Supplementary Information

Mo_2B_2 MBene-supported single-atom catalysts as bifunctional HER/OER and OER/ORR electrocatalysts

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Tables

Table. S1 The binding energy E_b (eV) of different transition metal atoms embedded in Mo monovacancy of Mo_2B_2.

TM	E_b
Ti	-6.99
V	-5.97
Cr	-5.38
Mn	-4.55
Fe	-5.02
Co	-4.74
Ni	-6.12
Cu	-5.73

Table. S2 The reaction Gibbs free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site I.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	-1.32	-0.25	3.86	2.63	2.63
V@Mo_2B_2	-0.98	-0.24	3.80	2.34	2.57
Cr@Mo_2B_2	-1.29	-0.05	3.32	2.94	2.09
Mn@Mo_2B_2	0.44	0.74	2.84	0.90	1.61
Fe@Mo_2B_2	-0.45	0.95	2.26	2.16	1.03
Co@Mo_2B_2	0.16	0.82	2.13	1.81	0.90
Ni@Mo_2B_2	0.63	1.17	1.75	1.37	0.52
Cu@Mo_2B_2	1.02	1.54	0.89	1.48	0.31

Table. S3 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site II.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	-0.37	-1.30	4.67	1.92	3.47
V@Mo_2B_2	-0.39	-0.83	4.16	1.94	2.93
Cr@Mo_2B_2	-1.18	-0.16	3.32	1.93	2.10
Mn@Mo_2B_2	-0.85	0.32	2.80	0.94	1.57
Fe@Mo_2B_2	-0.86	1.36	2.71	1.71	1.48
Co@Mo_2B_2	-0.84	1.82	2.31	1.63	1.08
Ni@Mo_2B_2	-0.46	2.26	1.63	1.49	1.03
Cu@Mo_2B_2	-0.32	2.87	0.76	1.60	1.64

Table. S4 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site III.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	-1.25	0.53	4.10	1.54	2.87
V@Mo_2B_2	-0.21	-0.63	3.89	1.87	2.66
Cr@Mo_2B_2	-1.24	-0.24	3.12	3.28	2.05
Mn@Mo_2B_2	-0.27	-0.27	2.31	1.93	1.08
Fe@Mo_2B_2	-0.98	-0.98	4.36	1.51	3.13
Co@Mo_2B_2	-0.52	-0.52	3.90	1.76	2.67
Ni@Mo_2B_2	-0.09	-0.09	3.98	1.26	2.75
Cu@Mo_2B_2	-0.13	-0.13	3.92	1.38	2.70

Table. S5 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site IV.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	-0.62	-0.19	3.98	1.37	2.75
V@Mo_2B_2	-0.27	-0.51	4.68	1.02	3.45
Cr@Mo_2B_2	-1.13	-0.30	5.17	1.18	3.94
Mn@Mo_2B_2	0.73	-0.15	-0.64	4.98	3.75
Fe@Mo_2B_2	-0.91	-0.09	3.59	2.32	2.36
Co@Mo_2B_2	-0.56	-0.46	4.36	1.58	3.13
Ni@Mo_2B_2	-0.33	-0.33	4.18	1.40	2.95
Cu@Mo_2B_2	-0.35	-0.18	4.00	1.45	2.77

Table. S6 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site V.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	2.22	1.42	-5.42	6.70	5.47
V@Mo_2B_2	-1.14	5.89	-4.93	5.10	4.66
Cr@Mo_2B_2	-1.46	1.06	0.49	4.83	3.60
Mn@Mo_2B_2	0.32	1.07	-0.32	3.85	2.62
Fe@Mo_2B_2	-1.33	0.87	1.18	4.21	2.98
Co@Mo_2B_2	-0.43	0.47	-1.07	5.95	4.72
Ni@Mo_2B_2	-0.75	0.94	-1.18	5.91	4.68
Cu@Mo_2B_2	-1.05	1.14	0.82	4.02	2.79

Table. S7 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site VI.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	-1.45	3.69	-3.51	6.19	4.96
V@Mo_2B_2	-1.17	6.00	-5.58	5.66	4.43
Cr@Mo_2B_2	-1.56	0.14	1.25	5.09	3.86
Mn@Mo_2B_2	0.91	0.50	2.55	0.95	1.32
Fe@Mo_2B_2	-0.41	-0.20	0.20	5.32	4.09
Co@Mo_2B_2	-0.29	0.13	0.70	4.37	3.14
Ni@Mo_2B_2	-0.39	0.79	-1.70	6.22	4.99
Cu@Mo_2B_2	-0.48	3.25	-4.21	6.35	5.12

Table. S8 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) of four elementary steps and overpotential (η_{OER}) for OER at site VII.

TM@Mo_2B_2	ΔG_1/eV	ΔG_2/eV	ΔG_3/eV	ΔG_4/eV	η_{OER}/V
Ti@Mo_2B_2	-1.63	0.36	0.23	5.96	4.73
V@Mo_2B_2	-1.06	-0.30	0.55	5.73	4.50
Cr@Mo_2B_2	-1.73	0.86	-1.00	6.80	5.57
Mn@Mo_2B_2	1.41	-0.30	-0.42	4.24	3.01
Fe@Mo_2B_2	-0.78	0.30	0.02	5.38	4.15
Co@Mo_2B_2	-0.59	-0.30	-0.86	6.67	5.44
Ni@Mo_2B_2	-0.48	-0.15	-0.81	6.37	5.14
Cu@Mo_2B_2	-0.07	-0.43	-0.88	6.31	5.08

Table. S9 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site I.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-2.63	-3.86	0.25	1.32	2.55
V@Mo_2B_2	-2.34	-3.80	0.24	0.98	2.21
Cr@Mo_2B_2	-2.94	-3.32	0.05	1.29	2.52
Mn@Mo_2B_2	-0.90	-2.84	-0.74	-0.44	0.79
Fe@Mo_2B_2	-2.16	-2.26	-0.95	0.45	1.68
Co@Mo_2B_2	-1.81	-2.13	-0.82	-0.16	1.07
Ni@Mo_2B_2	-1.37	-1.75	-1.17	-0.63	0.60
Cu@Mo_2B_2	-1.48	-0.89	-1.54	-1.02	0.34

Table. S10 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site II.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-1.92	-4.67	1.30	0.37	2.53
V@Mo_2B_2	-1.97	-4.16	0.83	0.39	2.06
Cr@Mo_2B_2	-2.93	-3.33	0.16	1.18	2.41
Mn@Mo_2B_2	-0.94	-2.80	-0.32	-0.85	0.91
Fe@Mo_2B_2	-1.71	-2.71	-1.36	0.86	2.09
Co@Mo_2B_2	-1.63	-2.31	-1.82	0.84	2.07
Ni@Mo_2B_2	-1.50	-1.63	-2.26	0.46	1.69
Cu@Mo_2B_2	-1.60	-0.76	-2.87	0.32	1.55

Table. S11 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site III.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-1.54	-4.10	-0.53	1.25	2.48
V@Mo_2B_2	-1.87	-3.89	0.63	0.21	1.86
Cr@Mo_2B_2	-3.28	-3.12	0.24	1.24	2.47
Mn@Mo_2B_2	-1.93	-2.31	-0.96	0.27	1.50
Fe@Mo_2B_2	-1.51	-4.36	-0.03	0.98	2.21
Co@Mo_2B_2	-1.76	-3.90	0.23	0.52	1.75
Ni@Mo_2B_2	-1.26	-3.98	0.23	0.09	1.46
Cu@Mo_2B_2	-1.38	-3.93	0.26	0.13	1.49

Table. S12 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site IV.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-1.37	-3.98	-0.19	0.62	1.85
V@Mo_2B_2	-1.02	-4.68	0.51	0.27	1.74
Cr@Mo_2B_2	-1.18	-5.17	0.30	1.13	2.36
Mn@Mo_2B_2	-4.98	0.64	0.15	-0.73	1.87
Fe@Mo_2B_2	-2.33	-3.59	0.09	0.91	2.14
Co@Mo_2B_2	-1.58	-4.36	0.46	0.56	1.79
Ni@Mo_2B_2	-1.40	-4.18	0.33	0.33	1.56
Cu@Mo_2B_2	-1.45	-4.00	0.18	0.35	1.58

Table. S13 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site V.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-6.70	5.42	-1.42	-2.22	6.65
V@Mo_2B_2	-5.10	4.93	-5.89	1.14	6.16
Cr@Mo_2B_2	-4.83	-0.49	-1.06	1.46	2.69
Mn@Mo_2B_2	-3.85	0.32	-1.07	-0.33	1.55
Fe@Mo_2B_2	-4.21	-1.18	-0.87	1.33	2.56
Co@Mo_2B_2	-5.95	1.07	-0.47	0.43	2.30
Ni@Mo_2B_2	-5.91	1.18	-0.94	0.75	2.41
Cu@Mo_2B_2	-4.02	-0.82	-1.14	1.05	2.28

Table. S14 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site VI.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-6.19	3.51	-3.69	1.45	4.74
V@Mo_2B_2	-5.66	5.58	-6.00	1.17	6.81
Cr@Mo_2B_2	-5.09	-1.25	-0.14	1.56	2.79
Mn@Mo_2B_2	-0.95	-2.55	-0.50	-0.91	0.73
Fe@Mo_2B_2	-5.32	-0.20	0.20	0.41	1.64
Co@Mo_2B_2	-4.37	-0.70	-0.13	0.29	1.52
Ni@Mo_2B_2	-6.22	1.70	-0.79	0.39	1.62
Cu@Mo_2B_2	-6.35	4.21	-3.25	0.48	1.71

Table. S15 The reaction free energy (ΔG_a, ΔG_b, ΔG_c and ΔG_d) of four elementary steps and overpotential (η_{ORR}) for ORR at site VII.

TM@Mo_2B_2	ΔG_a/eV	ΔG_b/eV	ΔG_c/eV	ΔG_d/eV	η_{ORR}/V
Ti@Mo_2B_2	-5.96	-0.23	-0.36	1.63	2.86
V@Mo_2B_2	-5.73	-0.56	0.30	1.06	2.29
Cr@Mo_2B_2	-6.80	1.00	-0.86	1.73	2.96
Mn@Mo_2B_2	-4.24	0.42	0.30	-1.41	1.65
Fe@Mo_2B_2	-5.38	-0.02	-0.30	0.78	2.01
Co@Mo_2B_2	-6.67	0.86	0.30	0.59	2.09
Ni@Mo_2B_2	-6.37	0.81	0.15	0.48	2.04
Cu@Mo_2B_2	-6.31	0.88	0.43	0.07	2.11

Table. S16 The reaction free energy (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) and overpotential (η) of pristine Mo_2B_2 for OER and ORR.

Mo_2B_2	$\Delta G_1(\Delta G_a)$/eV	$\Delta G_2(\Delta G_b)$/eV	$\Delta G_3(\Delta G_c)$/eV	$\Delta G_4((\Delta G_d))$/eV	η/V
OER	-0.27	-0.27	3.90	1.56	2.67
ORR	-1.56	-3.90	0.27	0.27	1.50

Table. S17 The total energy (E/eV) of H adsorbed on TM@Mo_2B_2 at different surface active sites.

TM@Mo_2B_2	E(I) /eV	E(II) /eV	E(III) /eV	E(IV) /eV	E(VII) /eV
Ti@Mo_2B_2	-335.68	-335.95	-335.96	-335.67	-336.87
V@Mo_2B_2	-335.72	-335.92	-335.47	-334.85	-336.55
Cr@Mo_2B_2	-335.81	-336.50	-335.42	-335.67	-336.26
Mn@Mo_2B_2	-334.92	-334.67	-334.86	-335.22	-335.53
Fe@Mo_2B_2	-333.72	-334.21	-334.62	-334.44	-334.87
Co@Mo_2B_2	-333.54	-333.38	-331.90	-332.65	-333.79
Ni@Mo_2B_2	-332.27	-332.35	-332.10	-332.50	-332.72
Cu@Mo_2B_2	-330.12	-331.19	-330.26	-330.85	-331.61

Table. S18 Adsorption free energies of *H (ΔG_H) at different surface active sites under 1/16 hydrogen coverage condition. The promising candidates ($|\Delta G_H| < 0.2$ eV) are highlighted in bold typeface.

$TM@Mo_2B_2$	ΔG_H(I) /eV	ΔG_H(II)/eV	ΔG_H(III)/eV	ΔG_H(IV)/eV	ΔG_H(VII)/eV
$Ti@Mo_2B_2$	**-0.04**	-0.31	-0.32	**-0.04**	-1.24
$V@Mo_2B_2$	**0.05**	**-0.15**	0.29	0.91	-0.78
$Cr@Mo_2B_2$	**-0.08**	-0.77	0.31	**0.06**	-0.53
$Mn@Mo_2B_2$	-0.68	-0.43	-0.62	-0.98	-1.29
$Fe@Mo_2B_2$	0.39	**-0.10**	0.51	-0.33	-0.76
$Co@Mo_2B_2$	-0.94	-0.77	0.71	**-0.04**	-1.18
$Ni@Mo_2B_2$	**0.18**	**-0.10**	0.35	**-0.05**	-0.27
$Cu@Mo_2B_2$	0.28	-0.79	**0.14**	-0.45	-1.21

Table. S19 The reaction free energy (ΔG_1, ΔG_2) of elementary step for $2e^-$ ORR at site I.

$TM@Mo_2B_2$	ΔG_1/eV	ΔG_2/eV
$Ni@Mo_2B_2$	-1.37	0.36
$Cu@Mo_2B_2$	-1.48	0.47

Table. S20 Adsorption free energies of *H (ΔG_H) under 1/16, 1/9 and 1/4 hydrogen coverage conditions at site I for Ni@Mo_2B_2.

hydrogen coverage	ΔG_H/eV
1/4	-0.09
1/9	0.12
1/16	0.18

Figures

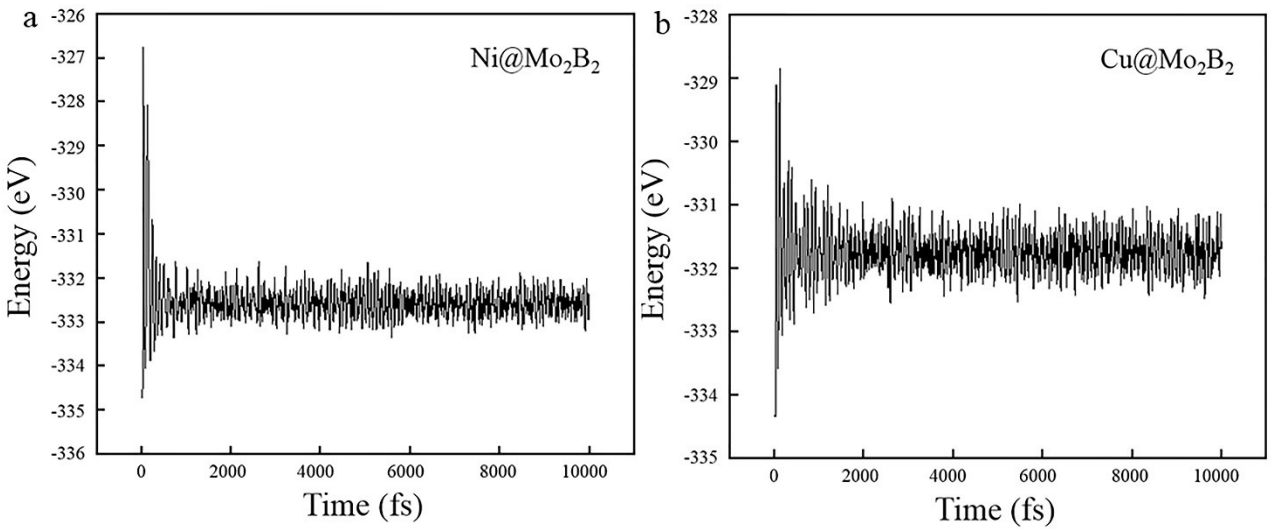

Fig. S1 Total potential energy fluctuations after equilibration for $Ni@Mo_2B_2$ and $Cu@Mo_2B_2$ in the AIMD simulation at 300 K after a time scale of 10 ps.

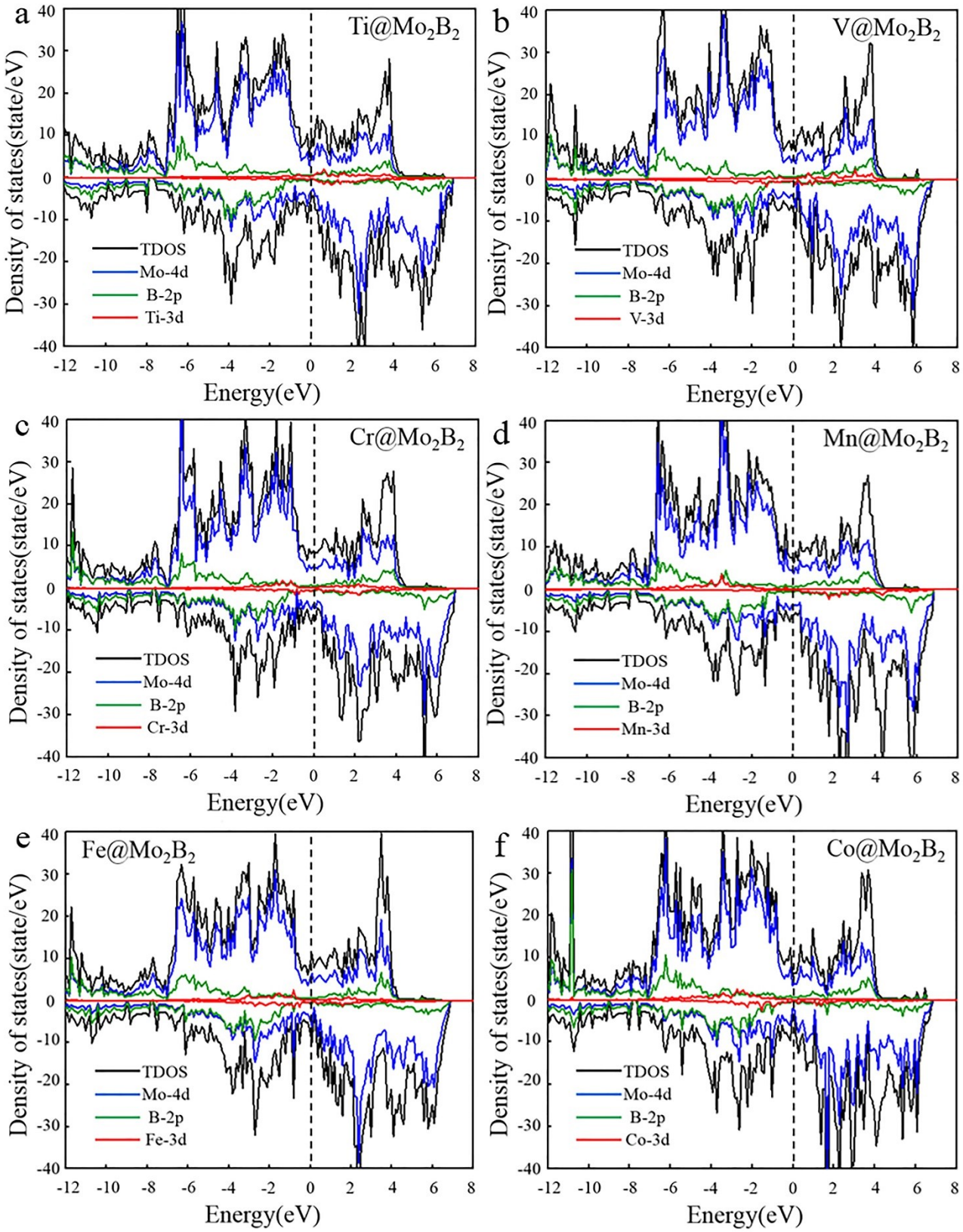

Fig. S2 The total density of states (TDOS) and projected density of states (PDOS) of (a) $Ti@Mo_2B_2$, (b) $V@Mo_2B_2$, (c) $Cr@Mo_2B_2$, (d) $Mn@Mo_2B_2$, (e) $Fe@Mo_2B_2$ and (f)

Co@Mo_2B_2, where the Fermi level is set to 0 eV

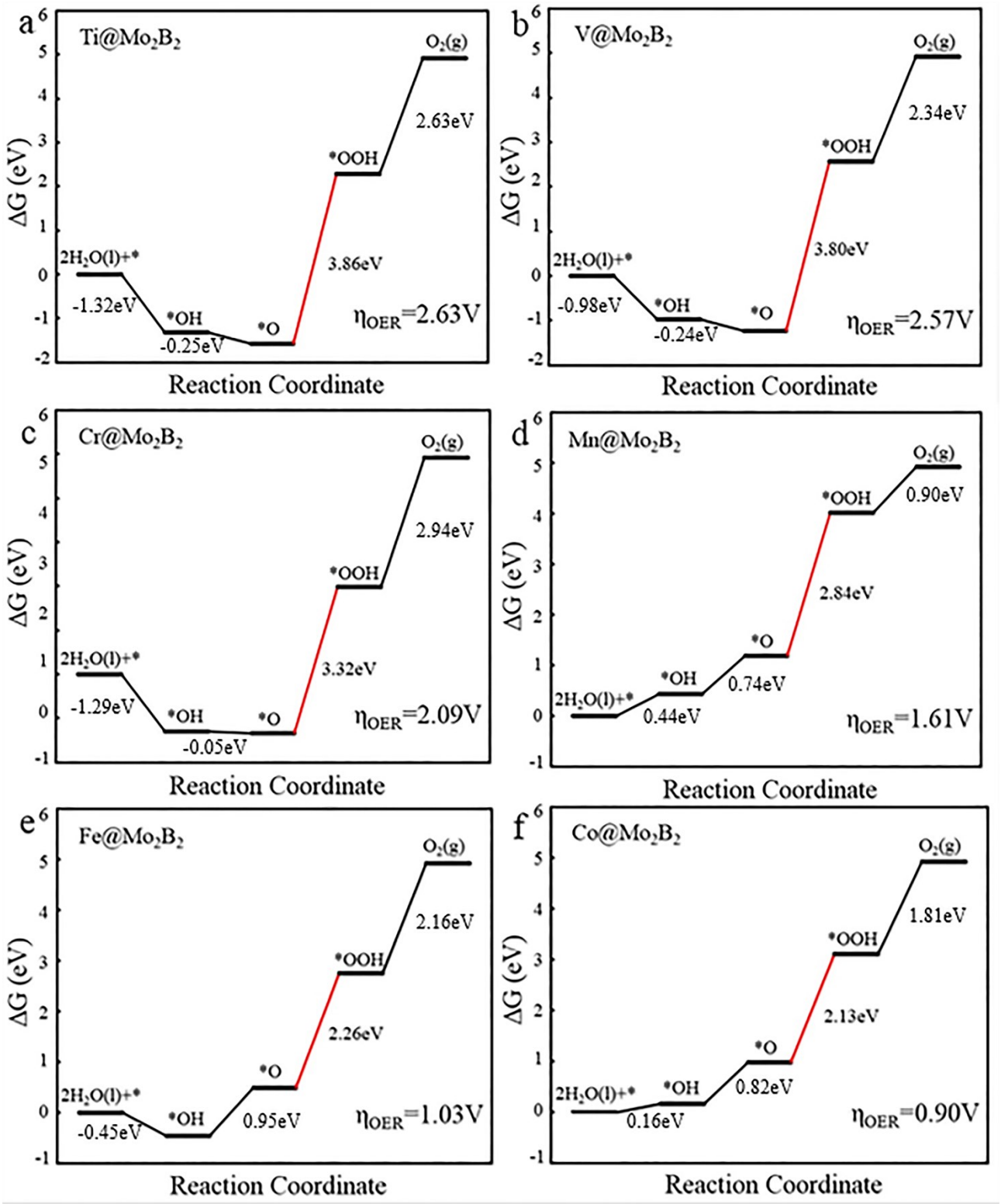

Fig. S3 Free energy diagram for the OER pathway of (a) Ti@Mo_2B_2, (b) V@Mo_2B_2, (c) Cr@Mo_2B_2, (d) Mn@Mo_2B_2, (e) Ti@Mo_2B_2 and (f) Co@Mo_2B_2 at site I, where the red lines represent the most energy-consuming step of OER.

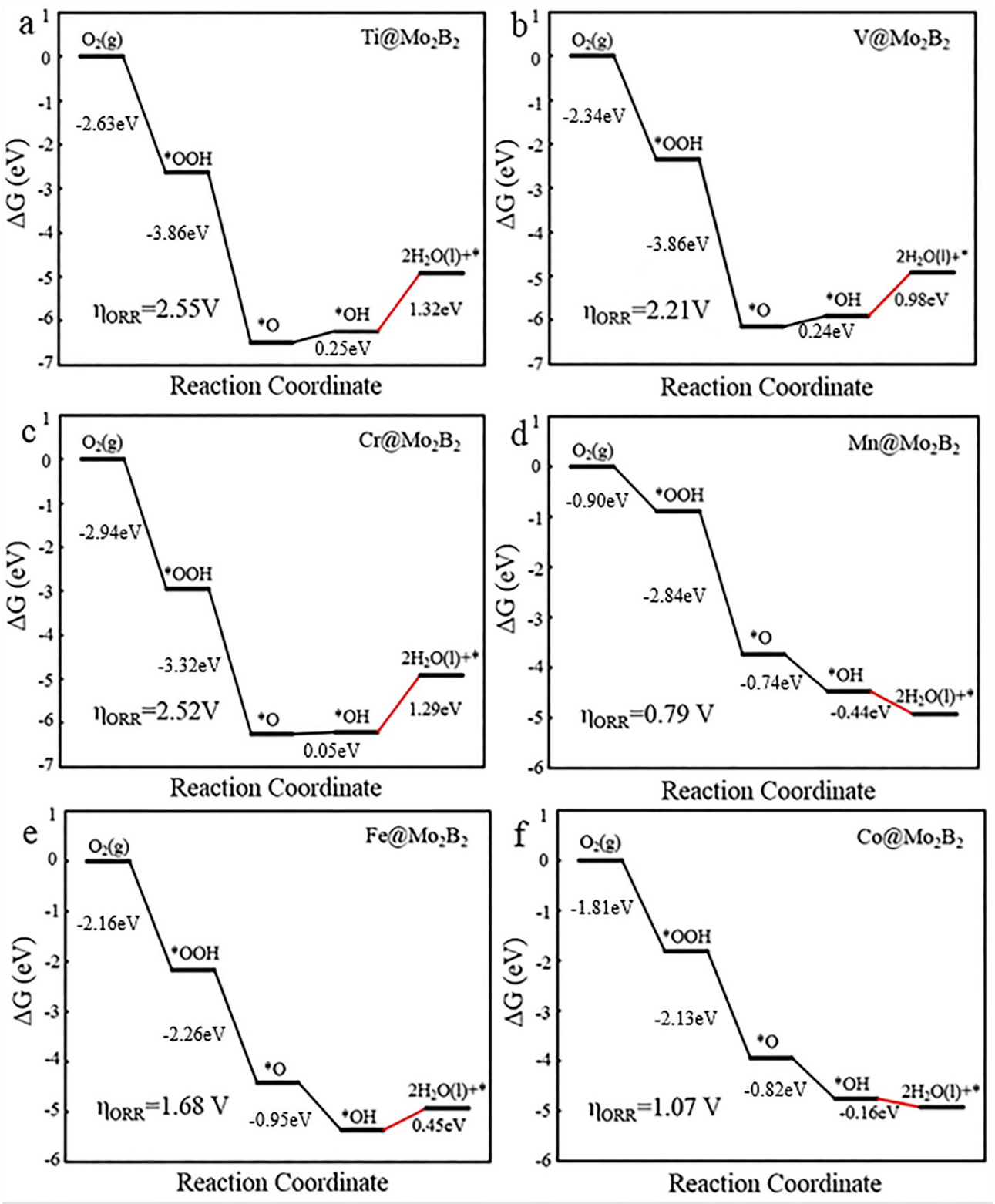

Fig. S4 Free energy diagram for the ORR pathway of (a) Ti@Mo_2B_2, (b) V@Mo_2B_2, (c) Cr@Mo_2B_2, (d) Mn@Mo_2B_2, (e) Ti@Mo_2B_2 and (f) Co@Mo_2B_2 at site I, where the red lines represent the most energy-consuming step of ORR.

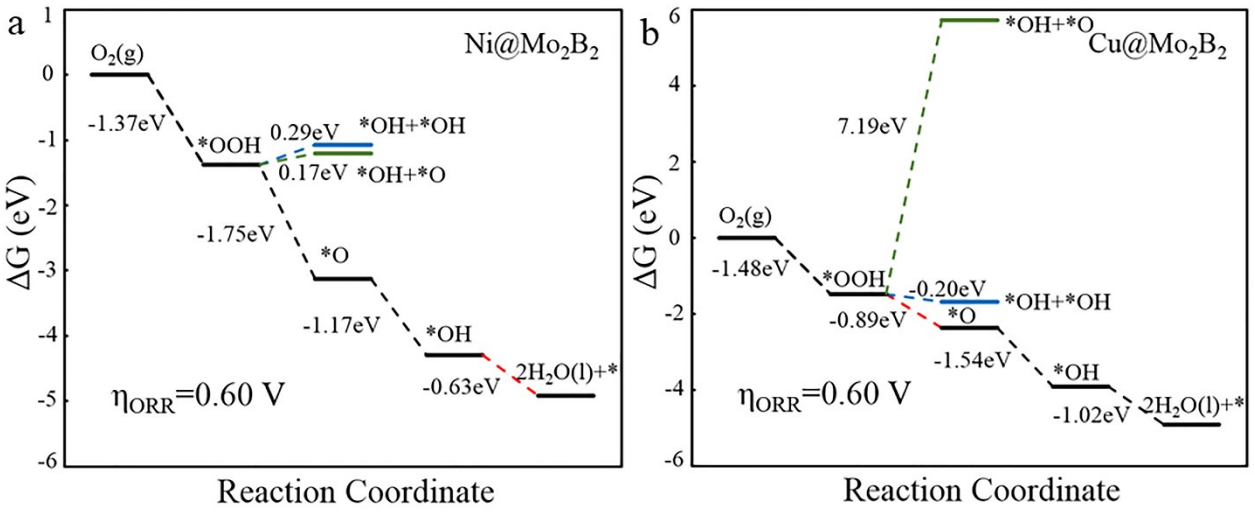

Fig.S5 The Gibbs free energy diagrams for the processes of forming *O, *OH+*OH and *OH+*O from *OOH for (a) Ni@Mo_2B_2 and (b) Cu@Mo_2B_2 at site I, where the blue lines represent the pathway of forming *OH+*OH from *OOH, the green lines represent the pathway of forming *OH+*O from *OOH, the black lines represent the pathway of forming *O from *OOH, and the red dashed lines represent the most energy-consuming step of ORR.

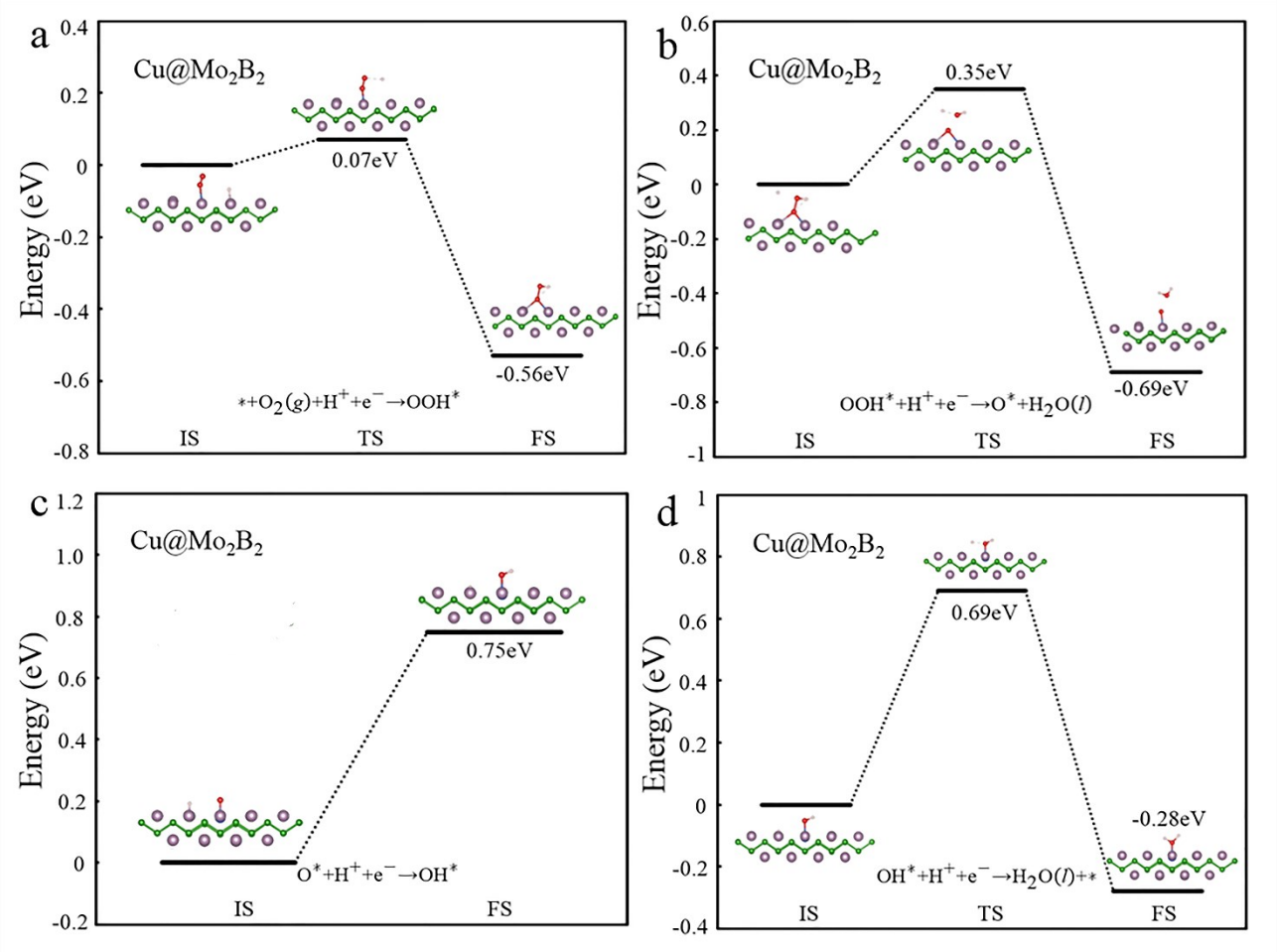

Fig. S6 Energy barrier of four elementary steps for ORR: (a) $*+O_2(g)+H^++e^-\rightarrow OOH^*$, (b) $OOH^*+H^++e^-\rightarrow O^*+H_2O(l)$, (c) $O^*+H^++e^-\rightarrow OH^*$ and (d) $OH^*+H^++e^-\rightarrow H_2O(l)+*$. The IS, TS, and FS represents initial state, transition state, and final state, respectively. It should be noted that if we reverse the IS and FS, the energy barrier of elementary steps for OER can be obtained.

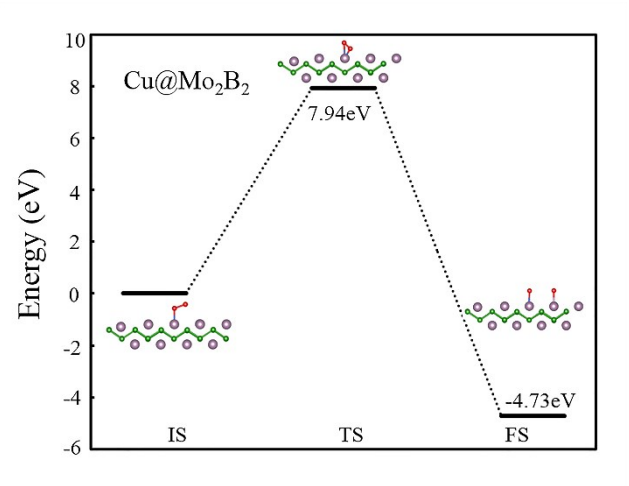

Fig. S7 Energy profile for the O_2 dissociation reaction on the surface of $Cu@Mo_2B_2$. The IS, TS, and FS represents initial state, transition state, and final state, respectively.

The strategy of dual volcano plots

By linear fitting, the linear relationship between ΔG_{O^*} and ΔG_{OH^*} is obtained：

$$\Delta G_{O^*} = 1.69\Delta G_{OH^*} + 0.74 \quad \text{(S1)}$$

Therefore, the overpotential (η) for the ORR processes determined by the maximum free energy change of the four elementary steps obeys the following equations:

$$\eta = -\Delta G_{OH^*}/e + 1.23\ \text{V} \quad (\Delta G_{OH^*} < 1.76\text{eV}) \quad \text{(S2)}$$

$$\eta = 1.01\Delta G_{OH^*}/e - 1.15\ \text{V} \quad (\Delta G_{OH^*} > 1.76\text{e} \quad \text{(S3)}$$

The overpotential (η) for the OER process obeys the equations:

$$\eta = -1.01\Delta G_{OH^*}/e + 1.15\ \text{V} \quad (\Delta G_{OH^*} < 0.96\text{eV}) \quad \text{(S4)}$$

$$\eta = 0.69\Delta G_{OH^*}/e - 0.49\ \text{V} \quad (0.96\text{eV} < \Delta G_{OH^*} < 2.\text{:} \quad \text{(S5)}$$

$$\eta = \Delta G_{OH^*}/e - 1.23\ \text{V} \quad (\Delta G_{OH^*} > 2.39\text{eV}) \quad \text{(S6)}$$