Supplementary Information

Accelerating 2D MXenes Catalyst Discovery for Hydrogen Evolution Reaction by Computer-Driven Workflow and Ensemble Learning Strategy

Xiaoxu Wang[1, 2, 5§], Changxin Wang[1, 3§], Shinan Ci[4], Yuan Ma[1, 3], Tong Liu[5], Lei Gao[1, 3], Ping Qian[1, 2*], Chunlin Ji[6], Yanjing Su[1,3*]

[1]Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, Beijing 100083, China

[2]Department of Physics, University of Science and Technology Beijing, Beijing 100083, China

[3]Corrosion and Protection Center, University of Science and Technology Beijing, Beijing 100083, China

[4]Science and Technology on Advanced High Temperature Structural Materials Laboratory, Beijing Institute of Aeronautical Materials, Beijing 100095, China

[5]Beijing Key Laboratory of Cloud Computing Key Technology and Application, Beijing Computing Center, Beijing Academy of Science and Technology, Beijing 100094, China

[6]Kuang-Chi Institute of Advanced Technology, Shenzhen, Guangdong 518000, China

E-mail address: qianping@ustb.edu.cn, yjsu@ustb.edu.cn

Author contributions: §Xiaoxu Wang, Changxin Wang.

Supplementary Tables

Supplementary Figures

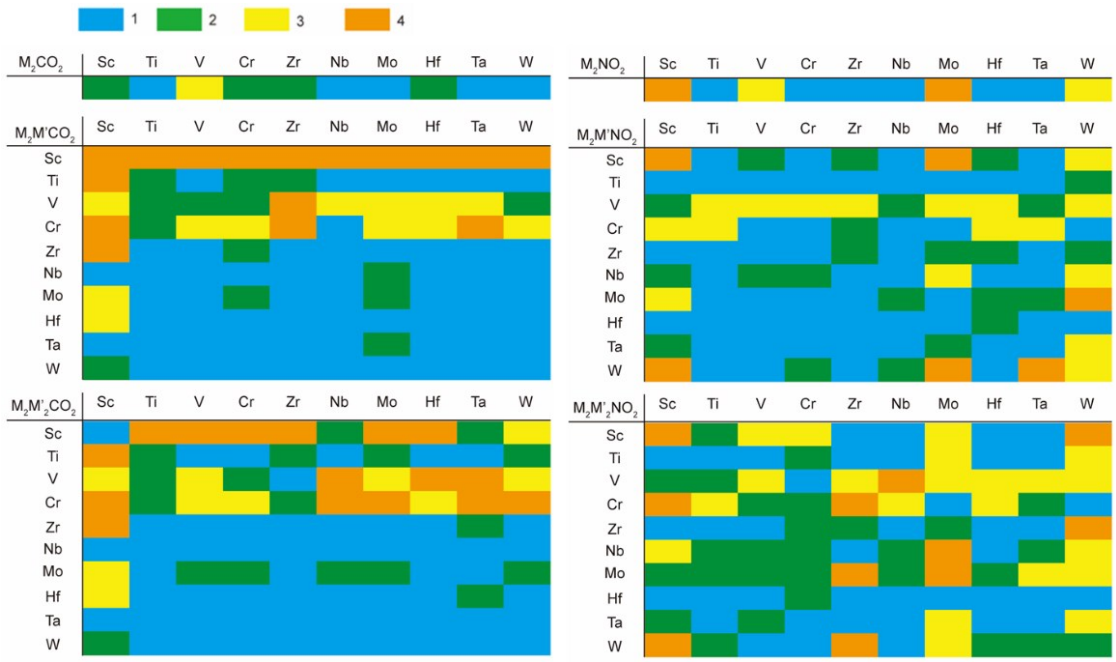
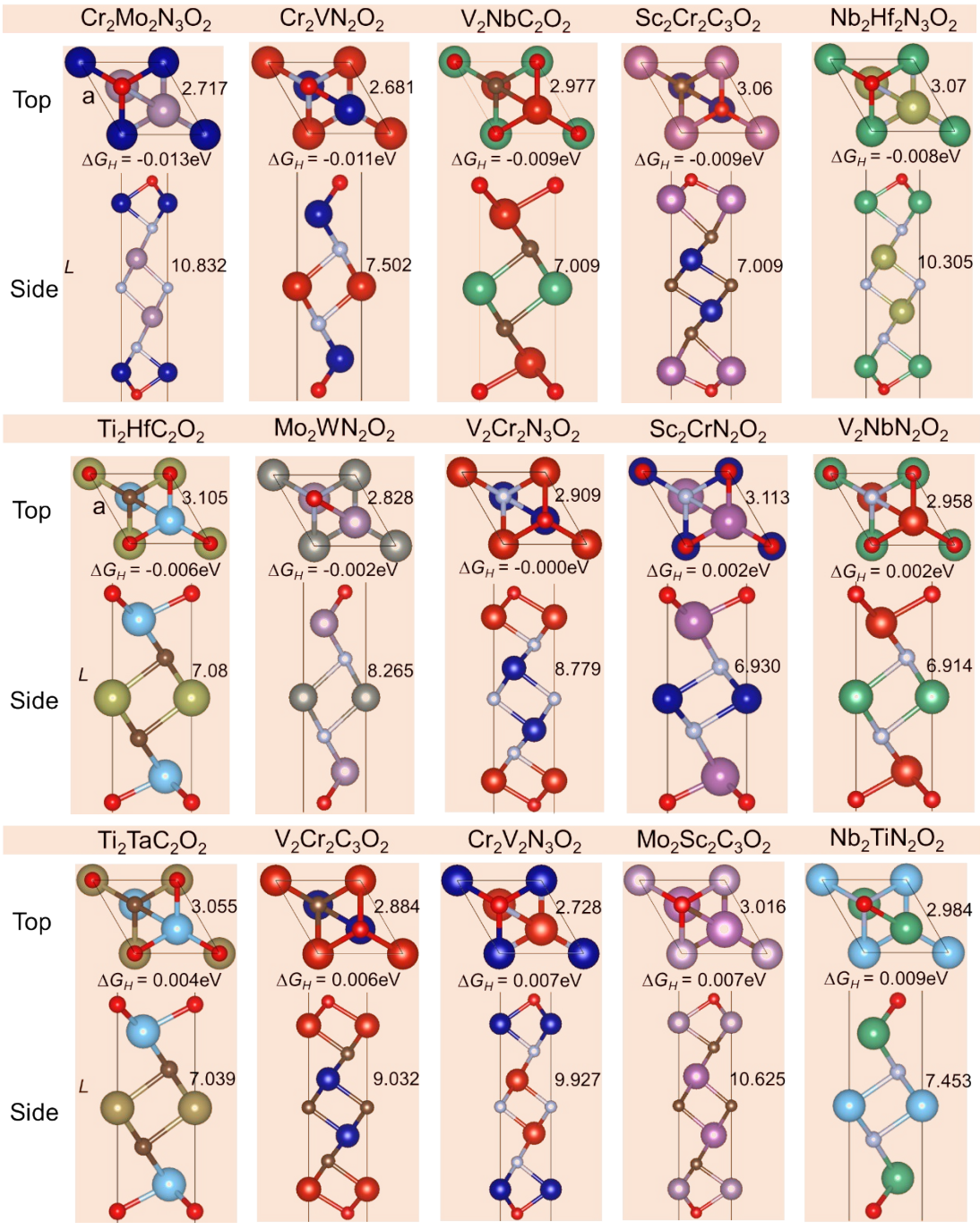


Fig. S1. Heat map showing the H equilibrium coverage for different MXenes. Under these conditions, the equilibrium coverage is defined as the coverage at which the free energy of hydrogen adsorption (ΔG_H) is closest to zero. 1, 2, 3, 4 denote the H coverage of 1/4, 2/4, 3/4 and 4/4, respectively.


Cr2Mo2N3O2
Cr2VN2O2
V2NbC2O2
Sc2Cr2C3O2
Nb2Hf2N3O2
Top
Side
a
L
2.717
ΔGH = -0.013eV
10.832
2.681
ΔGH = -0.011eV
7.502
2.977
ΔGH = -0.009eV
7.009
3.06
ΔGH = -0.009eV
7.009
3.07
ΔGH = -0.008eV
10.305
Ti2HfC2O2
Mo2WN2O2
V2Cr2N3O2
Sc2CrN2O2
V2NbN2O2
3.105
ΔGH = -0.006eV
7.08
2.828
ΔGH = -0.002eV
8.265
2.909
ΔGH = -0.000eV
8.779
3.113
ΔGH = 0.002eV
6.930
2.958
ΔGH = 0.002eV
6.914
Ti2TaC2O2
V2Cr2C3O2
Cr2V2N3O2
Mo2Sc2C3O2
Nb2TiN2O2
3.055
ΔGH = 0.004eV
7.039
2.884
ΔGH = 0.006eV
9.032
2.728
ΔGH = 0.007eV
9.927
3.016
ΔGH = 0.007eV
10.625
2.984
ΔGH = 0.009eV
7.453

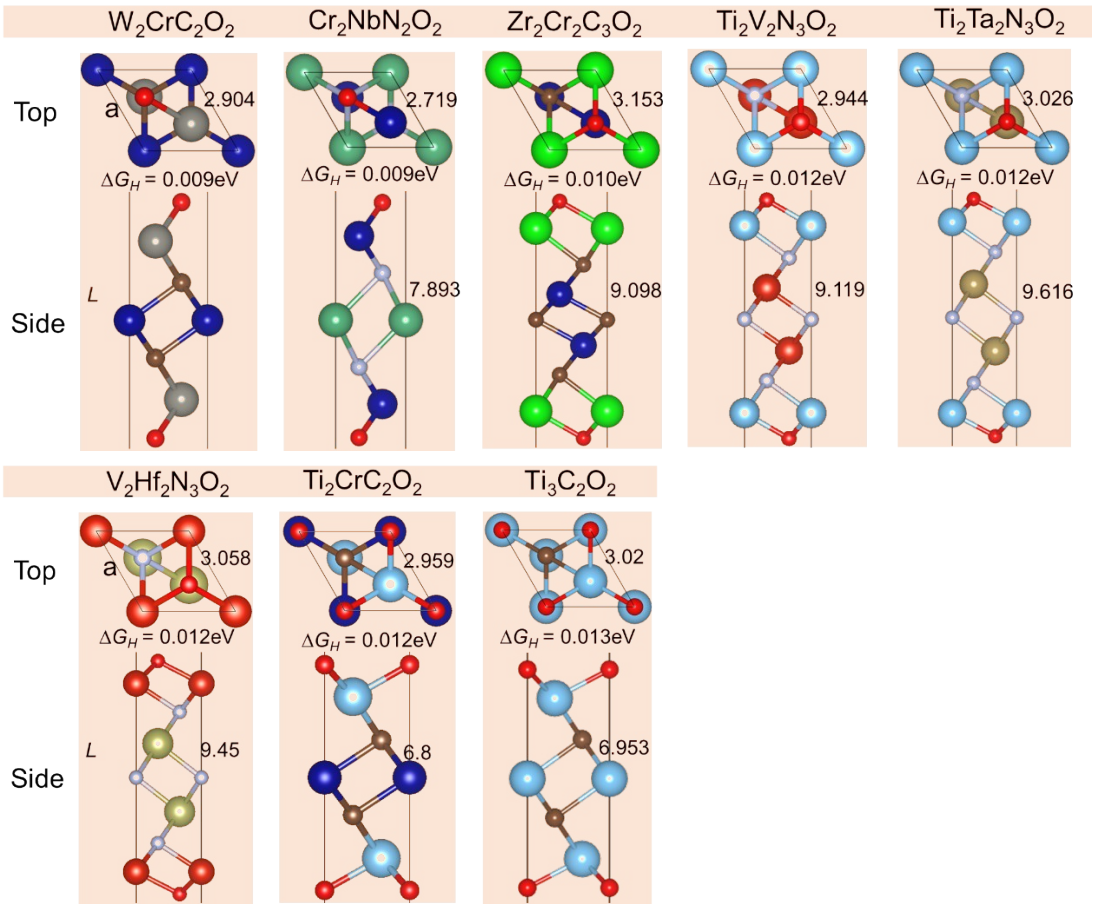
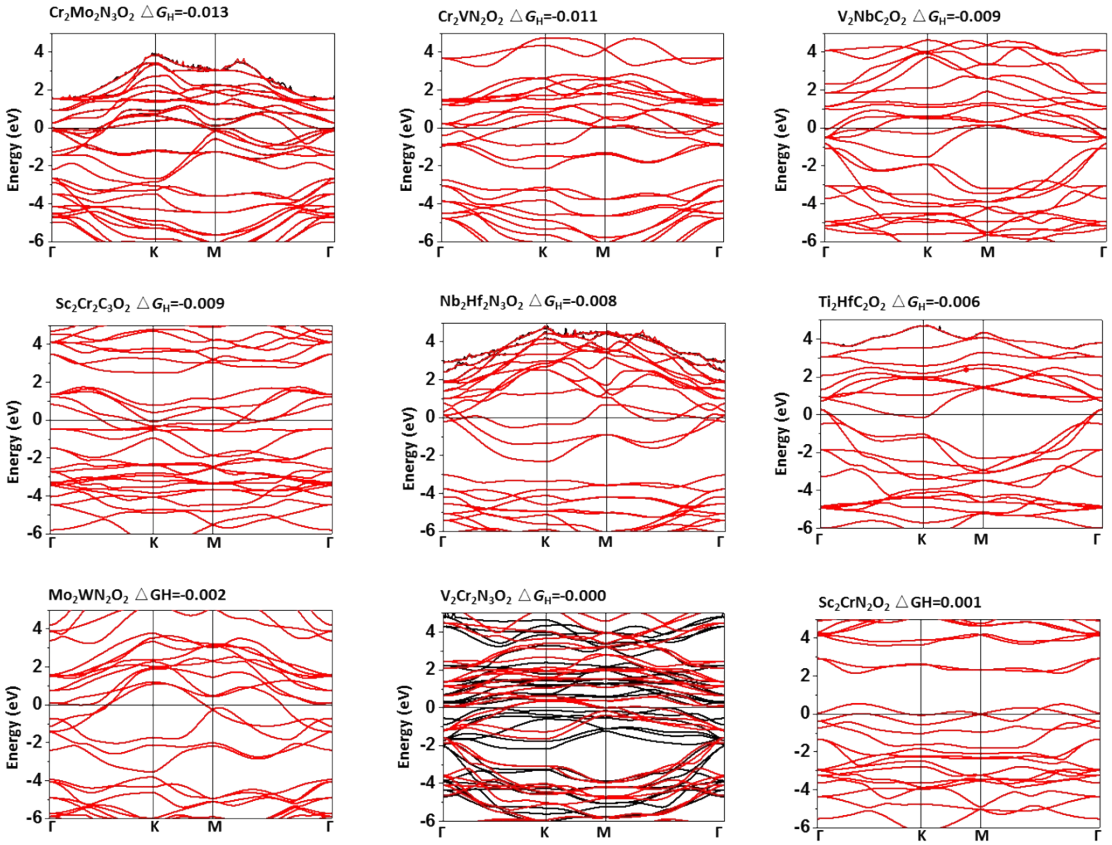
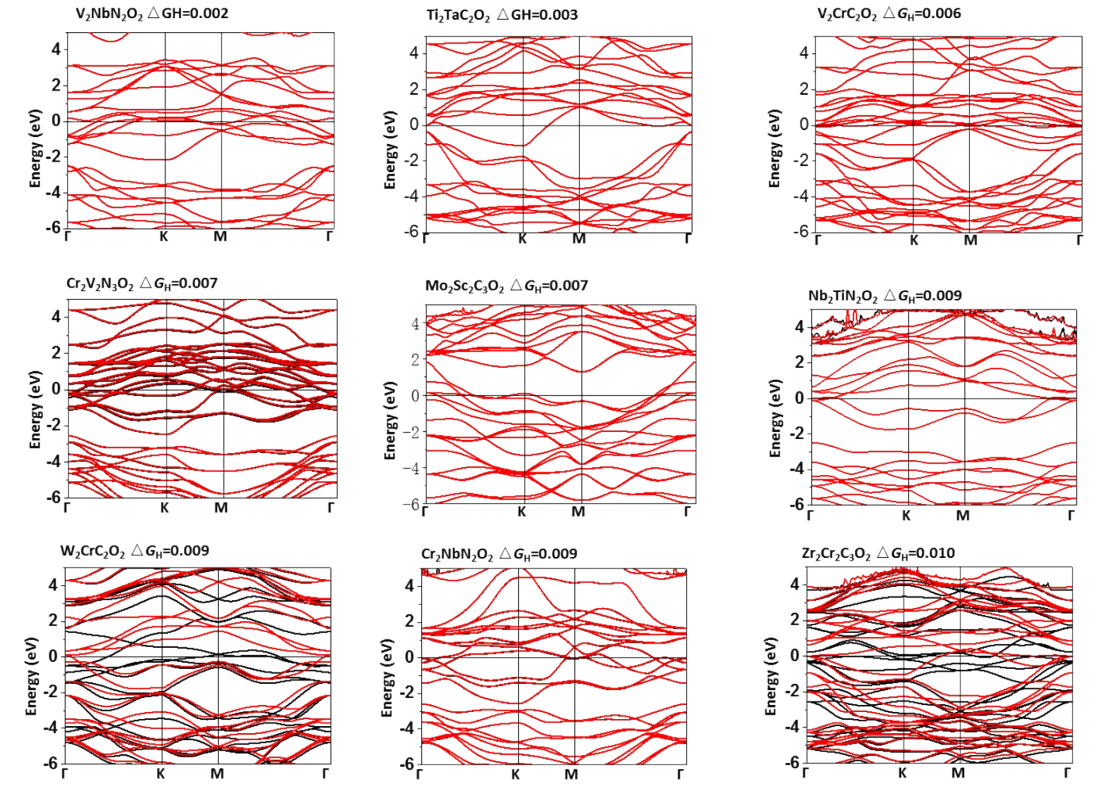


Fig. S2. The structure information of $Ti_3C_2O_2$ and 22 MXenes OBAs with better catalytic activity than $Ti_3C_2O_2$. Lattice parameters are expressed in terms of *a*, and *L* in terms of layer thickness. The top and side views of all structures are listed in the order of ΔG_H.


Cr2Mo2N3O2 △GH=-0.013
Cr2VN2O2 △GH=-0.011
V2NbC2O2 △GH=-0.009
Sc2Cr2C3O2 △GH=-0.009
Nb2Hf2N3O2 △GH=-0.008
Ti2HfC2O2 △GH=-0.006
Mo2WN2O2 △GH=-0.002
V2Cr2N3O2 △GH=-0.000
Sc2CrN2O2 △GH=0.001
Energy (eV)
Γ K M Γ

1-9


V2NbN2O2 △GH=0.002
Ti2TaC2O2 △GH=0.003
V2CrC2O2 △GH=0.006
Cr2V2N3O2 △GH=0.007
Mo2Sc2C3O2 △GH=0.007
Nb2TiN2O2 △GH=0.009
W2CrC2O2 △GH=0.009
Cr2NbN2O2 △GH=0.009
Zr2Cr2C3O2 △GH=0.010
Energy (eV)
Γ K M Γ

10-18

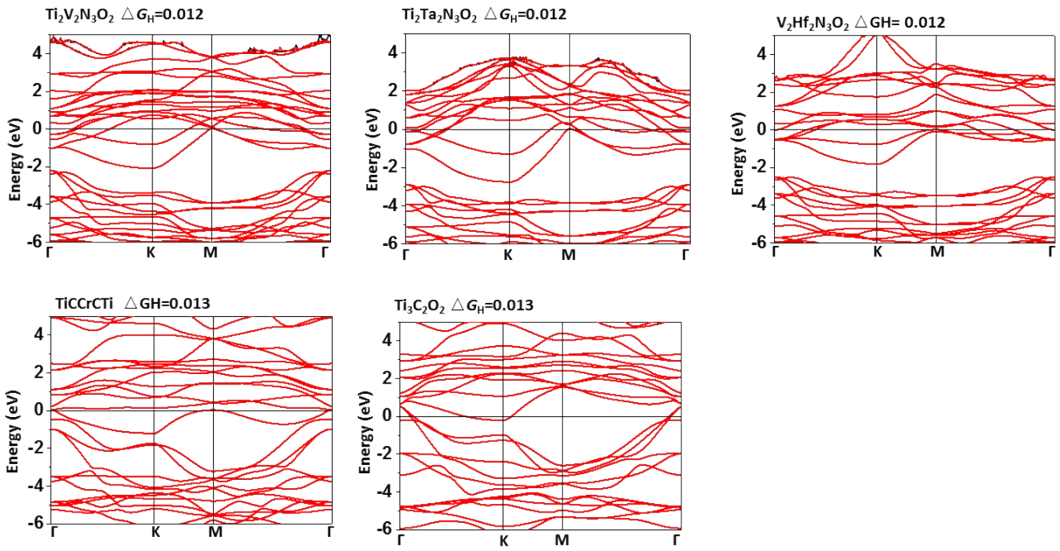


Fig. S3. Band structure of $Ti_3C_2O_2$ and 22 MXenes OBAs with better catalytic activity than $Ti_3C_2O_2$.

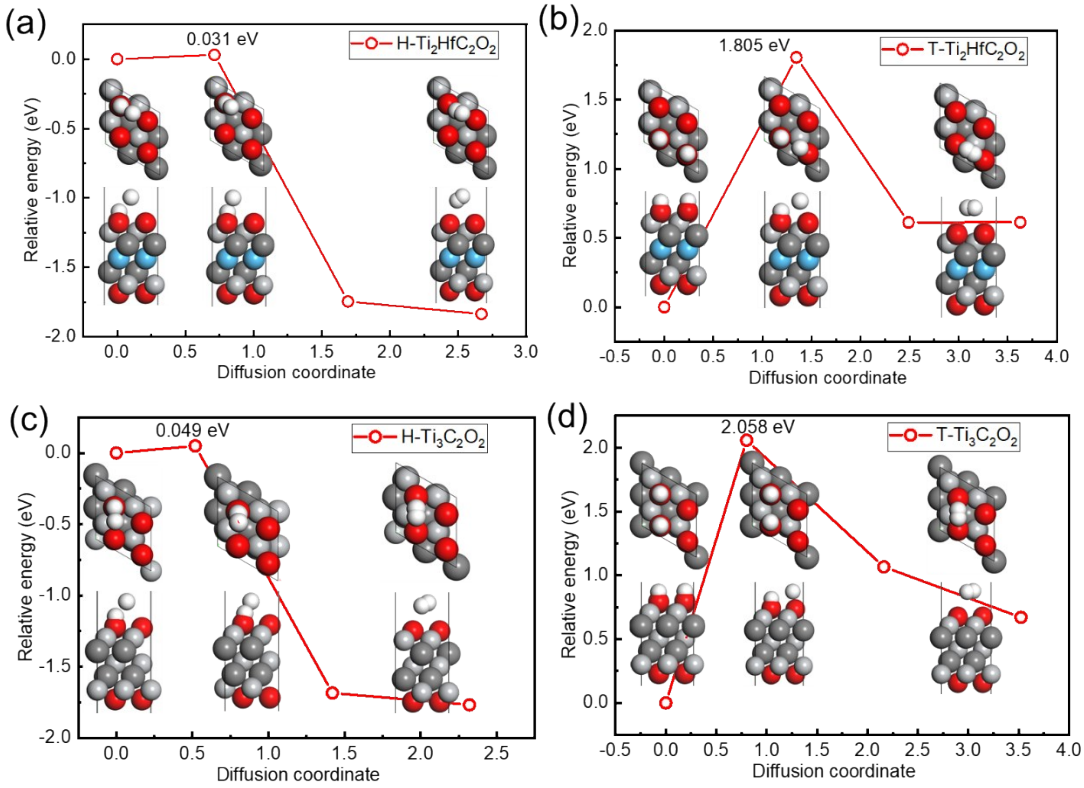


Fig. S4. The activation barriers of H on HfC_2O_2 (a-b); $Ti_3C_2O_2$ (c-d). The "T-" represents the Tafel reaction while the "H-" typifies the Heyrovsky reaction. The inserted structure diagrams are the reaction of initial state (IS), the transition state (TS) and the final state (FS).

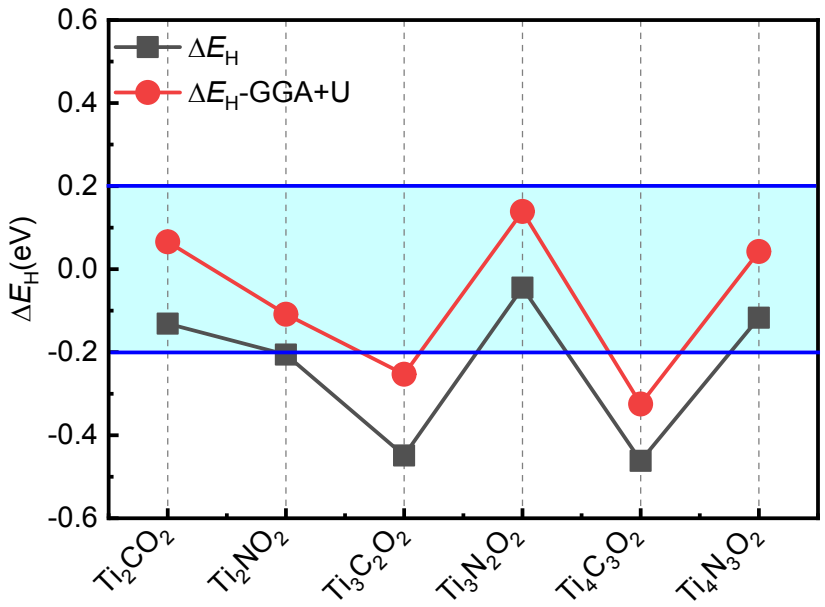


Fig. S5. Comparison of ΔE_H calculated by GGA and GGA + U for Ti-monometallic MXenes. The corresponding U_{eff} values were set to 2.58 for the Ti element[1].

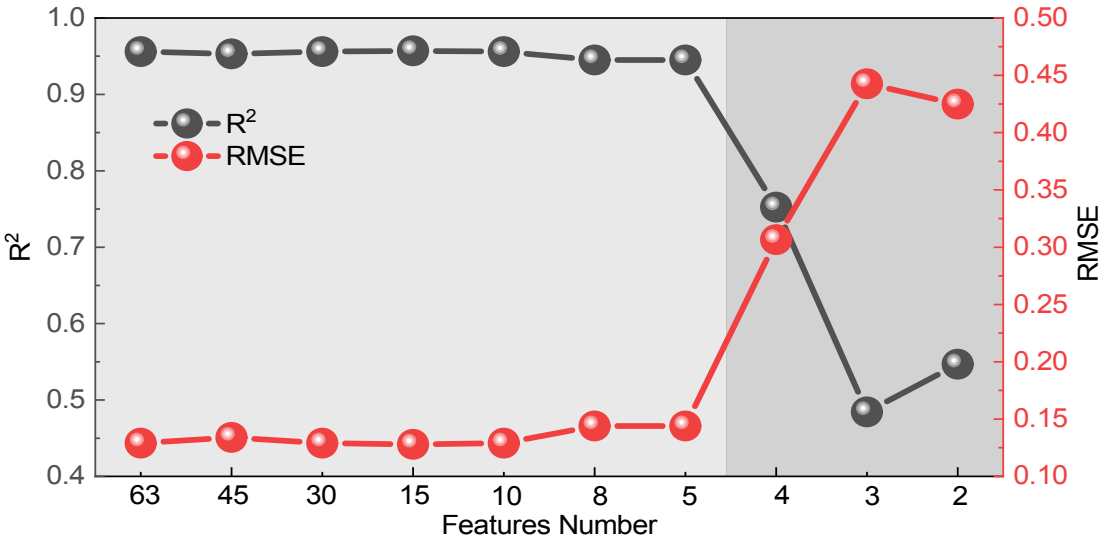


Fig. S6. The process of AdaBoost model dimension reduction and prediction accuracy evolution

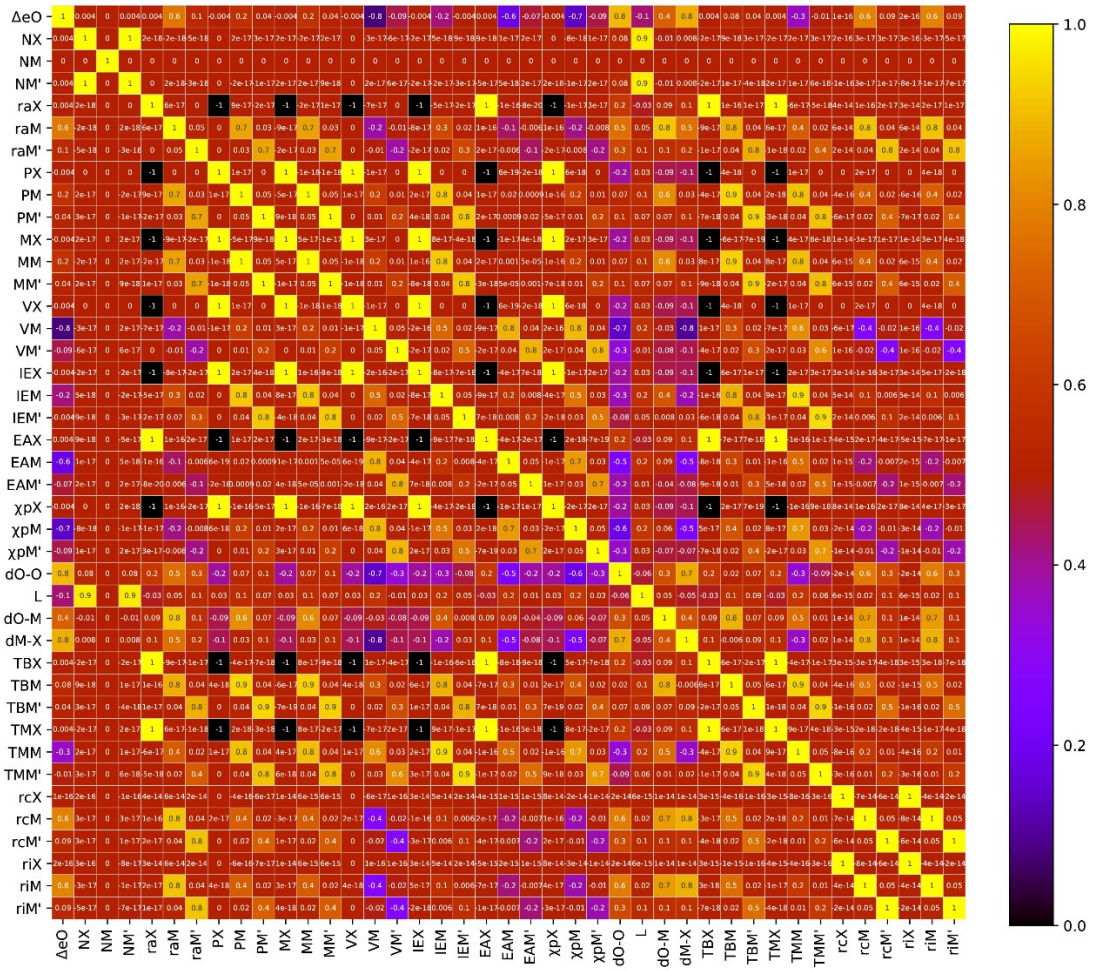


Fig. S7. Pearson correlation coefficient matrix for selected 41 primary features with annotated correlation values.

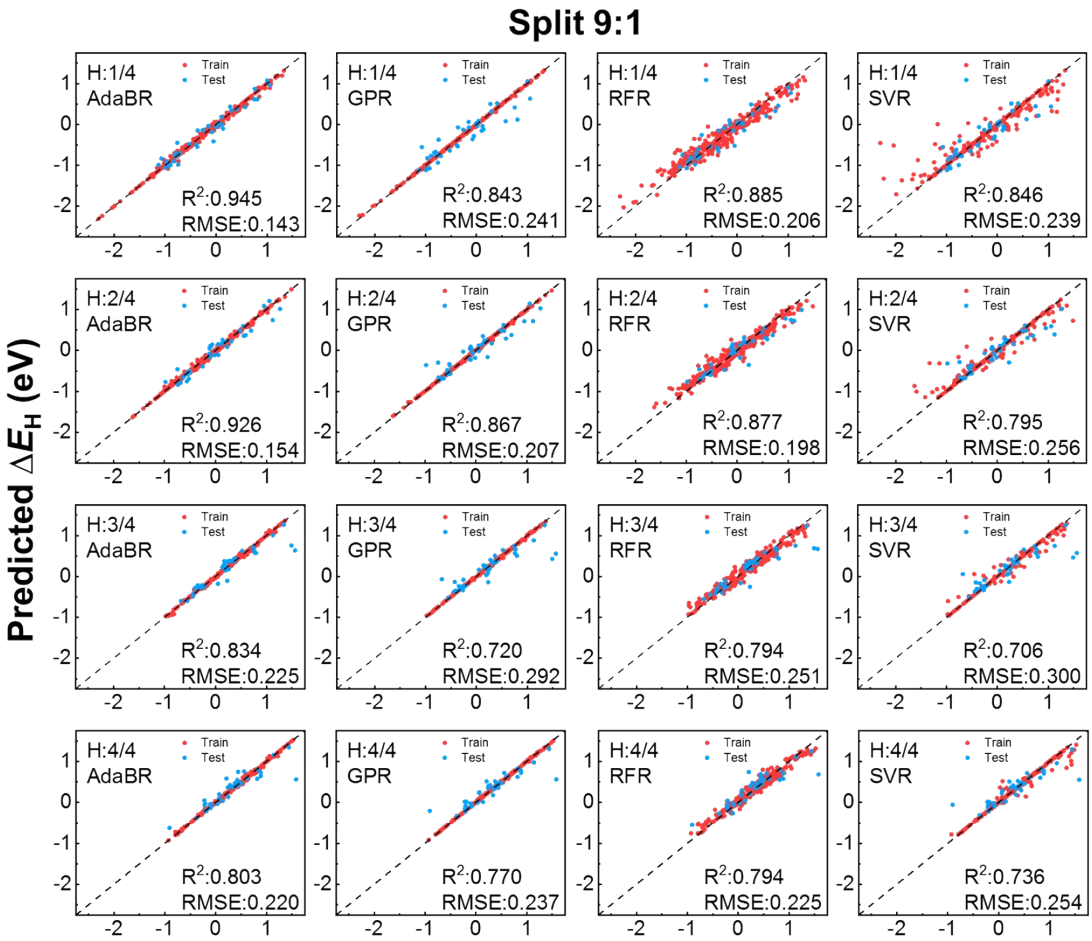


Fig. S8. Comparison of several typical machine learning models for four H coverages with 9:1 data split.

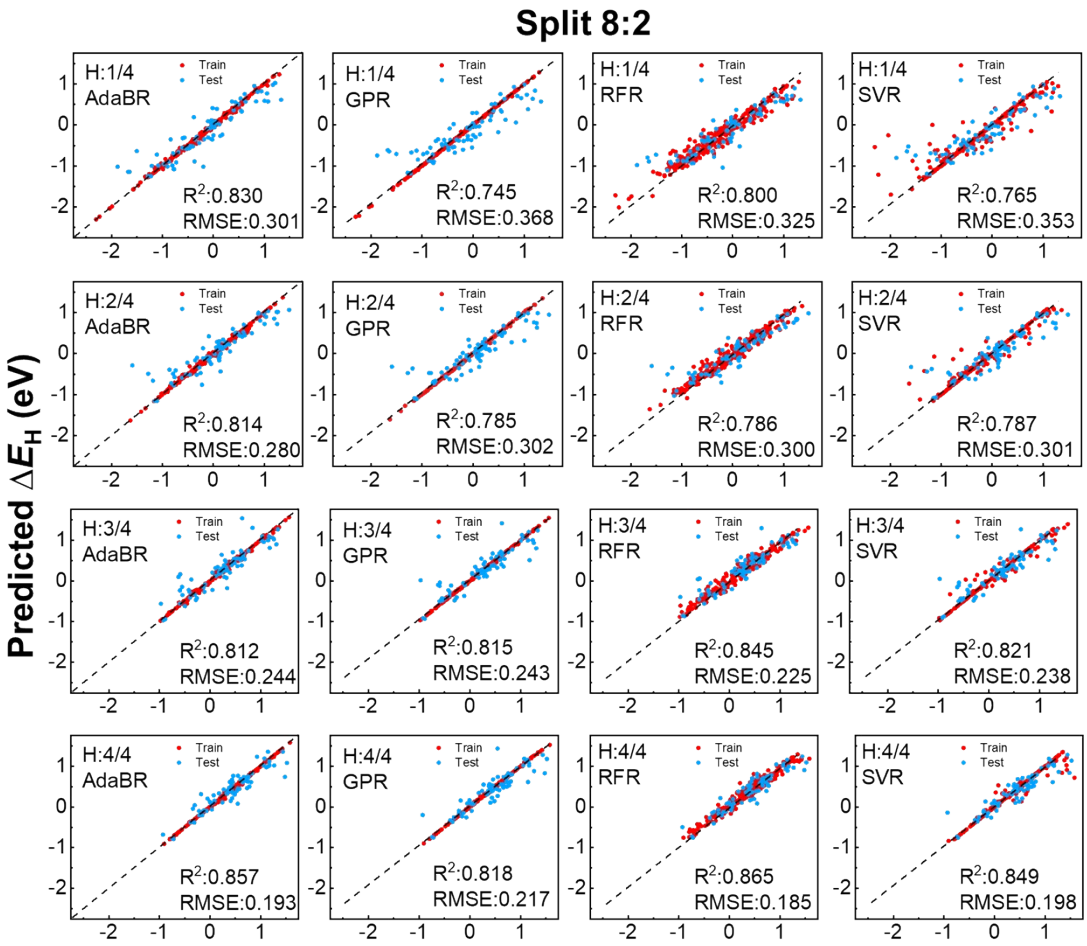


Fig. S9. Comparison of several typical machine learning models for four H coverages with 8:2 data split.

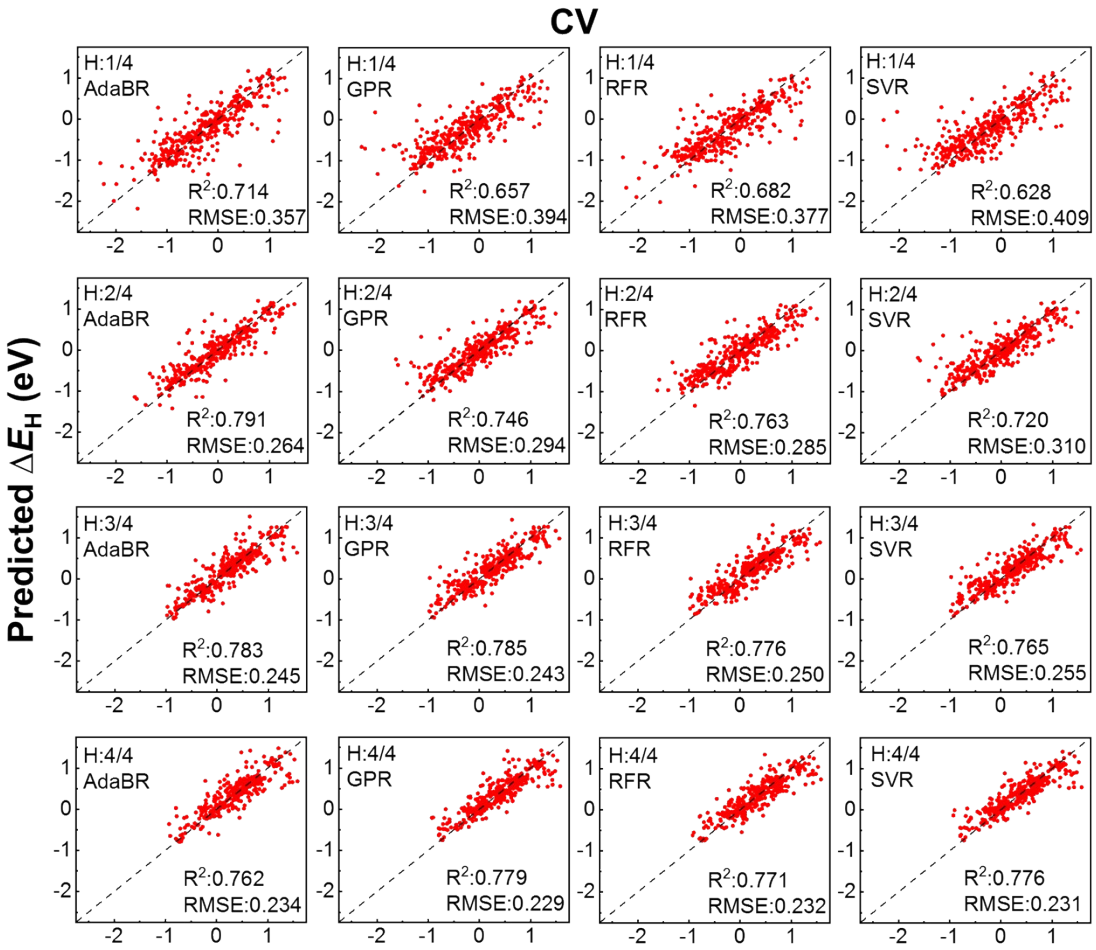


Fig. S10. Cross validation for several typical machine learning models for four H coverages.

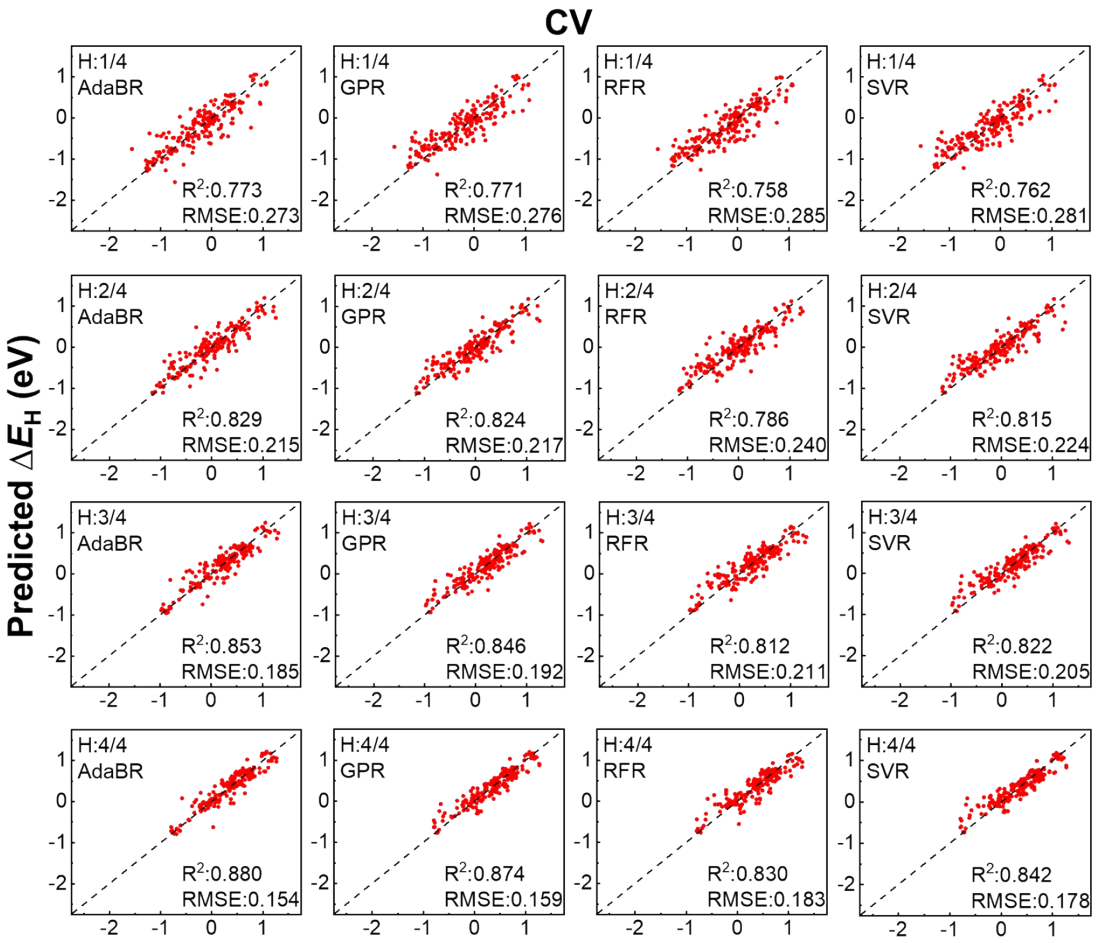


Fig. S11. Cross validation for several typical machine learning models for four H coverages without group-VIB $M_nX_{n+1}O_2$ (M = Cr, Mo, W; n = 1, 2, 3).

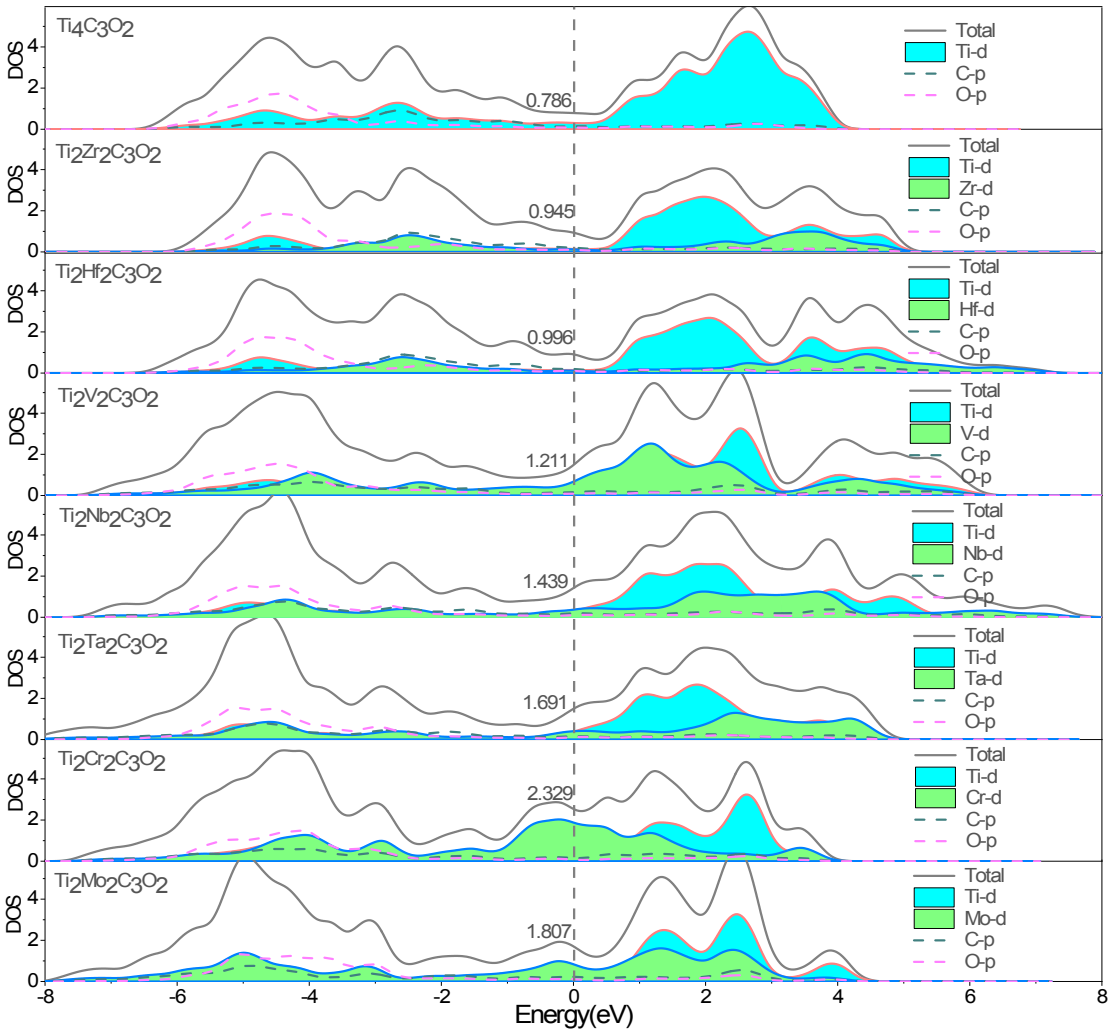


Fig. S12. TDOS and PDOS of $Ti_2M'_2C_3O_2$ MXenes OBAs.

Supplementary Tables

Table S1. 41 primary features of elemental and geometrical properties that are easily available in chemical repositories or calculated by faster DFT-PBE approach are considered. We have taken 5 DFT calculated properties, and standard deviation and mean of 22 properties, which result in total 63 features.

.

Symbol	Name	Symbol	Name
$d_{O\text{-}O}$	O-O distance in MXene	$d_{O\text{-}M}$	O-M distance in MXene
L	Layer thickness	Δe^{O}	O charge transfer
$d_{M\text{-}X}$	M-X distance in MXene	$\chi p_{M'}$	M′ Pauling's electroneativity
N_X	X atomic number	$N_{M'}$	M′ atomic number
$ra_{M'}$	M′ atomic radius	$ri_{M'}$	M′ ionic radius
$EA_{M'}$	M′ electron affinity	TB_X	X boiling point
$V_{M'}$	M′ valence	P_X	X period table number
V_X	X valence	M_X	X atomic mass
EA_X	X electron affinity	χp_X	X Pauling's electroneativity
IE_X	X first ionization potential	ra_X	X atomic radius
TM_X	X melting point	χp_M	M Pauling's electroneativity
TB_M	M boiling point	$TM_{M'}$	M′ melting point
raM	M atomic radius	ri_M	M ionic radius
rc_M	M crystal radius	$TB_{M'}$	M′ boiling point
MM'	M′ atomic mass	$P_{M'}$	M′ period table number
TM_M	M melting point	EA_M	M Electron affinity
M_M	M atomic mass	$IE_{M'}$	M′ first ionization potential
P_M	M period table number	IE_M	M first ionization potential
V_M	M valence	N_M	M atom number
rc_X	X crystal radius	ri_X	X ionic radius
$rc_{M'}$	M′ crystal radius		

Table S2. 22 kinds of 2D MXenes OBAs with better catalytic activity than $Ti_3C_2O_2$. corresponding cohesive energy (E_c in eV), hydrogen adsorption energy (ΔE_H in eV), zero-point energy (E_{ZEP} in eV) and free Energy of hydrogen adsorption at equilibrium H coverage for HER (ΔG_H in eV)[2], and electronic character of MXenes (Metallic or Semiconducting). The '*half*' respect semimetal.

NO.	***MXenes***	***Metallic***	E_c	ΔE_H	E_{ZEP}	ΔG_H
1	$Cr_2Mo_2N_3O_2$	yes	-4.456	-0.389	0.306	-0.013
2	$Cr_2VN_2O_2$	yes	-4.012	-0.385	0.304	-0.011
3	V_2NbCO_2	yes	-5.530	-0.387	0.308	-0.009
4	$Sc_2Cr_2C_3O_2$	yes	-5.168	-0.377	0.298	-0.009
5	$Nb_2Hf_2N_3O_2$	yes	-6.289	-0.383	0.305	-0.008
6	$Ti_2HfC_2O_2$	yes	-5.972	-0.377	0.300	-0.006
7	$Mo_2WN_2O_2$	yes	-4.869	-0.365	0.293	-0.002
8	$V_2Cr_2N_3O_2$	yes	-4.062	-0.381	0.311	0.000
9	$Sc_2CrN_2O_2$	*half*	-4.688	-0.368	0.299	0.002
10	$V_2NbN_2O_2$	yes	-5.093	-0.379	0.311	0.002
11	$Ti_2TaC_2O_2$	yes	-6.189	-0.368	0.301	0.004
12	$V_2Cr_2C_3O_2$	yes	-5.198	-0.369	0.305	0.006
13	$Cr_2V_2N_3O_2$	yes	-4.587	-0.368	0.305	0.007
14	$Mo_2Sc_2C_3O_2$	yes	-5.476	-0.369	0.306	0.007
15	$Nb_2TiN_2O_2$	yes	-5.722	-0.364	0.302	0.009
16	$W_2CrC_2O_2$	yes	-5.483	-0.365	0.304	0.009
17	$Cr_2NbN_2O_2$	yes	-4.186	-0.368	0.307	0.009
18	$Zr_2Cr_2C_3O_2$	yes	-5.663	-0.357	0.297	0.010
19	$Ti_2V_2N_3O_2$	yes	-5.696	-0.358	0.300	0.012
20	$Ti_2Ta_2N_3O_2$	yes	-6.259	-0.361	0.303	0.012
21	$V_2Hf_2N_3O_2$	yes	-5.774	-0.369	0.311	0.012
22	$Ti_2CrC_2O_2$	yes	-5.361	-0.356	0.299	0.013
23	$Ti_3C_2O_2$	yes	-5.852	-0.355	0.298	0.013

Supplementary References

1. Peng, Qiong, et al. Cu Single Atoms on Ti_2CO_2 as a Highly Efficient Oxygen Reduction Catalyst in a Proton Exchange Membrane Fuel Cell. *J. Mater. Chem. A*. **7**, 26062–26070 (2019).
2. Ling, C., Shi, L., Ouyang, Y., Wang, J. Searching for Highly Active Catalysts for Hydrogen Evolution Reaction Based on O-Terminated MXenes through a Simple Descriptor. Chem. Mater. **28**, 9026-9032(2016).