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Supporting Information

Rational design of 2D MBenes-based bifunctional OER/ORR dual-metal atom catalysts: A DFT study

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More calculation details

To describe the stability of the metal atoms (mono- or diatomic Mn/Fe/Co/Ni) adsorbed on $Mo_2B_2O_2$, the adsorption energy (E_{ad}) between the metal atoms and $Mo_2B_2O_2$ was calculated according to the following equation:

$$E_{ad} = E_{T\text{-}m} - E_T - E_m \quad (1)$$

$E_{T\text{-}m}$ is the total energy of SACs or DACs, E_m is the energy of the free MBenes substrate, and E_T is the energy of each metal atom in the metal bulk.

The 4-electron OER is described under acidic conditions as follows:

$$H_2O(l) \rightarrow OH^* + H^+ + e^- \quad (2)$$

$$OH^* \rightarrow O^* + H^+ + e^- \quad (3)$$

$$H_2O(l) + O \rightarrow OOH^* + H^+ + e^- \quad (4)$$

$$OOH^* \rightarrow O_2(g) + H^+ + e^- \quad (5)$$

Where * denotes the active site. l and g refer to the liquid phase and gas phase, respectively.

The ORR process can be considered the inverse of the OER, with the following elementary steps:

$$O_2(g) + H^+ + e^- + * \rightarrow OOH^* \quad (6)$$

$$OOH^* + H^+ + e^- \rightarrow O^* + H_2O(l) \quad (7)$$

$$O^* + H^+ + e^- \rightarrow OH^* \quad (8)$$

$$OH^* + H^+ + e^- \rightarrow H_2O(l) + * \quad (9)$$

The Gibbs free energy of intermediates (Δ_{OH^*}, Δ_{O^*} and Δ_{OOH^*}) was calculated by the equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (10)$$

The ΔE is the total energy change of the reaction by DFT calculations. The zero-point energy and entropy changes are denoted by ΔZPE and ΔS, respectively.

For the OER, the free energy change of the four elementary reactions may be stated as follows: $\Delta G_1 = \Delta G_{OH*}$, $\Delta G_2 = \Delta G_{O*} - \Delta G_{OH*}$, $\Delta G_3 = \Delta G_{OOH*} - \Delta G_{O*}$ and $\Delta G_4 = 4.92 - \Delta G_{OOH*}$. For the ORR step: $\Delta G_a = \Delta G_{OOH*} - 4.92$, $\Delta G_b = \Delta G_{O*} - \Delta G_{OOH*}$ $\Delta G_c = \Delta G_{OH*} - \Delta G_{O*}$ and $\Delta G_d = -\Delta G_{OH*}$. The following equation can be used to calculate the overpotential for evaluating the catalytic activity of OER/ORR of catalysts:

$$\eta^{OER} = \max\{\Delta G_1, \Delta G_2, \Delta G_3 \text{ and } \Delta G_4\}/e - 1.23 \quad (11)$$

$$\eta^{ORR} = \max\{\Delta G_a, \Delta G_b, \Delta G_c \text{ and } \Delta G_d\}/e + 1.23 \quad (12)$$

For the HER, the main metric used to evaluate its performance is the Gibbs free energy of hydrogen (ΔG_{H*}). In the earlier work, the value of $\Delta ZPE\text{-}T\Delta S$ was equal to 0.24 eV under acidic conditions; thus, the equation is stated as follows:

$$\Delta G_{H*} = \Delta E_{H*} + 0.24 \quad (13)$$

where ΔE_{H*} is the hydrogen adsorption energy, expressed as:

$$\Delta E_{H*} = E_{H*} - E_* - 1/2E_{H2} \quad (14)$$

where E_{H*}, E_*, and E_{H2} are the total energy of the H adsorbed on the catalyst, the energy of the catalyst itself, and the energy of the H_2, respectively.

Table S1. The total energy of TM/2TM/TM_1TM_2-$Mo_2B_2O_2$ (TM = Mn, Fe, Co, Ni), where the most stable configuration is marked in red.

Sample	model-1	model-2
2Mn-$Mo_2B_2O_2$	-472.288	-472.165
2Fe-$Mo_2B_2O_2$	-469.288	-469.033
2Co-$Mo_2B_2O_2$	-465.932	-465.574
2Ni-$Mo_2B_2O_2$	-462.814	-462.543
MnFe-$Mo_2B_2O_2$	-470.494	-470.570
MnCo-$Mo_2B_2O_2$	-469.297	-468.977
MnNi-$Mo_2B_2O_2$	-466.789	-467.434
FeCo-$Mo_2B_2O_2$	-467.772	-467.386
FeNi-$Mo_2B_2O_2$	-466.078	-465.836
CoNi-$Mo_2B_2O_2$	-464.460	-464.082
Mn-$Mo_2B_2O_2$	-462.262	
Fe-$Mo_2B_2O_2$	-460.549	
Co-$Mo_2B_2O_2$	-458.808	
Ni-$Mo_2B_2O_2$	-457.131	

Table S2. Calculated the Bader charge (Q_{TM}) of SACs and DACs. O denotes the average value of Bader electrons of O atoms in contact with TM/2TM/TM_1TM_2 (TM = Mn, Fe, Co, Ni).

Sample	Atoms	Bader electrons (e)	Q_{TM} (e)	Sample	Atoms	Bader electrons (e)	Q_{TM} (e)
Mn-$Mo_2B_2O_2$	Mn	5.685	-1.315	MnFe-$Mo_2B_2O_2$	Mn	5.830	-1.170
	O	6.915	0.915		Fe	6.880	-1.120
Fe-$Mo_2B_2O_2$	Fe	6.782	-1.218		O	6.925	0.925
	O	6.925	0.925	MnCo-$Mo_2B_2O_2$	Mn	5.767	-1.233
Co-$Mo_2B_2O_2$	Co	8.074	-0.926		Co	8.078	-0.922
	O	6.864	0.864		O	6.912	0.912
Ni-$Mo_2B_2O_2$	Ni	9.125	-0.875	MnNi-$Mo_2B_2O_2$	Mn	5.743	-1.257
	O	6.876	0.876		Ni	9.159	-0.841
2Mn-$Mo_2B_2O_2$	Mn_1	5.830	-1.170		O	6.930	0.930
	Mn_2	5.730	-1.270	FeCo-$Mo_2B_2O_2$	Fe	6.982	-1.018
	O	6.947	0.947		Co	8.090	-0.910
2Fe-$Mo_2B_2O_2$	Fe_1	6.838	-1.162		O	6.917	0.917
	Fe_2	6.836	-1.164	FeNi-$Mo_2B_2O_2$	Fe	6.763	-1.237
	O	6.966	0.966		Ni	9.152	-0.848
2Co-$Mo_2B_2O_2$	Co_1	8.089	-0.911		O	6.944	0.944
	Co_2	8.094	-0.906	CoNi-$Mo_2B_2O_2$	Co	8.093	-0.907
	O	6.891-	0.891		Ni	9.151	-0.849
2Ni-$Mo_2B_2O_2$	Ni_1	9.143	-0.857		O	6.902	0.902
	Ni_2	9.148	-0.852				
	O	6.904	0.904				

Table S3. The Gibbs free energy of intermediates (ΔG_{OH*}, ΔG_{O*} and ΔG_{OOH*}), and the Gibbs free energy change of elementary step (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) as well as overpotential (η) for the OER, where the highest energy step of SACs and DACs is marked in red.

Sample	ΔG_{OH*} (eV)	ΔG_{O*} (eV)	ΔG_{OOH*} (eV)	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{OER} (V)
Mn-$Mo_2B_2O_2$	0.56	1.65	3.64	0.56	1.09	1.99	1.28	0.76
Fe-$Mo_2B_2O_2$	0.35	1.63	3.73	0.35	1.63	1.75	1.19	0.52
Co-$Mo_2B_2O_2$	0.65	2.09	3.82	0.65	1.44	1.73	1.10	0.50
Ni-$Mo_2B_2O_2$	1.26	2.22	4.01	1.26	0.96	1.79	0.91	0.56
2Mn-$Mo_2B_2O_2$	-0.04	1.10	3.23	-0.04	1.14	2.12	1.69	0.89
2Fe-$Mo_2B_2O_2$	0.14	1.59	4.02	0.14	1.45	2.43	0.90	1.20
2Co-$Mo_2B_2O_2$	0.51	1.79	3.49	0.51	1.28	1.70	1.43	0.47
2Ni-$Mo_2B_2O_2$	0.96	2.68	3.91	0.96	1.72	1.24	1.01	0.49
MnFe-$Mo_2B_2O_2$	-0.27	0.96	3.00	-0.27	1.23	2.04	1.92	0.81
MnCo-$Mo_2B_2O_2$	0.67	1.89	3.32	0.67	1.22	1.43	1.60	0.37
MnNi-$Mo_2B_2O_2$	-0.54	0.69	2.65	-0.54	1.24	1.95	2.27	1.04
FeCo-$Mo_2B_2O_2$	0.33	1.76	3.31	0.33	1.43	1.55	1.61	0.38
FeNi-$Mo_2B_2O_2$	0.33	1.75	3.60	0.33	1.42	1.85	1.32	0.62
CoNi-$Mo_2B_2O_2$	0.73	2.00	3.44	0.73	1.27	1.44	1.48	0.25

Table S4. The Gibbs free energy of intermediates (ΔG_{OH*}, ΔG_{O*} and ΔG_{OOH*}), and the Gibbs free energy change of elementary step (ΔG_a, ΔG_b, ΔG_c and ΔG_d) as well as overpotential (η) for the ORR, where the highest energy step of SACs and DACs is marked in red.

Sample	ΔG_{OH*} (eV)	ΔG_{O*} (eV)	ΔG_{OOH*} (eV)	ΔG_a (eV)	ΔG_b (eV)	ΔG_c (eV)	ΔG_d (eV)	η^{ORR} (V)
Mn-$Mo_2B_2O_2$	0.56	1.65	3.64	-1.28	-1.99	-1.09	-0.56	0.67
Fe-$Mo_2B_2O_2$	0.35	1.63	3.73	-1.19	-1.75	-1.63	-0.35	0.88
Co-$Mo_2B_2O_2$	0.65	2.09	3.82	-1.10	-1.73	-1.44	-0.65	0.58
Ni-$Mo_2B_2O_2$	1.26	2.22	4.01	1.26	0.96	1.79	0.91	0.32
2Mn-$Mo_2B_2O_2$	-0.04	1.10	3.23	-1.69	-2.12	-1.14	0.04	1.27
2Fe-$Mo_2B_2O_2$	0.14	1.59	4.02	-0.90	-2.43	-1.45	-0.14	1.09
2Co-$Mo_2B_2O_2$	0.51	1.79	3.49	-1.43	-1.70	-1.28	-0.51	0.72
2Ni-$Mo_2B_2O_2$	0.96	2.68	3.91	-1.01	-1.24	-1.72	-0.96	0.27
MnFe-$Mo_2B_2O_2$	-0.27	0.96	3.00	-1.92	-2.04	-1.23	0.27	1.50
MnCo-$Mo_2B_2O_2$	0.67	1.89	3.32	-1.60	-1.43	-1.22	-0.67	0.56
MnNi-$Mo_2B_2O_2$	-0.54	0.69	2.65	-2.27	-1.95	-1.24	0.54	1.77
FeCo-$Mo_2B_2O_2$	1.22	1.95	3.77	-1.15	-1.81	-0.73	-1.22	0.50
FeNi-$Mo_2B_2O_2$	0.33	1.75	3.60	-1.32	-1.85	-1.42	-0.33	0.90
CoNi-$Mo_2B_2O_2$	0.73	2.00	3.44	-1.48	-1.44	-1.27	-0.73	0.51

Table S5. Calculated the ΔE_{H^*} and ΔG_{H^*} of DACs.

Sample	Adsorption sites	ΔE_{H^*} (eV)	ΔG_{H^*} (eV)
2Mn-$Mo_2B_2O_2$	Mn	0.28	0.52
2Fe-$Mo_2B_2O_2$	Fe	0.61	0.85
2Co-$Mo_2B_2O_2$	Co	0.42	0.66
2Ni-$Mo_2B_2O_2$	Ni	0.67	0.91
MnFe-$Mo_2B_2O_2$	Mn	0.64	0.88
	Fe	0.35	0.59
MnCo-$Mo_2B_2O_2$	Mn	0.53	0.77
	Co	0.52	0.76
MnNi-$Mo_2B_2O_2$	Mn	-0.33	-0.09
	Ni	-0.33	-0.09
FeCo-$Mo_2B_2O_2$	Fe	0.67	0.91
	Co	0.55	0.79
FeNi-$Mo_2B_2O_2$	Fe	0.70	0.94
	Ni	0.59	0.83
CoNi-$Mo_2B_2O_2$	Co	0.59	0.83
	Ni	0.63	0.87

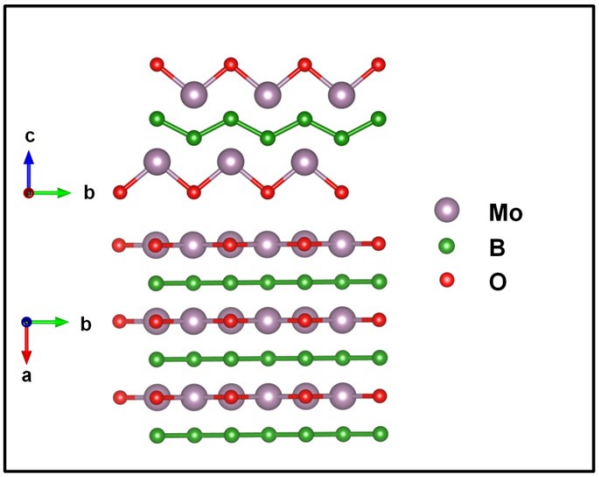

Fig. S1. The most stable atomic structures of $Mo_2B_2O_2$.

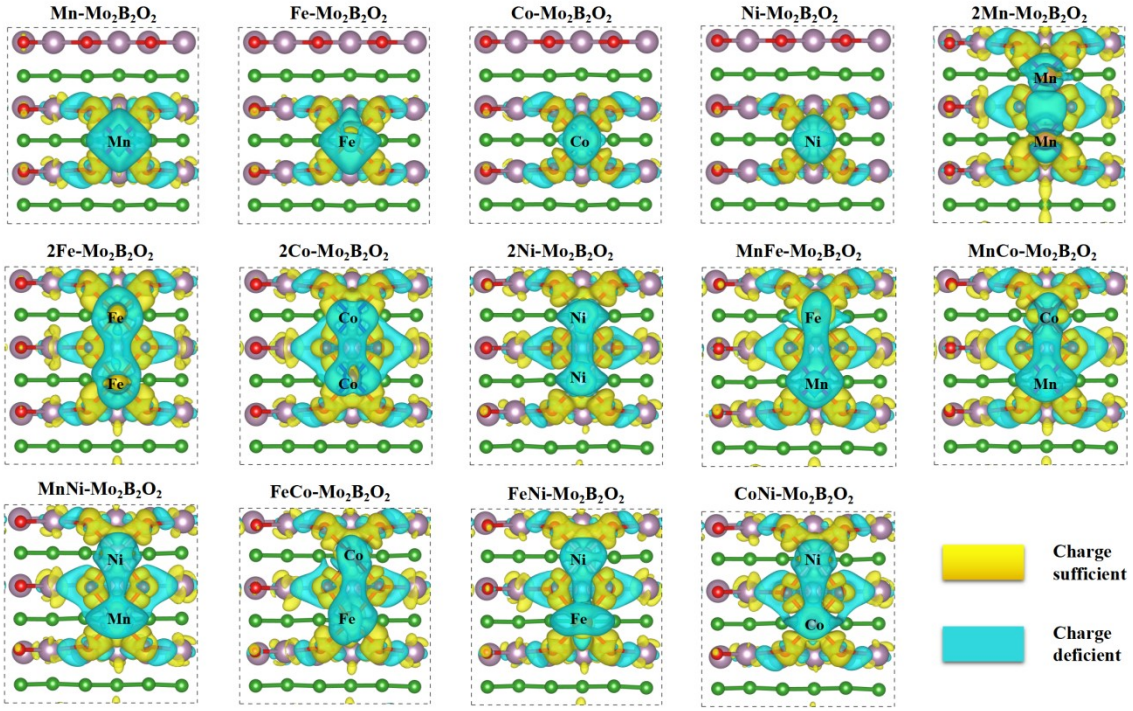

Fig. S2. The charge density difference of SACs and DACs. The isosurface level was 0.003 e $Å^{-3}$.

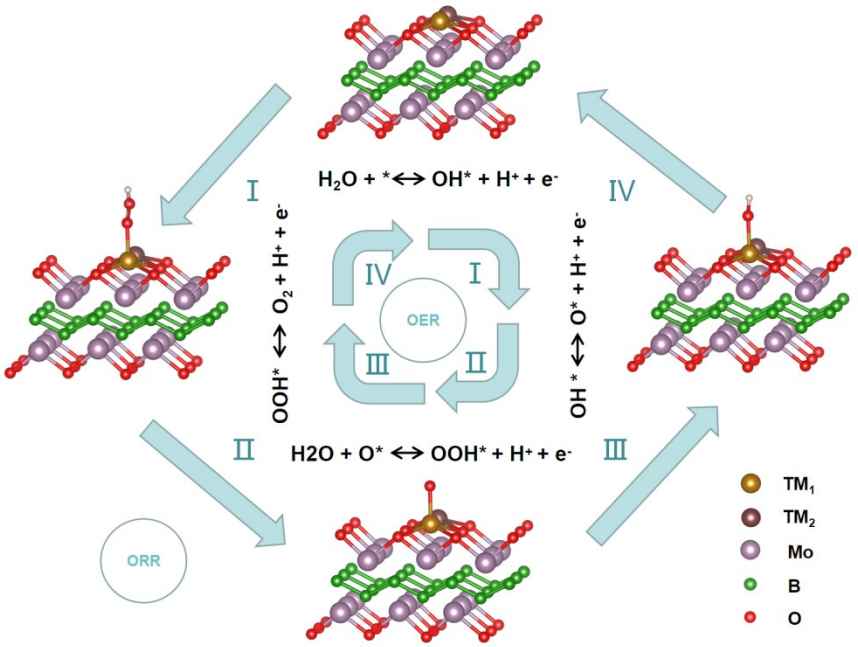

Fig. S3. The elementary reaction steps of OER/ORR on the surface of TM_1TM_2-$Mo_2B_2O_2$.

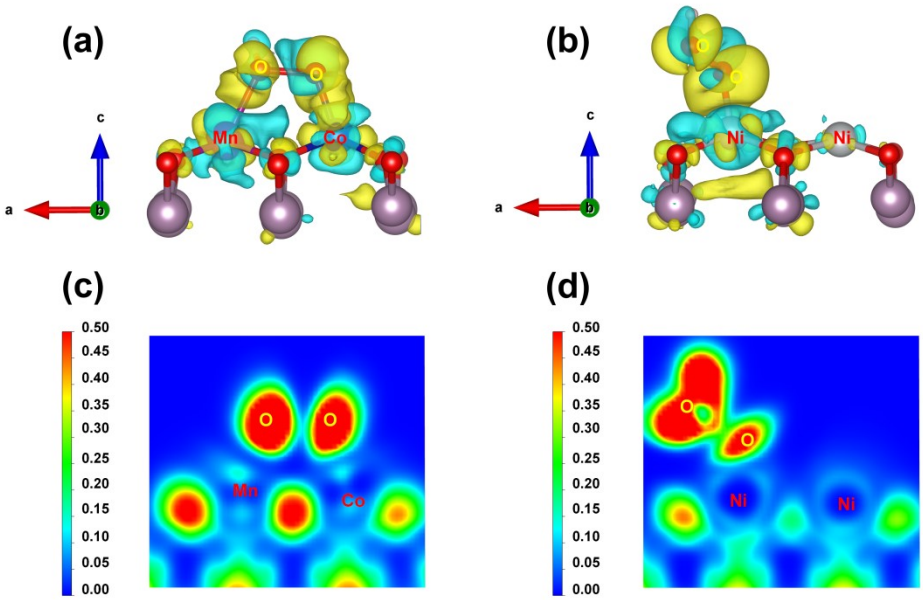

Fig. S4. Calculated the charge density differences of OOH* adsorbed on the surface of (a) MnCo-$Mo_2B_2O_2$ and (b) 2Ni-$Mo_2B_2O_2$ with the isosurfaces value of 0.0015 e $Å^{-3}$. Blue and yellow colors represent positive and negative charges, respectively. Electron localization function (ELF) plots of (c) OOH*-MnCo-$Mo_2B_2O_2$ and (d) OOH*-2Ni-$Mo_2B_2O_2$.

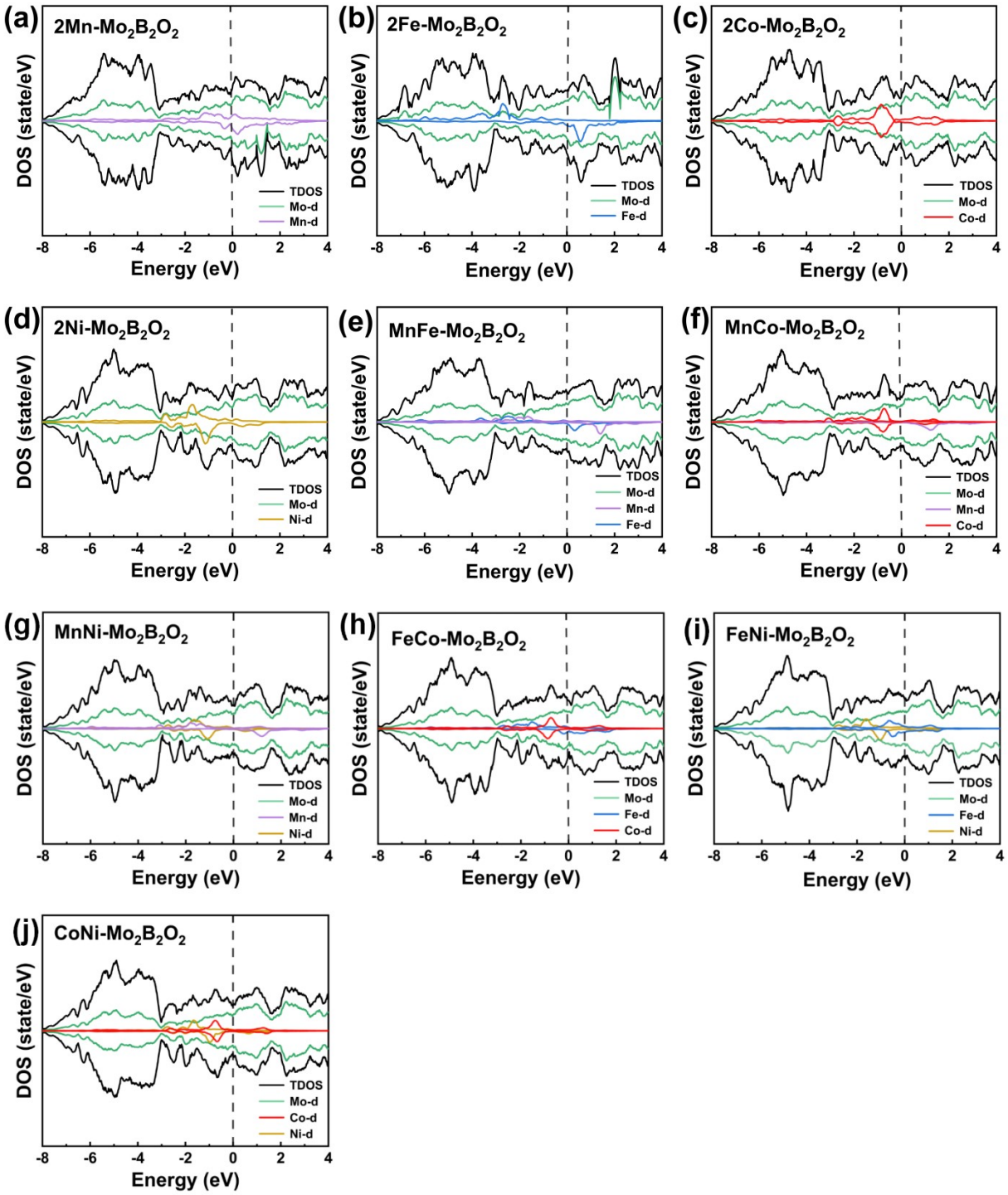

Fig. S5. The total density of states (TDOS) and the projected density of states (PDOS) of (a) 2Mn-$Mo_2B_2O_2$, (b) 2Fe-$Mo_2B_2O_2$, (c) 2Co-$Mo_2B_2O_2$, (d) 2Ni-$Mo_2B_2O_2$, (e) MnFe-$Mo_2B_2O_2$, (f) MnCo-$Mo_2B_2O_2$, (g) MnNi-$Mo_2B_2O_2$, (h) FeCo-$Mo_2B_2O_2$, (i) FeNi-$Mo_2B_2O_2$ and (j) CoNi-$Mo_2B_2O_2$, where the Fermi level is set to 0 eV.

References

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