Supporting Information Oxygen Evolution on MoS₂ edges: Activation through Surface Oxidation

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S-I. Hybrid explicit/continuum solvation simulations

The hybrid explicit/implicit solvation model used to calculate the aqueous stability (Figure 2(b) in main article) and reaction free energies comprises of two regions: a bulk region defined as a continuum polarizable environment with dielectric permittivity of 78.3, and an interface region, modelled by a statistical ensemble of water bilayer configurations containing 16 water molecules and determined with the *ab* initio molecular dynamics (AIMD) simulations (Figure S1(a)).¹ The implicit region is modelled using Self-Consistent Continuum Solvation (SCCS) method;² implemented in the ENVIRON-1.1 module³ coupled with the Quantum Espresso code.⁴ In this continuum model, the cavity is defined by two electron density cut-off parameters ρ_{max} and ρ_{min} corresponding to electron density of the quantum mechanical region. For the simulations performed in this work we have used the water interface denoted a SCCS (water) model implemented in the Environ package, which corresponds to the ρ_{max} and ρ_{min} values equivalent to 0.005 and 0.0001 respectively.

The simulations with the basal surface is performed with 3x2 orthorhombic supercell containing 12 Mo and 24 S atoms. A vacuum space of 20 Å is added along the non-periodic



Figure S1: The simulation set up for the MoS_2 basal surface (a) and ZZ- Mo_{S-100} edge (b) with the explicit layer of water molecules at the solid/solvent interface region.



Figure S2: The schematic representation for theoretical procedures used to cleave the edges from the MoS_2 basal surface and set up the simulation unit cells with H_2O molecules. The detail descriptions are given in the computational details (section S-I). In this Figure, the theoretical procedure is shown for one of the zigzag edges, ZZ-Mo_{S-100}. Similar method has been followed for the other zigzag edges.

z-direction, in order to remove fictitious interactions between the periodic images. The edges as shown in Figure 1 (main article) are constructed by cleaving the 3x2 orthorhombic basal surface along the zigzag and armchair directions. The simulations in vacuum are performed with the one-dimensional (1D) 3x1 nanoribbons. Along both the non-periodic axes of the nanoribbons, a vacuum space of 20 Å has been added.

As the solvent interactions for 1D nanoribbons are expected along both the non-periodic axes, the simulations in aqueous medium are performed by adding water molecules along both the directions. Figure S1 (b) shows the simulation cell for ZZ-Mo_{S-100} edge. The simulation cells for ZZ edges are set up in the following steps:

(1) We have relaxed the z-direction of $3x^2$ orthorhombic cell with explicit water layers containing 16 water molecules, placed above and below the monolayer MoS₂ (Figure S2 A).

(2) Then the relaxed geometry is cleaved along the zigzag (xz-plane) direction and reoriented such that non-periodic cleaved direction is aligned along the z-direction (B, Figure S2) to obtain the ZZ-Mo edges.

(3) We further add 16 water molecules on top of the cleaved edge surfaces. The schematic arrangement for one of the zigzag edges (ZZ-Mo_{S-100}) with the water molecules is shown in Figure S1 (b).

(4) The implicit region in the hybrid solvent model for the edges is defined in the similar way using the SCCS (water) model as defined earlier for the MoS_2 basal surface.

Prior to AIMD simulations, the atomic positions of the MoS_2 edges and the basal surface atoms with the reaction intermediates are relaxed in vacuum and presence of the water molecules. The atomic positions for bottom half of the nanoribbons are freezed during these simulations. Starting from the relaxed structures with the H₂O molecules, AIMD simulations are performed. In this study, since the main goal of the AIMD simulations is to determine the arrangement of the H₂O molecules at the interfacial region, the atomic positions of the reaction intermediates and the substrates are kept fixed. Only the arrangement of H₂O molecules are allowed to vary during the AIMD simulations. To evaluate the precision of this hybrid solvation model, benchmark calculations for the interfacial surface-free energy of MoS_2 monolayer in aqueous medium is performed as shown in section S-II, with different continuum and hybrid (explicit/continuum) models and compared with the experimental value.

S-II. Aqueous surface free energy (γ) calculations of MoS₂ monolayer

The different solvent models considered to calculate the surface free energy value (γ) for MoS₂ are shown in Table S1. The free energy value is determined with the eq. S1

$$\gamma = \frac{1}{2A} \left(\mu_{surface} - \mu_{MoS_2}^{bulk} - n\mu_{H_2O} + \Delta E_{im/ex}^{corr} \right)$$
(S1)

Here, $\mu_{surface}$ corresponds to the DFT calculated formation free energy for the MoS₂ surface with respect to reference bulk Mo and S allotropes and A is the interfacial surface area. $\mu_{MoS_2}^{bulk}$ is the formation free energy of the 3D-bulk from which the surface has been exfoliated and μ_{H_2O} denotes the formation free energy of liquid water, determined based upon the all-explicit *ab*-initio molecular dynamics simulation trajectories previously reported.⁵ The $\Delta E_{im/ex}^{corr}$ is the energy correction term added due to the potential offset in the hybrid explicit/implicit solvation model as reported in a recent study by Hormann et. al.¹ The correction term is determined from the statistical estimation of the water/vacuum interfacial interactions as determined from the simulations of explicit water slabs in vacuum following the similar approach as in ref.¹ $\Delta E_{im/ex}^{corr} = 0$ for full implicit solvation.

A symmetric slab set up is used with solvent interactions considered on both sides of the basal surface. The two models denoted as impl1 and impl2 in TableS1 are the full implicit solvent medium with dielectric cavity defined using the SCCS model. The impl1 corresponds to SCCS (water) model as described earlier, whereas for impl2 we have used ρ_{max} and ρ_{min}

values of 0.01025 and 0.0013 respectively. For impl2, the non-electrostatic contributions due to the solvation free energy has been neglected. The hybrid models are denoted by hyb. While the implicit region in these models is defined by SSCS (water) model, the explicit region is modelled in three different ways as:

(1) Hyb1: the explicit water region is modelled with a single water molecule adsorbed on the surface.

(2) Hyb2: Bilayer water region near to the slab surface with the H_2O arrangements forming a hexagonal ice like network.

(3) Hyb3: Bilayer water region with the arrangement of the H₂O molecules determined using AIMD simulations at 350 K.

The experimental value of 6.34 meV/Å² is obtained for the as-exfoliated MoS₂ basal surface using the Young-Dupre equation considering the experimental water contact angle of around 69° as reported in ref.^{6–8}

Table S1: The Interfacial surface energy (γ) of MoS₂ monolayer in presence of different solvent models. The experimental value is obtained from ref.^{6–8} The corresponding γ are obtained using eq. S1 in SI. A correction term has been added to the energy values obtained from hybrid simulations in order to correct for the explicit-implicit energy difference.

Solvent model type	Description	$\gamma_{sl}(meV/{ m \AA}^2)$
impl1	SCCS (water)	14.02
impl2	$\mathrm{SCCS}\;(ho_{max}=0.01025\; ho_{min}=0.0013)$	10.79
hyb1	Hybrid [SCCS (water) / Single water molecule]	11.75
hyb2	Hybrid [SCCS (water)/ Hexagonal water bilayer]	3.54
hyb3	Hybrid [SCCS (water) /water bilayer $(MD)^a$]	9.31
experiment	-	6.34

Among the different solvent models, the solvation effect in hyb1, hyb2 and the implicit imp1 models do not provide satisfying estimation of the experimental interfacial interactions. While imp1 and hyb1 models underestimate the interfacial interactions, hyb2 model due to ordered arrangement of the water molecules and greater intra-molecular H-bonding interactions underestimate the interfacial free energy value. The hybrid model hyb3 and full implicit model imp2 give the closest estimation with respect to the experimental value.

The continuum SCCS solvation model impl2 with the ρ_{max} and ρ_{min} parameters corresponding to 0.01025 and 0.0013 respectively have shown in previous studies to provide a better accuracy for the solvent effects at the solid-aqueous interfaces.^{9,10} Though for the MoS₂ surface, the electrostatic effects at the aqueous interface form the greater contribution to the interfacial surface energy compared to the explicit hydrogen bond interactions with the water molecules, with the reaction intermediates (OH^{*}, O^{*} and OOH^{*}) adsorbed on the surface the explicit water interaction would be important. Therefore, we choose the hybrid continuum/explicit model denoted as hyb3 to study the stability and reactivity of the catalytic activity for OER on MoS₂ catalytic sites.

S-III Formation Energy calculation of the edges in aqueous medium

The formation energy of the edges are calculated using the following equation¹¹

$$\Delta G_{form} = \frac{\left(\mu_{Mo_x S_y} - x\mu_{Mo} + -y\mu_{S} - n\mu_{H_2O} + \Delta E_{im/ex}^{corr}\right)}{(x+y)},\tag{S2}$$

where $\mu_{Mo_xS_y}$ is the calculated free energy obtained from the AIMD simulations of the MoS₂ sheet fragment having the chemical formula Mo_xS_y with n explicit H₂O molecules over a timescale of 4 ps. μ_S and μ_{Mo} are the reference state of the elemental Mo and S, approximated from the DFT calculated free energy of the most stable elemental state of the bulk Mo and S allotropes.

In order to express the ΔG_{form} (eq. S2) with respect to μ_S as plotted in Figure 2B (main text), the equilibrium formation energy of bulk MoS₂ ($\mu_{MoS_2}^{bulk} = \mu_{Mo} + 2\mu_S$) is used to substitute the value of μ_{Mo} in eq. S2. The resulting expression is denoted in the following

eq. S3

$$\Delta G_{form} = \frac{\left(\mu_{Mo_x S_y} - x\mu_{MoS_2}^{bulk} + (2x - y)\mu_S - n\mu_{H_2O} + \Delta E_{im/ex}^{corr}\right)}{(x + y)},$$
(S3)

 $\mu_{MoS_2}^{bulk}$ is the DFT calculated formation free energy of the 3D-bulk. For S-rich condition $\mu_S = 0$ (corresponding to the most stable S allotrope), whereas for Mo rich conditions μ_S is obtained from equilibrium formation energy of bulk MoS₂ ($\mu_{MoS_2}^{bulk} = \mu_{Mo} + 2\mu_S$), where for μ_{Mo} we have used the chemical potential of the most stable bulk phase of Mo. $\Delta E_{im/ex}^{corr}$ is the energy correction term added due to the hybrid explicit/implicit solvation model as defined earlier in section S-II.

S-IV. Structural Distortions of ZZ edges

The different structural possibilities for ZZ edges are determined by varying the arrangements of the S-atoms. We have considered 3x1 supercell to calculate the relative stabilities of the edges as shown in Figure S3 to S9. The relative stability of these edges in vacuum is shown in eV.



Figure S3: ZZ- Mo_{S-0}



Figure S4: ZZ- Mo_{S-17}



Figure S5: ZZ-Mo $_{S-33}$



Figure S6: ZZ- Mo_{S-50}





Figure S7: ZZ- Mo_{S-66}





Figure S8: ZZ-Mo $_{S-83}$



Figure S9: ZZ-Mo $_{S-100}$

S-V. Reaction free energy values for OER

The reaction free energy values ΔG_1 , ΔG_2 , ΔG_3 and ΔG_4 for the four proton coupled electron transfer step as shown in eq. S4 to eq. S7:

$$* + \mathrm{H}_{2}\mathrm{O} \to \mathrm{OH}^{*} + \mathrm{H}^{+} + e^{-} , \ \Delta G_{1} = \Delta G_{OH^{*}}$$
(S4)

$$OH^* \to O^* + H^+ + e^-, \ \Delta G_2 = \Delta G_{O^*} - \Delta G_{OH^*}$$
 (S5)

$$O^* + H_2O \to OOH^* + H^+ + e^- , \ \Delta G_3 = \Delta G_{OOH^*} - \Delta G_{O^*}$$
(S6)

$$OOH^* \to O_2 + * + H^+ + e^- , \ \Delta G_4 = \Delta G_{O_2} - \Delta G_{OOH^*}$$
(S7)

These equations are obtained from the formation free energies of the different intermediates $\Delta G_{OH}*$, $\Delta G_{O}*$ and $\Delta G_{OOH}*$ as given in Table S2. These free energy values are expressed in terms of the following electro-catalytic reactions, Eqs. S7 - S10.

$$* + \mathrm{H}_{2}\mathrm{O} \xrightarrow{\Delta G_{OH*}} \mathrm{OH}^{*} + \mathrm{H}^{+} + e^{-}$$
(S8)

$$* + \mathrm{H}_{2}\mathrm{O} \xrightarrow{\Delta G_{O*}} \mathrm{O}^{*} + 2\mathrm{H}^{+} + 2e^{-}$$
(S9)

$$* + 2H_2O \xrightarrow{\Delta G_{OOH*}} OOH^* + 3H^+ + 3e^-$$
 (S10)

In these equations the $\Delta G_{OH}*$, $\Delta G_{O}*$ and $\Delta G_{OOH}*$ are calculated from the adsorption energies of OH*, O* and OOH* intermediates, $\Delta E_{OH}*$, $\Delta E_{O}*$ and $\Delta E_{OOH}*$ on the catalytic sites respectively as given in eq. S11 - S13. The $\Delta E_{OH*/O*/OOH*}^{ZPE}$ represents the Zero Point Energy values and $T\Delta S_{OH*/O*/OOH*}$ corresponds to the entropy correction term. Since the vibrational entropy for the adsorbed state is small, the entropy term $\Delta S_{OH*/O*/OOH*}$ is considered almost equivalent to experimental entropy of gaseous reactants at standard state, from which the intermediates have been formed. The $\Delta E_{OH*/O*/OOH*}^{ZPE}$ values are calculated using harmonic approximations of the vibrational frequencies of the adsorbed intermediates $(OH^*, O^* \text{ and } OOH^*)$ and gaseous H_2O and H_2 molecules following the relationships in ref.¹²

$$\Delta G_{OH} * = \Delta E_{OH} * + \Delta E_{OH}^{ZPE} - T\Delta S_{OH} *$$
(S11)

$$\Delta G_O * = \Delta E_O * + \Delta E_{O^*}^{ZPE} - T\Delta S_O * \tag{S12}$$

$$\Delta G_{OOH} * = \Delta E_{OOH} * + \Delta E_{OOH}^{ZPE} - T\Delta S_{OOH} *$$
(S13)

The catalytic performance is determined by the overpotential (η_{TD}) for the reaction, which is defined by the maximum potential needed to downhill all the intermediate reaction steps. The overpotential value (η_{TD}) at standard condition is defined by eq. S14

$$\eta_{TD} = \frac{\Delta G_{pds}}{e} - 1.23 \mathrm{V} \tag{S14}$$

In eq. S14, ΔG_{pds} corresponds to the free energy for the potential determining step and e is the electronic charge. 1.23 V is the oxidation potential required for the ideal catalyst surface for the oxidation of H₂O to O₂ at standard electrochemical conditions. The ΔG_{pds} is free energy of the potential determining step and obtained using the eq. S15

$$\Delta G_{pds} = max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4] \tag{S15}$$

Table S2: The reaction free energies ($\Delta G_{OH}*$, $\Delta G_{O}*$ and $\Delta G_{OOH}*$) in eV on the MoS₂ basal surface, ZZ-Mo_{S-100}, ZZ-Mo_{S-50}, and ZZ-Mo^{ox}_{S-0} edges, as obtained following eqs. S8 to S10. The values are calculated for acidic medium at zero external potential.

site name	$\Delta G_{\rm OH^*}$	ΔG_{O^*}	$\Delta G_{\rm OOH^*}$
$MoS_2(basal)$	1.92	1.49	4.85
$ZZ-Mo_{S-100}$	1.44	2.15	5.5
$ZZ-Mo_{S-50}$	1.21	1.9	4.79
$ZZ-Mo_{S-0}^{ox}$	one-site pathways		
Path I	0.1	1.07	2.94
Path II	0.80	2.19	4.15
Path III	1.31	2.46	4.26
$ZZ-Mo_{S-0}^{ox}$	two-site pathways		
Path IV	0.80	2.46	4.26
Path V	0.80	2.19	4.26
Path VI	0.80	2.46	4.15
Path VII	1.31	2.19	4.15
Path VIII	1.31	2.46	4.15
Path IX	1.31	2.19	4.26

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