

Supporting Information:

How Stable are 2H-MoS₂ Edges under Hydrogen Evolution Reaction Conditions?

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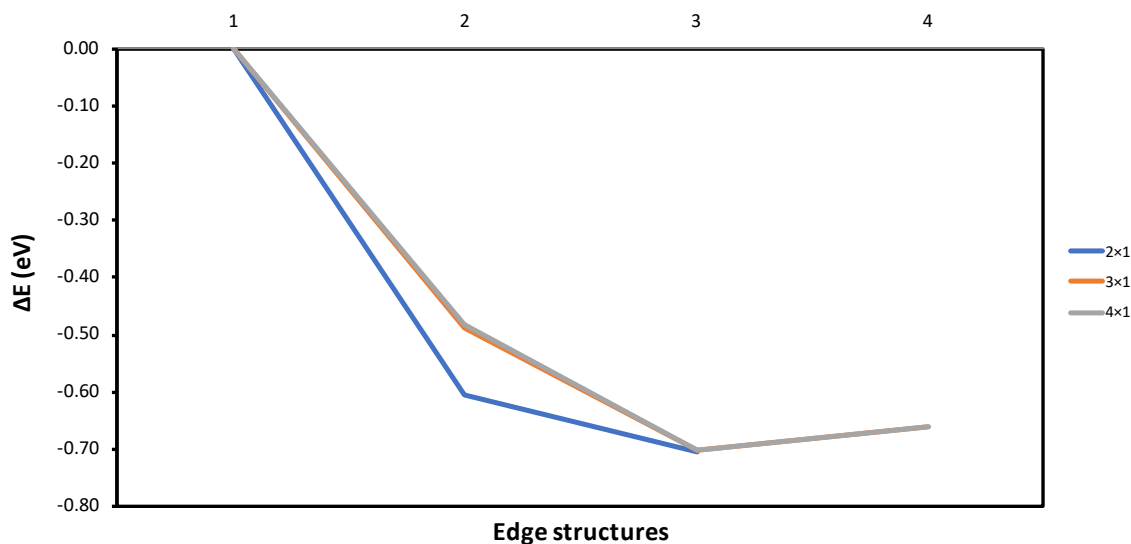
S1 Reconstruction of the 50%S S-edge, 50%S Mo-edge

The (100) surface of the hexagonal polytype of MoS₂ is well-accepted as the catalytically active surface representing the zigzag edges. Our previous study considered only the idealized 0%S Mo-edge and 100%S S-edge (X) as cut from the bulk. Here, we calculate the relative energies of different 50%S S-edges and 50%S Mo-edges (Y). Different surface sizes $p(2 \times 1)$, $p(3 \times 1)$ and $p(4 \times 1)$ are tested. To decide which structure is the most stable, we calculate ΔE according to the following equation:

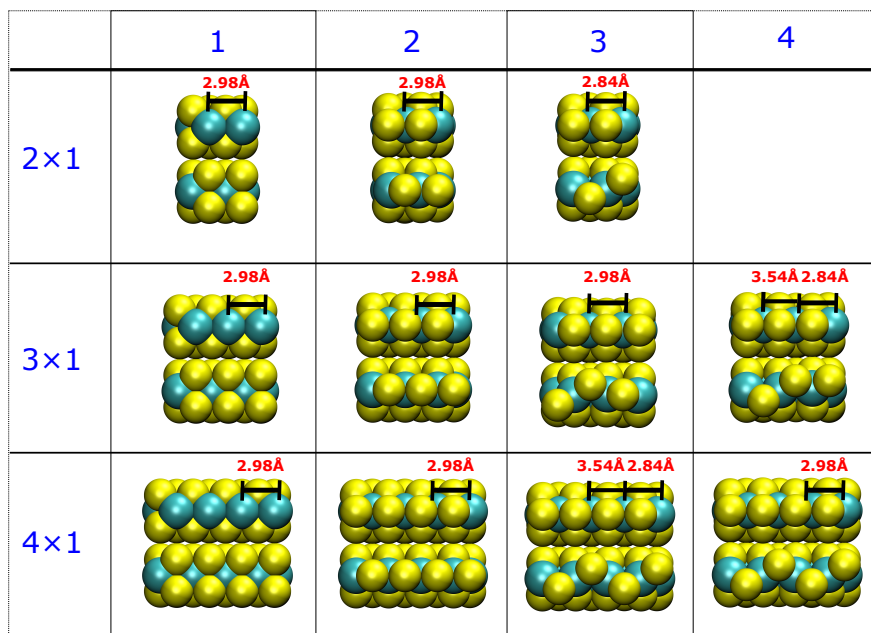
$$\Delta E_{rel} = \frac{1}{n}(E_Y - E_X) \quad (S1)$$

Where E_X and E_Y are the energies of the symmetric 0%S Mo-edge; 100%S S-edge, and the 50%S S-edge; 50%S Mo-edge, respectively. n is the number of Mo atoms at the edge, so that ΔE_{rel} corresponds to a relative stability per Mo-edge atoms. The most negative ΔE corresponds to the most stable edge structure.

DFT calculations were used to simulate various edge structures to identify the most stable one. Figure S1 shows the different edges 2×1 , 3×1 and 4×1 . We observe that the combination of 50%S Mo-edge with the 50%S S-edge are always more stable than the bulk-cleaved 100%S S-edge, 0%S Mo-edge combination. As suggested in the literature,^{S1} many reconstructions can occur on the 50%S edges with unequal Mo-Mo and S-S distances. These re-constructed surfaces are stabilized by up to 0.2 eV per surface Mo compared to the undistorted 50%S edges. We find that the 50%S S-edge with a wave-like S-S configuration and with alternating short/long Mo-distances at the 50%S Mo-edge (number 3 in Fig. S1) is the most stable configuration for all cell sizes. This is in agreement with many previous studies.^{S1-S4} Therefore, we adopted the most stable $p(2 \times 2)$ unit cell as our reference surface to investigate its stability under HER conditions.



(a) Evolution of the surface energy of the MoS₂ edges with different atomistic constructions and cell sizes.



(b) Visualization of the different systems studied with Mo-Mo distances

Figure S1: Comparison between the surfaces energies of 2x1, 3x1 and 4x1 cells and the different types of edges existed starting from 1 which is the 100%S and 100%Mo to 2, 3, and 4 the different structures of the 50%S MoS₂ edges . The color code for atoms is yellow for S and greenish for Mo.

S2 Hydrogen adsorption on 50%S S-edge

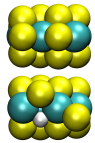
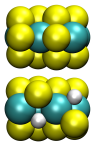
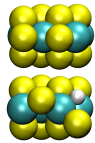
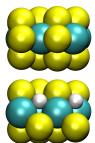
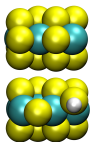
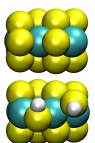
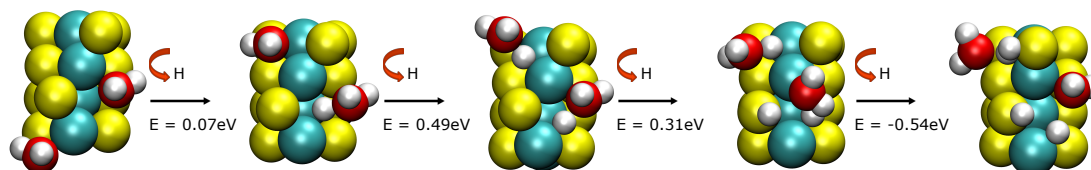
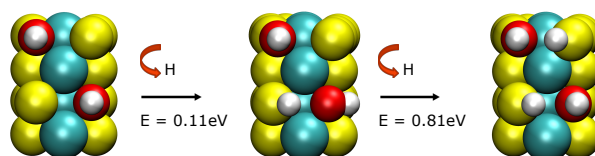
Structure	Hydrogen adsorption energy
	$G_H = 0.04 \text{ eV}$
	$G_H = -0.01 \text{ eV}$
	$G_H = 0.05 \text{ eV}$
	$G_H = 0.18 \text{ eV}$
	$G_H = 0.38 \text{ eV}$
	$G_H = -0.14 \text{ eV}$

Figure S2: Adsorption energies of Hydrogen on different sites of the 50%S S-edge. The color code for atoms is yellow for S, greenish for Mo and white for Hydrogen

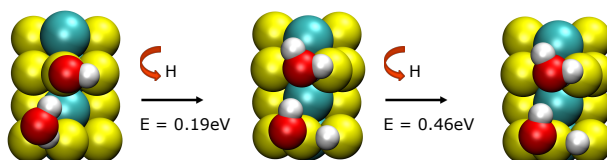
S3 Hydrogen adsorption on 50%S S-edge in presence of OH and H₂O



(a) Adsorption of hydrogen number 2, 3, 4 and 5 respectively, on 50%S S-edge in presence of H₂O



(b) Adsorption of hydrogen number 4 and 5 respectively, on 50%S S-edge in presence of OH



(c) Adsorption of hydrogen number 1 and 6 respectively, on 50%S Mo-edge in presence of H₂O

Figure S3: Influence of the presence of H₂O and OH on ΔG_H at both 50%S S-edge and 50%S Mo-edge.

S4 Independence of the 50%S S-edge and 50%S Mo-edge

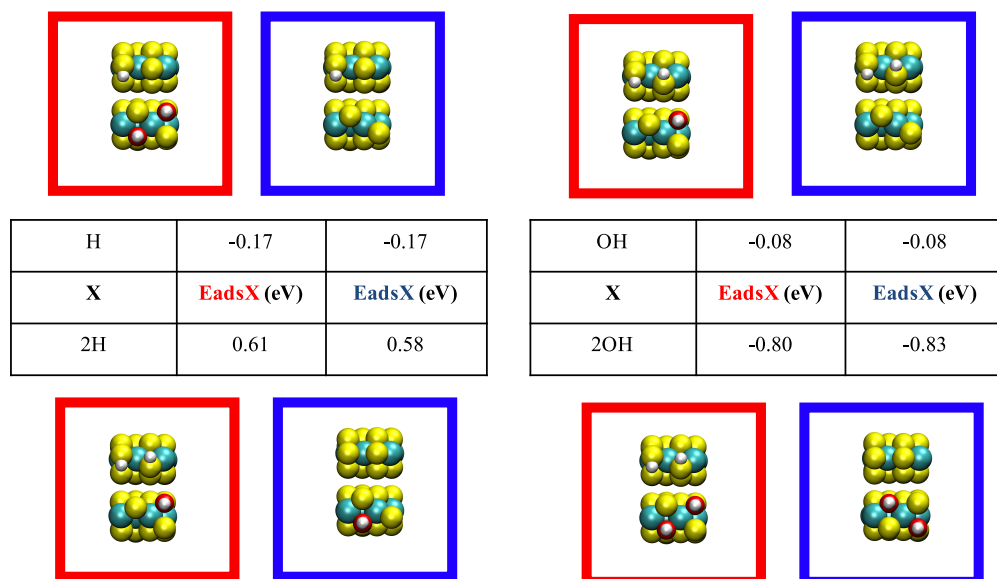


Figure S4: Adsorption energies of Hydrogen and OH. The red color indicates the structures with adsorbates on both edges and the blue color is for the structures with adsorbates on one edge

S5 Production of H₂ on the OH covered 0%S S-edge

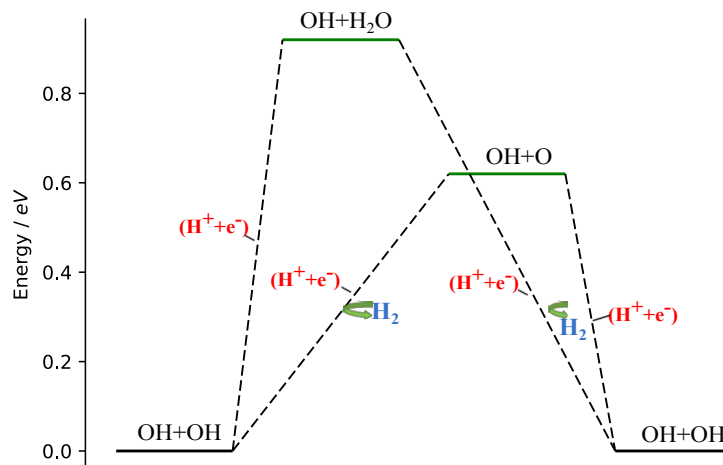


Figure S5: Possible production of H₂ on the OH covered 0%S S-edge, involving OH, O and H₂O at 0 V vs SHE. According to the reaction energy profile the OH+OH surface state is too stable compared to OH+O and OH+ H₂O. Thus, the hydrogen production is hampered.

S6 Production of H₂ and H₂S on the OH covered 50%S S-edge

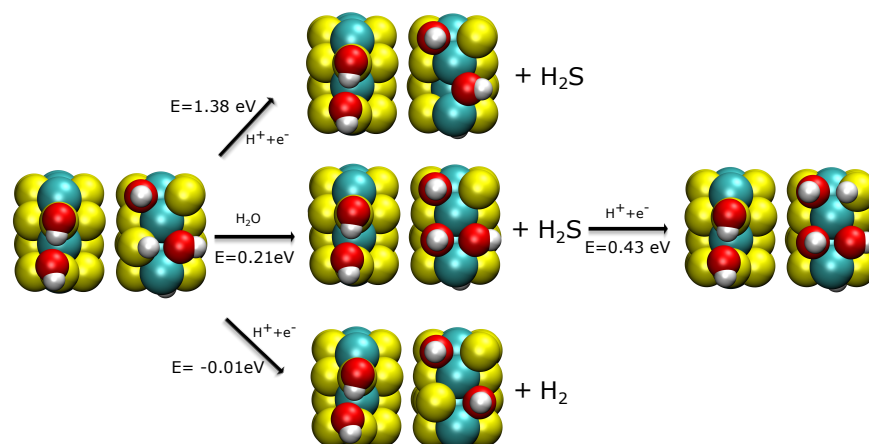


Figure S6: The release of H₂ and H₂S at the 50% S-edge with two adsorbed OH.

References

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