Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

First-principles study of the sodium adsorption and diffusion on phosphorene

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1. Configurations of phosphorene with single Na atom

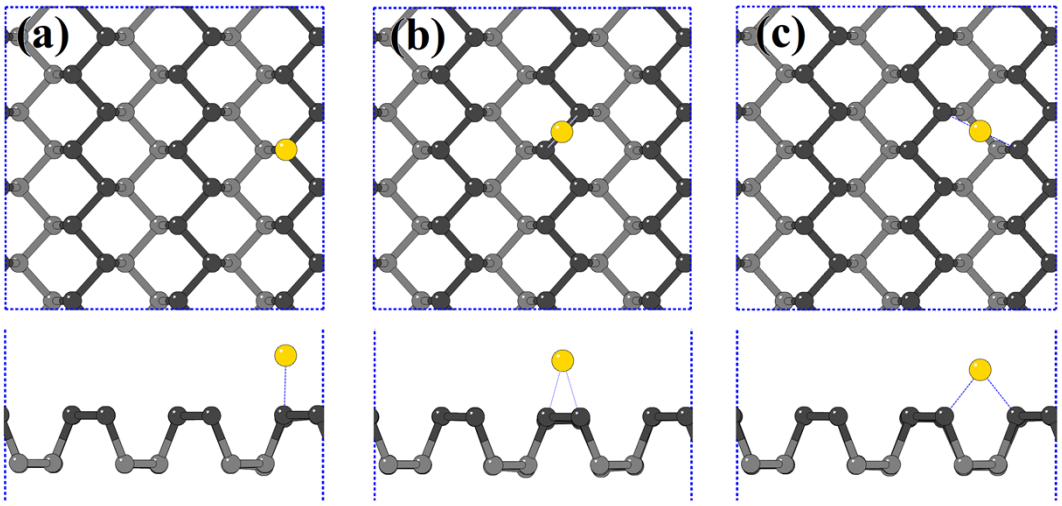

Fig. S1. (color online) Top-view and side-view of phosphorene with single Na atom adsorbed on (a) *T*-site, (b) *B*-site and (c) *Br*-site.

2. Na intercalation structures of phosphorene with different Na concentrations

Based on the discussion about the interaction of Na atoms on phosphorene, we have adhered two rules to filter the most stable configurations at different Na intercalation concentrations: one is that Na atoms are preferable to be intercalated on both-side of phosphorene as the configuration in Fig. 2(e) and the other one is that larger distance between Na atoms in the same side of phosphorene will decrease the total energy of whole structure. We have listed all the configurations of different Na patterns in a 3 × 4 supercell and their corresponding binding energies with different Na concentrations in Fig. S2-S10.

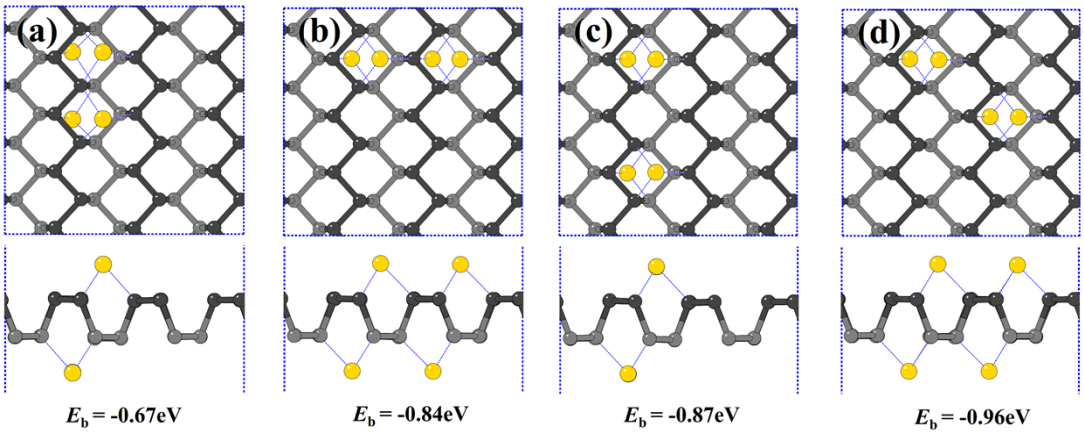

Fig. S2. (color online) Top-view and side-view of Na_4P_{48}

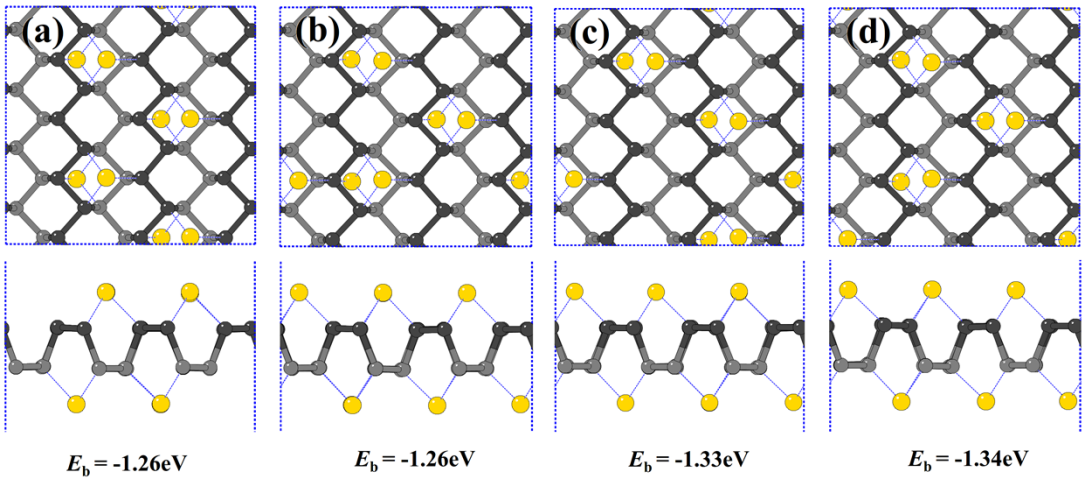

Fig. S3. (color online) Top-view and side-view of Na_8P_{48}

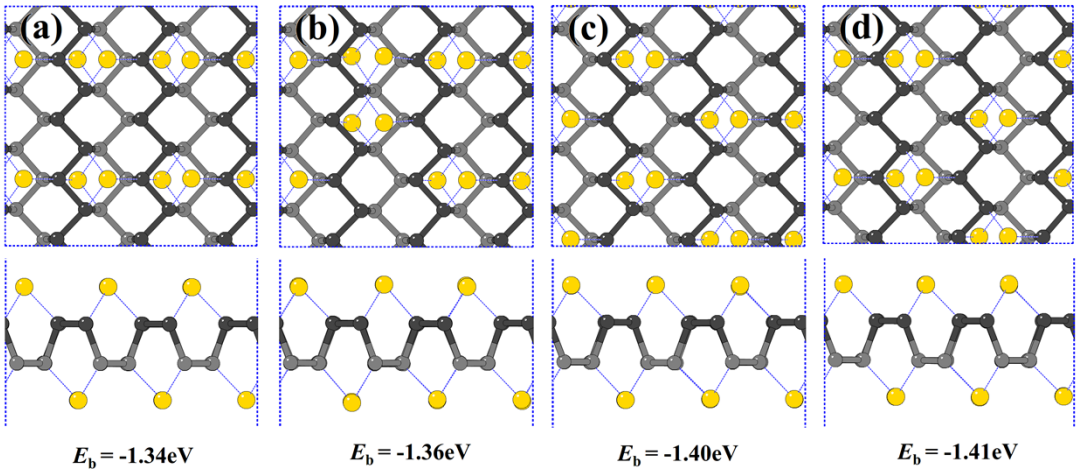

Fig. S4. (color online) Top-view and side-view of $Na_{12}P_{48}$

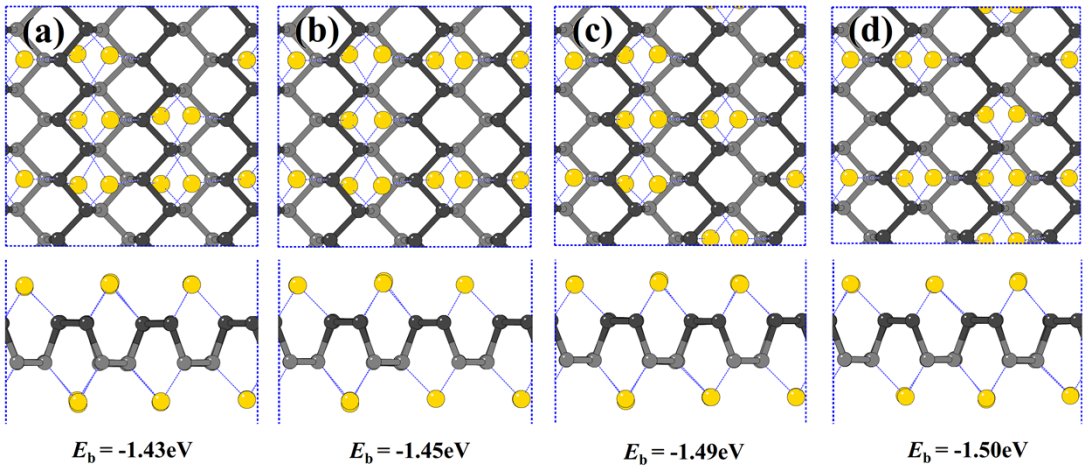

Fig. S5. (color online) Top-view and side-view of $Na_{14}P_{48}$

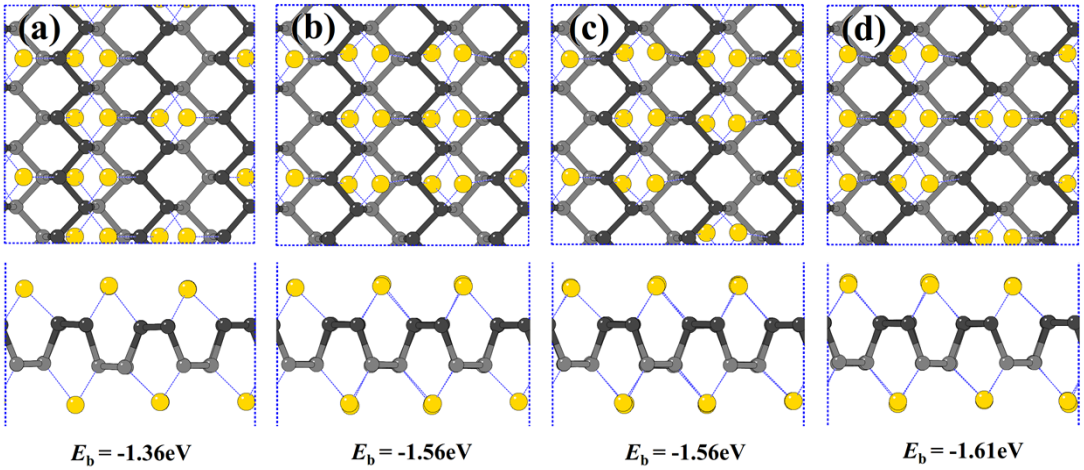

Fig. S6. (color online) Top-view and side-view of $Na_{16}P_{48}$

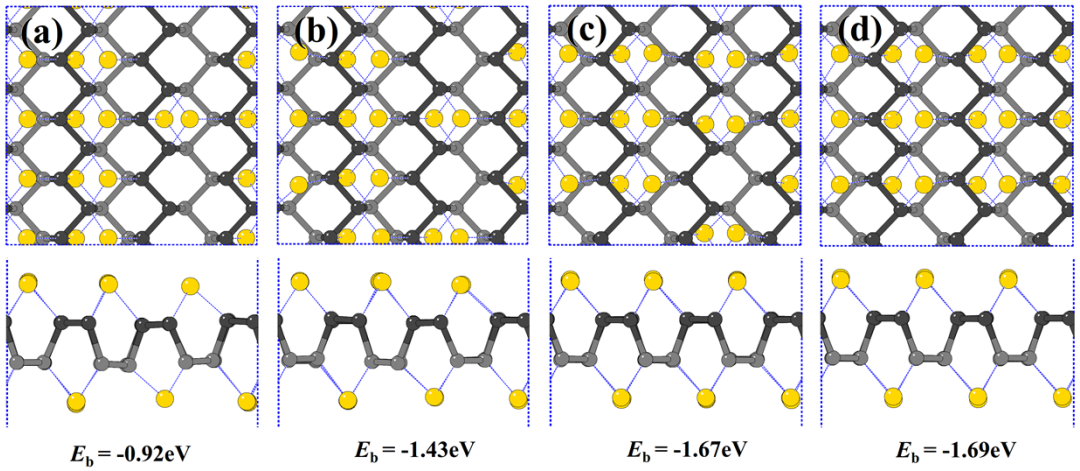

Fig. S7. (color online) Top-view and side-view of $Na_{18}P_{48}$

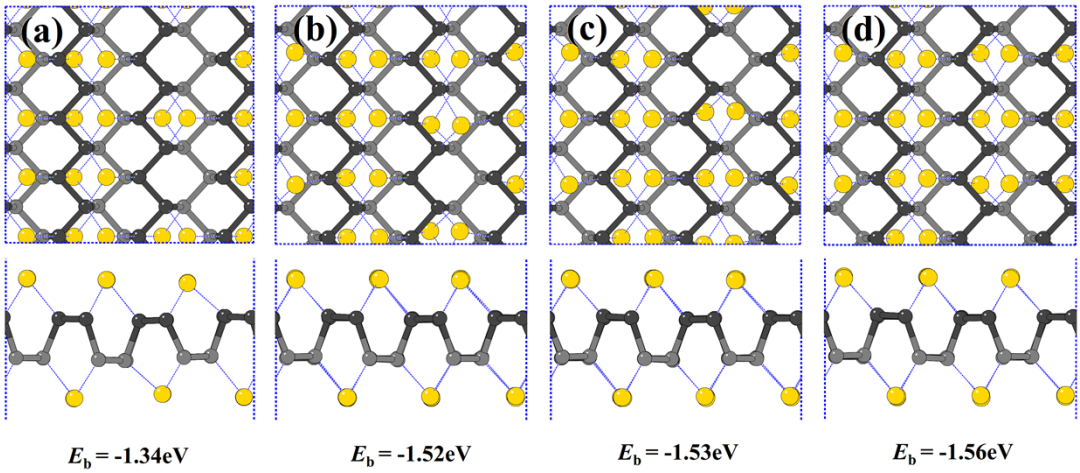

Fig. S8. (color online) Top-view and side-view of $Na_{20}P_{48}$

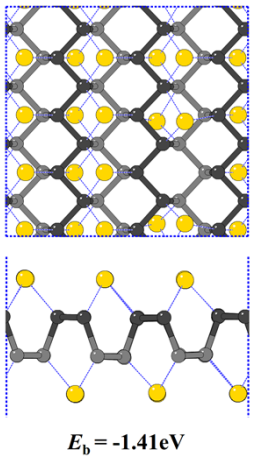

Fig. S9. (color online) Top-view and side-view of $Na_{22}P_{48}$

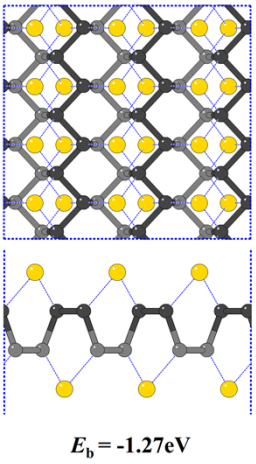

Fig. S10. (color online) Top-view and side-view of $Na_{24}P_{48}$

3. The structural stability study of pristine phosphorene and $Na_{18}P_{48}$

Ab initio molecule dynamic simulations have been performed to study the structural stability of phosphorene under full Na^+ discharge/charge. All structures are simulated under a NVT ensemble at room temperature (300K). Firstly, as shown in Fig. S11, the stability of pristine phosphorene is evaluated and the results show that the structure of pristine phosphorene is well retained, which indicates it is stable at room temperature. Then the Na doped phosphorene $Na_{18}P_{48}$ is chosen as the highest Na concentration to investigate the structural stability of fully charged phosphorene. Fig. S12 gives the snapshots of 0.5 ps and 1 ps and it is clear that adsorbed Na atoms avoid to be clustered on the surface of the phosphorene. In addition, we can find a few Na atoms are intercalated into the channels of the phosphorene and cause the nearest P atoms deviating off the layer with a very low proportion in some local regions. However, we notice that the phosphorene still keeps the overall framework of 2D structure and the side-view of the snapshot indicates almost all Na atoms reside on the surface of the phosphorene rather than substitute the P atoms in the layered structure. Moreover, we have considered the structural stability of fully discharged phosphorene by removing the adsorbed Na atoms in the last configuration of Fig. S12. Fig. S13 shows the structural evolution of the phosphorene without Na atoms and the results show that the monolayer phosphorene can self-repair to recover to the initial structure.

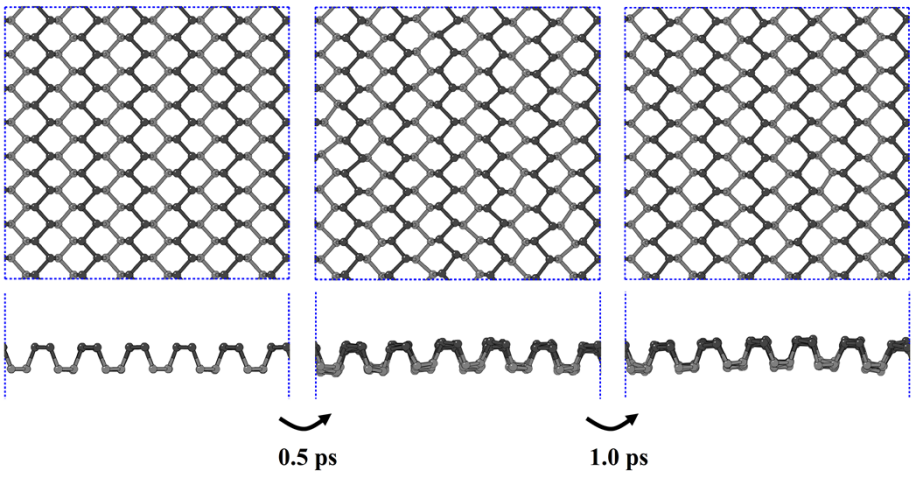

Fig. S11. (color online) Simulation snapshots for the evolution of pristine phosphorene at 300K.

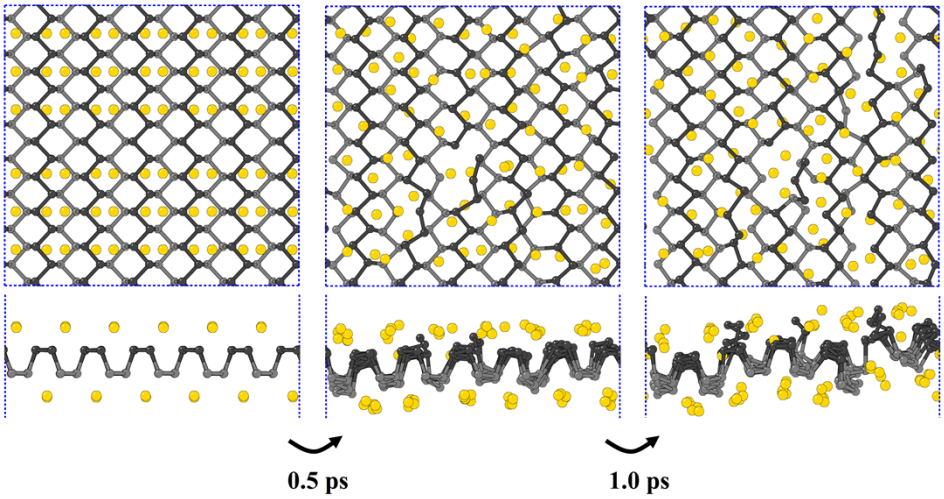

Fig. S12. (color online) Simulation snapshots for the evolution of $Na_{18}P_{48}$ at 300K.

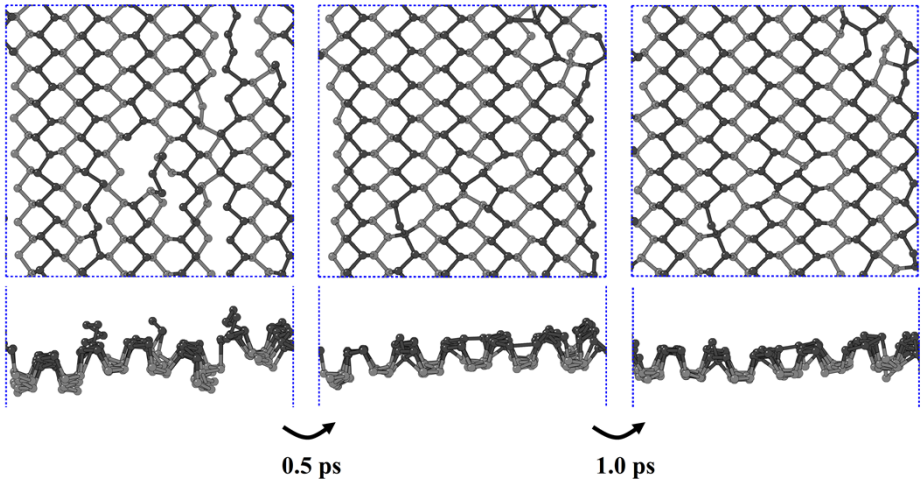

Fig. S13. (color online) Simulation snapshots for the evolution of $Na_{18}P_{48}$ after all Na atoms being released at 300K.