Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

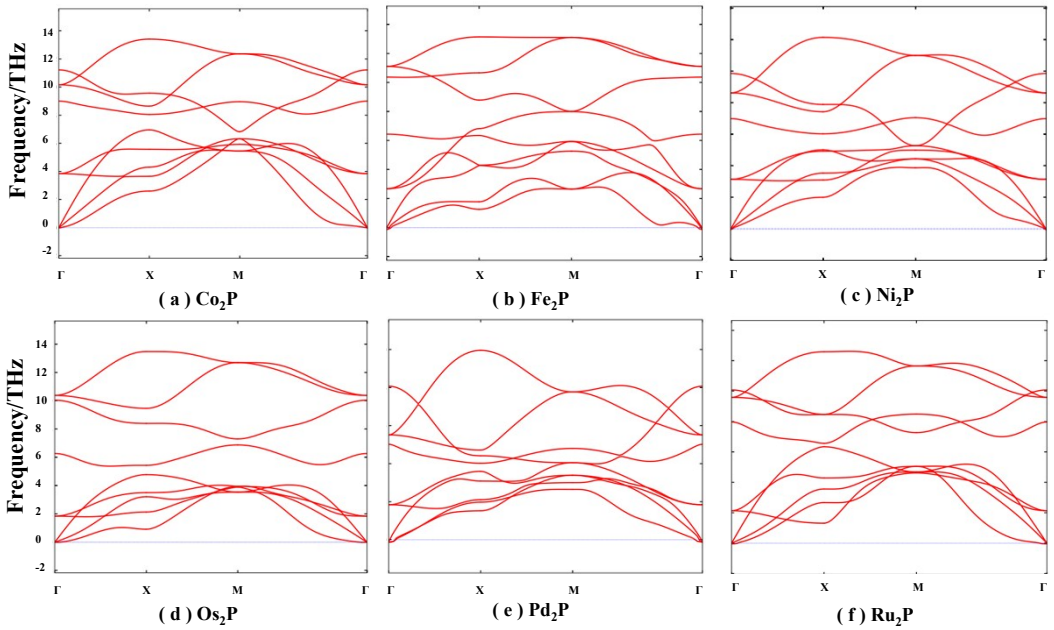

Fig. S1 Phonon dispersions of TM_2P monolayers along $\Gamma - X - M - \Gamma$ directions in Brillouin zone.

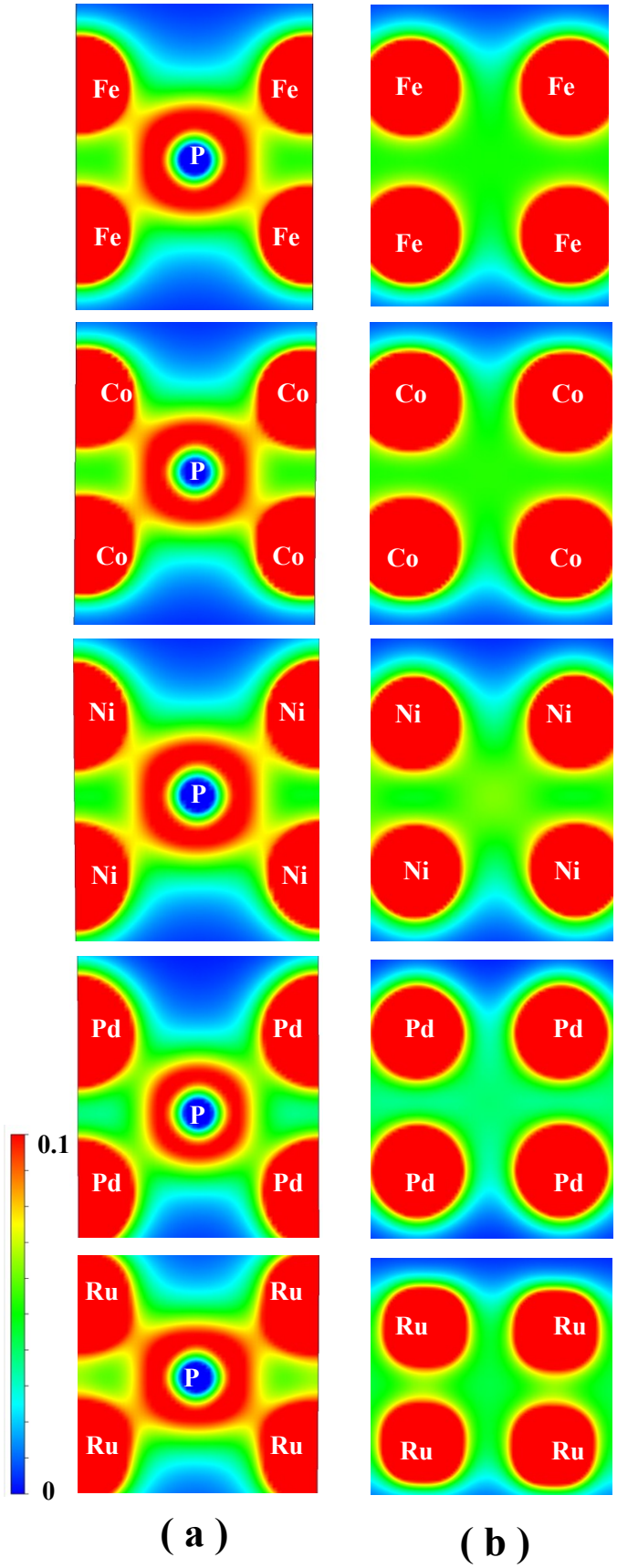

Fig. S2 The charge density for TM_2P monolayers on (a) (1 1 0) and (b) (0 1 0) face.

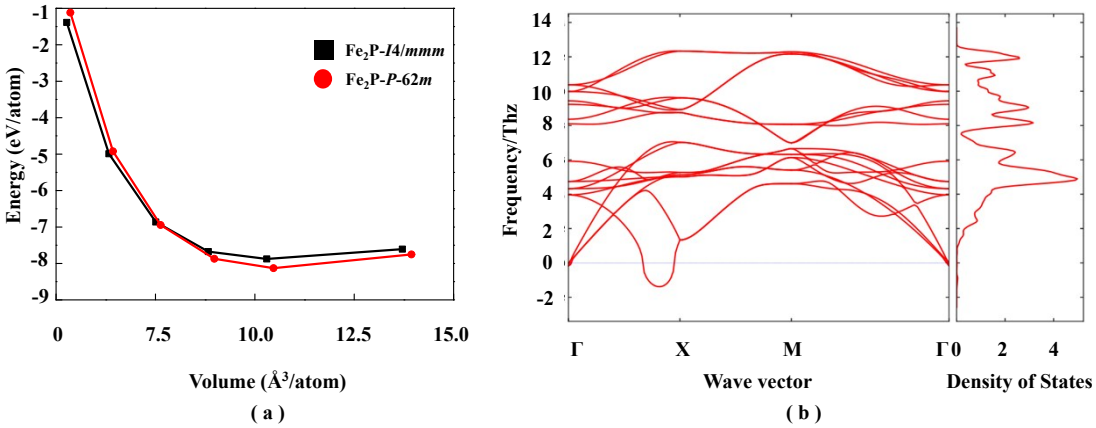

Fig. S3 (a) Total energy variations along with unit cell volume change for the *I*4/*mmm* and *P*-62*m* phase. (b)Phonon dispersions of *I4/mmm* Fe_2P along $\Gamma - X - M - \Gamma$ directions in Brillouin zone.

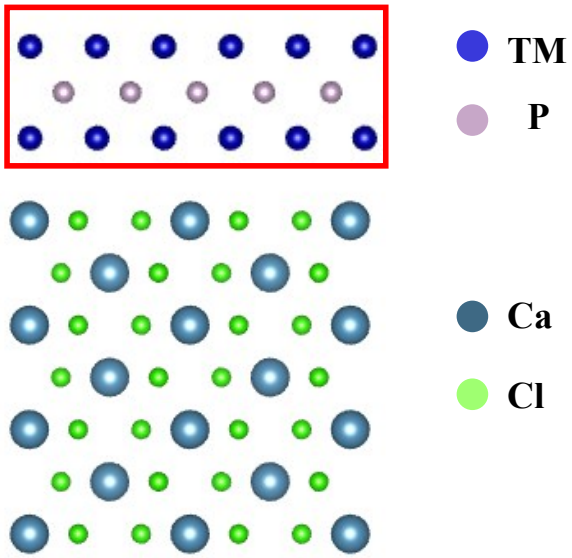

Fig. S4 Schematic representation of TM_2P grown on the surface of $CaCl_2$.

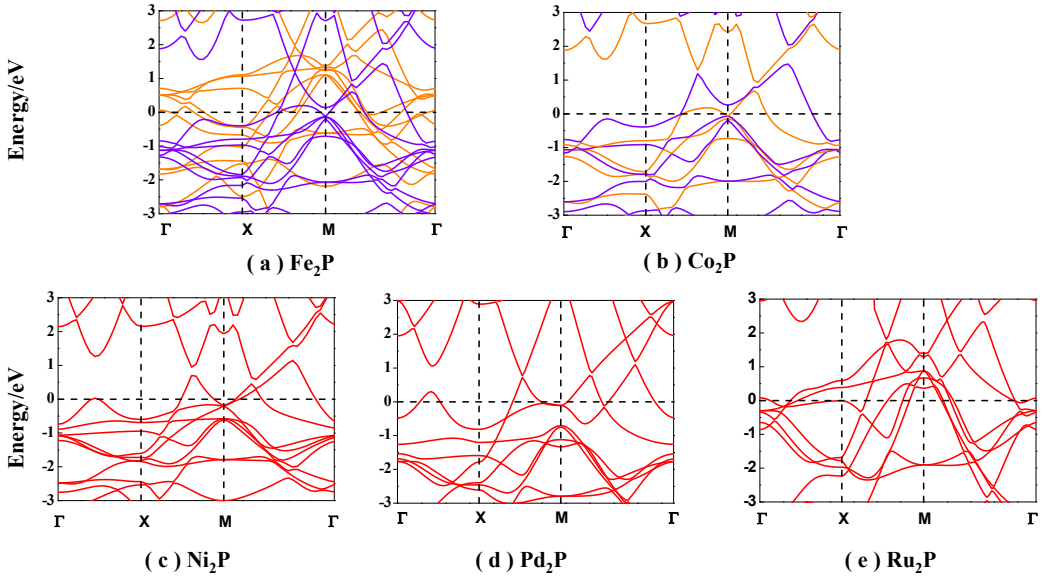

Fig. S5 The band structures of 2D (a) Fe_2P, (b) Co_2P, (c) Ni_2P, (d) Pd_2P and (e) Ru_2P. The purple and orange lines are spin-up and down bands. The Fermi level is set to zero.

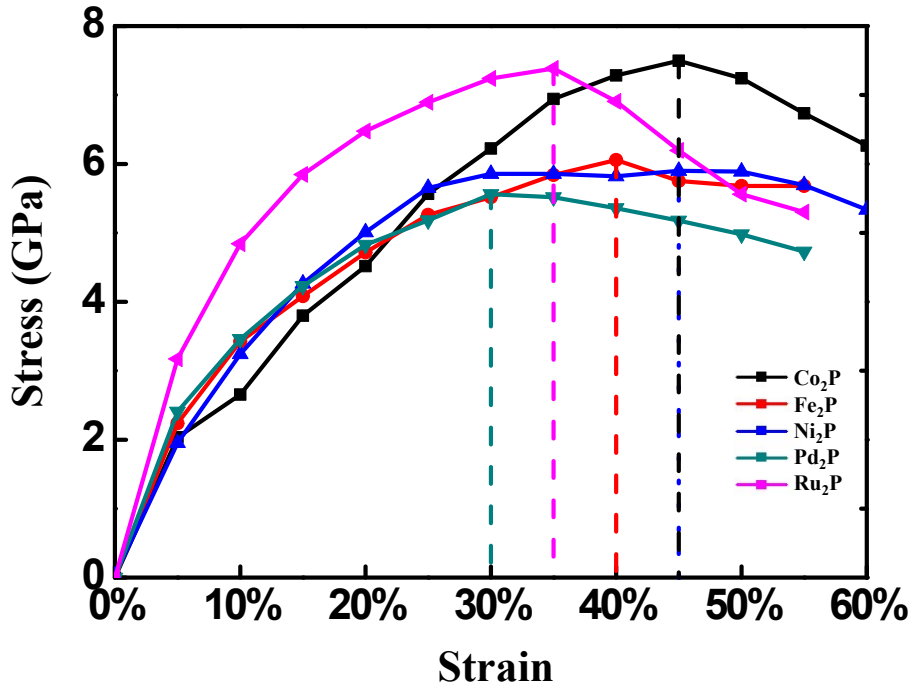

Fig. S6 The uniaxial tensile stress-strain response of 2D TM_2P monolayers along [100] direction.

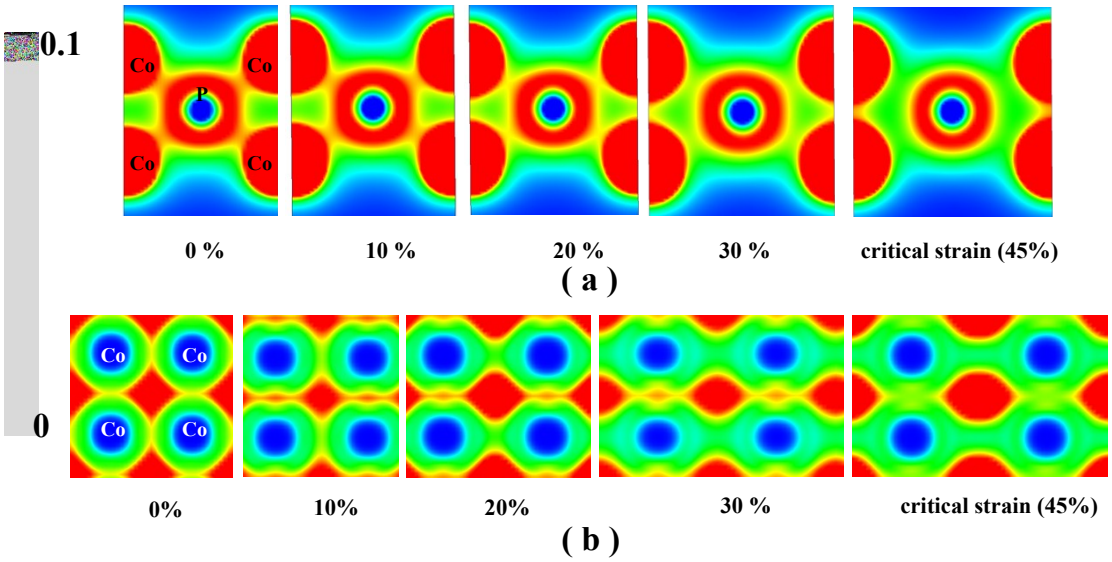

Fig. S7 (a) Charge density on (1 1 0) face and (b) isosurface of electron localization function (ELF) on (0 0 1) face of Co_2P under various tensile strains.

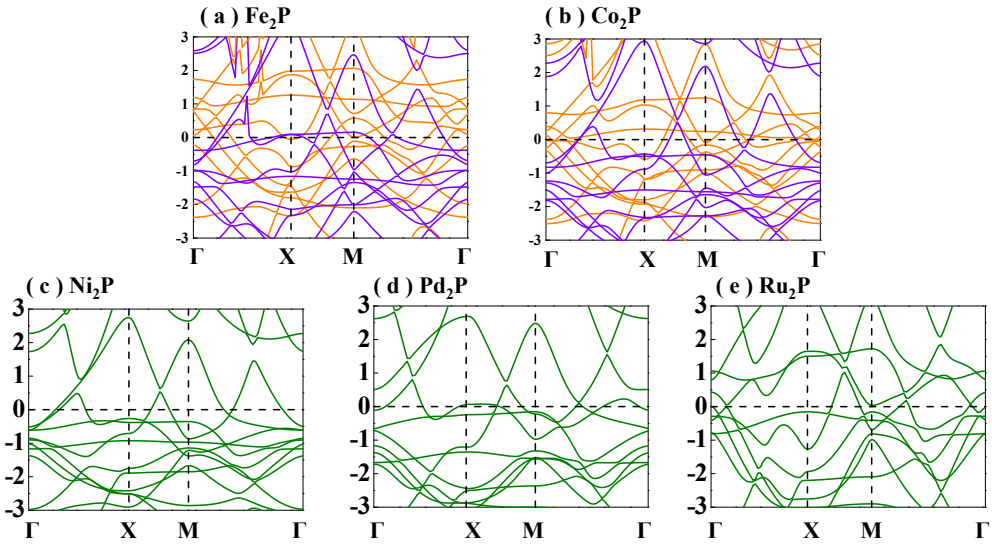

Fig. S8 The band structures of 2D (a) Fe_2P and (b) Co_2P, (c) Ni_2P, (d) Pd_2P and (e) Ru_2P under critical tensile strain, respectively. The Fermi level is set to zero.

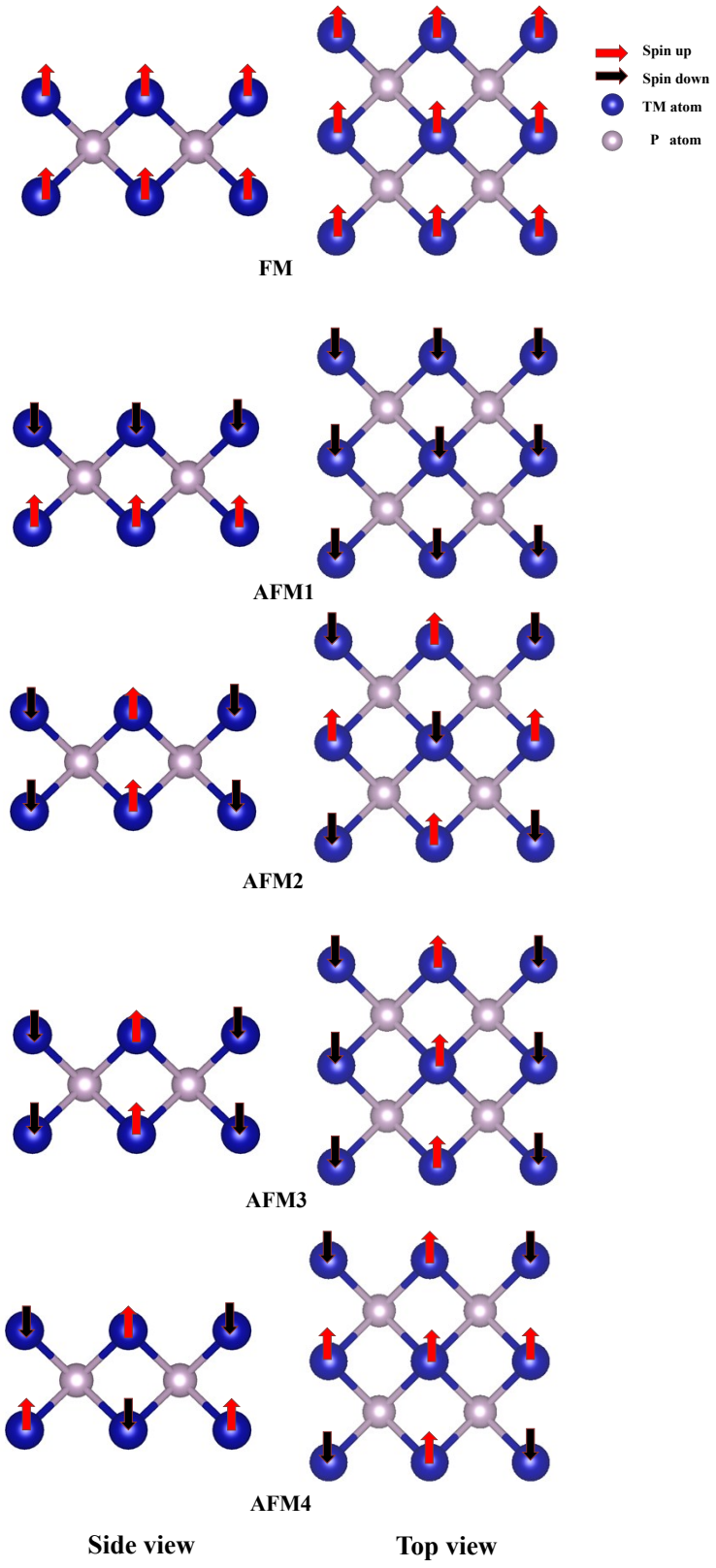

Fig. S9 Schematic diagrams for Fe_2P and Co_2P monolayers in FM and various AFM magnetic configurations. The blue and pink balls represent TM (Fe, Co) and P atoms, respectively.

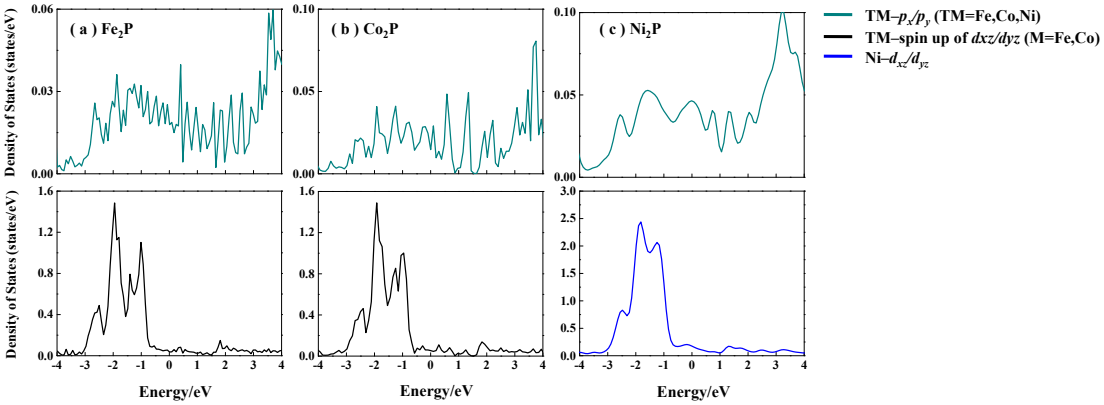

Fig. S10 The orbital project density of states of (a) Fe_2P, (b) Co_2P and (c) Ni_2P, respectively. The Fermi level is set zero.

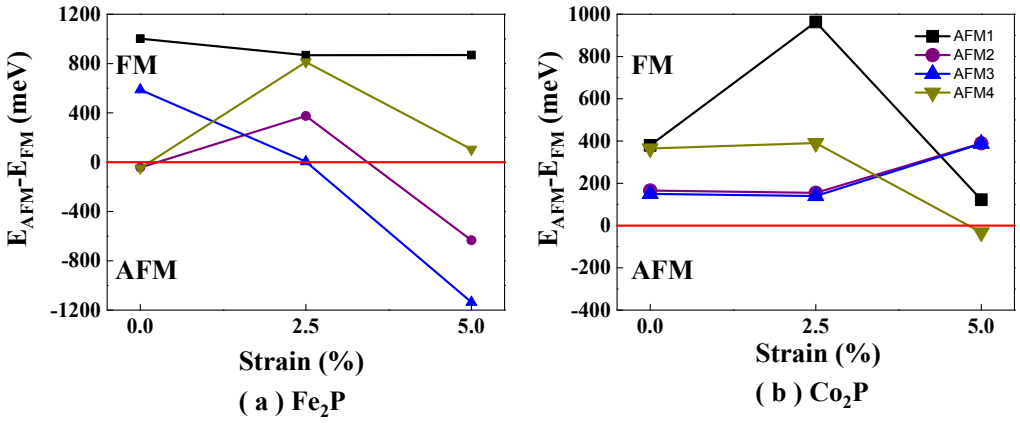

Fig. S11 Energy difference between the FM and AFM phases for (a) Fe_2P and (b) Co_2P. The AFM phase region is below the red line.

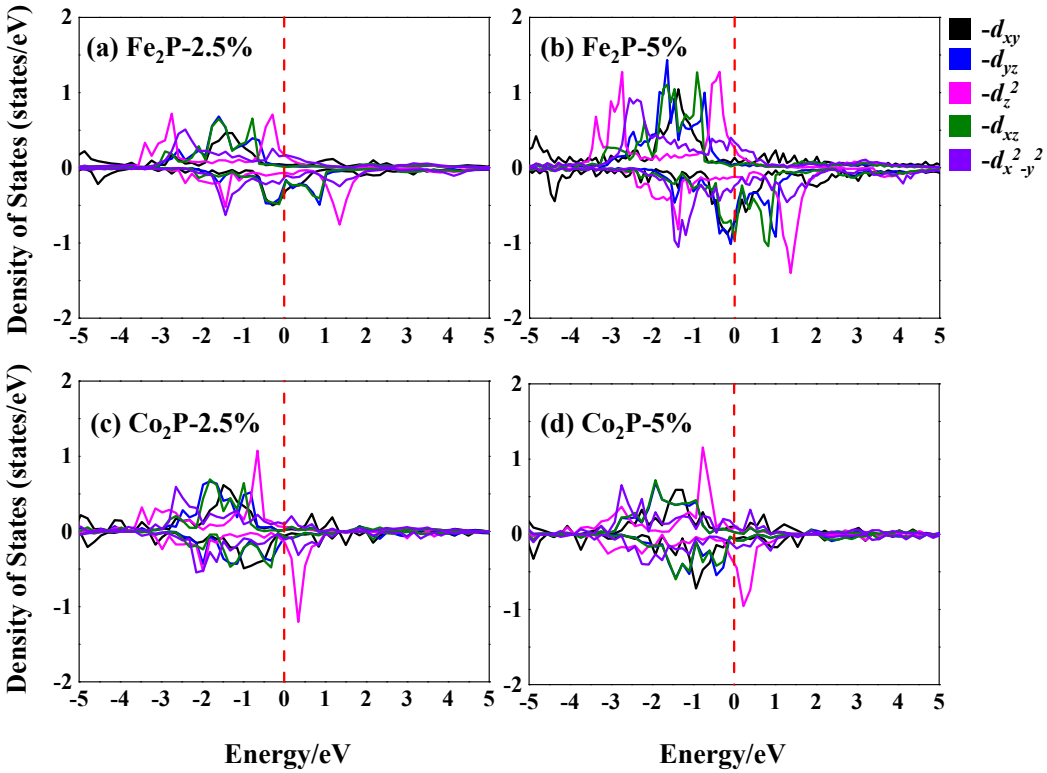

Fig. S12 The orbital projected density of states for Co_2P and Fe_2P monolayers under tensile strains.

Table S1. The corresponding formation energy per atom (E_f) of TM_2P monolayers.

	Fe_2P	Co_2P	Ni_2P	Pd_2P	Ru_2P	Os_2P
E_f (eV/atom)	–0.32	–0.44	–0.53	–0.59	–0.15	0.36

Table S2. Elastic constants C_{11}, C_{12}, and C_{66} of 2D TM_2P systems.

	C_{11} (N/m)	C_{12} (N/m)	C_{66} (N/m)
Fe_2P	119	59	30
Co_2P	141	55	24
Ni_2P	90	42	19
Pd_2P	97	27	9
Ru_2P	167	88	13

Table S3. Mulliken bond population of 2D TM_2P monolayers from PBE calculations.

Bond	Co-P	Co-Co	Fe-P	Fe-Fe	Ni-P	Ni-Ni	Pd-P	Pd-Pd	Ru-P	Ru-Ru
Bond population	0.57	-0.71	0.69	-0.91	0.67	-0.89	0.57	-1.40	0.68	-0.87

Table S4. The adsorption energy ΔE_H and ΔE_{ZPE} - $T\Delta S_H$ of TM_2P monolayers for hydrogen evolution from DTF calculations.

	Fe_2P	**Co_2P**	**Ni_2P**	**Pd_2P**	**Ru_2P**
ΔE_H /eV	–0.49	–0.65	–0.50	–0.20	–0.52
ΔE_{ZPE} - $T\Delta S_H$ /eV	0.20	0.23	0.23	0.22	0.22

Table S5 Atomic Mulliken charges in TM_2P monolayers

Species		*s*	*p*	*d*	Charge (*e*)
Fe_2P	P	1.52	3.44	0.00	0.04
	Fe	0.53	0.44	7.05	0.02
Co_2P	P	1.54	3.44	0.00	0.02
	Co	0.58	0.43	8.01	–0.01
Ni_2P	P	1.55	3.41	0.00	0.04
	Ni	0.58	0.51	8.94	–0.02
Ru_2P	P	1.64	3.38	0.00	–0.01
	Ru	0.72	-0.17	7.44	0.01
Pd_2P	P	1.66	3.08	0.00	0.25
	Pd	0.63	0.11	9.39	–0.13

Table S6 Exchange coupling parameters (J_1, J_2, J_3, and J_4) for Co_2P and Fe_2P monolayers.

	J_1/meV	**J_2/meV**	**J_3/meV**	**J_4/meV**
Co_2P	31.06	1.08	4.11	2.10
Fe_2P	–44.08	–43.70	42.33	19.04