

## Electronic Supporting Information

### **Machine-Learning-Accelerated Screening of Single Metal Atoms Anchored on MnPS<sub>3</sub> Monolayer as Promising Bifunctional Oxygen Electrocatalysts**

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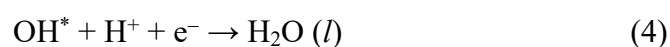
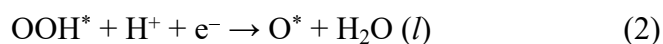
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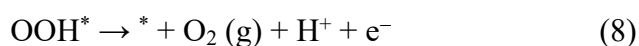
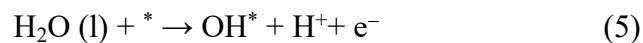
## Computational Details on Free Energy Changes

In the acid electrolyte, the ORR process can be decomposed into the following elementary steps:



where  $*$  is the active site on the surfaces of the catalysts,  $l$  and  $g$  represent the liquid phase and the gas phase, respectively.

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



For each elementary step of ORR and OER, the free energy has been calculated according to the method proposed by Nørskov *et al.* The free energy change from initial state to final state of the reaction is defined as:  $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{U}}$ , where  $\Delta E$  is the reaction energy difference of reactant and product, which can be directly computed from DFT computations.  $\Delta E_{\text{ZPE}}$  and  $\Delta S$  are the changes in zero point energies and entropy at room temperature ( $T = 298.15$  K). The entropy ( $S$ ) was obtained from vibrational frequency calculations. Specifically,  $S$

$$= \Sigma R \left\{ \frac{\beta h \nu}{e^{\beta h \nu} - 1} - \ln \left( \frac{1}{1 - e^{\beta h \nu}} \right) \right\}$$
, in which h represents Planck's constant,  $\nu$  refers the vibrational frequencies of adsorbed species, R refers gas constant,  $\beta = \frac{1}{k_B T}$ , and e represents mathematical constant. The Gibbs free energy of O<sub>2</sub> ( $G_{O_2}$ ) will be obtained by  $G_{O_2} = G_{H_2O} - 2G_{H_2} + 4.92$  eV because the DFT method fails to accurately describe the high-spin ground state of the O<sub>2</sub> molecule.

Therefore, where \* denotes an active site on the catalyst. According to Eqs. (1)–(8), the reaction Gibbs free energy can be written as  $\Delta G_1 = \Delta G_{\text{ads}}(\text{OOH}^*) - 4.92$  eV,  $\Delta G_2 = \Delta G_{\text{ads}}(\text{O}^*) - \Delta G_{\text{ads}}(\text{OOH}^*)$ ,  $\Delta G_3 = \Delta G_{\text{ads}}(\text{OH}^*) - \Delta G_{\text{ads}}(\text{O}^*)$ ,  $\Delta G_4 = -\Delta G_{\text{ads}}(\text{OH}^*)$ ,  $\Delta G_5 = \Delta G_{\text{ads}}(\text{OH}^*)$ ,  $\Delta G_6 = \Delta G_{\text{ads}}(\text{O}^*) - \Delta G_{\text{ads}}(\text{OH}^*)$ ,  $\Delta G_7 = \Delta G_{\text{ads}}(\text{OOH}^*) - \Delta G_{\text{ads}}(\text{O}^*)$ ,  $\Delta G_8 = 4.92$  eV  $- \Delta G_{\text{ads}}(\text{OOH}^*)$ . The overpotential that evaluates the performance of OER and ORR is applied according to the following equations:

$$\eta^{\text{ORR}} = \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \} / e^- + 1.23 \quad (9)$$

$$\eta^{\text{ORR}} = \max \{ \Delta G_5, \Delta G_6, \Delta G_7, \Delta G_8 \} / e^- + 1.23 \quad (10)$$

where 1.23 is the equilibrium potential. Based on previous reports, a lower  $\eta$  value on a given catalyst suggests a less energy input for ORR/OER, thus demonstrating its higher ORR/OER catalytic activity. Indeed, more exact predictions of catalytic activity will require calculations not just of free energies, but of reaction barriers between steps along the pathway. However, each electrochemical step involves the transfer of a proton from a solution to an adsorbed species on the surface. According to previous studies on ORR on Pt benchmark, the barriers for electrochemical proton transfers for the reduction O<sub>2</sub> to OOH on Pt<sup>1</sup> and for the reduction of OH to H<sub>2</sub>O on

Pt<sup>2</sup> were calculated to be small (0.15 eV to 0.25 eV) at the potential needed to make the elementary step exergonic and were found to diminish with higher applied voltages. Similarly, as a first approximation we expected that barriers for electrochemical proton transfers to adsorbed species in this study will be small and easily surmountable at room temperature.”

For non-electrochemical step  $i$ , the equilibrium constant ( $K_i$ ) can be expressed as :

$$K_i = \exp\left(-\frac{\Delta G_i}{k_B T}\right) \quad (\text{S1})$$

where  $\Delta G_i$  is the free energy change of step  $i$ , and  $k_B$  is the Boltzmann constant.

The rate constant ( $k_i$ ) is given by:

$$k_i = v_i \exp\left(-\frac{E_{a,i}}{k_B T}\right) \quad (\text{S2})$$

where  $v_i$  is the pre-exponential factor, and  $E_{a,i}$  is the activation energy.

For the electrochemical step,  $K_i$  is associated with the reaction potential ( $U$  vs. RHE) and is given by:

$$K_i = \exp\left(-\frac{e(U - U_i)}{k_B T}\right) \quad (\text{S3})$$

where  $U_i$  is the reversible potential of step  $i$  deduced by  $U_i = -\Delta G_i / e$ .  $k_i$  is written as:

$$k_i = A_i \exp\left(-\frac{E_{a,i}}{k_B T}\right) \exp\left(-\frac{e\beta_i(U - U_i)}{k_B T}\right) \quad (\text{S4})$$

where  $A_i$  is an effective pre-exponential factor taken as  $1.23 \times 10^9$ , and  $\beta_i$  is the symmetric factor taken as 0.5. Since the  $E_{a,i}$  values of electrochemical ORR steps are

generally small, ranging from 0.10 to 0.26 eV, we adopted  $E_{a,i} = 0.26$  eV for all the electrochemical steps of the ORR on Rh/MnPS<sub>3</sub> monolayer.

Moreover, the rate constants for all the reverse reactions ( $k_{-i}$ ), can be deduced by:

$$k_{-i} = \frac{k_i}{K_i} \quad (\text{S5})$$

Finally, the current density ( $j$ ) can be computed by :

$$j = e\rho TOF_e \quad (\text{S6})$$

**Table S1.** The computed binding energies ( $E_{\text{bind}}$ , eV) of all considered SACs on MnPS<sub>3</sub> monolayer.

TM	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$E_{\text{bind}}$	-3.94	-4.95	-5.92	-4.28	-4.16	-5.03	-5.53	-5.09	-4.24
TM	Zn	Nb	Mo	Ru	Rh	Pd	Ag	W	Os
$E_{\text{bind}}$	-1.11	-6.31	-6.51	-7.45	-5.81	-3.93	-2.28	-9.04	-8.71
TM	Ir	Pt	Au						
$E_{\text{bind}}$	-7.91	-5.89	-4.50						

**Table S2.** The computed adsorption Gibbs free energies ( $\Delta G_{\text{OOH}^*}$ ,  $\Delta G_{\text{O}^*}$ , and  $\Delta G_{\text{OH}^*}$ )

of all catalysts.

	$\Delta G_{\text{OH}^*}$ ( eV )	$\Delta G_{\text{O}^*}$ ( eV )	$\Delta G_{\text{OOH}^*}$ ( eV )
Sc	-1.58	-0.57	2.38
Ti	-1.40	-0.97	2.59
V	-0.90	-0.86	1.96
Cr	-2.03	1.98	2.80
Mn	-0.42	0.78	2.94
Fe	0.18	1.39	3.32
Co	0.20	1.58	3.58
Ni	0.94	2.65	4.05
Cu	0.64	2.98	4.00
Zn	0.09	2.04	3.68
Nb	-1.47	-1.62	1.70
Mo	-0.90	-1.08	2.33
Ru	0.32	1.12	2.93
Rh	0.96	2.33	4.01
Pd	1.23	3.25	4.23
Ag	0.86	2.03	3.80
W	-1.30	0.03	2.23
Os	0.41	1.16	4.59
Ir	0.12	1.26	3.01
Pt	0.10	1.61	3.28
Au	-0.12	1.98	3.27

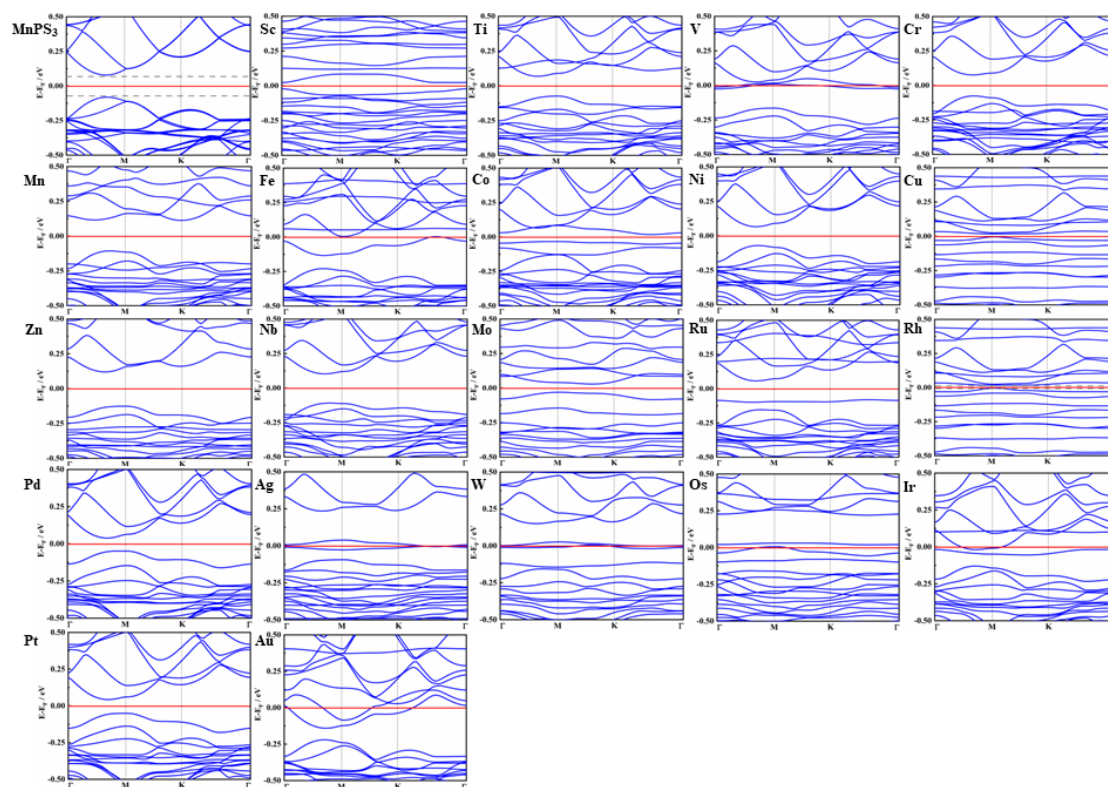
**Table S3.** The computed free energy change of each step during ORR/OER on all TM/MnPS<sub>3</sub> systems.

	$\Delta G_1$ ( eV )	$\Delta G_2$ ( eV )	$\Delta G_3$ ( eV )	$\Delta G_4$ ( eV )
Sc	-2.95	-2.54	-1.02	1.58
Ti	-2.33	-3.56	-0.43	1.40
V	-2.83	-2.96	-0.04	0.90
Cr	-0.47	-2.10	-2.47	0.12
Mn	-2.15	-1.98	-1.21	0.42
Fe	-1.60	-1.93	-1.21	-0.18
Co	-1.34	-2.00	-1.38	-0.20
Ni	-0.87	-1.41	-1.71	-0.94
Cu	-0.92	-1.02	-2.34	-0.64
Zn	-1.23	-1.24	-2.34	-0.09
Nb	-3.22	-3.32	0.15	1.47
Mo	-2.58	-3.42	0.19	0.90
Ru	-1.99	-1.81	-0.80	-0.32
Rh	-0.91	-1.68	-1.37	-0.96
Pd	-0.69	-0.98	-2.02	-1.23
Ag	-0.77	-0.62	-2.67	-0.86
W	-0.14	-0.75	-2.73	-1.30
Os	-0.43	-3.42	-0.65	-0.41
Ir	-0.71	-2.95	-1.14	-0.12
Pt	-1.67	-1.64	-1.51	-0.10
Au	-1.64	-1.30	-2.10	0.12

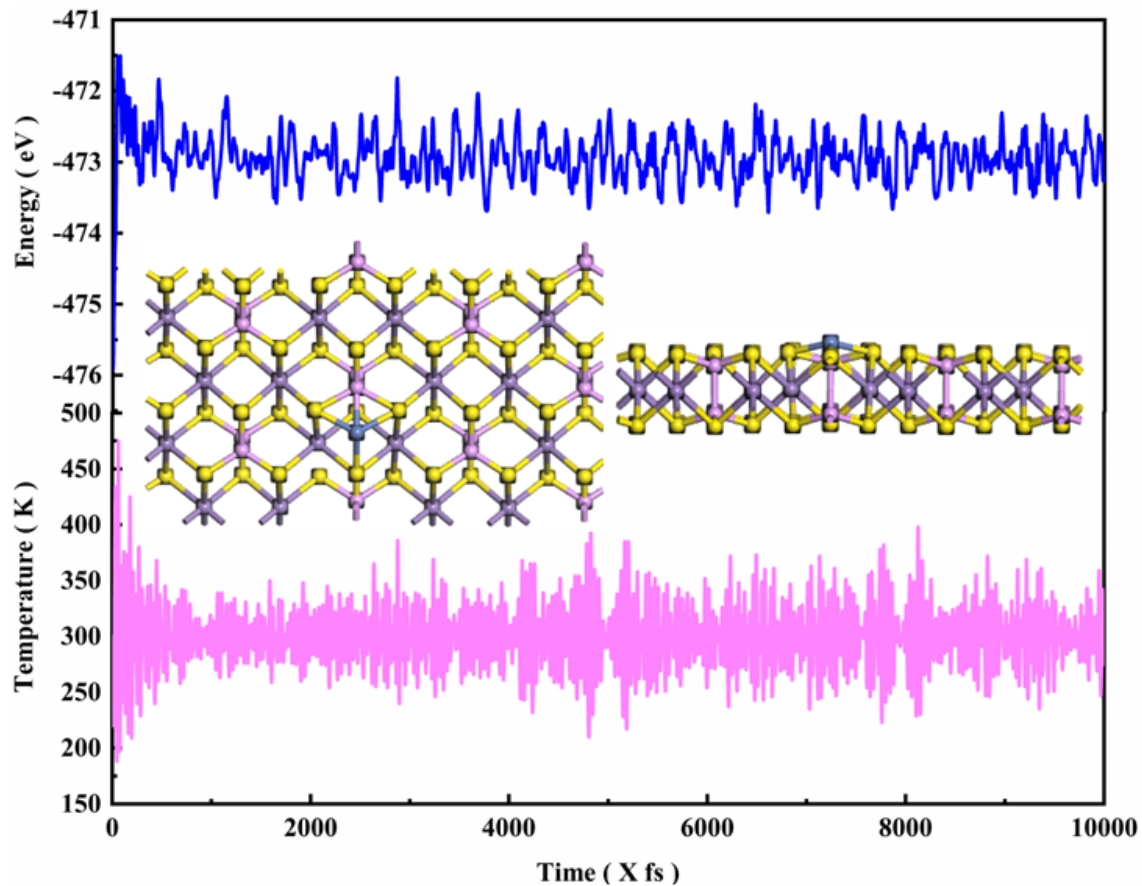


**Table S4.** The computed the bond length of TM atoms and adsorbed O species ( $d_{TM-O}$ ), the  $d$ -band center ( $\varepsilon_d$ ), the first ionization energy ( $I_m$ ), the radius of TM atoms ( $r_d$ ), the electronegativity ( $N_m$ ), the charge transfer of TM atoms ( $Q_e$ ), the magnetic moment of TM atoms ( $\mu_B$ ), and the number of TM- $d$  electrons ( $N_e$ ).

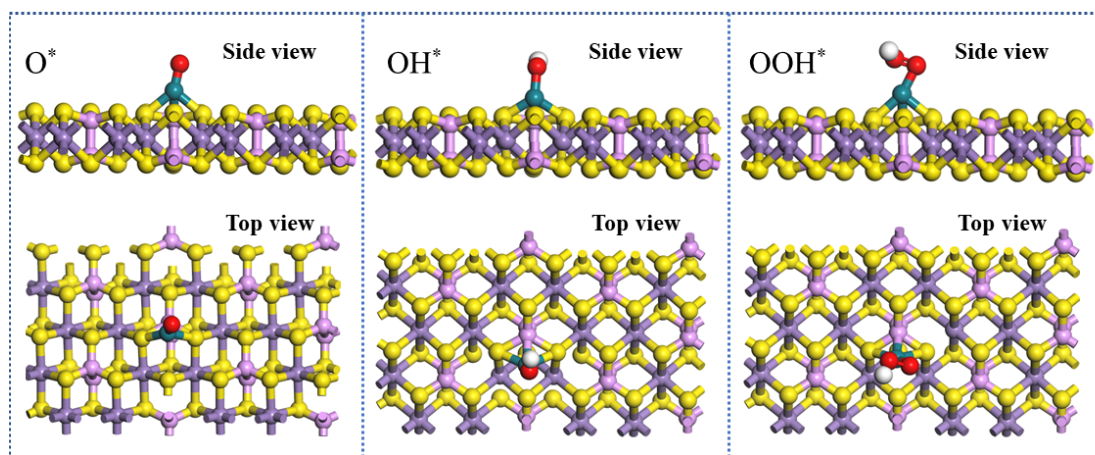
	$d_{TM-O}/\text{\AA}$	$\varepsilon_d/\text{eV}$	$Q_e/e^-$	$\mu_B$	$r_d/\text{\AA}$	$N_e$	$N_m$	$I_m$
Sc	1.84	-3.20	0.65	0.23	162	1	1.36	633.1
Ti	1.81	-4.20	0.78	0.73	147	2	1.54	658.1
V	1.76	-3.97	0.94	1.84	134	3	1.63	650.9
Cr	1.79	-3.65	0.89	3.10	128	5	1.66	652.9
Mn	1.82	-1.03	0.74	3.58	127	5	1.55	717.3
Fe	1.80	-1.35	0.59	2.09	126	6	1.83	762.5
Co	1.77	-1.33	0.33	0.12	125	7	1.88	760.4
Ni	1.80	-1.55	0.29	0.27	124	8	1.91	737.1
Cu	1.79	-2.93	0.50	0.05	128	10	1.90	745.5
Zn	1.82	-3.48	0.43	0.01	134	10	1.65	906.4
Nb	1.89	-3.98	0.27	0.84	146	4	1.60	652.1
Mo	1.91	-3.62	0.81	1.23	139	5	2.16	684.3
Ru	1.94	-1.36	0.30	0.62	134	7	2.20	710.2
Rh	1.96	-1.44	0.47	0.06	134	8	2.28	719.7
Pd	2.00	-2.36	0.11	0.16	137	10	2.20	804.4
Ag	2.03	-1.99	0.79	0.03	144	10	1.93	731.0
W	1.90	-4.01	0.75	0.24	139	4	2.38	758.8
Os	1.98	-0.5-	0.93	0.02	135	6	2.20	814.2
Ir	1.93	-0.97	0.90	0.04	136	7	2.28	865.2
Pt	1.52	-2.78	0.08	0.19	139	9	2.20	864.4
Au	1.98	-2.31	0.51	0.03	144	10	2.54	890.1



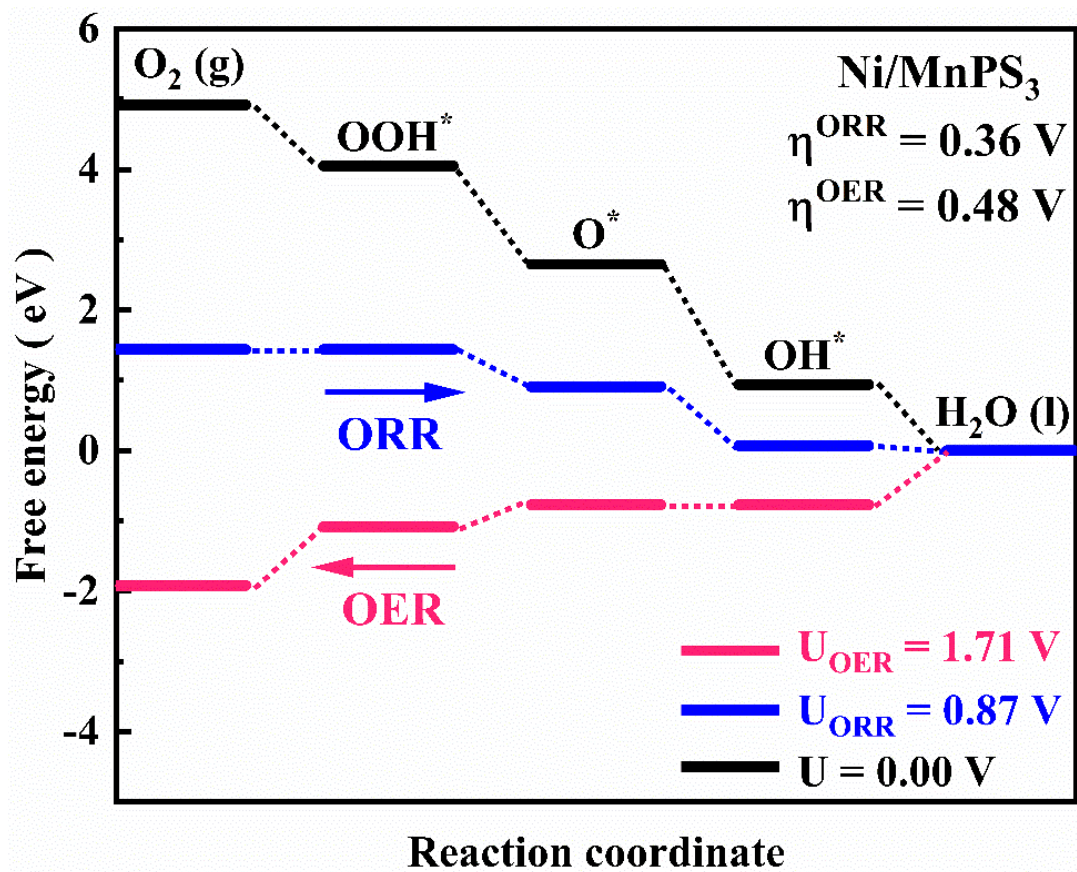
**Figure S1.** The computed band structures of MnPS<sub>3</sub> and other candidate catalysts. The Fermi level was set to zero in red line.



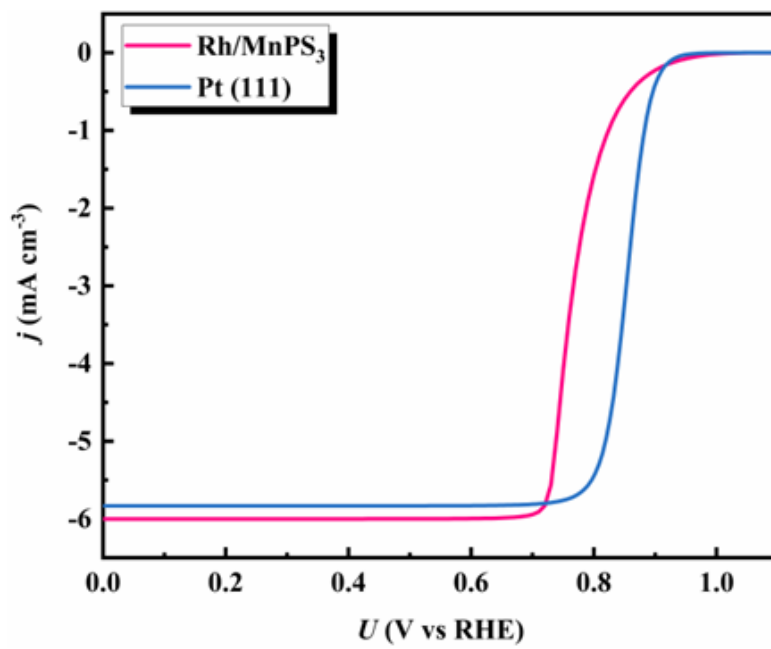
**Figure S2.** The variations of temperature and energy versus the time for AIMD simulations of Rh/MnPS<sub>3</sub>, which is run under 300 K for 10 ps with a time step of 1 fs. Schematic diagrams of the atomic configurations after dynamics simulation (top and side views) are also given.



**Figure S3.** The optimized configurations of  $O^*$ ,  $OH^*$ , and  $OOH^*$  on Rh/MnPS<sub>3</sub> catalyst.



**Figure S4.** The computed free energy profiles for ORR/OER on Ni/MnPS<sub>3</sub> monolayer.



**Figure S5.** The obtained polarization curves of ORR on Rh/MnPS<sub>3</sub> and Pt (1 1 1).

## References:

- 1 M. Janik, C. Taylor, M. Neurock, *J. Electrochem. Soc.*, 2009, **156**, B126-B135.
- 2 V. Tripković, E. Skúlason, S. Siahrostami, J. K. Nørskov, J. Rossmeisl, *Electrochim. Acta*, 2010, **55**, 7975-7981.