Supporting Information

Selective Growth of Two Dimensional Phosphorene on Catalyst Surface

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S1. Method of Calculation

In all the calculations, the original lattice parameters of α, β, γ, and δ-phosphorene were adopted from reference,[1] and then were further optimized (shown in Figure S1). The seven transition metal surfaces were simulated by three atomic layer thick slab models with all the atoms in the bottom layer fixed. Then the four types of phosphorenes were placed on the surfaces by carefully choosing the supercell size of the system, which ensures the lattice mismatch between phosphorene and substrate to be lower than 3%. As an example, the models of α-, β-, γ- and δ-phorphorenes on β-Sn(100) surface are shown in Figure 1 and more detailed parameters of other models are here shown in the table S1. In order to avoid the interaction between neighboring images, the neighboring slabs were separated by a vacuum layer of ~15 Å.

Density functional theory (DFT) calculations were performed *via* the Vienna ab initio Simulation Package (VASP),[2,3] with projected augmented wave (PAW) method[4] describing the interactions between valence electrons and ion cores. Generalized gradient approximation (GGA) energy was used for the exchange-correlation[5]. To apply the weak van der Waals interaction into the system, the DFT-D3 method[6] was applied. A plane-wave cutoff energy of 400 eV was adopted and all the structures were fully relaxed with energy and force convergence criteria of 10^{-4} eV and 10^{-2} eV/Å, respectively. The Brillouin zone was sampled with different Monkhorst–Pack mesh k-points[7] with a separation criterion of 0.03.

S2. Optimized atomic structures of α, β, γ, and δ-phosphorene in vacuum and on transition metal surfaces.

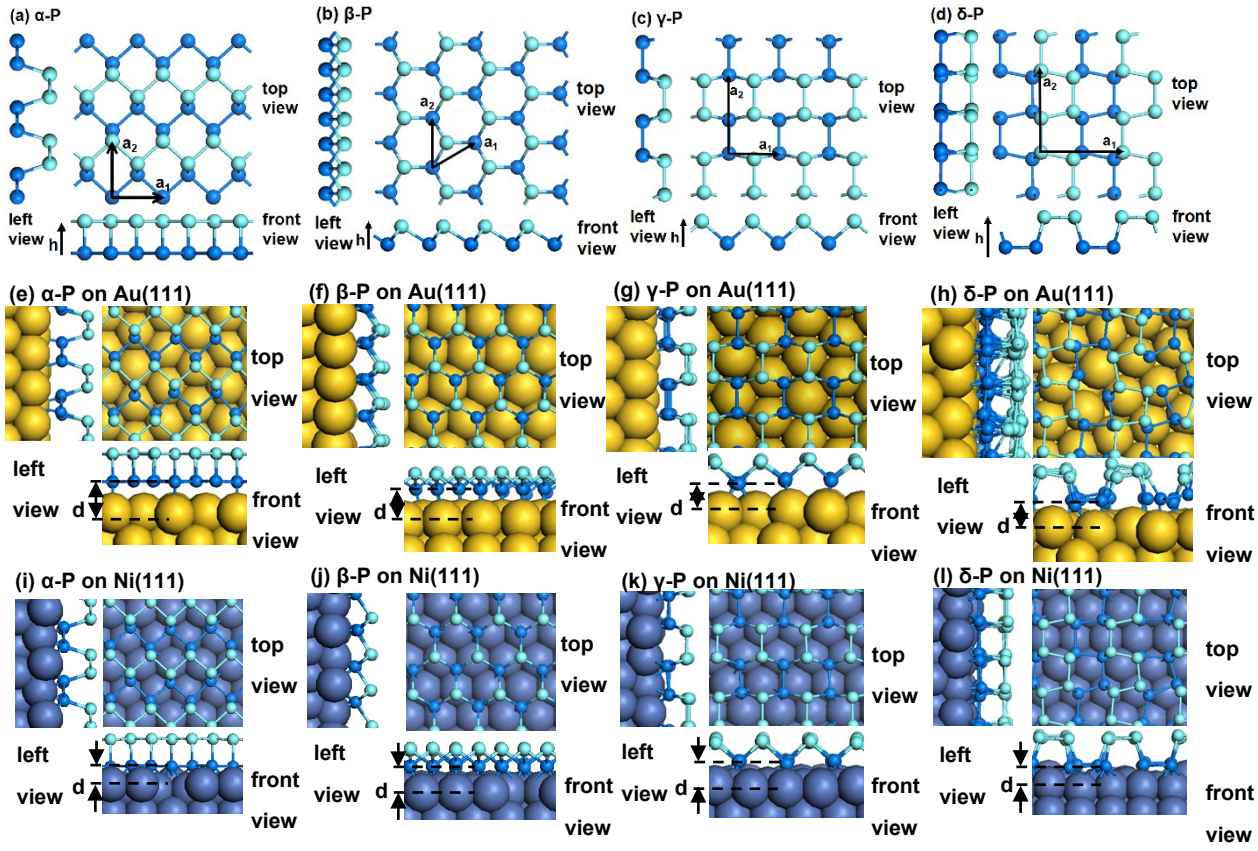

Figure S1. Optimized atomic structures of α, β, γ, and δ-phosphorene in vacuum (a, b, c, and d), on Au(111) (e, f, g, h) and Ni(111) (i, j, k, and l) surfaces.. The optimized lattice parameters are shown in table S1.

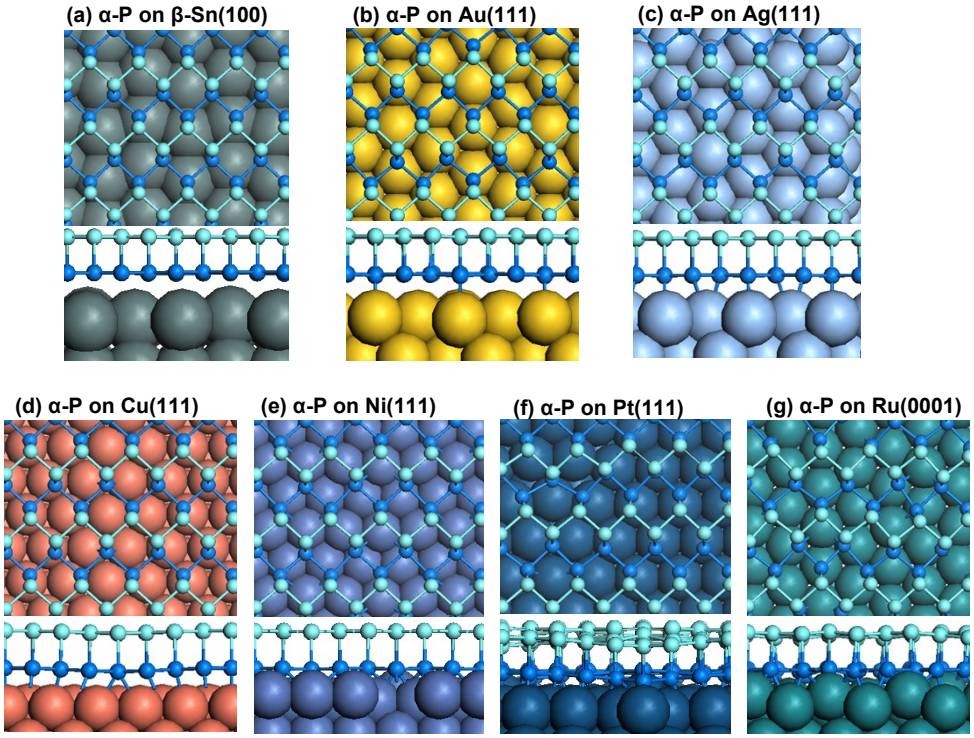

Figure S2. Optimized atomic structures of α-phosphorene on β-Sn(100), Au(111), Ag(111), Cu(111), Ni(111), Pt(111), and Ru(0001) surfaces in top and front views, respectively.

S3. A summary of the calculated parameters.

Table S1. Calculated parameters of all the phosphorene-on-substrate models. a and b are the lattice parameters of the modelled supercells. a_p, b_p, a_m and b_m represent the lattice mismatches (along a and b directions) in percentage for phosphorenes and the metal substrates, respectively, in comparison with the freestanding phosphorene and bulk metal; d is the distance between the phosphorene and the metal substrate after optimization; E_f and E_b are the formation energy and binding energy as defined in this main text.

		Supercell a (Å)	supercell b (Å)	mismatch a_p; b_p (%)	mismatch a_m; b_m (%)	distance d(Å)	E_f (eV/atom)	E_b (eV/atom)
vacuum	α	3.31	4.38	/	/	/	0.0	/
	β	3.28	3.28	/	/	/	0.034	/
	γ	3.37	5.28	/	/	/	0.133	/
	δ	5.52	5.52	/	/	/	0.078	/
β-Sn(100)	α	23.17	21.90	0;0	0.5;1.4	2.98	-0.155	-0.155
	β	22.96	22.72	0;0	1.4;2.3	2.66	-0.127	-0.161
	γ	23.58	15.83	0;0	1.3;0.0	2.52	-0.088	-0.222
	δ	22.06	5.60	0;0.3	0.7;3.0	2.90	-0.096	-0.175
Au(111)	α	9.93	8.76	0;0	2.9;1.0	2.63	-0.226	-0.226
	β	22.96	22.96	0;0	2.8;2.8	2.40	-0.287	-0.321
	γ	10.11	21.10	0;0	1.0;2.1	2.44	-0.261	-0.395
	δ	55.16	11.03	0;0.1	0.3;3.0	2.42	-0.231	-0.309
Ag(111)	α	9.93	8.76	0;0	0.7;1.1	2.61	-0.243	-0.243
	β	19.96	19.96	0;0	1.3;1.3	2.39	-0.300	-0.335
	γ	10.23	26.70	0;0	2.2;2.6	2.26	-0.255	-0.388

	δ	5.56	49.14	0.2;0	3.0;1.8	2.57	-0.179	-0.258
Cu(111)	α	13.24	13.14	0.5;0	3.0;1.1	2.24	-0.381	-0.381
	β	9.98	9.98	0;0	2.4;2.4	2.16	-0.536	-0.570
	γ	10.23	26.70	0;0	0.1;0.5	2.00	-0.454	-0.587
	δ	22.24	21.84	0.1;0	3.0;1.3	2.20	-0.337	-0.415
Ni(111)	α	9.93	8.76	0;0	0.4;1.5	1.75	-0.795	-0.795
	β	9.98	9.98	0;0	1.1;1.1	1.88	-0.931	-0.965
	γ	10.23	21.36	0;0	2.6;1.0	1.83	-0.857	-0.991
	δ	22.24	21.84	0;0	0.8;1.2	1.83	-0.755	-0.834
Pt(111)	α	16.55	39.42	0;0	0.6;2.5	2.20	-0.618	-0.618
	β	16.63	16.63	0;0	0.1;0.1	1.99	-0.816	-0.850
	γ	13.64	37.38	0;0	1.7;2.8	1.90	-0.690	-0.824
	δ	33.36	5.52	0;0	0.8;1.6	2.05	-0.569	-0.648
Ru(0001)	α	23.17	13.14	0;0	1.1;2.8	1.95	-0.649	-0.649
	β	13.30	13.30	0;0	1.7;1.7	1.98	-0.821	-0.855
	γ	23.87	10.68	0;0	1.8;1.3	1.97	-0.828	-0.962
	δ	27.80	10.92	0;0	1.1;0.9	1.93	-0.698	-0.777

Reference

1) J. Guan, Z. Zhu, and D. Tománek, *Phys. Rev. Lett.*, 2014, **113**, 046804

2) G. Kresse, and J. Hafner, *Phys. Rev. B.*, 1993, **48**, 13115.

3) G. Kresse, and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.

4) G. Kresse, and D. Joubert, *Phys. Rev. B.*, 1999, **59**, 1758.

5) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

6) S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.

7) H. Monkhorst, and J. Pack, *Phys. Rev. B.*, 1976 , **13**, 5188–5192.