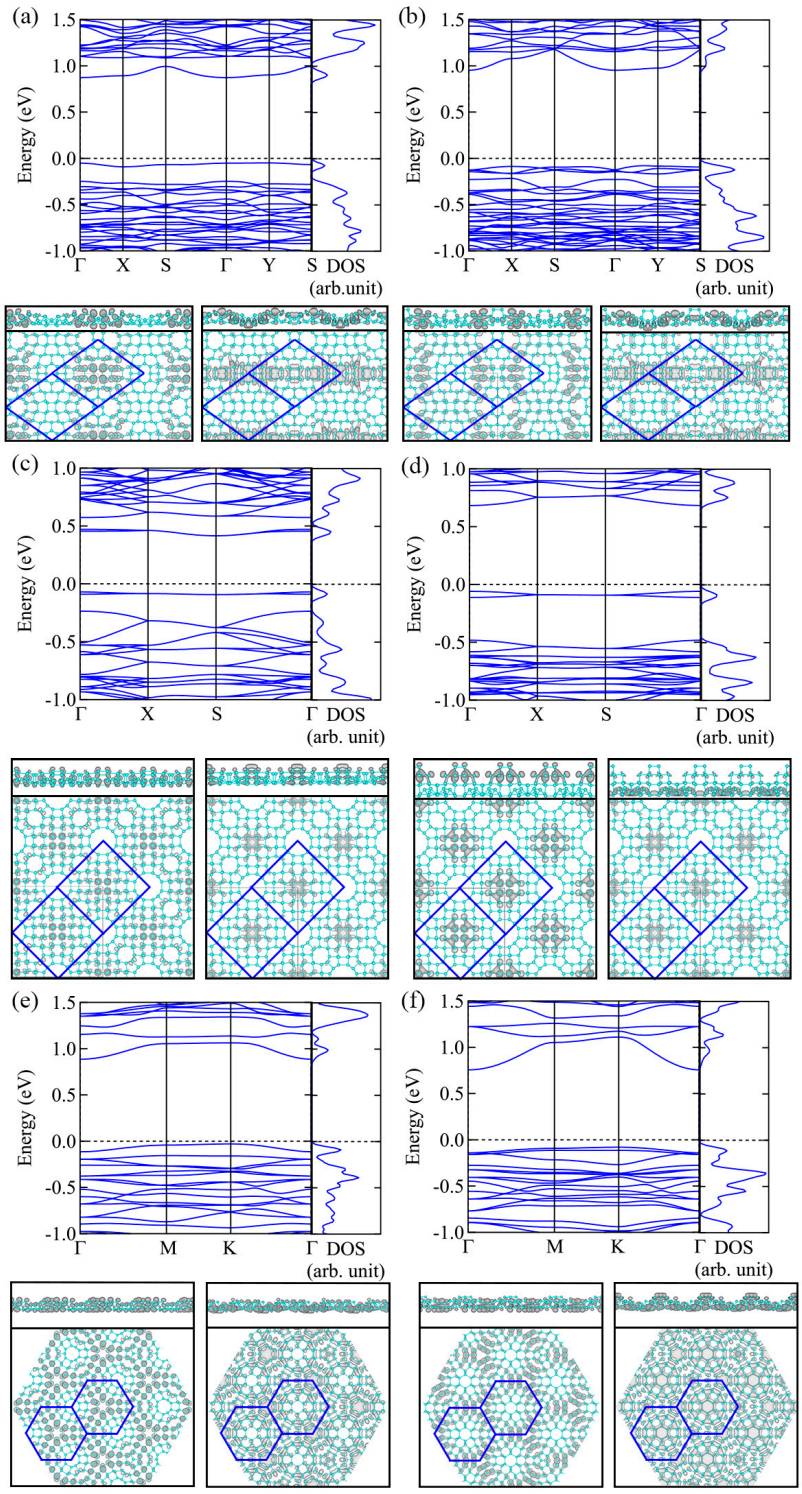

FIG. S3. (Color online) Calculated band structures, density-of-states, and partial electron densities at valence band edge (bottom-left) and conduction band edge (bottom-right) of *ho*-flexagons; (a) *ho*-2F-*t*, (b) *ho*-2F-*s*, (c) *ho*-4F-*t*, (d) *ho*-4F-*s*, (e) *ho*-6F-*t*, and (f) *ho*-6F-*s*. Blue lines are to show same vertical arrangement of adjacent flakes.

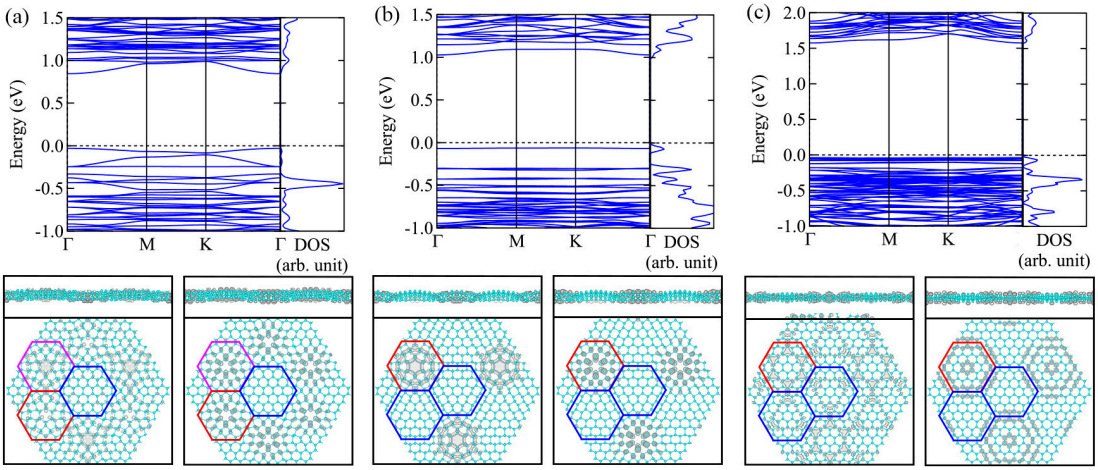

FIG. S4. (Color online) Calculated band structures, density-of-states, and partial electron densities at valence band edge (bottom-left) and conduction band edge (bottom-right) of β-P combination flexagons; (a) *he*-6F-β^1, (b) *he*-6F-β^2, and (c) *he*-6F-β^3. Red, blue, and purple lines are to show different vertical arrangements and consisting phases of adjacent flakes.

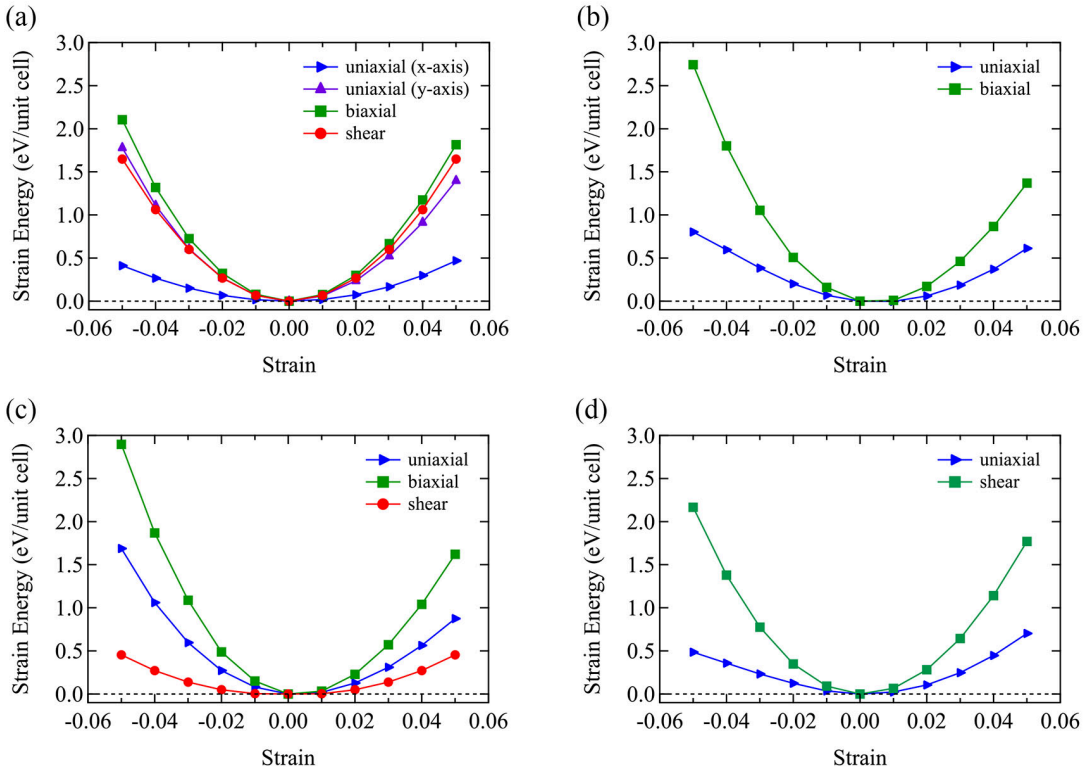

FIG. S5. (Color online) Calculated strain energy of phosphorene flexagons with respect to the applied strain; (a) *he*-2F-*t*, (b) *he*-3F-*t*, (c) *he*-4F-*t*, and (d) *ho*-6F-*t*.

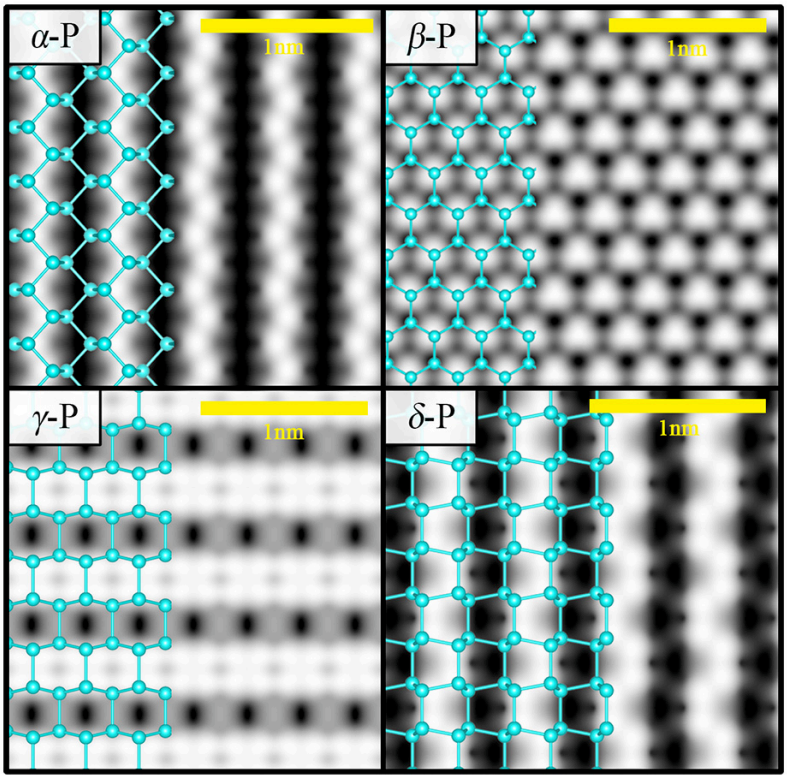

FIG. S6. (Color online) Simulated STM images and corresponding atomic positions of normal phosphorene phases; (a) α-, (b) β-, (c) γ-, and (d) δ-P.