Electronic Supplementary Material (ESI) for Nanoscale Advances.

Water dissociation and association on mirror twin boundaries in two-dimensional $MoSe_2$: insights from density functional theory calculations

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1 Oxygen Reduction Reaction

The free energy of reactions detailed in Eq.(3) to Eq.(4) in the paper can be expressed using Eq.(2) as (see Ref. [1] for detail):

$$\Delta G_1 = G_{^*\mathrm{OOH}} - G_{^*\mathrm{O_2}} - 0.5G_{\mathrm{H_2}} + U_{\mathrm{eq}} \tag{S1}$$
$$\Delta G_2 = G_{^*\mathrm{O}} + G_{\mathrm{H_2O}} - G_{^*\mathrm{OOH}} - 0.5G_{\mathrm{H_2}} + U_{\mathrm{eq}} \tag{S2}$$
$$\Delta G_3 = G_{^*\mathrm{OH}} - G_{^*\mathrm{O}} - 0.5G_{\mathrm{H_2}} + U_{\mathrm{eq}} \tag{S3}$$
$$\Delta G_4 = G_{\mathrm{H_2O}} + G_{*} - G_{^*\mathrm{OH}} - 0.5G_{\mathrm{H_2}} + U_{\mathrm{eq}} \tag{S4}$$

where $U_{\mathrm{eq}} = eU - k_{\mathrm{B}}T\ln 10 \times pH$. However, due to the high-spin ground state of the O_2 molecule, the free energy is poorly described within the framework of DFT. To circumvent this problem when using the Eq.S1-S4, the reaction free energy of following equations is used:

$$^* + 2\,\mathrm{H_2O} \longleftrightarrow {}^*\mathrm{OOH} + \frac{3}{2}\,\mathrm{H_2} \tag{S5}$$
$$^* + \mathrm{H_2O} \longleftrightarrow {}^*\mathrm{O} + \mathrm{H_2} \tag{S6}$$
$$^* + \mathrm{H_2O} \longleftrightarrow {}^*\mathrm{OH} + \frac{1}{2}\,\mathrm{H_2} \tag{S7}$$

Thus, the reaction free energies, Eqs. S5 to Eq. S7, can be expressed as:

$$\Delta G_{^*\mathrm{OOH}} = 1.5G_{\mathrm{H_2}} + G_{^*\mathrm{OOH}} - 2G_{\mathrm{H_2O}} - G_{*} \tag{S8}$$
$$\Delta G_{^*\mathrm{O}} = G_{\mathrm{H_2}} + G_{^*\mathrm{O}} - G_{\mathrm{H_2O}} - G_{*} \tag{S9}$$
$$\Delta G_{^*\mathrm{OH}} = 0.5G_{\mathrm{H_2}} + G_{^*\mathrm{OH}} - G_{\mathrm{H_2O}} - G_{*} \tag{S10}$$

At equilibrium potential of 1.23 V, the reaction free energy of $O_2 + 4\,H^+ + 4\,e^- \longleftrightarrow 2\,H_2O$ is 4.92 eV. Combining with Eqs. S8 – S10, the free energy in Eqs. S1 – S4 can be rewritten as:

$$\Delta G_1 = \Delta G_{^*\mathrm{OOH}} - 4.92 + U_{\mathrm{eq}} \tag{S11}$$
$$\Delta G_2 = \Delta G_{^*\mathrm{O}} - \Delta G_{^*\mathrm{OOH}} + U_{\mathrm{eq}} \tag{S12}$$
$$\Delta G_3 = \Delta G_{^*\mathrm{OH}} - \Delta G_{^*\mathrm{O}} + U_{\mathrm{eq}} \tag{S13}$$
$$\Delta G_4 = -\Delta G_{^*\mathrm{OH}} + U_{\mathrm{eq}} \tag{S14}$$

References

[1] S. Tian, C. Deng, Y. Tang, and Q. Tang. Effect of adatom doping on the electrochemical performance of 1t-mos2 for oxygen reduction reactions. *The Journal of Physical Chemistry C*, 124(45):24899–24907, Nov 2020.

Table S1: Bond length .

Bond length	Pristine	44|P	44|E	55|8
H_2O	2.6 Å	2.6 Å	2.5 Å	2.4 Å
OH [O−Se]	2.1 Å	2.1 Å	1.9 Å	1.9 Å
O [O−Se]	1.7 Å	1.7 Å	1.7 Å	2.0 Å [O−Mo]
H [H−Mo]	1.9 Å	1.9 Å	1.9 Å	1.8 Å

Table S2: Overpotential.

Overpotential	Pristine	44|P	44|E	55|8
-	1.34 V	1.26 V	1.19 V	1.25 Å

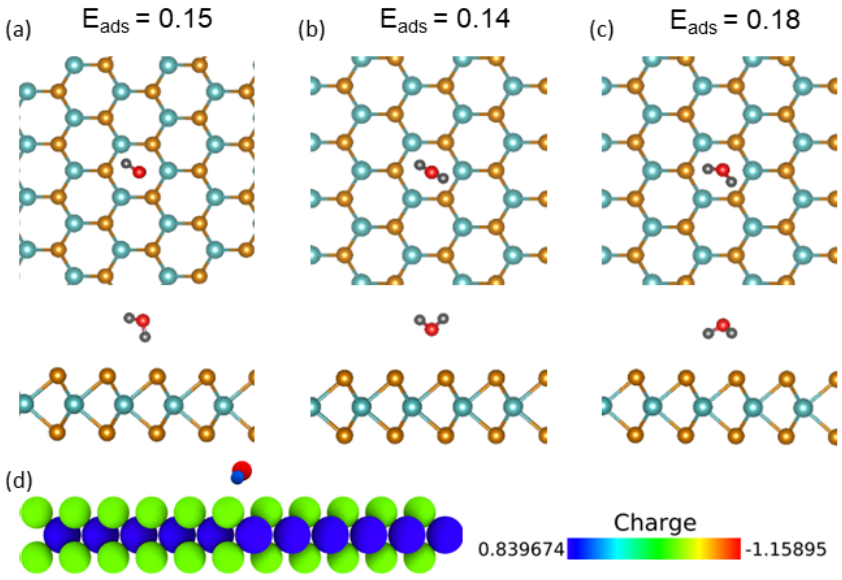

Figure S1: (a)-(c) Water adsorption on $MoSe_2$ at various sites. (d) Bader analysis of H_2O on $MoSe_2$. The charge analysis shows slight polar behaviour of $MoSe_2$ indicating that the electrostatic attraction is the main reason for orientation of H_2O in the most favourable absorption configuration i.e. schematic (c).

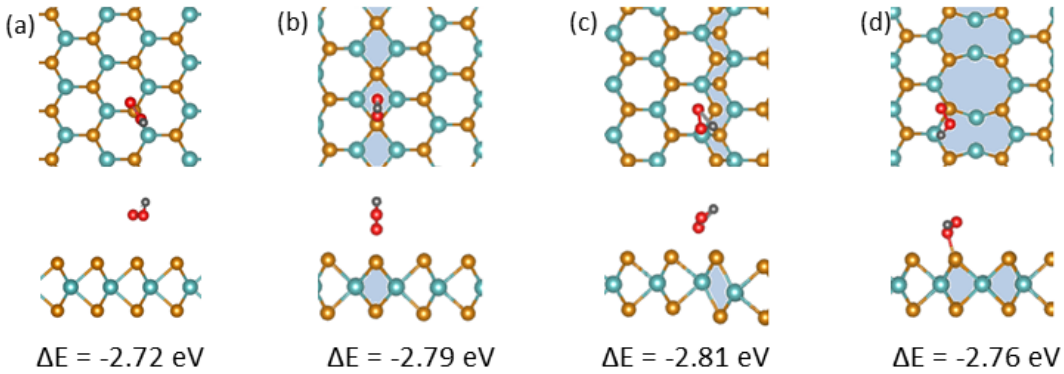

Figure S2: (a)-(d) OOH adsorption on $MoSe_2$ at various sites. (a) Pristine (b) 44|P (c) 44|E (d) 55|8.

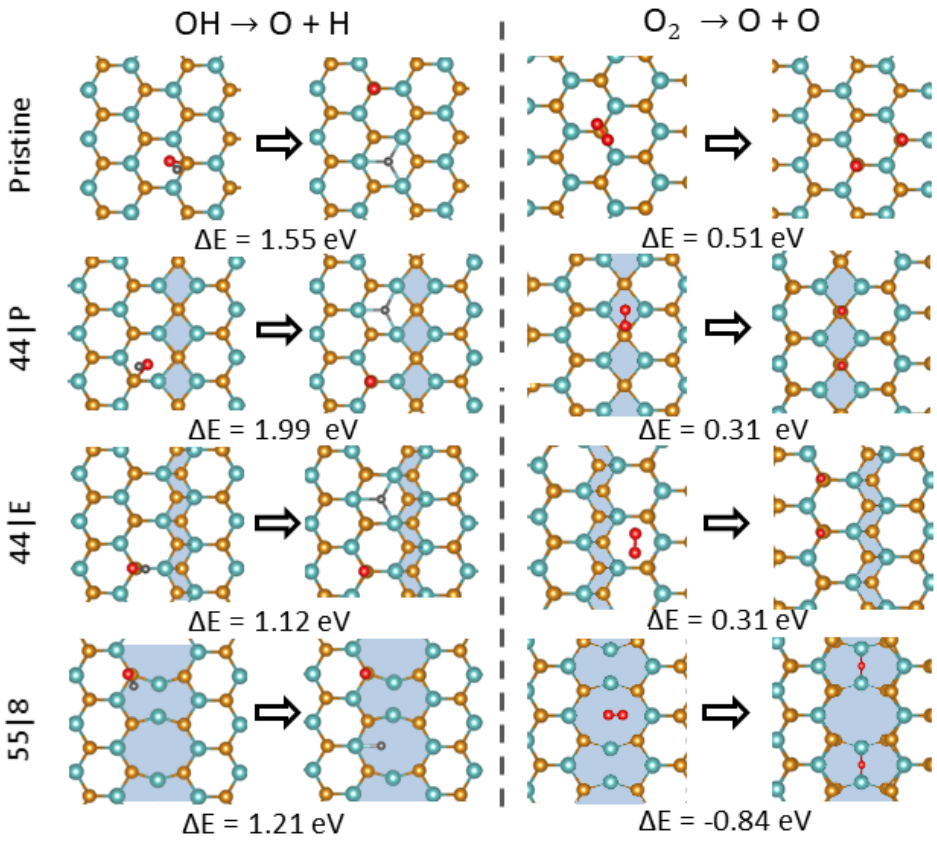

Figure S3: Schematic view of OH and O_2 association and dissociation reactions: on Pristine, 44|P, 44|E and 55|8 systems.

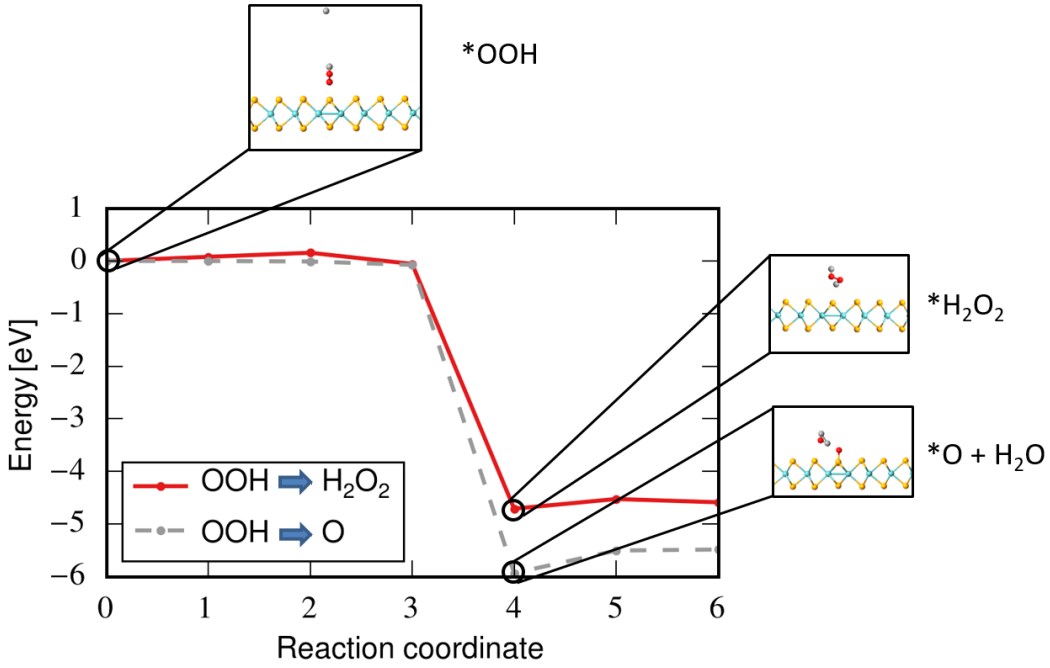

Figure S4: The energy diagram for the 2- (red) and 4-electron (gray) oxygen reduction, on 44|P MTB. The electrochemical barrier for *OOH to *O is slightly lower than that for *OOH to H_2O_2.

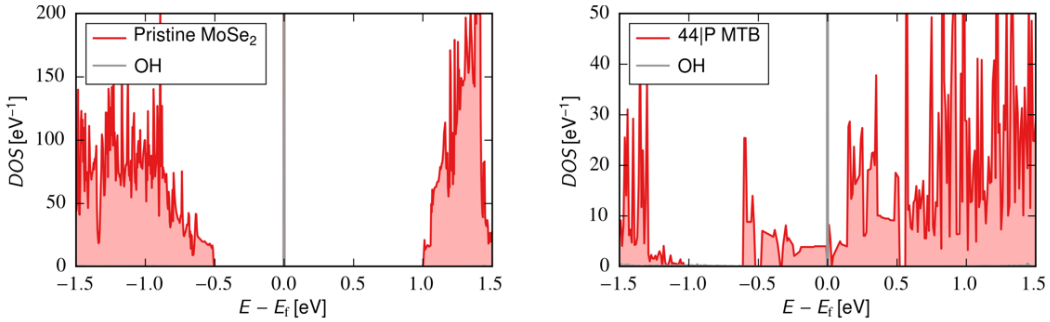

Figure S5: Projected density of states (PDOS) for OH adsorbed on pristine and 44|P MTB $MoSe_2$. The red and gray lines indicate the states for the MoSe2 monolayer and adsorbate, respectively..