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Supporting data:

Exploring new two-dimensional monolayers: pentagonal transitional metal borides/carbides (penta-TMB/Cs)

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Table S1. Lattice parameters of 2D TMBs and TMCs: a/b is lattice constant (a=b) and d is the distance between two neighboring boron/carbon atoms in vertical direction.

TMBs	a/b (Å)	d (Å)	TMCs	a/b (Å)	d (Å)
TiB	5.66	1.66	TiC	5.44	1.49
ZrB	6.15	1.63	ZrC	5.92	1.47
HfB	6.07	1.67	HfC	5.85	1.51
VB	5.25	1.70	VC	5.13	1.54
NbB	5.70	1.71	NbC	5.59	1.57
TaB	5.69	1.75	TaC	5.58	1.61

CrB	5.01	1.76	CrC	4.91	1.58
MoB	5.45	1.78	MoC	5.35	1.60
WB	5.46	1.82	WC	5.36	1.68
MnB	4.85	1.76	MnC	4.77	1.57
FeB	4.78	1.74	FeC	4.80	1.53
CoB	4.83	1.68	CoC	4.82	1.57
NiB	4.88	1.75	NiC	5.04	1.45

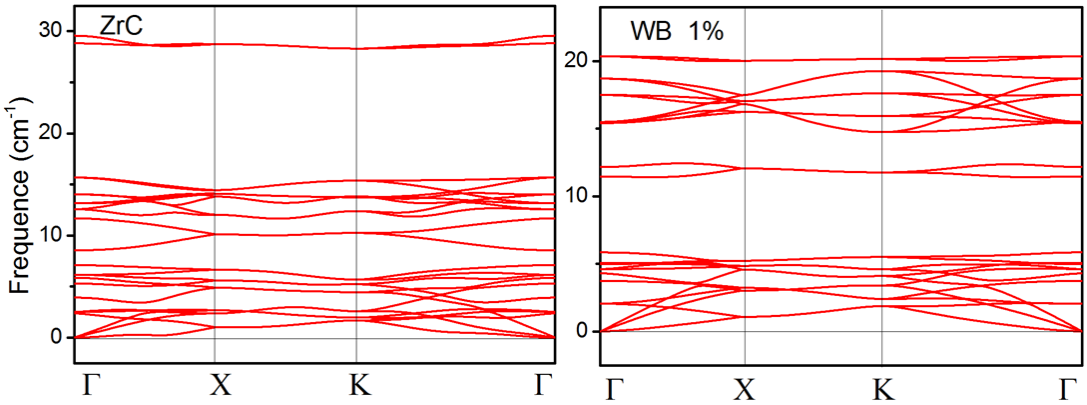

Fig. S1 Calculated phonon dispersions of ZrC and WB.

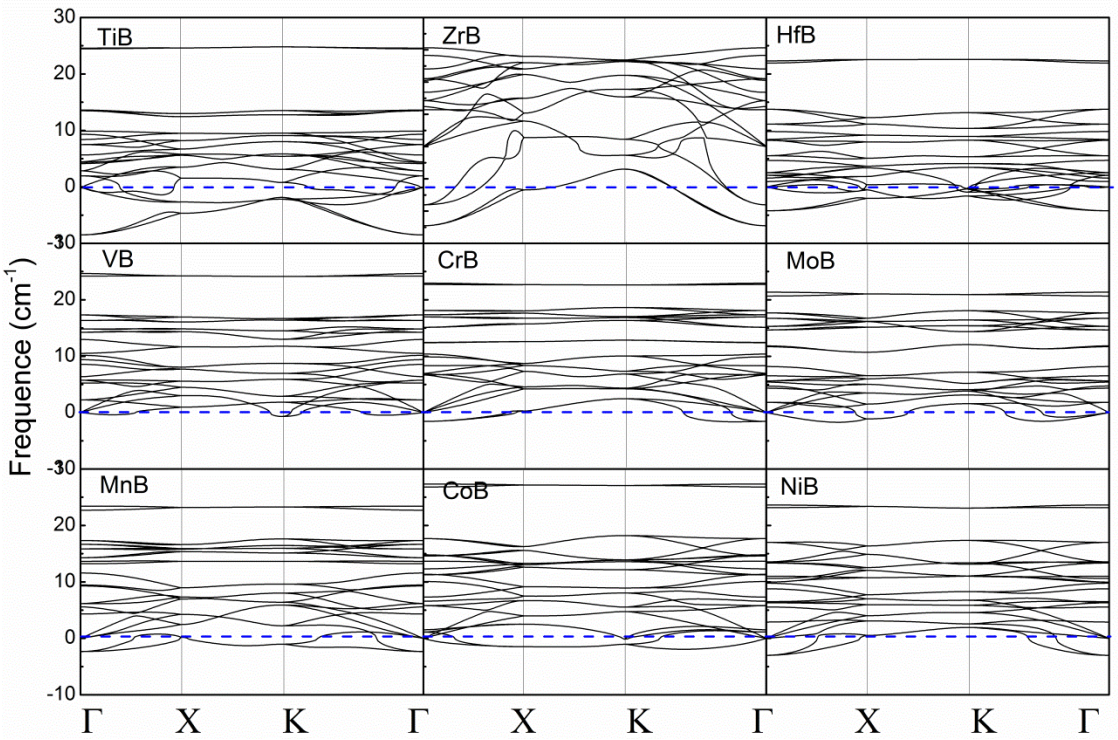

Fig. S2 Calculated phonon dispersions of penta-TMBs.

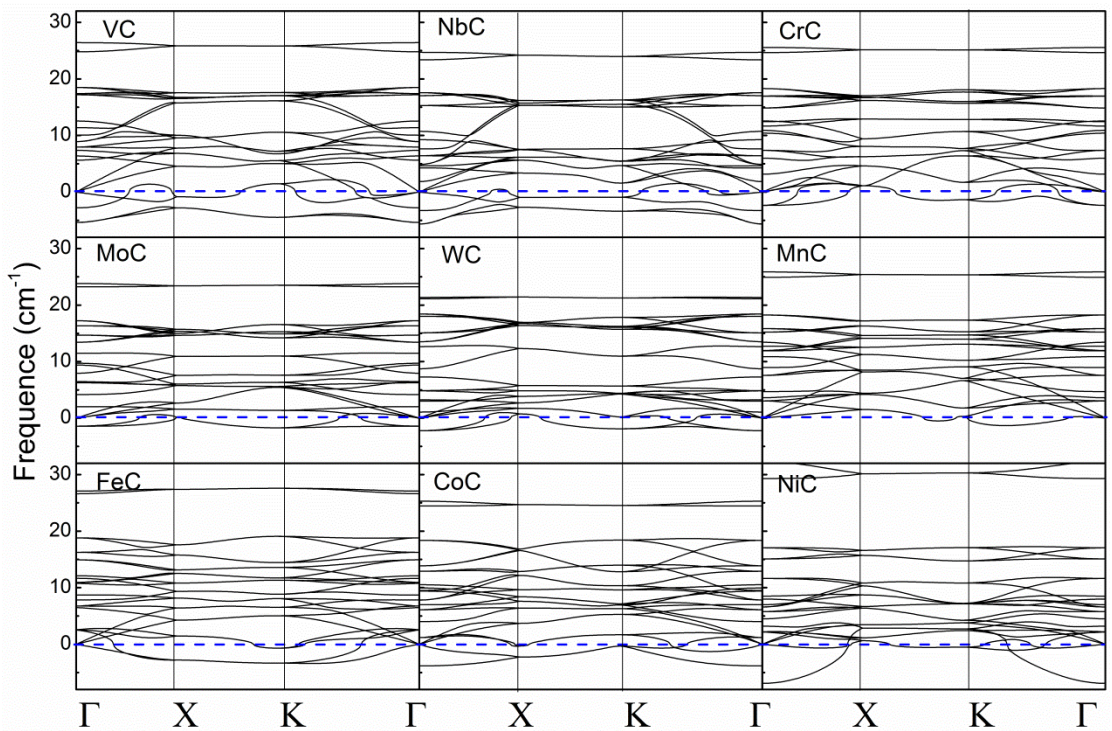

Fig. S3 Calculated phonon dispersions of penta-TMCs.

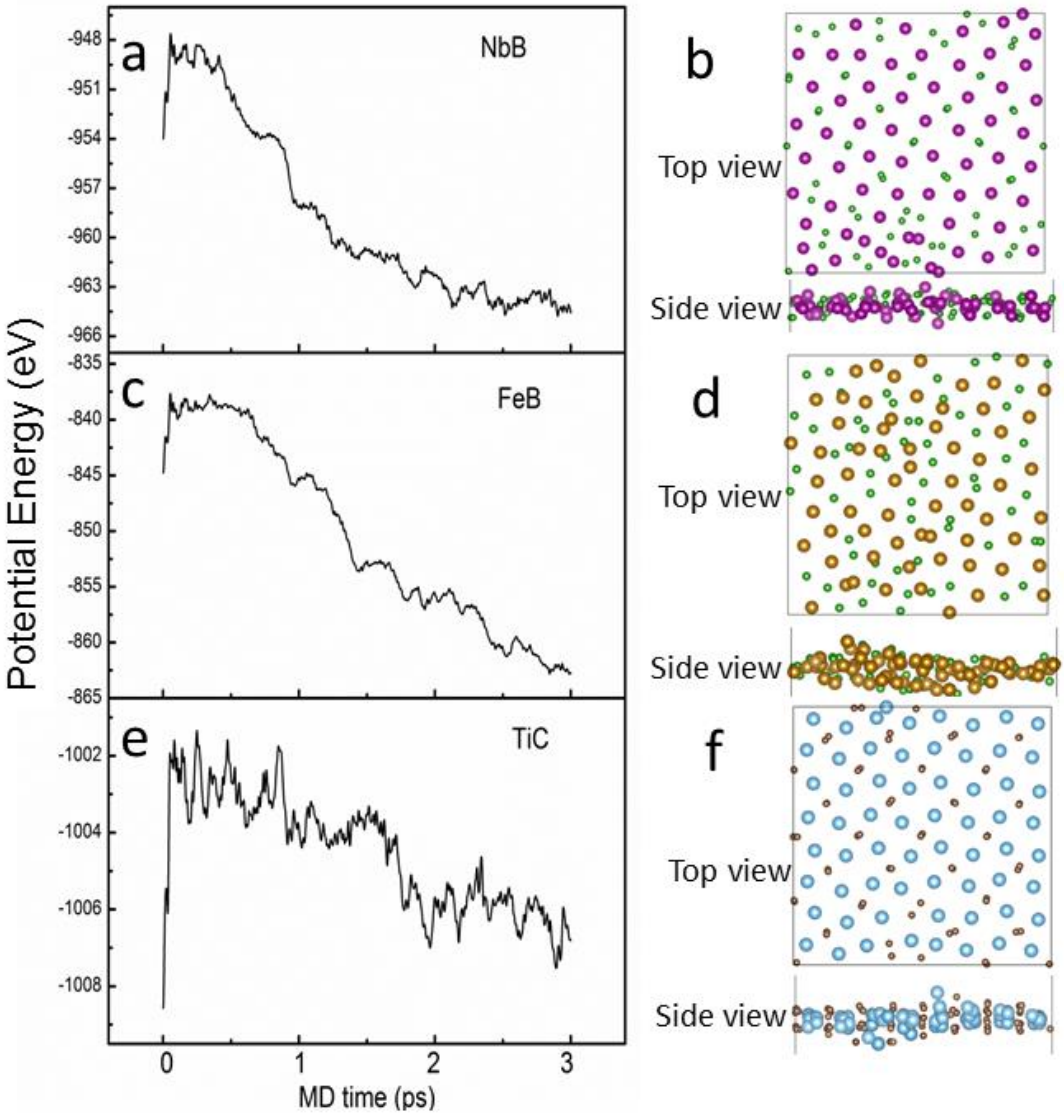

Fig. S4 Total potential energy as a function of MD time at temperature of 300 K (a, c & e). Top and side views of (b) NbB, (d) FeB, and (f) TiC after 3 ps.

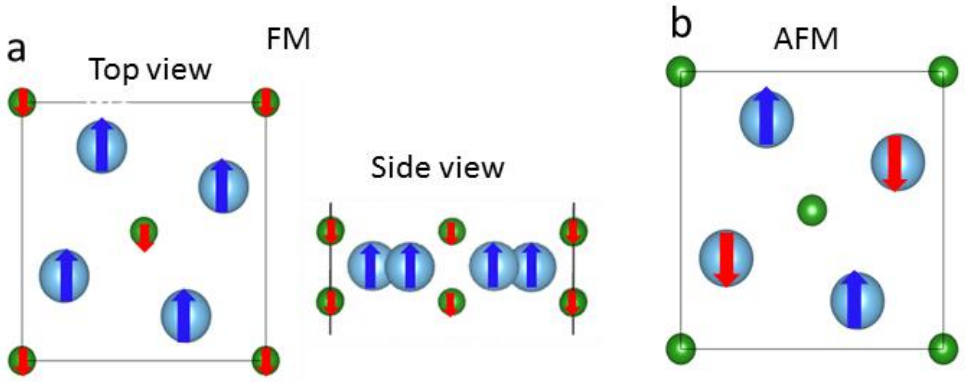

Fig. S5 (a) Top and side view of FM configuration. (b) Top view of AFM configuration. Blue and red arrows indicate the spin up and down states, respectively.

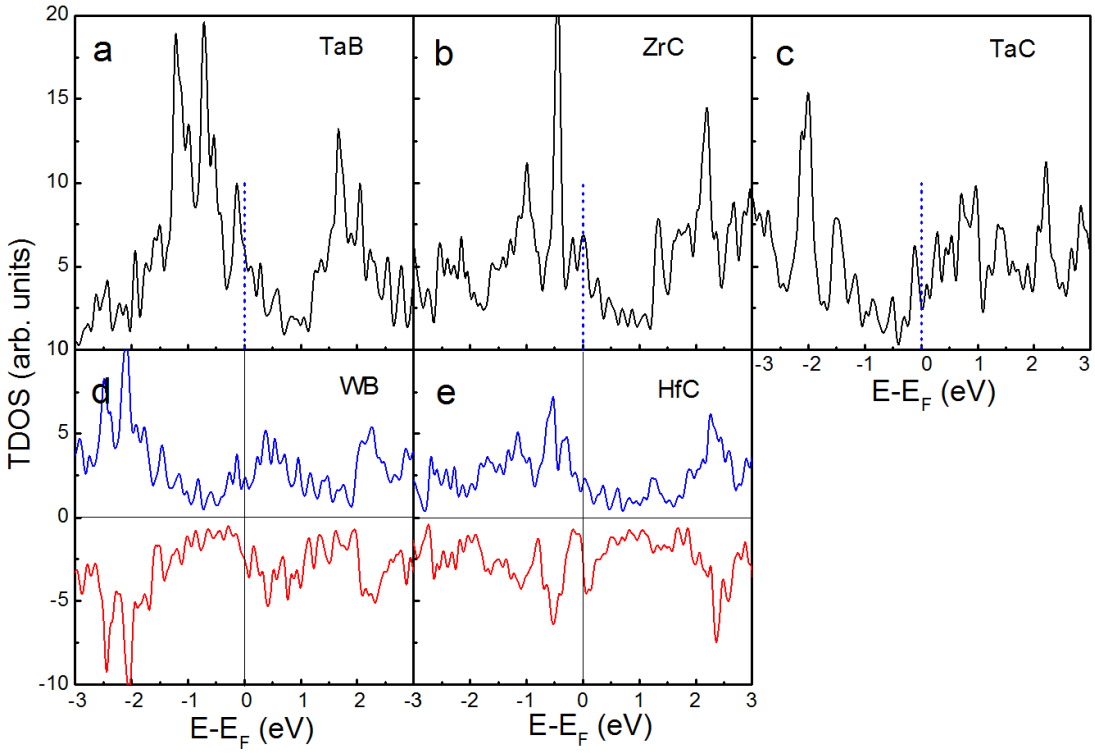

Fig. S6 Calculated total density of states (TDOSs) of (a) TaB, (b) ZrC, (c) TaC, (d) WB, and (e) HfC, respectively.

Table S2 Calculated ΔE_{ZPE} (eV) of Penta-TMB/TMCs.

H-coverage	TaB	WB	ZrC	TaC	HfC
1/4	0.052	0.063	0.090	0.083	0.091
2/4	0.093	0.065	0.090	0.094	0.099
3/4	0.065	0.084	0.132	0.181	0.121
4/4	0.060	0.082	0.111	0.122	0.114

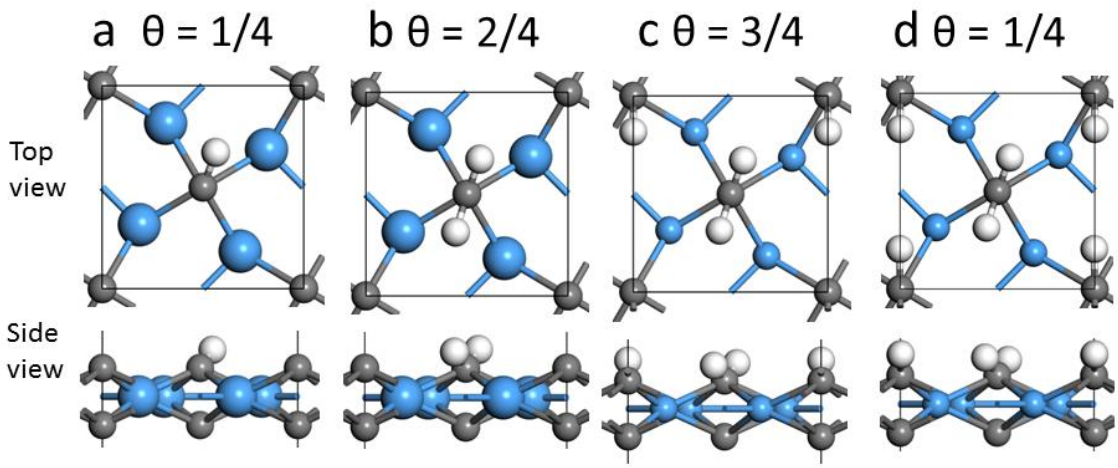

Fig. S7 Top and side views of the structure of penta-TMBs and penta-TMCs with hydrogen

adsorption at hollow site.

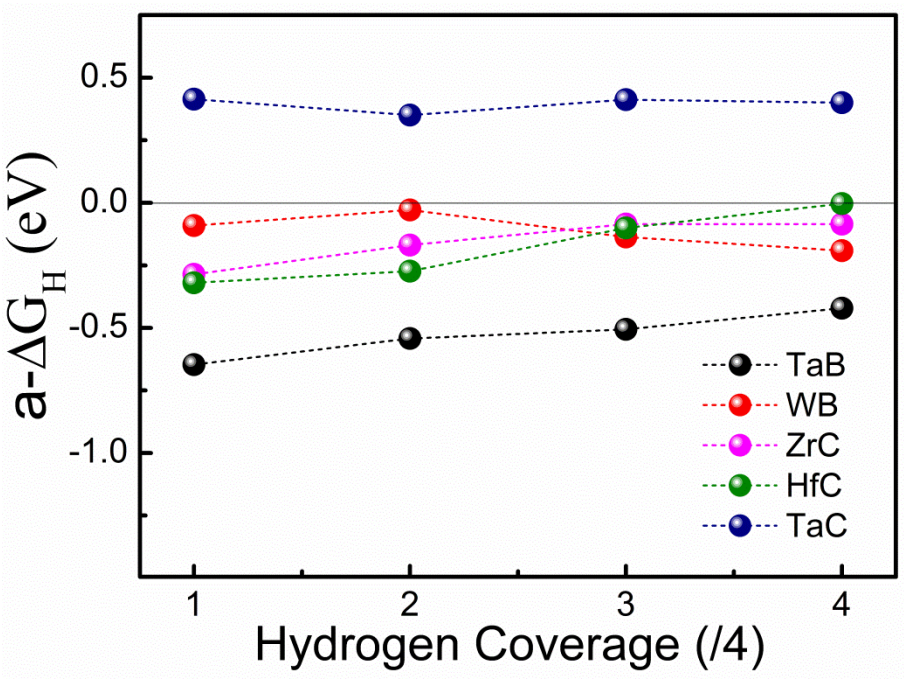

Fig. S8 Calculated average Gibbs free energies of penta-TMBs and penta-TMCs monolayers as a function of H coverage: collective (a-ΔG_H) processes.

Effect of defect on HER

WB and ZrC were used as examples to study the effect of defect on the HER performance of penta-TMB/TMCs. We removed one metal atom to investigate the effect of vacancy in WB and ZrC on their catalytic performance (Fig. S9a-d). From the calculated Gibbs free energies, the i-ΔG_H of defective WB and ZrC are far away from zero than those of perfect WB and ZrC except at a hydrogen coverage of $\theta = 3/4$, indicating their HER activities reduced slightly (Fig. S9e). For collective process, the a-ΔG_H of defective WB and ZrC are closer to zero than perfect structures at high H-coverage, indicating the HER activities improved (Fig. S9f). However, at low H-coverage, the catalytic performance reduced (Fig. S9f).

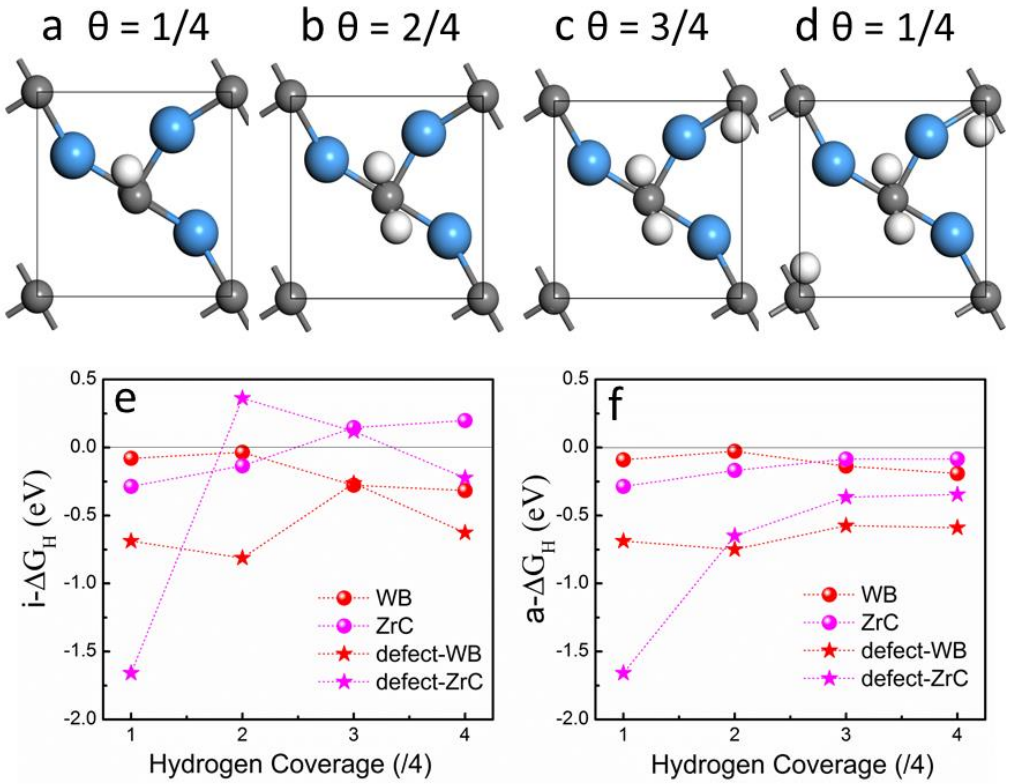

Fig. S9 (a-d) Top view of the structure of penta-TMBs and penta-TMCs with hydrogen adsorption. (e) Calculated differential Gibbs free energies (i-ΔG_H) of perfect and defective in WB and ZrC monolayers as a function of H-coverage in individual processes. (f) Calculated average Gibbs free energies (a-ΔG_H) of perfect and defective WB and ZrC monolayers as a function of H-coverage in collective processes.

Generally, the catalytic activity depends on the carrier density near the Fermi level, which is related to the H-coverage. To reveal the origin of HER performance of penta-MB/MCs, we calculated the total densities of states of TaB, WB, ZrC, HfC, and TaC. All the penta-MB/MCs are metallic from calculated DOSs. The carrier density can be estimated from the TDOSs. We see that the carrier density changes depend on their compositions and H-coverage, which affect their HER activities in individual/collective process. The high conductivity indicates the high catalytic ability. From the calculated total DOSs of penta-MB/MCs, their HER performance depends on the carrier density estimated from the total DOS (Fig. S10).

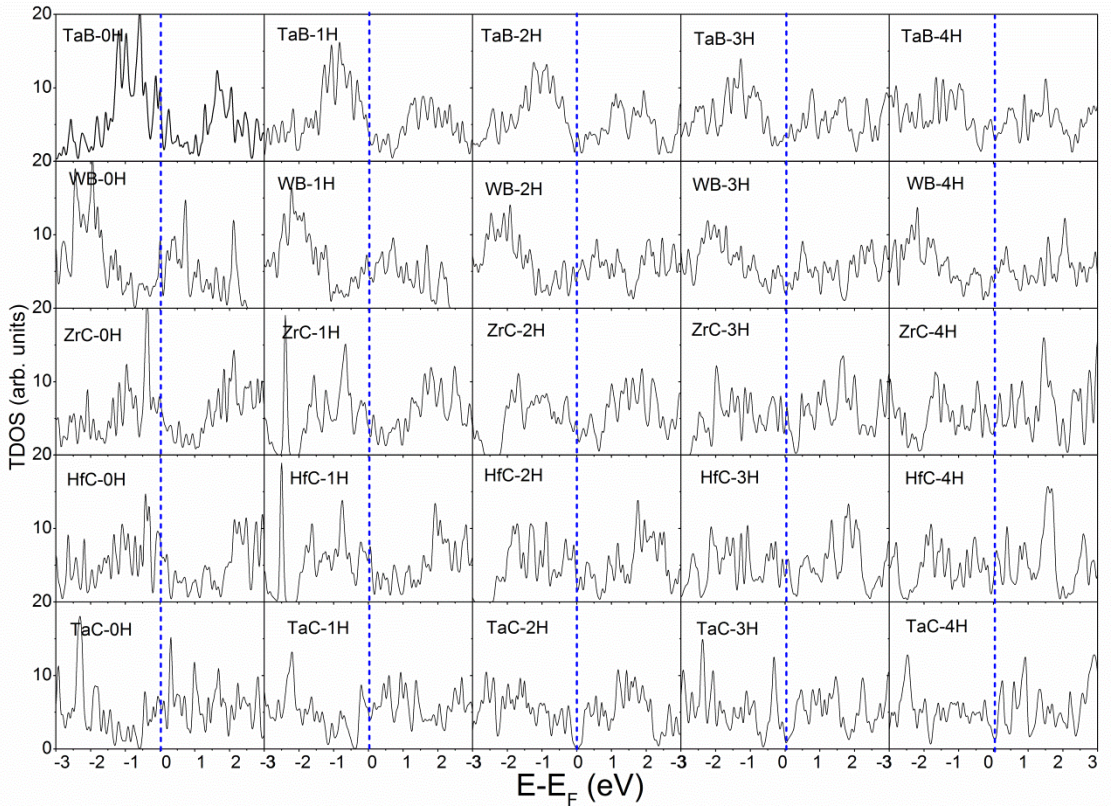

Fig. S10 Calculated TDOSs of TaB, WB, ZrC, HfC, and TaC at different H-coverage.

Table S3 Calculated Gibbs free energies on MXenes and MX_2 monolayers from literatures. Tx – functional group; I – Individual process; A – Average process

Materials	Phase	**Adsorption site**	**Hydrogen coverage**	**T_x**	**ΔG_H (eV)**	I or A	ref
Ti_2C	1T	*Basal Plane*	*1/8*	O2	-0.04	I	1
			2/8	O2	-0.13	I	1
			3/8	O2	0.13	I	1
			4/8	O2	0.10	I	1
			Full	Pure	-1.13	A	1
V_2C	1T	*Basal Plane*	*1/8*	O2	-0.54	I	1
			2/8	O2	-0.47	I	1
			3/8	O2	-0.02	I	1
			4/8	O2	-0.05	I	1
			Full	Pure	-0.77	A	1
Nb_2C	1T	*Basal Plane*	*1/8*	O2	0.02	I	1
			2/8	O2	0.11	I	1
			3/8	O2	0.38	I	1
			4/8	O2	0.38	I	1
			Full	Pure	-0.82	A	1
W_2C	1T	*HC*	*Full*	Pure	-0.15	I	2
		TX	*Full*	Pure	-0.05	I	2
		TM	*Full*	Pure	-0.02	I	2
W_2N	1T	*HC*	*Full*	Pure	-0.21	I	2
		TX	*Full*	Pure	0.09	I	2
Mo_2C	1T	*TM*	*1/4*	Pure	-0.1	I	2
			1/2	Pure	-0.06	I	2
Mo_2N	1T	*TM*	*1/4*	Pure	-0.008	I	2
			1/2	Pure	-0.001	I	2
MoS_2	1T	*TX*	*1/16*	Pure	0.13	A	3
			1/8	Pure	0.16	A	3
			1/4	Pure	0.18	A	3
			1/2	Pure	0.255	A	3
	2H	*TX*	*1/16*	Pure	1.6	A	3
VS_2	2H	*TX*	*1/12*	Pure	0.007	I	4
			1/6	Pure	0.051	I	4
WS_2	1T	*TX*	*1/16*	Pure	0.28	I	5
			2/16	Pure	0.36	I	5

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