

**Theoretical study of Mo₂N supported transition metal
single-atom catalyst for OER/ORR bifunctional
electrocatalysis**

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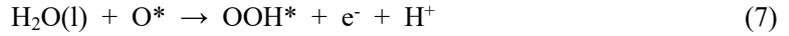
DFT Calculation

For ORR calculation, the four electrons pathway by which the ORR occurs under base condition are generally reported to proceed according to the following steps [S1]:



In which * denoted an activity site on the catalyst, (l) and (g) represented liquid and gas phases, respectively.

The OER process can be regarded as the inverse process of the ORR process, which can proceed via the following pathway:



The computational hydrogen electrode (CHE) model [1,2] was used to compute the change in the Gibbs free energy change (ΔG) of each elementary step of ORR/OER, in which one-half of the chemical potential of hydrogen molecule is equal to the chemical potential of proton-electron pair. In this CHE model, the ΔG value of each elementary step was determined by: $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$, where ΔE that represents the reaction energy difference of reactant and product, which can be directly computed from DFT computations. ΔE_{ZPE} and ΔS are the change in the zero-point energies and entropy at room temperature ($T = 298.15\text{K}$), which can be computed from the vibrational frequencies. In this work, the pH of the solution is assumed to be zero for an acid medium and the free energy contribution caused by changing the H concentration was neglected. The entropies of the free molecules, such as H_2 and H_2O , were taken from the NIST database. Since the DFT method failed to accurately describe the high-spin ground state of the O_2 molecule, the Gibbs free energy of O_2 (G_{O_2}) will be obtained by $G_{\text{O}_2} = G_{\text{H}_2\text{O}} - 2G_{\text{H}_2} + 4.92 \text{ eV}$. The effects of electrode potential (U) and pH on ORR/OER can be treated as the energy shifts to free energy change in the electrochemical steps: $\Delta G_{\text{U}} = -eU$ and $\Delta G_{\text{pH}} = k_{\text{B}}T \ln 10 \times \text{pH}$. In this work the value of pH was assumed to be zero for acidic medium. The thermodynamic activity of ORR/OER was evaluated by examining the overpotential of the reaction (η) according to the following equations:

$$\eta^{\text{ORR}} = (\Delta G_{\text{ORR}/\text{e}}^{\text{max}}) + 1.23$$

$$\eta^{\text{OER}} = (\Delta G_{\text{OER}/\text{e}}^{\text{max}}) - 1.23$$

where ΔG represents the free energy change of reaction (1)-(8), 1.23 is the equilibrium potential of ORR/OER. According to the above definition, a small η on a given catalyst suggests a higher catalytic activity for ORR/OER.

The Solvation effect

Based on previous studies, a single ice-like bilayer of water is a reasonable model able to provide sufficient water molecules to describe solvation effects, As shown in Fig.S3. We also

calculate the solvation energy (ΔSol), whose energy correction is defined by the following equations (equation 1-2):

$$\Delta Sol = E_{tot} - E_{(sur + adsorbate)} - E_{water} + E_{(sur + water)} \quad (1)$$

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta Sol + xeU - 4eU \quad (2)$$

where E_{tot} , $E_{(sur + adsorbate)}$, E_{water} , and $E_{(sur + water)}$ represent the computed electronic energies of the surface with the adsorbates as well as the single water layer, the surface with the adsorbates only, the single water layer, and the surface with single water layer only, respectively. The number of transferred electrons x was 1-3 for the OOH*, O*, and OH* intermediates, respectively.

The calculated results are shown in Table.S3. The results show that the intermediates involved in ORR and OER are stabilized to varying degrees by the interaction of hydrogen bonds with environmental water molecules. The figure shows that OOH* has a larger solvation energy than OH*. The adsorption of these intermediates can maintain the binding network in the water bilayer by forming hydrogen bonds with adjacent *H₂O molecules. The hydrogen bond interaction between the water bimolecular layer and the intermediate has a certain influence overall. In the ORR process of Au@Mo₂N, the overpotential changes by 0.02 V. In addition, the OER overpotential shifted from 0.37 V to 0.56 V. The above results show that although water does affect the absolute adsorption energy and free energy of the reaction, it does not significantly affect the overall trend of intrinsic catalytic properties.

Table S1. Gibbs adsorption free energies of OH*, O* and OOH* (ΔG_{OH^*} , ΔG_{O^*} and ΔG_{OOH^*}) as well as the overpotentials for OER/ORR($\eta^{\text{ORR/OER}}$) on TM@Mo₂N systems

System	ΔG_{OH^*} (eV)	ΔG_{O^*} (eV)	ΔG_{OOH^*} (eV)	η^{ORR} (V)	η^{OER} (V)
Fe@Mo ₂ N	-0.58	0.41	2.83	1.81	1.19
Co@Mo ₂ N	-0.45	0.65	2.90	1.68	1.02
Ni@Mo ₂ N	0.12	1.41	3.28	1.11	0.64
Cu@Mo ₂ N	0.23	2.27	3.58	1.00	0.80
Zn@Mo ₂ N	0.04	2.44	3.46	1.19	1.16
Ru@Mo ₂ N	-0.39	0.46	2.95	1.62	1.26
Rh@Mo ₂ N	-0.01	1.11	3.30	1.24	0.96
Pd@Mo ₂ N	0.54	2.17	3.80	0.69	0.40
Ag@Mo ₂ N	0.92	3.21	4.13	0.44	1.06
Cd@Mo ₂ N	0.81	2.89	3.75	0.42	0.85
Os@Mo ₂ N	-0.82	-0.18	2.57	2.05	1.52
Ir@Mo ₂ N	-0.49	0.29	2.89	1.72	1.37
Pt@Mo ₂ N	0.44	1.13	3.39	0.79	1.03
Au@Mo ₂ N	0.83	2.31	3.91	0.40	0.37
Hg@Mo ₂ N	0.71	2.90	4.04	0.52	0.95

Table.S2. The solvation energies corrections (ΔSol) and the free energies after considering the solvation effect (ΔG_{Sol}) on the selected catalysts (Au@Mo₂N).

	ΔSol			ΔG_{Sol}		
	*OOH	*O	*OH	*OOH	*O	*OH
Au@Mo ₂ N	-0.55	-0.34	-0.54	4.08	2.29	0.81

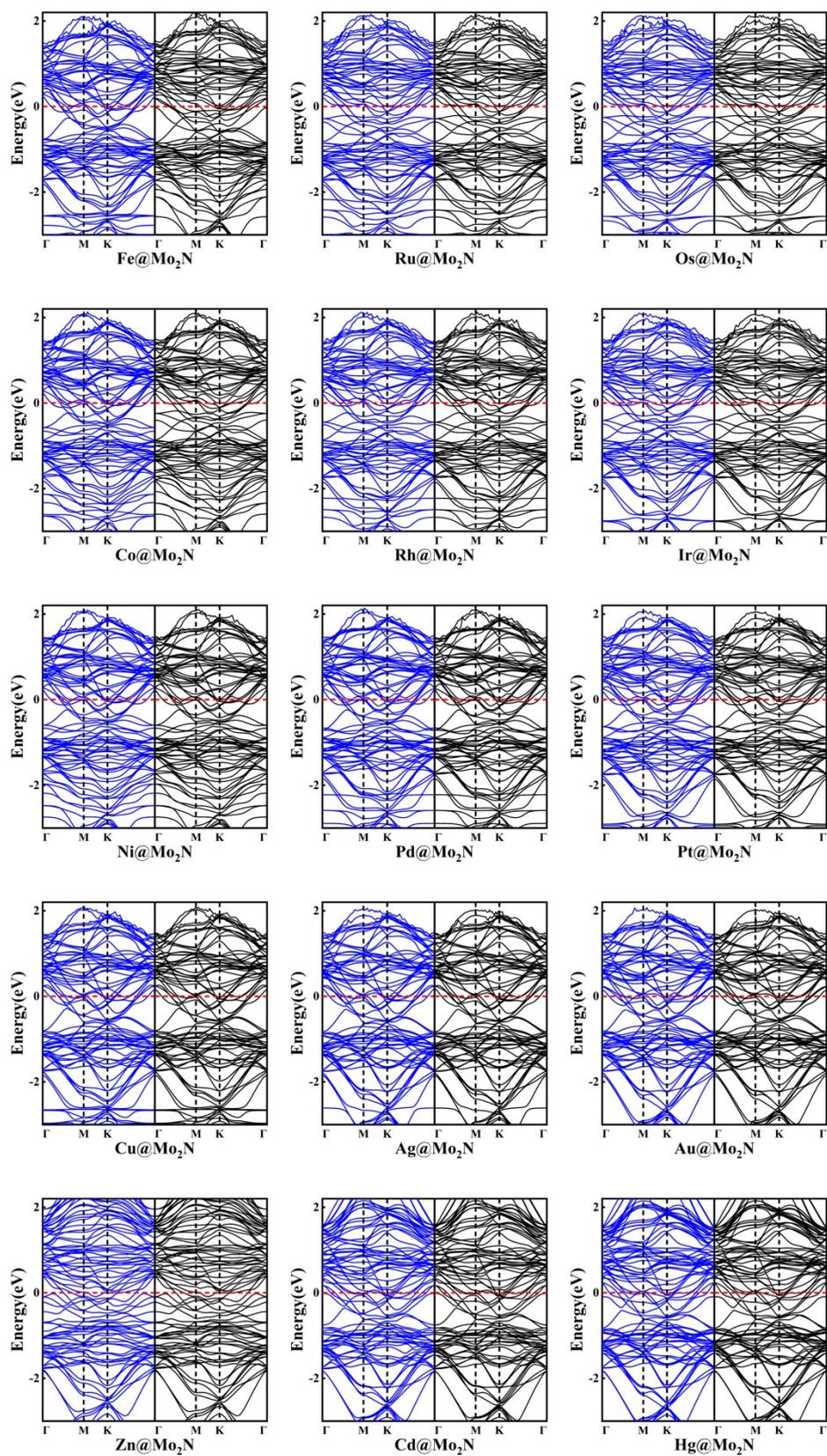


Fig.S1. Spin-polarized band structures of various TM-embedded Mo₂N monolayers. The Fermi level is set as zero in red dashed lines.

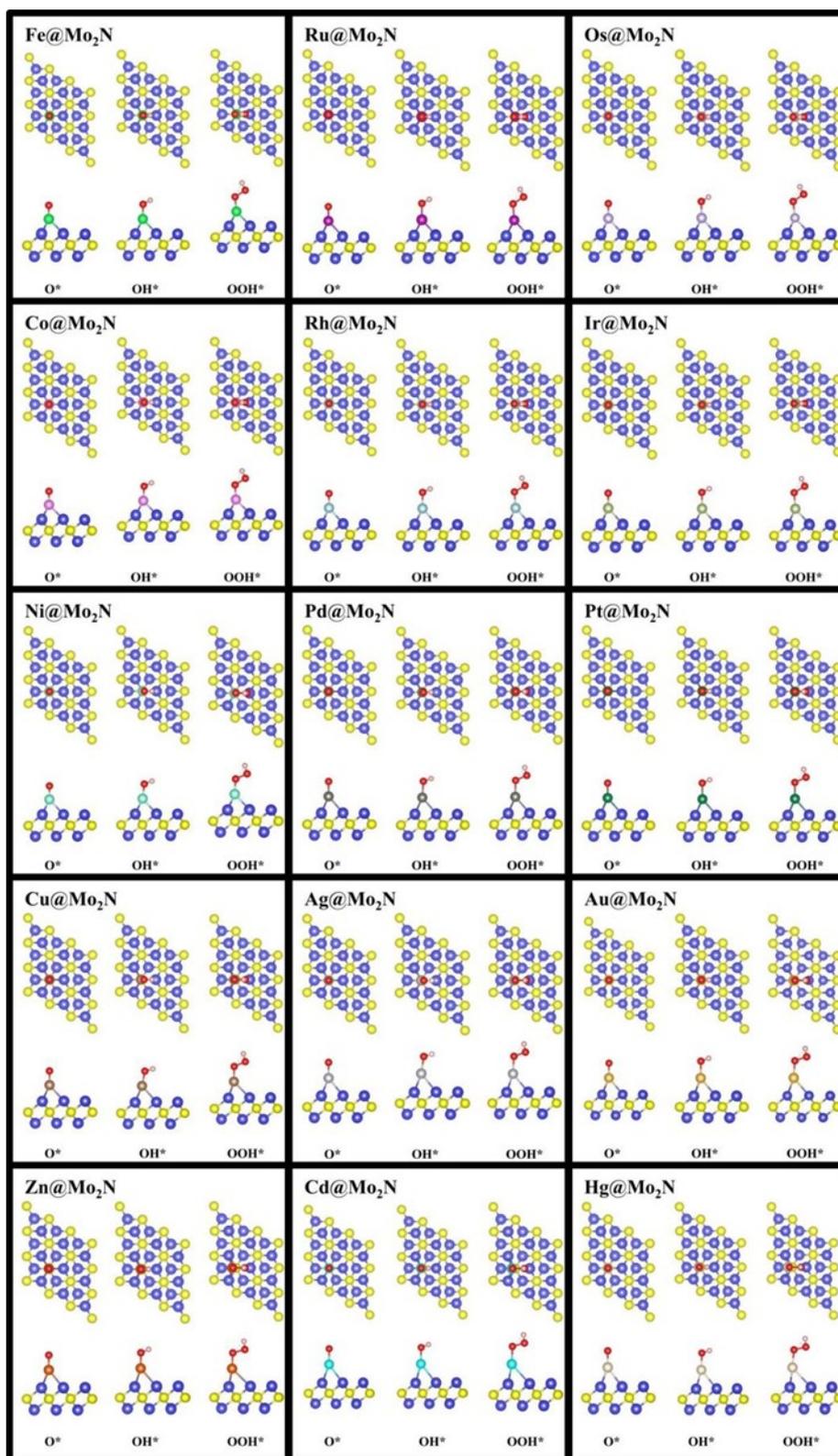


Fig.S2. Catalytic structure diagram of 15 kinds of catalyst reaction intermediates.

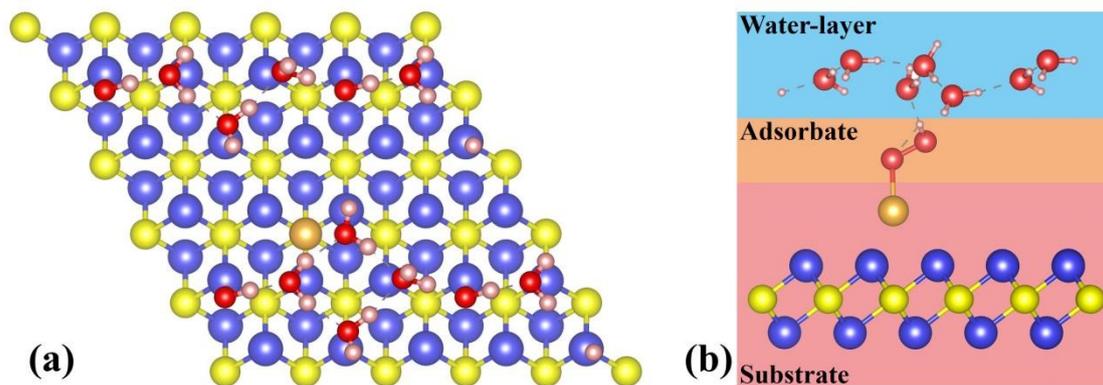


Fig.S3. (a) The top view of the solvation system and (b) the solvation model with adsorbed intermediates.

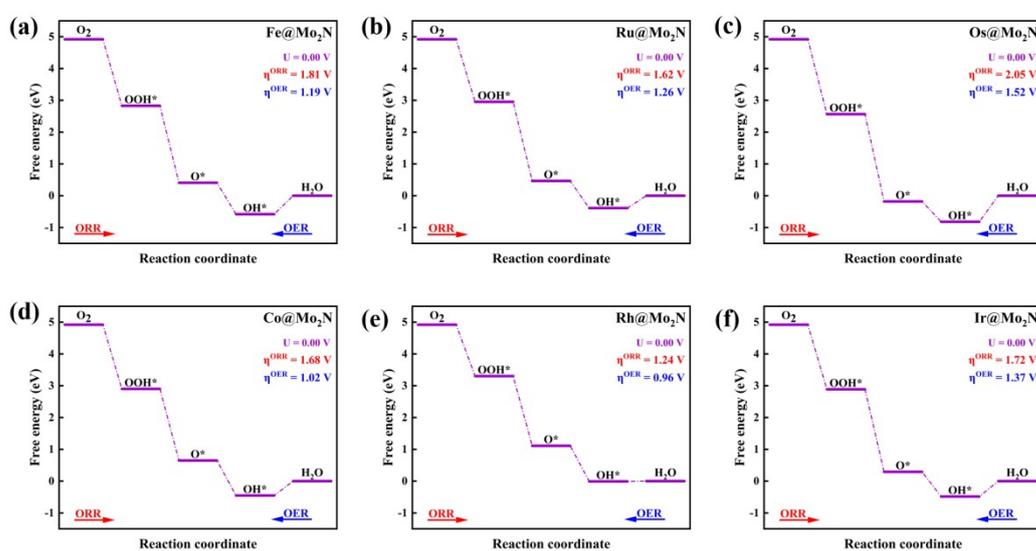


Fig.S4. Changes in Gibbs free energy differences (ΔG) of elementary reaction steps along the $4e^-$ pathway toward ORR and OER of six excluded atoms (Fe, Ru, Os, Co, Rh, Ir).