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

Electronic Supplementary Information

Adsorption of Metal Adatoms on Single-Layer Phosphorene

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S1. Computational Details

We use an orthorhombic supercell ($\alpha = \beta = \gamma = 90°$) with periodic boundary conditions to model adatom-phosphorene structure. Vacuum spacing of 20 Å is used to create isolated single-layer conditions. The typical simulation cell is shown in Figure S1.

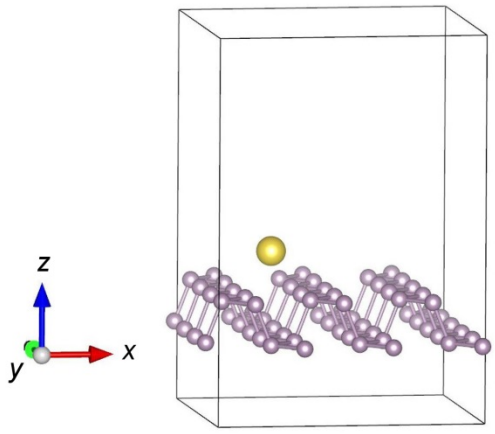

Figure S1. Typical (3×4) simulation supercell containing single-layer phosphorene and adatom.

S2. Calculated structural properties of the relevant bulk phases.

The accuracy of used pseudopotentials has been tested by calculating the lattice constants and cohesive energies for bulk structures of the studied elements. To determine the optimal lattice constant, the total energy of the given structure is calculated as a factor of the unit cell size. The lattice constant is then defined as a unit cell size, for which the total energy is minimal. The cohesive energy is defined as

$$E_{coh} = \frac{E_{bulk}}{N_{atoms}} - E_{atom},$$

where $E_{bulk}$and E_{atom} are total energies of bulk crystal and free atom, respectively. N_{atoms} is the number of atoms in the bulk crystal.

The obtained results are summarized and compared to the experimental data in Table S1. The best agreement between theory and experiment is achieved for *s*- and *p*-valence systems, such as Si, Ge, alkali metals. The description of transition metals with many *d* electrons is more complicated (this is well expected). Nevertheless, we have achieved a good level of consistency with the experimental

values and available modeling results at the same level of theory. The results of these benchmark calculations support our choice of pseudopotentials.

Table S1. Calculated structural parameters for the bulk phases of studied elements

Element	**Crystal structure**	**Lattice constant (this work)**	**Lattice constant (exp)[1]**	**Cohesive energy (this work)**	**Cohesive energy (exp)[1]**	**Cohesive energy (theory)[2] LDA (PW)**
Li	*bcc*	3.54	3.49	1.54	1.63	
Na	*bcc*	4.20	4.22	1.05	1.113	
K	*bcc*	5.28	5.22	0.83	0.934	
Cu	*fcc*	3.67	3.61	3.28	3.49	
Ag	*fcc*	4.16	4.09	2.53	2.95	
Au	*fcc*	4.17	4.08	3.01	3.81	
Pd	*fcc*	3.95	3.89	3.71	3.89	
Pt	*fcc*	3.99	3.92	5.43	5.84	
Ti	*hcp*	a = 2.95 c = 4.61	a = 2.95 c = 4.68	5.23	4.85	6.29 (5.09)
V	*bcc*	3.00	3.03	5.17	5.31	6.49 (5.12)
Cr	*bcc*	2.87	2.88	3.97	4.10	5.22 (3.80)
Mn	*bcc*	2.82	3.08 (Ref[3])	3.70	2.92	5.19 (3.73)
Fe	*bcc*	2.83	2.87	4.95	4.28	6.25 (4.78)
Co	*hcp*	a = 2.50 c = 4.02	a = 2.51 c = 4.07	5.08	4.39	6.51 (4.88)
Ni	*fcc*	3.52	3.52	4.82	4.44	5.98 (4.52)
Si	*diamond*	5.47	5.43	4.60	4.63	
Ge	*diamond*	5.76	5.66	3.74	3.85	

S3. Adsorption of adatoms on monolayer and bilayer phosphorene

We have performed a series of calculations on the adsorption of alkali adatoms on the monolayer and bilayer phosphorene. We have chosen Li, Na and K adatoms as examples due to their relevance to Li-ion and Na-ion batteries (note that P is a promising anode material). The obtained results are summarized in Table S2.

Table S2. Calculated adsorption energies for alkali adatoms on monolayer and bilayer phosphorene

Adatom	E_a@Bilayer (eV)	E_a@Monolayer (eV)	dE (eV)
Li	-1.91	-1.88	-0.03
Na	-1.35	-1.31	-0.04
K	-1.67	-1.61	-0.06

We find that the adsorption energy is slightly larger on bilayer than monolayer phosphorene. This is result is consistent with the recent experimental studies. Using cyclic voltammetry and in situ Raman spectroscopy, Pollak et al. demonstrated that the interaction of Li with few-layer graphene is stronger than with monolayer.[4] However, our calculated difference in adsorption energy is relatively small (-0.03…-0.06 eV, see Table S2). This is consistent with the theoretical study of Ling et al, which suggested that the Na adsorption voltage on BC_3 is only little affected by the number of BC_3 layers.[5]

S4. Spin density distribution in TM-phosphorene

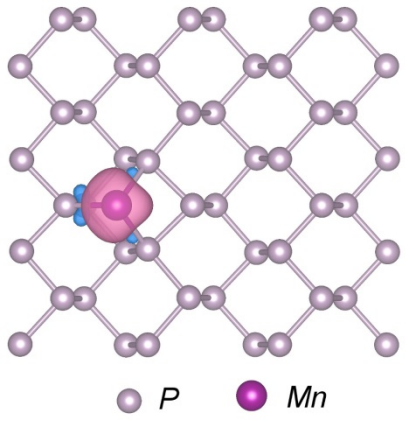

Figure S2. Isosurface of the total spin density for the Mn-phoshorene system. Pink isosurface color corresponds to positive values of the spin density, blue – to the negative values.

S5. Additional density of states (DOS) figures

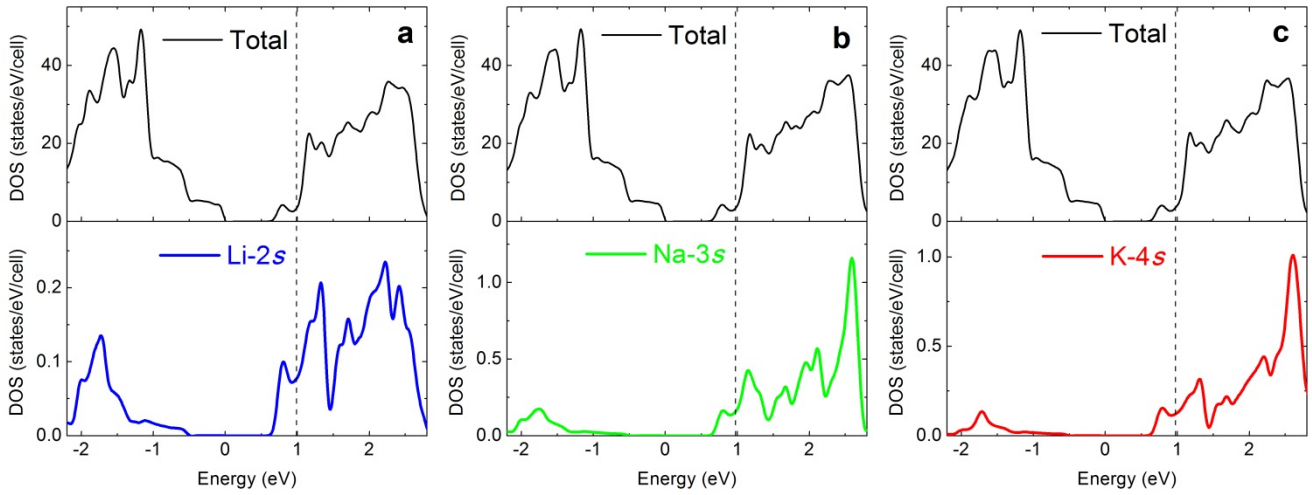

Figure S3. Total and projected DOS for alkali adatoms on single-layer phosphorene: (a) Li, (b) Na, and (c) K. The zero energy corresponds to the VBM. The dashed vertical line indicates the Fermi level.

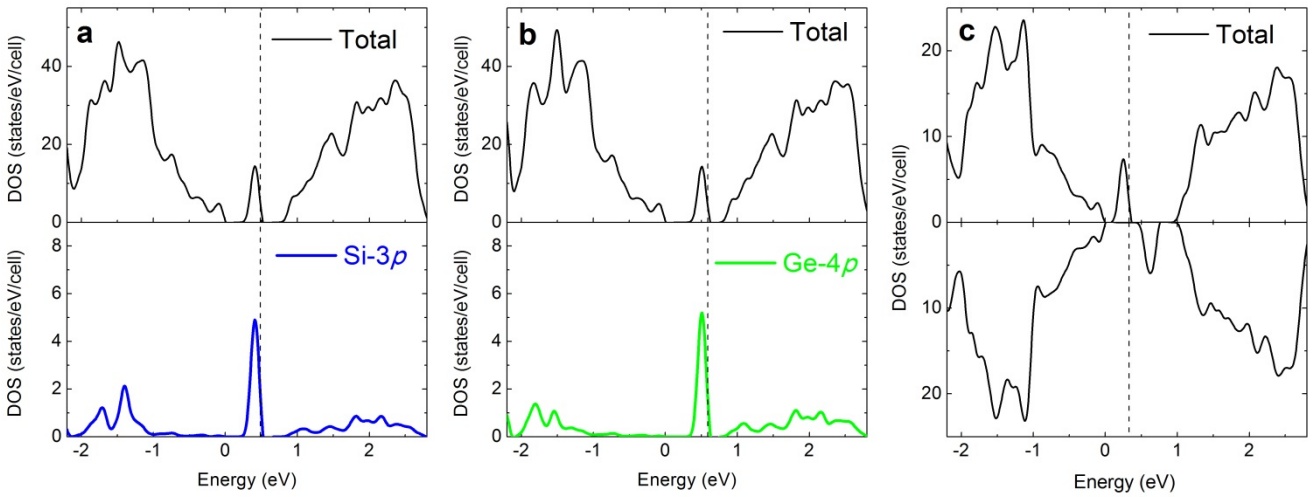

Figure S4. Total and projected DOS for semiconductor adatoms and hydrogen on single-layer phosphorene: (a) Si, (b) Ge, and (c) H. The zero energy corresponds to the VBM. The dashed vertical line indicates the Fermi level.

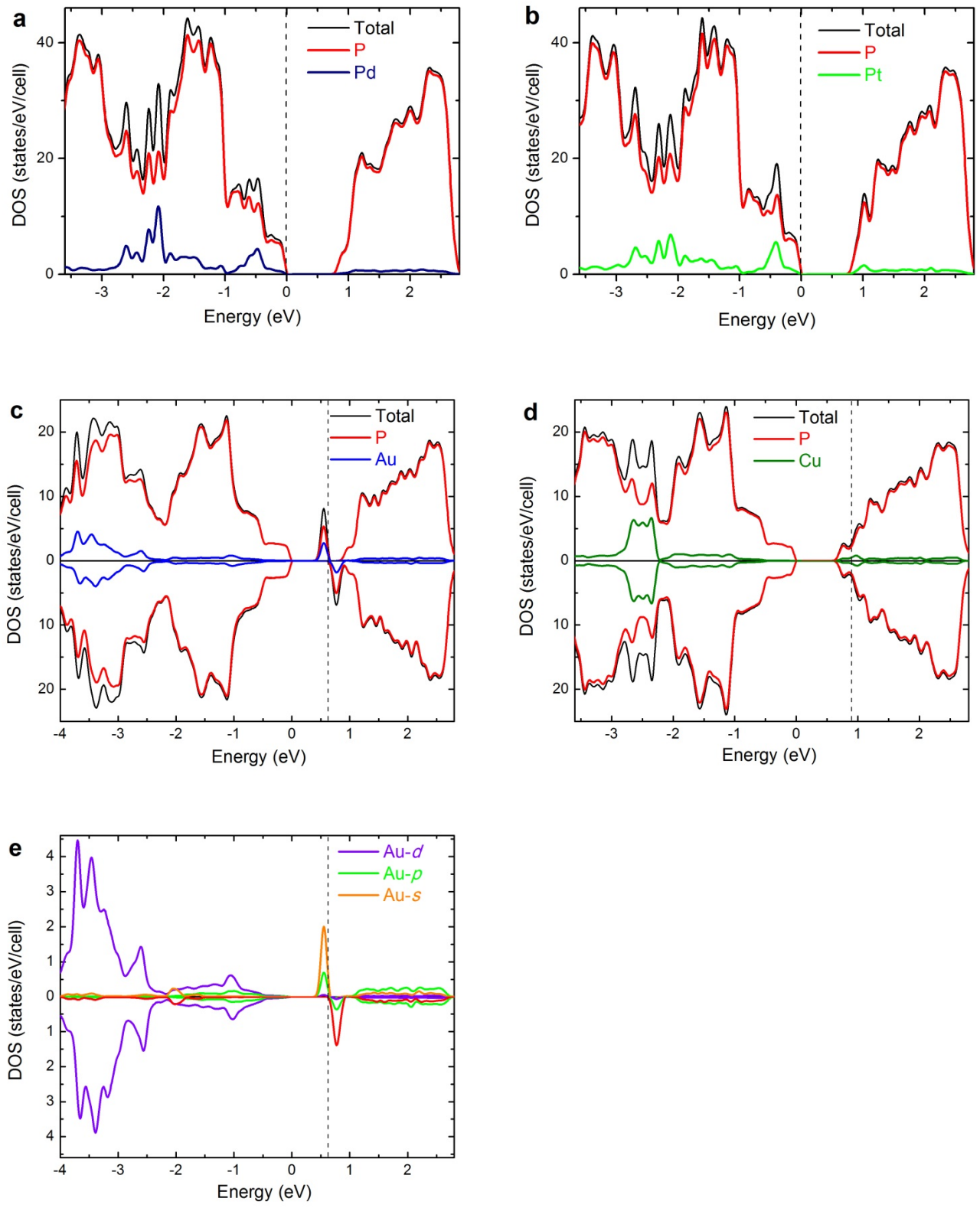

Figure S5. Total DOS for noble metal adatoms on single-layer phosphorene: (a) Pd, (b) Pt, (c) Au, and (d) Cu. (e) Projected DOS for Au adatom on phosphorene. The zero energy corresponds to the VBM. The dashed vertical line indicates the Fermi level.

References:

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5. C. Ling and F. Mizuno, *Phys. Chem. Chem. Phys.*, 2014.