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Constructing Dual Active Sites for Synergistic Electrocatalysis of Hydrogen Oxidation: Single-Metal-Atoms Anchored on WC_2O_2 MXene

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Table S1 Lattice constant *a* and bond length *d* (in Å) of W_2C and W_2CO_2.

Species	Parameters	This work	Other works
W_2C	*a*	2.878	2.874 (ref. 1) 2.87 (ref. 2) 2.857 (ref. 3)
	d(W–C)	2.121	2.121 (ref. 3)
W_2CO_2	d(W–O)	2.093	2.06 (ref. 2)
	d(W–C)	2.184	2.17 (ref. 2)

References

1 H. Pan, Ultra-high electrochemical catalytic activity of MXenes, *Sci. Rep.*, 2016, **6**, 1–10.

2 S. A. Khan, G. Rehman, I. Ahmad, M. Maqbool, C. Franchini, B. Amin, Intriguing electronic and optical properties of M_2CX_2 (M= Mo, W; X= O, F) MXenes and their van der Waals heterostructures, *Chem. Phys. Lett.*, 2019, **731**, 136614.

3 D. Wu, S. Wang, S. Zhang, J. Yuan, B. Yang, H. Chen, Highly negative Poisson's ratio in a flexible two-dimensional tungsten carbide monolayer, *Phys. Chem. Chem. Phys.*, 2018, **20**, 18924–18930.

Table S2 Mulliken charge *q* (in e) for W_2CO_2-M_{sa}.

Catalysts	$q(M_{sa})$	q(*ortho*-O)	q(*ortho*-W)
W_2CO_2-Cr_{sa}	0.356	-0.635	0.678
W_2CO_2-Mn_{sa}	0.418	-0.643	0.668
W_2CO_2-Fe_{sa}	0.160	-0.633	0.709
W_2CO_2-Co_{sa}	0.059	-0.633	0.749
W_2CO_2-Ni_{sa}	0.177	-0.634	0.705
W_2CO_2-Cu_{sa}	0.216	-0.638	0.706
W_2CO_2-Zn_{sa}	0.414	-0.641	0.650
W_2CO_2-Ru_{sa}	0.109	-0.626	0.719
W_2CO_2-Pd_{sa}	0.072	-0.631	0.743
W_2CO_2-Ir_{sa}	0.048	-0.622	0.723
W_2CO_2-Pt_{sa}	0.009	-0.625	0.742
W_2CO_2-Au_{sa}	0.114	-0.634	0.717
W_2CO_2	-	-0.628	0.940

Table S3 Adsorption energy E_{ads} (in eV) for different species at the most stable site of W_2CO_2-M_{sa}.

Catalysts	H*	H_2*	H_2O*	OH*
W_2CO_2-Cr_{sa}	-0.16	-0.44	-1.71	-4.32
W_2CO_2-Mn_{sa}	-0.21	-0.51	-1.72	-4.20
W_2CO_2-Fe_{sa}	-0.22	-0.59	-1.66	-3.80
W_2CO_2-Co_{sa}	-0.22	-0.61	-1.63	-3.47
W_2CO_2-Ni_{sa}	-0.19	-0.59	-1.59	-3.21
W_2CO_2-Cu_{sa}	-0.11	-0.51	-1.55	-2.95
W_2CO_2-Zn_{sa}	-0.07	-0.32	-1.60	-3.53
W_2CO_2-Ru_{sa}	-0.26	-0.45	-1.32	-3.22
W_2CO_2-Pd_{sa}	-0.20	-0.44	-1.19	-2.19
W_2CO_2-Ir_{sa}	-0.26	-0.54	-1.32	-3.21
W_2CO_2-Pt_{sa}	-0.21	-0.48	-1.23	-2.64
W_2CO_2-Au_{sa}	-0.08	-0.32	-1.17	-2.46

Table S4 Adsorption energy E_{ads} (in eV) of H_2 and H_2O with a hydroxyl group on W_2CO_2-M_{sa}.

Catalysts	H_2*	H_2O*
W_2CO_2-Cr_{sa}	-0.13	-1.59
W_2CO_2-Mn_{sa}	-0.18	-1.35
W_2CO_2-Fe_{sa}	-0.29	-1.29
W_2CO_2-Co_{sa}	-0.37	-1.23
W_2CO_2-Ni_{sa}	-0.38	-1.19
W_2CO_2-Cu_{sa}	-0.34	-1.12
W_2CO_2-Zn_{sa}	-0.22	-1.21
W_2CO_2-Ru_{sa}	-0.33	-1.24
W_2CO_2-Pd_{sa}	-0.35	-1.02
W_2CO_2-Ir_{sa}	-0.32	-1.08
W_2CO_2-Pt_{sa}	-0.33	-1.04
W_2CO_2-Au_{sa}	-0.23	-0.94

Table S5 Rate constants k (in s^{-1} $site^{-1}$) of the elementary reactions for HOR on W_2CO_2-M_{sa}.

Catalysts	Heyrovsky	H*+OH*
W_2CO_2-Cr_{sa}	7.44E+04	2.95E+07
W_2CO_2-Mn_{sa}	1.45E+12	6.50E+09
W_2CO_2-Fe_{sa}	6.03E+09	6.39E+10
W_2CO_2-Co_{sa}	5.43E+09	4.50E+10
W_2CO_2-Ni_{sa}	3.55E+09	1.60E+11
W_2CO_2-Cu_{sa}	6.44E+08	1.05E+10
W_2CO_2-Zn_{sa}	2.19E+10	6.94E+11
W_2CO_2-Ru_{sa}	6.16E+06	5.55E+11
W_2CO_2-Pd_{sa}	2.52E+06	1.42E+10
W_2CO_2-Ir_{sa}	8.14E+09	6.62E+11
W_2CO_2-Pt_{sa}	1.02E+12	1.11E+12
W_2CO_2-Au_{sa}	3.58E+07	7.96E+10

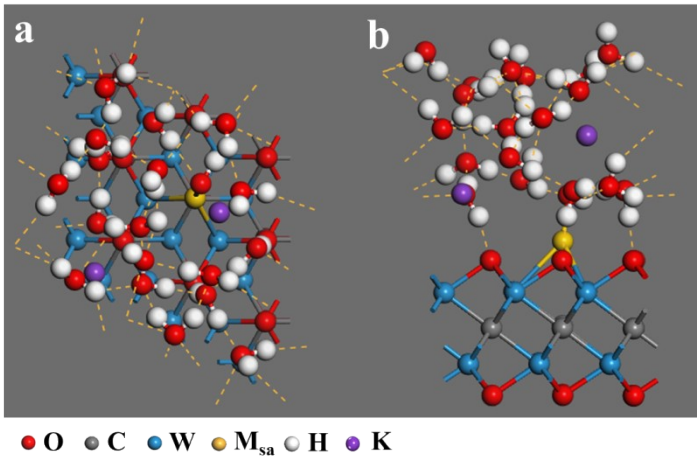

Fig. S1. (a) Side and (b) top views of the configuration for the W_2CO_2-M_{sa} catalysts with the K^+OH^- solution. The yellow dashed lines indicate the hydrogen bonding.

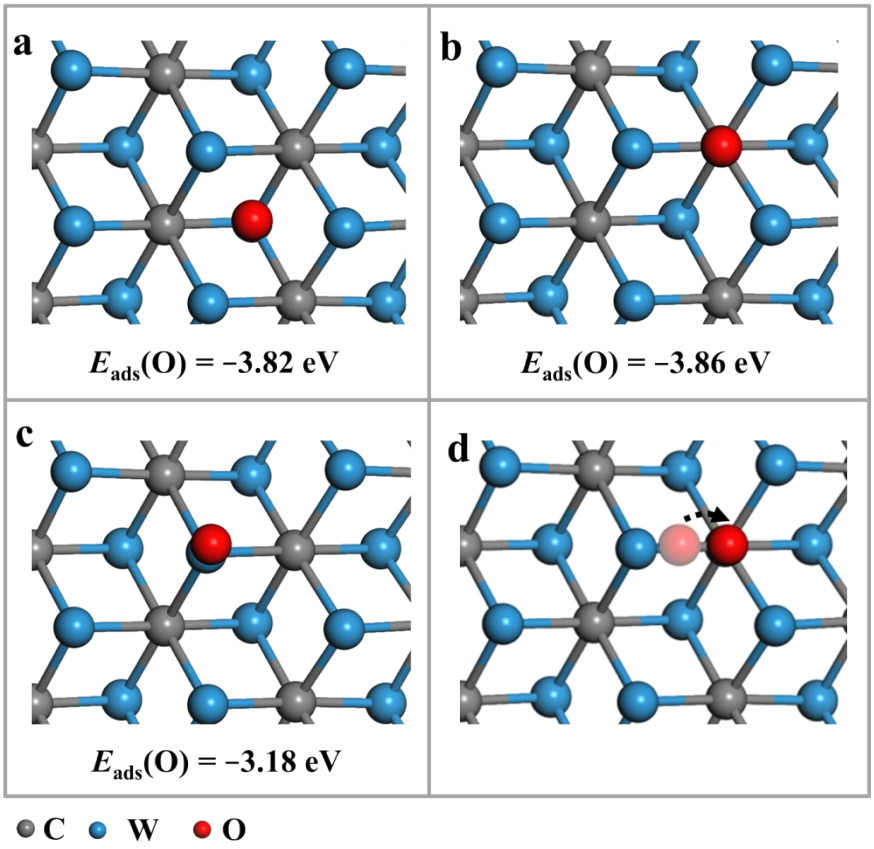

Fig. S2. Adsorption configurations of oxygen at the (a) fcc, (b) hcp, (c) top, and (d) bridge sites of W_2C MXene. Note that the O atom initially located at the bridge site will be transferred to the hcp site after optimization. Bottom values are the O adsorption energy on W_2C MXene.

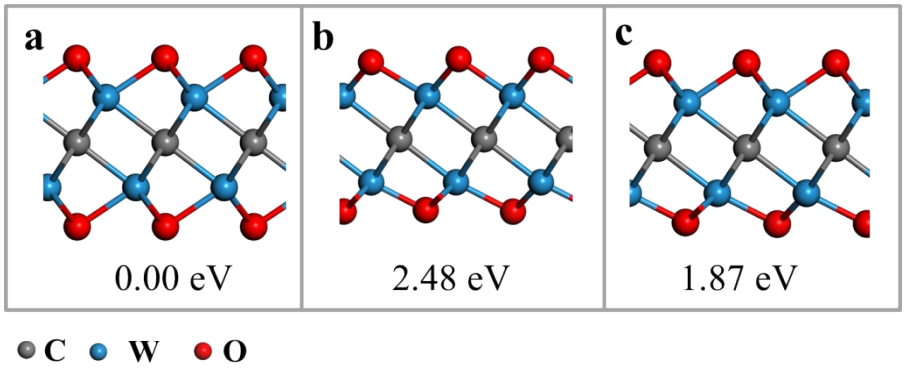

Fig. S3. W_2CO_2 models fully terminated by –O groups, that is, the –O groups on the top and bottom surfaces are located at (a) the hcp sites, (b) the fcc sites, and (c) the fcc and hcp sites, respectively. Bottom values indicate the energy differences relative to the most stable structure.

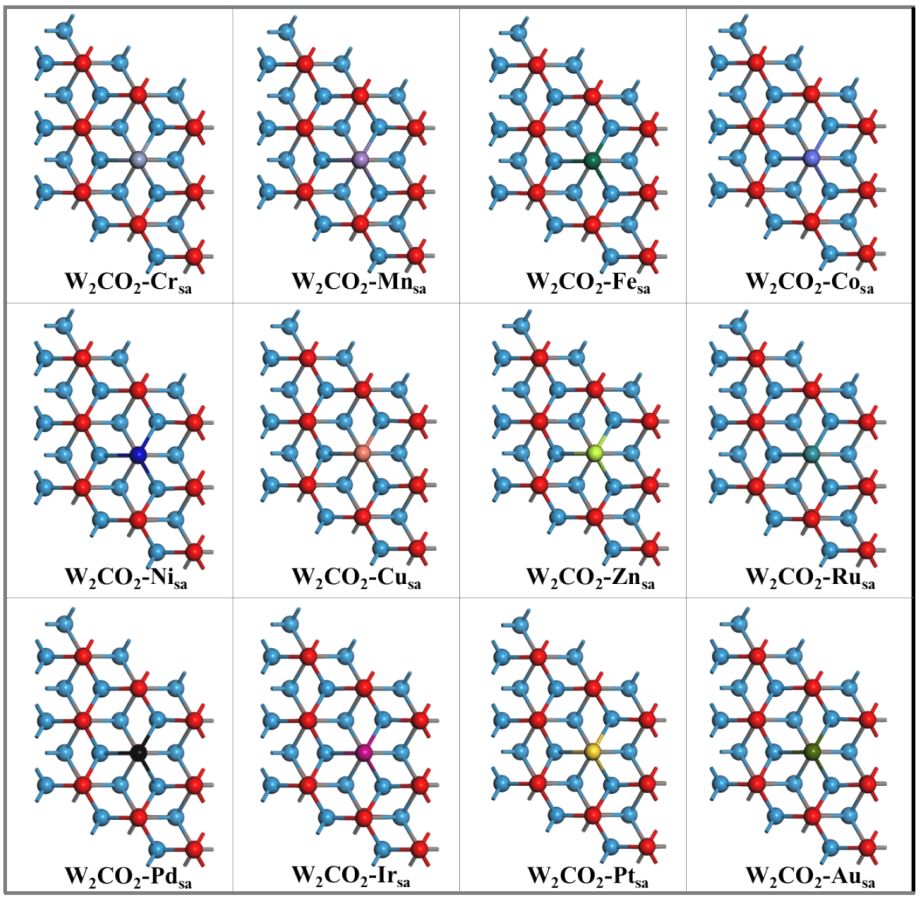

Fig. S4. Optimized structures of W_2CO_2-M_{sa}. The light blue, grey, and red balls denote W, C, and O, respectively, while the balls with other colors represent the corresponding M_{sa} atoms.

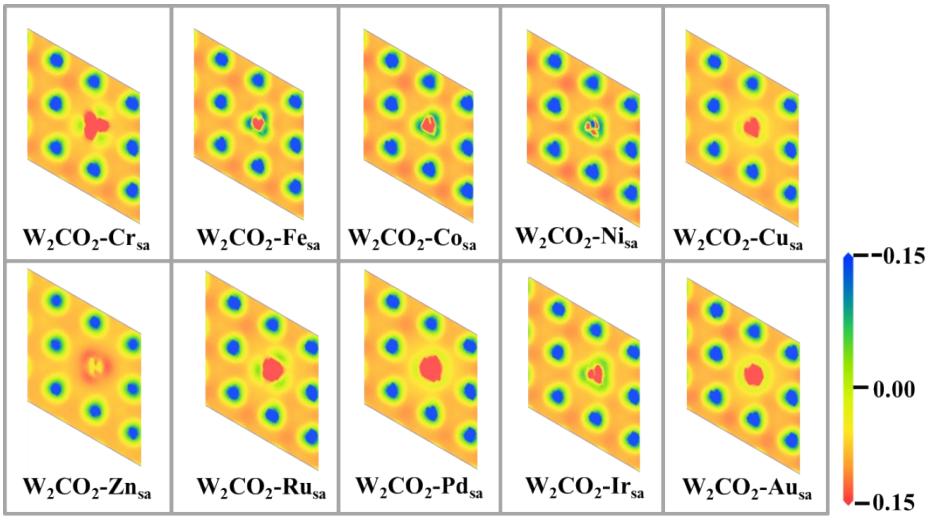

Fig. S5. The sliced deformation electron density (DED) map for W_2CO_2-M_{sa}, M_{sa} = Cr, Fe, Co, Ni, Cu, Zn, Ru, Pd, Ir, and Au.

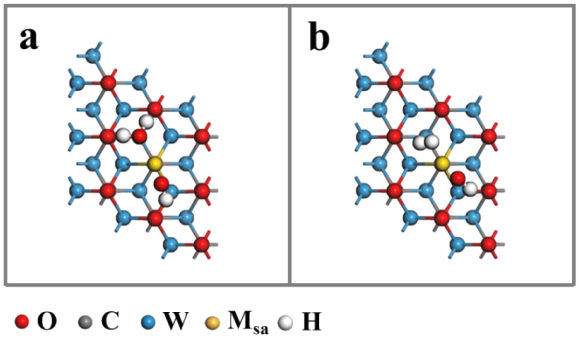

Fig. S6. Co-adsorption configurations of (a) H_2O*+OH* and (b) H_2*+OH* on W_2CO_2-M_{sa}.

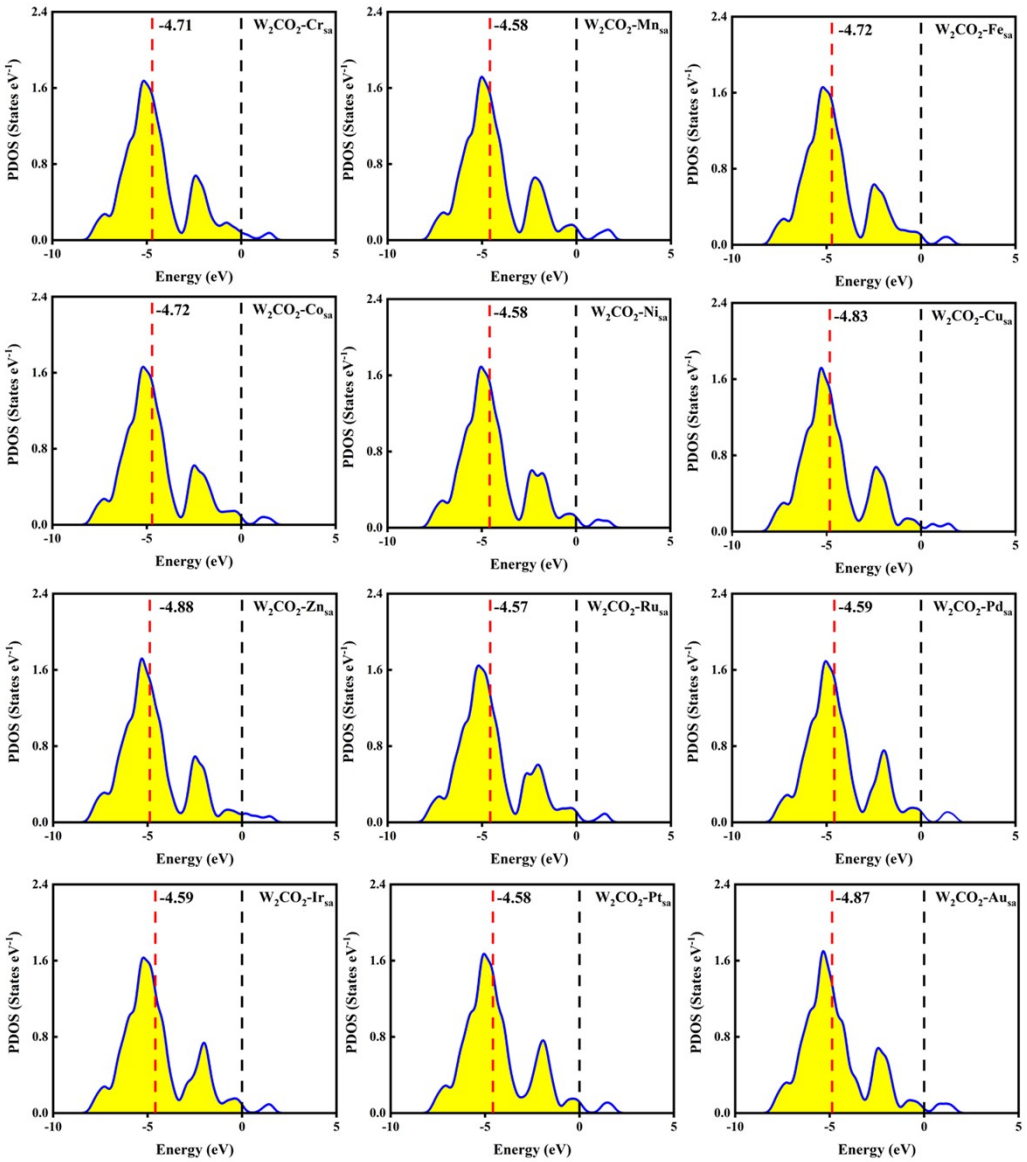

Fig. S7. PDOS for the p-band of the *ortho*-O atoms for W_2CO_2-M_{sa}. The Fermi level marked by dashed black lines is set as the energy zero. The p-band centers (in eV) are shown by dashed red lines. The shadows indicate the integrate interval from the minimum energy to the Fermi level.

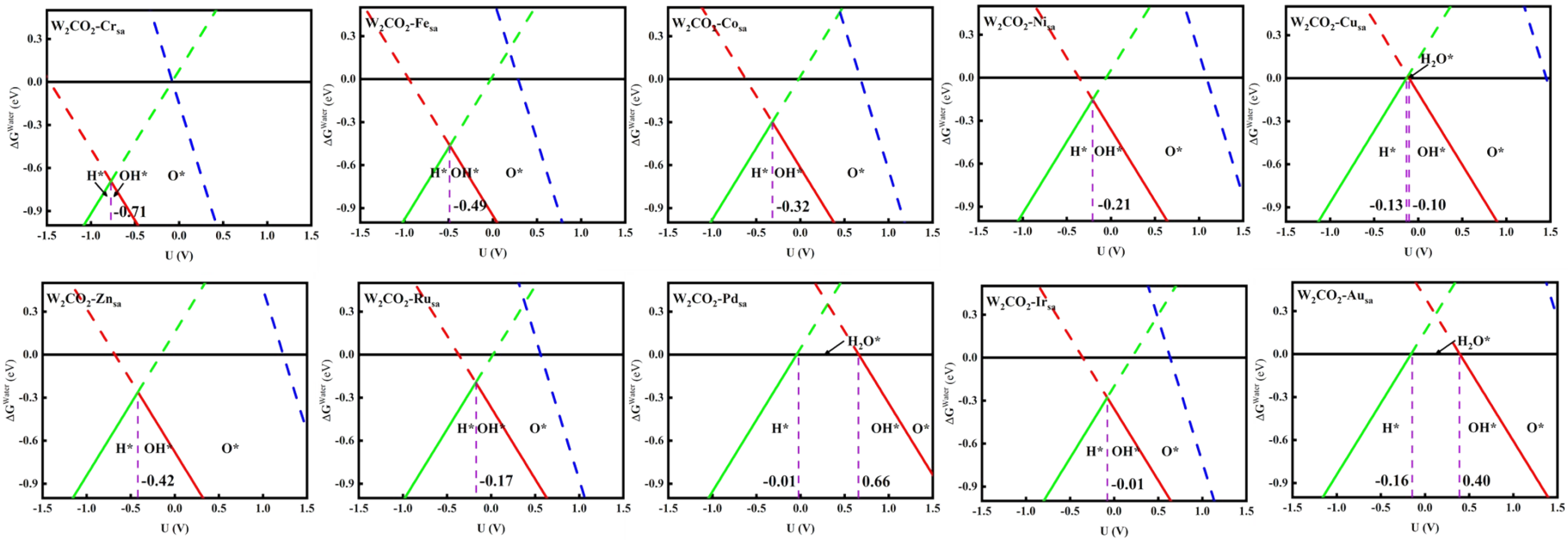

Fig. S8. Phase diagram showing the free energy for different surface structures for water in contact with W_2CO_2-M_{sa}, M_{sa} = Cr, Fe, Co, Ni, Cu, Zn, Ru, Pd, Ir, and Au. The free energy for liquid water at 298 K is defined as $\Delta G^{\text{water}}(U) = 0$ (black line). $\Delta G_{H^*}^{water}(U) = \Delta G_{H^*}^{water}(0) + eU$ (green line), $\Delta G_{OH^*}^{water}(U) = \Delta G_{OH^*}^{water}(0) - eU$ (red line), and $\Delta G_{O^*}^{water}(U) = \Delta G_{O^*}^{water}(0) - 2eU$ (blue line).

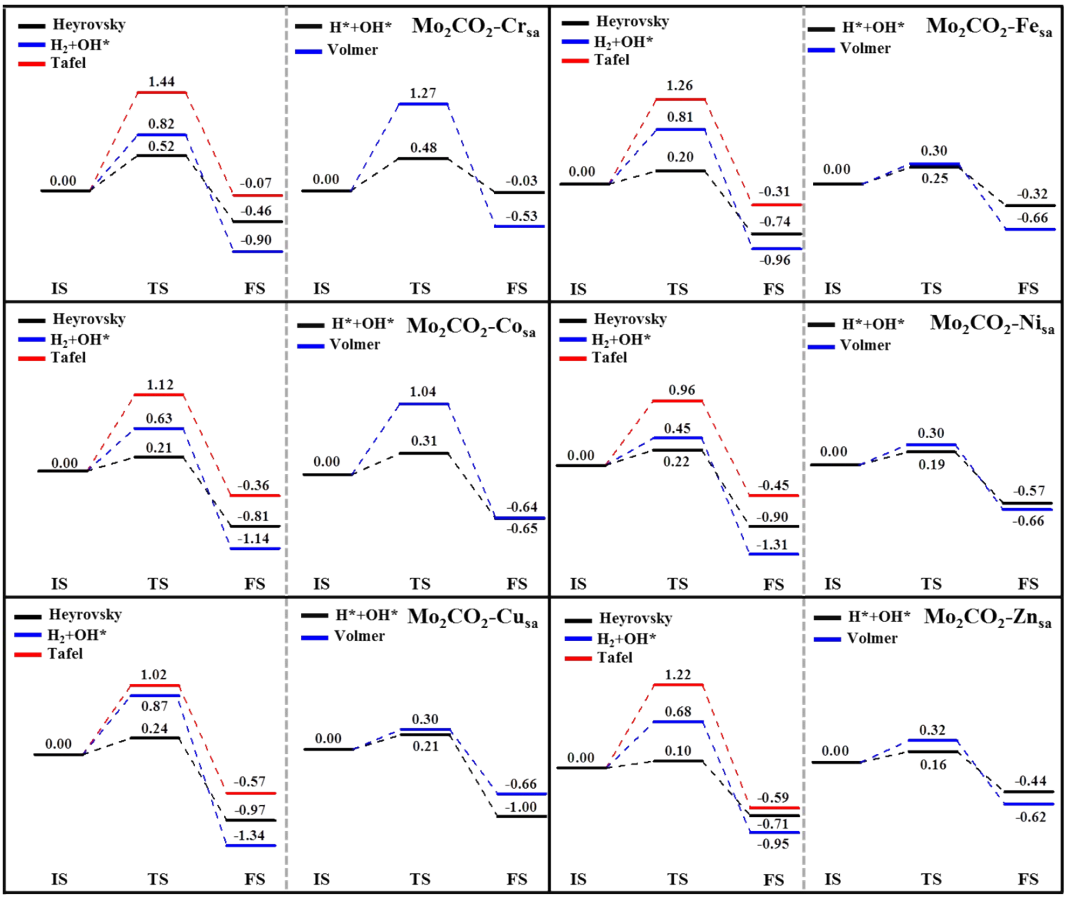

Fig. S9. Free energy diagrams (in eV) of the elementary reactions for the HOR on W_2CO_2-M_{sa}, M_{sa} = Cr, Fe, Co, Ni, Cu, and Zn. IS, TS, and FS are the initial state, transition state, and final state in the reactions, respectively.

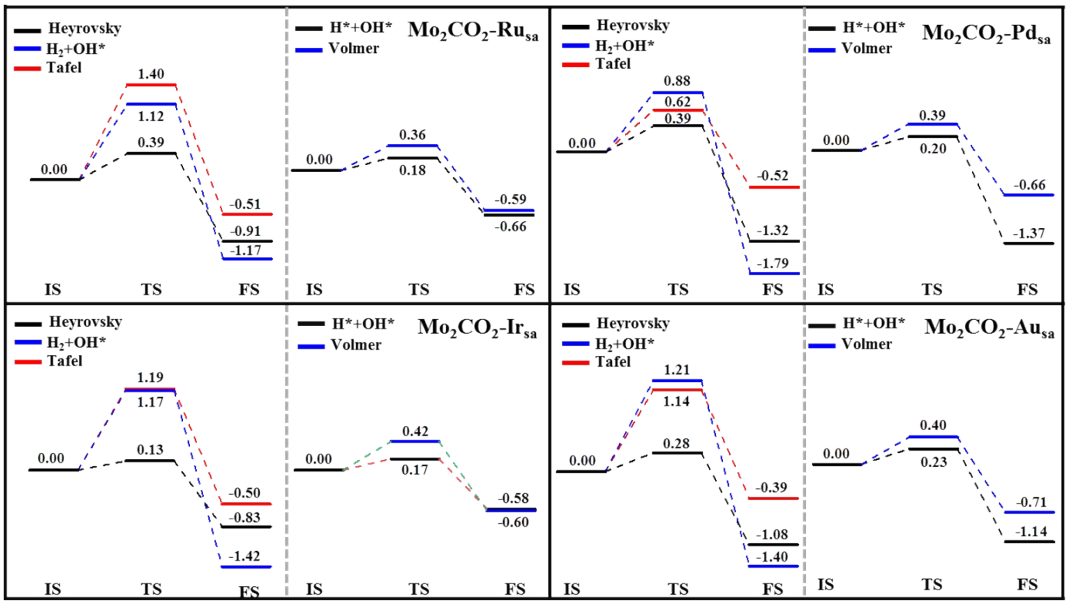

Fig. S10. Free energy diagrams (in eV) of the elementary reactions for the HOR on W_2CO_2-M_{sa}, M_{sa} = Ru, Pd, Ir, and Au. IS, TS, and FS are the initial state, transition state, and final state in the reactions, respectively.