Supporting Materials

Machine Learning-Guided Discovery of Thermodynamically Stable Single-Atom Catalysts on Functionalized MXenes for Enhanced Oxygen Reduction and Evolution Reactions

Hengquan Guo[a] and Seung Geol Lee[a,b,*]

[a] *Department of Materials Science and Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea*

[b] *Graduate School of Semiconductor Materials and Devices Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea*

*Corresponding author:

seunggeol.lee@unist.ac.kr (S.G.L.)

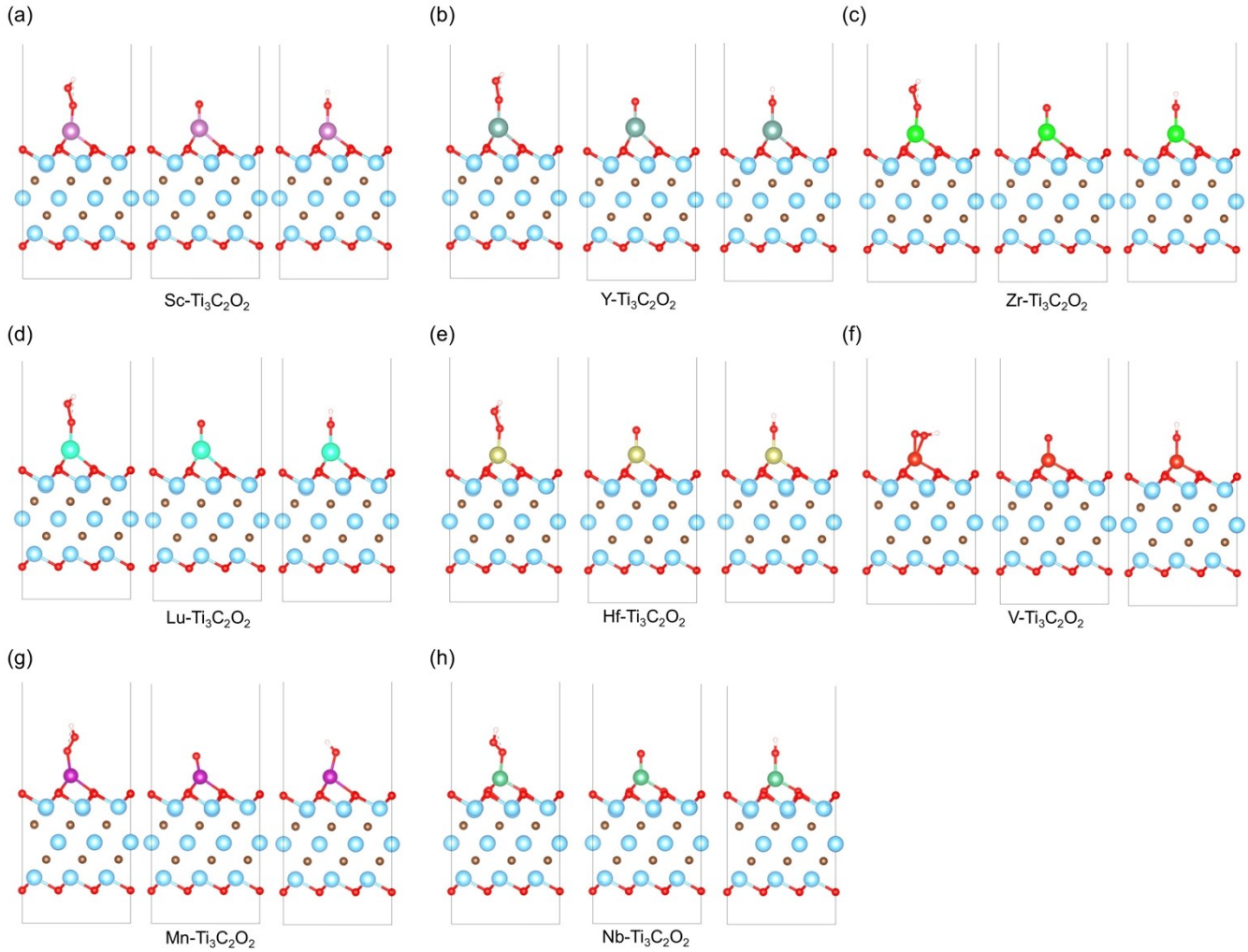

Figure S1 Side views of optimized adsorption configurations for *OOH, *O, and *OH intermediates on single-atom-decorated $Ti_3C_2O_2$ surfaces, including (a) Sc-$Ti_3C_2O_2$, (b) Y-$Ti_3C_2O_2$, (c) Zr-$Ti_3C_2O_2$, (d) Lu-$Ti_3C_2O_2$, (e) Hf-$Ti_3C_2O_2$, (f) V-$Ti_3C_2O_2$, (g) Mn-$Ti_3C_2O_2$, and (h) Nb-$Ti_3C_2O_2$.

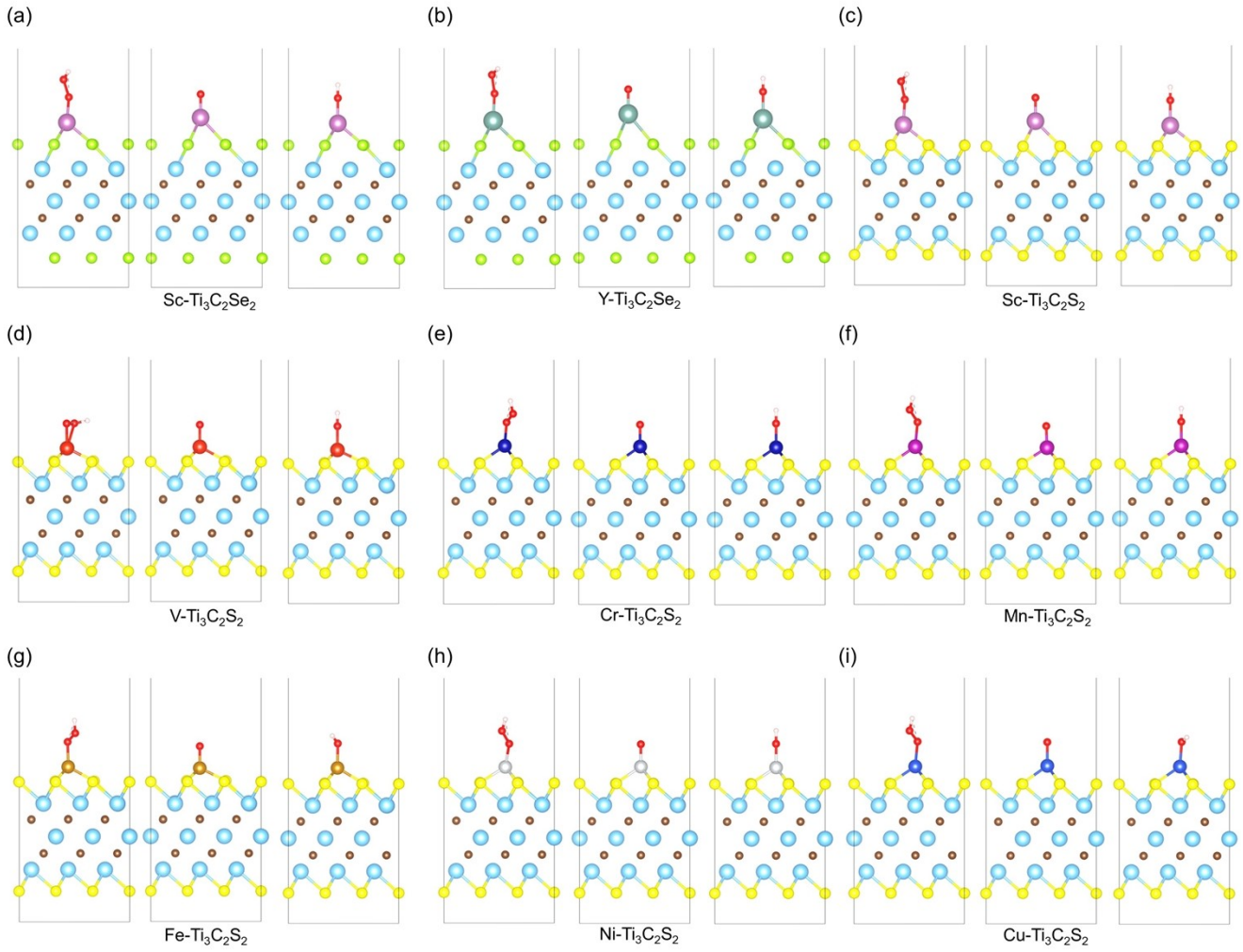

Figure S2 Side views of optimized adsorption configurations for *OOH, *O, and *OH intermediates on single-atom-decorated $Ti_3C_2Se_2$ and $Ti_3C_2S_2$ surfaces, including (a) Sc-$Ti_3C_2Se_2$, (b) Y-$Ti_3C_2Se_2$, (c) Sc-$Ti_3C_2S_2$, (d) V-$Ti_3C_2S_2$, (e) Cr-$Ti_3C_2S_2$, (f) Mn-$Ti_3C_2S_2$, (g) Fe-$Ti_3C_2S_2$, (h) Ni-$Ti_3C_2S_2$, and (i) Cu-$Ti_3C_2S_2$.

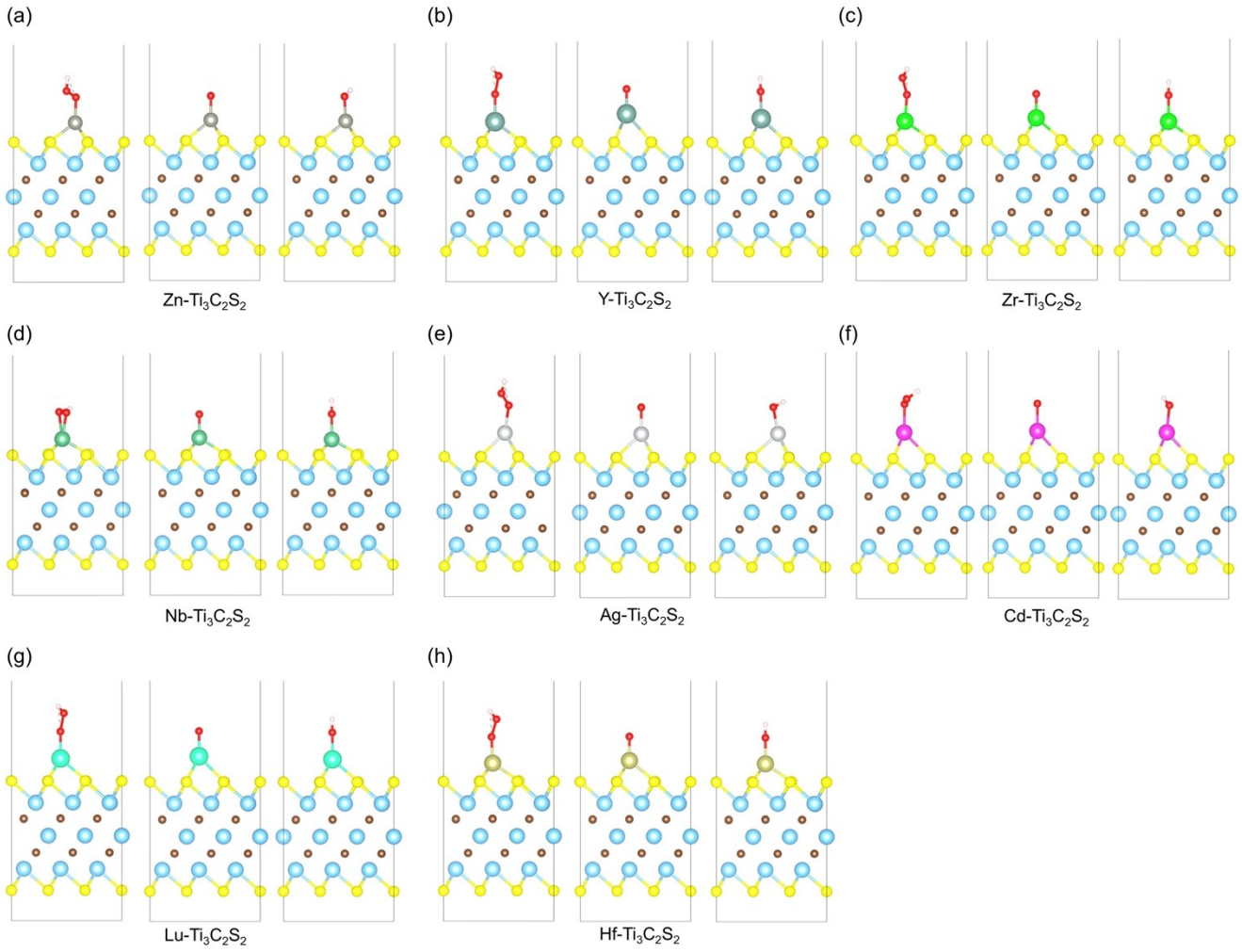

Figure S3 Side views of optimized adsorption configurations for *OOH, *O, and *OH intermediates on single-atom-decorated $Ti_3C_2S_2$ surfaces, including (a) Zn-$Ti_3C_2S_2$, (b) Y-$Ti_3C_2S_2$, (c) Zr-$Ti_3C_2S_2$, (d) Nb-$Ti_3C_2S_2$, (e) Ag-$Ti_3C_2S_2$, (f) Cd-$Ti_3C_2S_2$, (g) Lu-$Ti_3C_2S_2$, and (h) Hf-$Ti_3C_2S_2$.

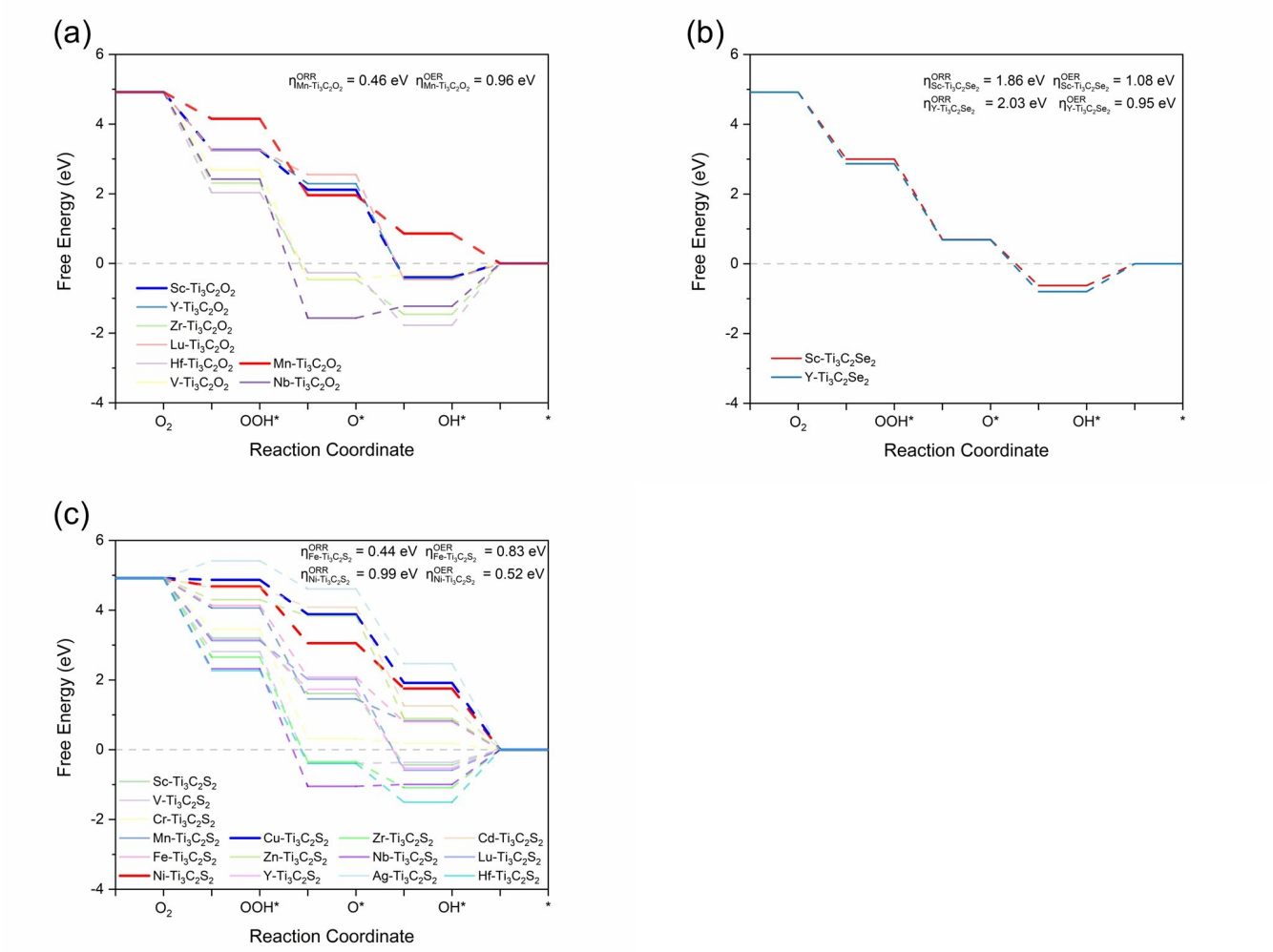

Figure S4 Free energy diagrams of transition metal promoted (a) $Ti_3C_2O_2$, (b) $Ti_3C_2Se_2$, and (c) $Ti_3C_2S_2$ for ORR/OERs (pH= 14, U = 0 V).

Table S1 O_2 adsorption energy with and without D3 correction on Ni-$Ti_3C_2S_2$ and Cu-$Ti_3C_2S_2$.

E_{ads} (eV)	DFT	DFT–D3
Ni-$Ti_3C_2S_2$	-0.92	-0.97
Cu-$Ti_3C_2S_2$	-0.54	-0.63

Table S2 Relative energies of transition metal atoms placed on three distinct adsorption sites (1 site, 2 site, and 3 site) of functionalized $Ti_3C_2T_2$ MXene surfaces (T = S, O, F, Cl, Se), calculated via density functional theory (DFT). For each metal–surface combination, the energy is referenced to the most stable configuration (set as 0 eV).

eV	$Ti_3C_2S_2$			$Ti_3C_2O_2$			$Ti_3C_2F_2$		
	1 site	2 site	3 site	1 site	2 site	3 site	1 site	2 site	3 site
Sc	0.29	0.00	0.29	0.58	0.00	0.58	0.00	0.00	1.47
V	0.10	0.00	0.10	0.60	0.00	2.76	0.00	0.00	0.42
Cr	0.00	0.10	1.87	0.41	0.00	1.24	0.06	0.00	0.03
Mn	0.00	0.03	2.18	0.38	0.00	1.64	0.05	0.00	0.29
Fe	0.04	0.00	2.45	0.33	0.00	1.82	0.17	0.00	0.16
Co	0.01	0.00	2.39	0.53	0.00	1.72	0.00	0.07	0.15
Ni	0.00	0.13	2.35	0.33	0.00	1.18	0.03	0.00	1.23
Cu	0.00	0.26	1.35	0.26	0.00	0.65	0.00	0.02	0.03
Zn	0.00	0.17	0.97	0.32	0.00	0.52	0.00	0.00	0.03
Y	0.28	0.00	3.09	0.50	0.00	3.36	0.35	0.00	1.57
Zr	0.30	0.00	4.00	0.46	0.00	3.76		0.00	2.64
Nb	0.30	0.00	3.85	0.54	0.00	3.37		0.00	1.94
Mo	0.08	0.00	2.74	0.63	0.00	2.15	0.01	0.00	-0.04
Tc	0.00	0.00	2.80	0.63	0.00	1.75	0.00	0.03	0.12
Ru	0.00	0.36	3.02	0.58	0.00	1.59	1.24	0.00	2.31
Rh	0.00	0.38	2.48	0.21	0.00	1.10	0.00	0.86	0.91
Pd	0.00	0.59	1.32	0.00	0.12	0.31	0.15	0.00	0.40
Ag	0.00	0.09	0.55	0.03	0.00	0.32	0.01	0.00	0.05
Cd	0.00	0.00	0.36	0.09	0.00	0.07	0.00	0.00	0.03
Lu	0.28	0.00	3.00	0.54	0.00	3.11	0.04	0.00	-0.28
Hf	0.37	0.00	0.00	0.58	0.00	3.82		0.00	0.19
Ta	0.40	0.00	4.33	0.55	0.00	3.98	0.00	0.03	0.44
W	0.25	0.00	3.64	0.77	0.00	3.08	0.00	0.04	-0.02
Re	0.17	0.00	3.41	1.00	0.00	2.21	0.09	0.00	0.01
Os	0.00	0.09	3.49	1.15	0.00	1.84	0.00	0.49	0.49
Ir	0.00	0.06	3.11	0.56	0.00	1.30	0.00	0.30	2.79
Pt	0.00	0.27	1.82	0.07	0.00	0.11	0.00	0.59	0.59
Au	0.00	0.16	0.21	0.00	0.03	-0.17	0.00	0.01	0.04
Hg	0.00	0.00	0.06	0.01	0.00	0.04	0.00	0.00	0.03
eV	$Ti_3C_2Cl_2$			$Ti_3C_2Se_2$					
	1 site	2 site	3 site	1 site	2 site	3 site			
Sc	0.00	0.08	1.17	0.08	0.00	2.81			
V	0.56	0.00	0.56	0.04	0.00	2.06			
Cr	0.00	0.10	0.44	0.00	0.30	1.49			
Mn	0.00	0.09	0.52	0.00	0.20	4.00			

Fe	0.00	0.69	0.80	0.00	0.32	2.21	
Co	0.02	0.00	1.22	0.00	0.30	2.52	
Ni	0.14	0.00	1.31	0.00	0.31	2.19	
Cu	0.00	0.10	0.52	0.00	0.34	1.20	
Zn	0.00	0.00	0.04	0.10	0.00	0.04	
Y	0.00	0.13	0.78	0.07	0.00	2.27	
Zr	0.00	0.34	0.96	0.00	0.03	3.02	
Nb	0.00	0.00	0.64	0.00	0.25	2.87	
Mo	0.00	0.05	0.25	0.00	0.41	2.29	
Tc	0.00	0.16	0.45	0.00	0.54	2.70	
Ru	0.00	0.60	1.08	0.00	0.59	3.09	
Rh	0.00	0.32	0.64	0.00	0.50	2.59	
Pd	0.00	0.10	0.19	0.00	0.49	1.20	
Ag	0.05	0.00	0.17	0.00	0.02	0.46	
Cd	0.00	0.00	0.04	0.02	0.00	0.11	
Lu	0.00	0.11	0.20	0.10	0.00	1.78	
Hf	0.00	0.41	0.11	0.09	0.00	0.09	
Ta	0.00	0.28	0.91	0.00	0.16	3.25	
W	0.00	0.11	0.20	0.00	0.33	2.88	
Re	0.00	0.08	0.15	0.00	0.45	3.10	
Os	0.00	0.11	0.37	0.00	0.49	3.50	
Ir		0.00	0.02	0.00	0.19	3.09	
Pt	-0.15	0.00	-0.21	0.00	0.92	1.69	
Au	0.07	0.00	0.06	0.07	0.00	0.15	
Hg	0.00	0.00	0.03	0.00	0.00	0.05	

Table S3 O-O bond length of oxygen molecular adsorbed TM-$Ti_3C_2T_2$(T = O, S, and Se, TM = transition metal).

O-O bond length/Å		End on	Side on			End on	Side on
$Ti_3C_2S_2$	Sc	1.300	1.384	$Ti_3C_2O_2$	Sc	1.301	1.359
	Zn	1.296	1.296		Y	1.300	1.398
	Y	1.312	1.421		Zr	1.325	1.491
	Zr(noD3)	1.315	1.487		Lu	1.301	1.362
	Lu	1.301	1.418		Hf	1.326	1.504
	Hf	1.316	1.506		V	1.281	1.452
	Mn	1.266	1.391		Mn	1.263	1.382
	V	1.278	1.435		Nb	1.310	1.483
	Cr	1.276	1.420		Hg	1.233	1.233
	Fe	1.263	1.379	$Ti_3C_2Se_2$	Sc	1.311	1.481
	Ni	1.260	1.325		Y	1.325	1.481
	Cu	1.266	1.267		Hg	1.233	1.233
	Nb	1.298	1.472				
	Ag	1.246	1.258				
	Cd	1.294	1.288				
	Hg	1.234	1.234				

Table S4 Calculated Gibbs free energy changes (ΔG_{OOH*}, ΔG_{O*}, and ΔG_{OH*}) for *OOH, *O, and *OH intermediates at pH = 0 and U = 0 V.

eV	ΔG_{OOH*}	ΔG_{O*}	ΔG_{OH*}
Sc-$Ti_3C_2S_2$	2.38	0.78	-1.26
V-$Ti_3C_2S_2$	1.98	-1.22	-1.19
Cr-$Ti_3C_2S_2$	2.62	-0.51	-0.64
Mn-$Ti_3C_2S_2$	3.23	0.63	0.00
Fe-$Ti_3C_2S_2$	3.30	1.25	-0.03
Ni-$Ti_3C_2S_2$	3.85	2.23	0.92
Cu-$Ti_3C_2S_2$	4.04	3.05	1.09
Zn-$Ti_3C_2S_2$	3.47	3.00	0.06
Y-$Ti_3C_2S_2$	2.32	0.90	-1.36
Zr-$Ti_3C_2S_2$	1.83	-1.17	-1.92
Nb-$Ti_3C_2S_2$	1.49	-1.88	-1.82
Ag-$Ti_3C_2S_2$	4.59	3.78	1.64
Cd-$Ti_3C_2S_2$	3.81	3.26	0.43
Lu-$Ti_3C_2S_2$	2.30	1.19	-1.42
Hf-$Ti_3C_2S_2$	1.44	-1.22	-2.33
Sc-$Ti_3C_2S_2$	2.43	1.28	-1.23
V-$Ti_3C_2O_2$	1.86	-1.26	-1.16
Mn-$Ti_3C_2O_2$	3.32	1.13	0.03
Y-$Ti_3C_2O_2$	2.43	1.46	-1.26
Zr-$Ti_3C_2O_2$	1.48	-1.29	-2.29
Nb-$Ti_3C_2O_2$	1.59	-2.40	-2.06
Lu-$Ti_3C_2O_2$	2.43	1.72	-1.30
Hf-$Ti_3C_2O_2$	1.20	-1.10	-2.60
Sc-$Ti_3C_2Se_2$	2.17	-0.14	-1.46
Y-$Ti_3C_2Se_2$	2.04	-0.14	-1.63