Supporting Information

Large Diffusion Anisotropy and Orientation Sorting of Phosphorene Nanoflakes under Temperature Gradient

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S1. Potential energy of the system as a function of BP-graphene separation and sliding distance. Comparison of DFT and empirical force field calculation results.

S2. BP nanoflakes with infinite width on graphene substrate.

S3. BP-graphene average separation as a function of temperature.

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S5. Description of movies.

S1. Potential energy of the system as a function of BP-graphene separation and sliding distance. Comparison of DFT and empirical force field calculation results.

The first-principles calculations were performed by using the Vienna *ab initio* simulation package (VASP) code [S1]. We used the van der Waals (vdW)-corrected functionals with Becke88 optimization (optB88) [S2] to consider the vdW interaction between phosphorene and graphene. A vacuum region with thickness greater than 15 Å was created to avoid the spurious interaction due to the periodic image. All the structures were optimized until the force exerted on each atom was less than 0.005 eV/Å. The kinetic energy cutoff of 400 eV and a $1 \times 2 \times 1$ Monkhorst-Pack grid for k-points sampling were adopted.

The Stillinger-Weber (SW) potential [S3] and the adaptive intermolecular reactive empirical bond order (AIREBO) potential [S4] were employed to describe the covalent interaction between the phosphorous (P) atoms in phosphorene nanoflake and the carbon (C) atoms in graphene substrate, respectively. The non-bonded van der Waals (vdW) interaction between phosphorene nanoflake and graphene substrate in the computational model was described by the Lennard-Jones (LJ) potential [S5].

In DFT calculation, the y-axis is total energy per phosphorous atom, with 10 P atoms and 32 C atoms in the supercell. In addition to the van der Waals interaction, the total energy from DFT calculation also contains electrostatic interaction and exchange-correlation energy. The MD simulation was conducted at 0.01 K, and the potential energy contains the interlayer interaction and potential energy in phosphorene and graphene, respectively. To suppress the statistic fluctuation, a larger supercell with 10560 C atoms and 190 P atoms is adopted. Here the number of P atoms is much smaller than the number of C atoms because the same system is also used to study the potential energy versus sliding distance relationship. To increase the comparability, a shift in the potential energy curve is adopted, and the minimum energy point is set as zero. The equilibrium BP-graphene separation from empirical potential calculation is 0.35 nm, which is very close to that from DFT calculation (0.34 nm). Although the absolute values of y-axis are different because of the different benchmarks in computational method, such as the different number of C atoms and the number of P atoms, the results from these two methods match well.

[S1] Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *ab initio* Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 1996, 54, No. 11169.

[S2] Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A 1988, 38, No. 3098.

[S3] Jiang, J.-W. Nanotechnology 2015, 26 (31), 315706.

[S4] Stuart, S. J. S. S. J.; Tutein, A. B. A.; Harrison, J. A. J.; Introduction, I. Chem. Phys. 2000, 112 (14), 6472–6486.

[S5] Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. Journal of the American Chemical Society 1992, 114 (25), 10024–10035.
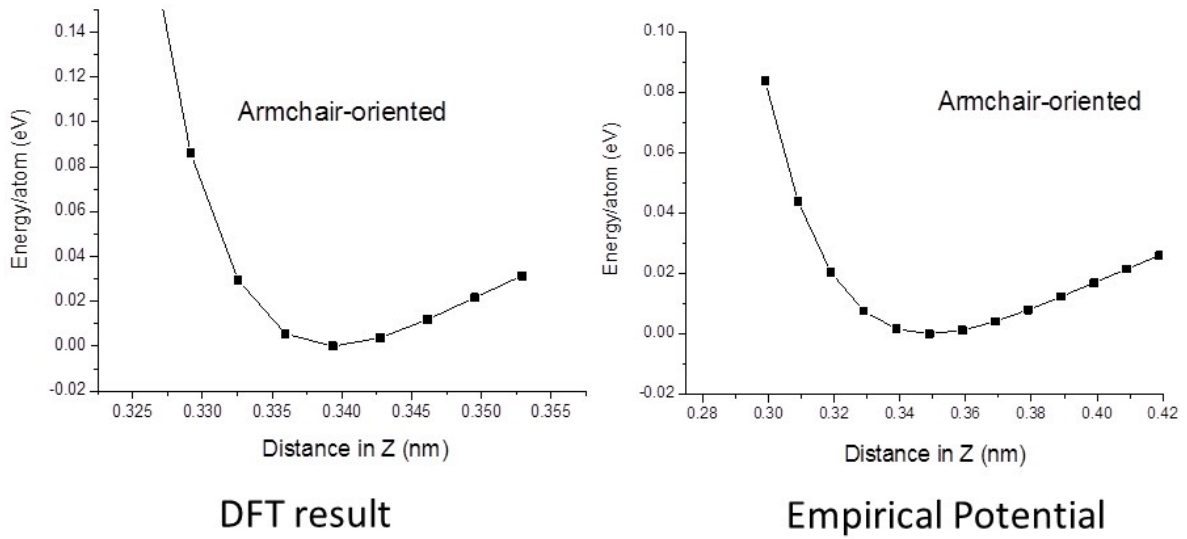
Figure S1. Comparison of potential energy per phosphorous atom as a function of BP-graphene separation calculated by DFT and empirical potential, respectively. Here the absolute values of y-axis are different because the different benchmarks in various calculations. The equilibrium BP-graphene separation calculated from empirical potential is consistent with that from DFT.
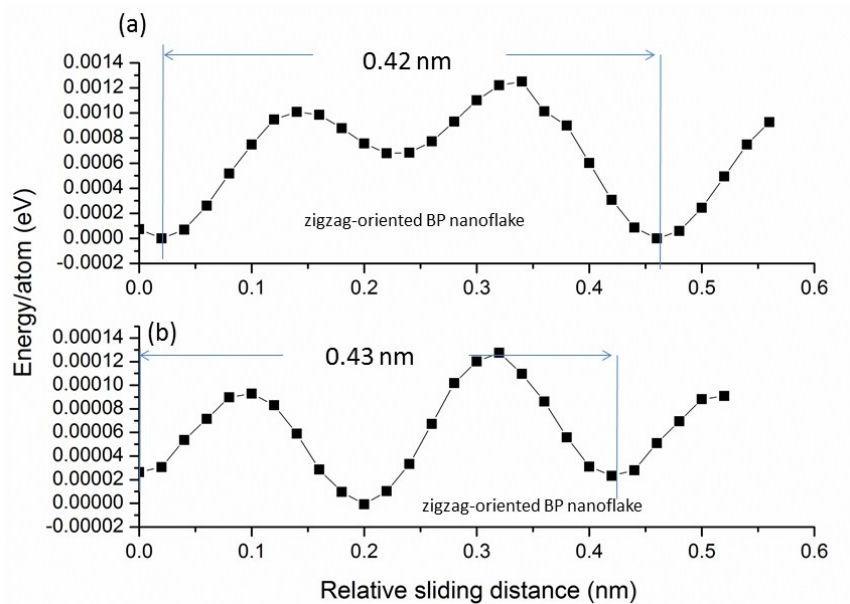

Figure S2. Potential energy as a function of sliding distance. (a) DFT calculation result. (b) MD result based on empirical potential. Comparison between (a) and (b) indiacates that the empirical potential calculations are able to accurately capture the shape of potential barrier (one small potential peak and one high potential peak within each periodicity), and the periodic length (0.42 nm from DFT, 0.43 nm from empirical potential). Here, the absolute values of y-axis are different because the different benchmarks are used in various calculations.

S2. BP nanoflakes with infinite width on graphene substrate. Here, periodic boundary condition is applied in the y-direction.
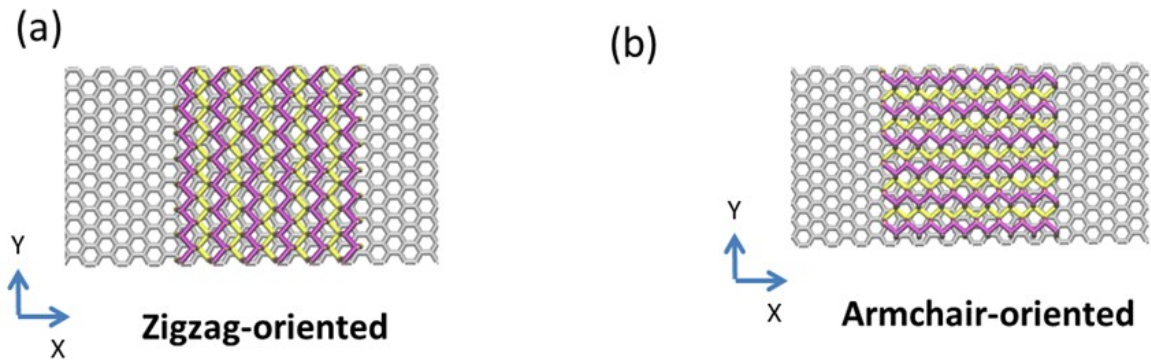

Figure S3. (a) Top view of the zigzag-oriented phosphorene nanoflake on graphene substrate along armchair direction. (b) Top view of the armchair-oriented phosphorene nanoflake on graphene substrate along armchair direction. The atoms in graphene are colored in "gray", and atoms of phosphorene in different colors represent atoms in different sublayers.

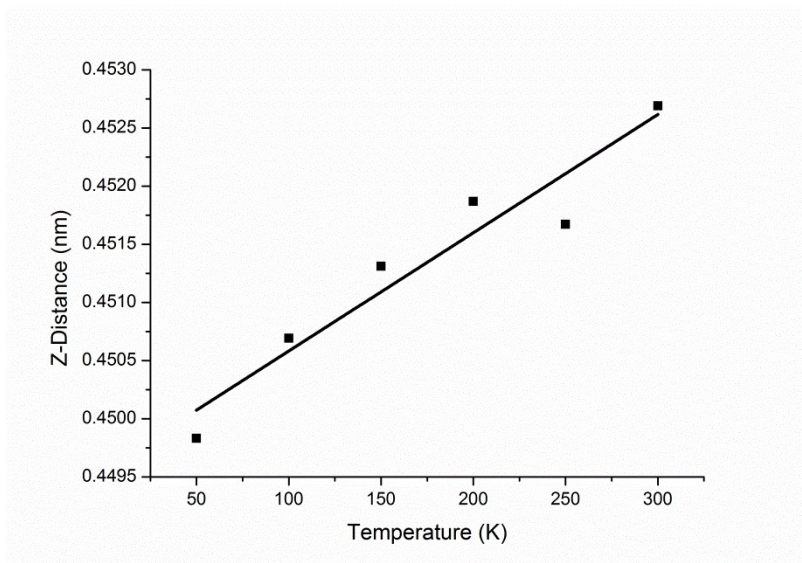## S3. BP-graphene average separation as a function of temperature.

Figure. S4 Time-averaged BP-graphene separation in Z-direction at different temperatures. The square symbols denote the calculation results. The line in the figure is drawn to guide the eyes.

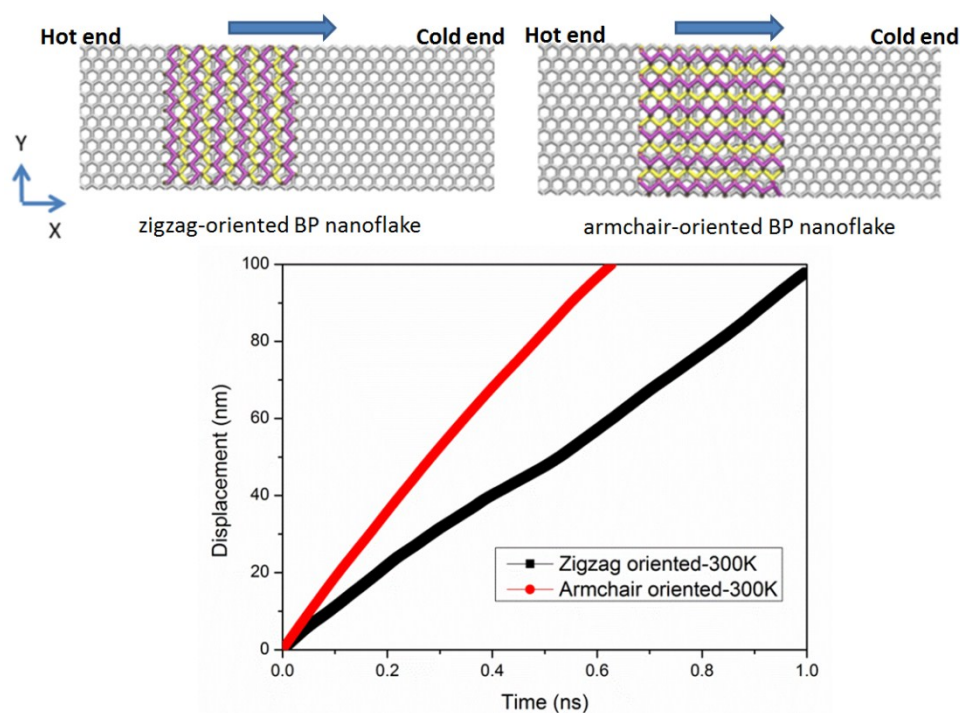## S4. BP diffusion on graphene substrate with zigzag orientation.

Figure S5. Configurations and displacements of the zigzag-oriented BP nanoflake (top left panel) and armchair-oriented BP nanoflake (top right panel) on graphene substrate with

zigzag orientation along x-direction. The temperatures of the two ends are 300K and 270K, respectively.

S5. Description of the movies.

Description of movie-1: Diffusion of the zigzag-oriented BP flake with sizes of 5×5 nm^2 on a graphene substrate with sizes of 50×15 nm^2. Temperatures of the two ends are 15 K and 5 K, respectively.

Description of movie-2: Diffusion of the armchair-oriented BP flake with sizes of 5×5 nm^2 on a graphene substrate with sizes of 50×15 nm^2. Temperatures of the two ends are 15 K and 5 K, respectively.

Description of movie-3: Top: Diffusion of the zigzag-oriented BP nanoflake; Bottom: Diffusion of the armchair-oriented BP nanoflake. Temperatures at two ends are 300 K (left) and 270K (right), respectively. The graphene substrate has been repeated for 3 unit cells along the y-direction.