

Supporting Information:
Electrochemical potential-dependent stability
and activity of MoS₃ during the hydrogen
evolution reaction

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S1 Models and methods

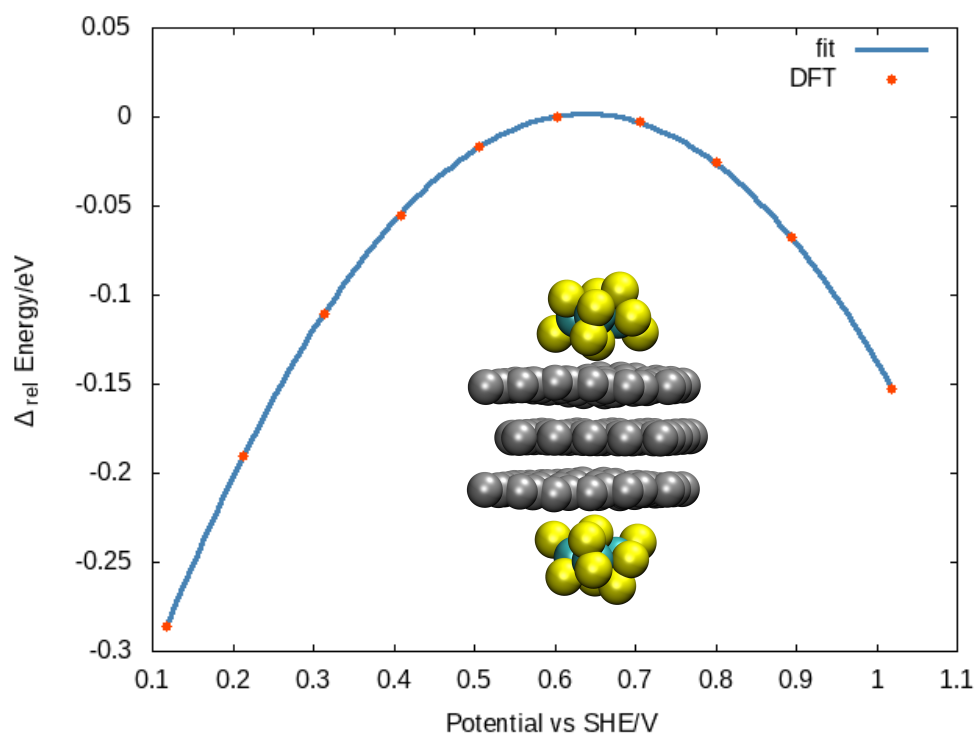


Figure S1: Variation of the total energy as a function of the electrochemical potential of Mo_3S_9 nanocluster on the graphite support.

S2 Adsorption Energies in Vacuum

S2.1 Hydrogen adsorption on Mo_3S_9 without support

The first step of the work consists on adsorbing hydrogen on the different atoms of Mo_3S_9 without the graphite support. We observe that not all of the sites are favourable for hydrogen adsorption. For example, it is impossible to adsorb hydrogen on the different Mo atoms and on S1, S2, S8 and S9.

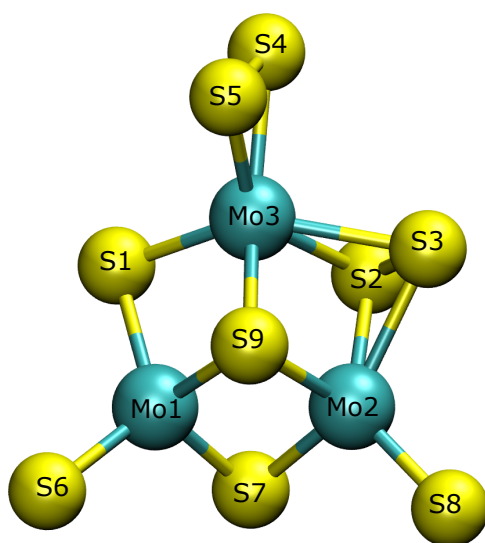


Figure S2: Mo_3S_9 with the different labels of the atoms. The color code for atoms is yellow for S and greenish for Mo.

1st H		2nd H		3rd H		4th H		5th H		6th H	
Site	Ads. Energy (eV)	Site	Ads. Energy (eV)	Site	Ads. Energy (eV)	Site	Ads. Energy (eV)	Site	Ads. Energy (eV)	Site	Ads. Energy (eV)
S1	0.49	S6S6	0.67	S6S8S9	1.75	S6S8S4S6	1.51	S6S8S4S5S6	1.29	S6S8S3S4S2S1	0.44
S2	0.40	S6S3	0.62	S6S6S8	1.17	S6S8S5S5	0.88	S6S8S4S5S8	1.02	S6S8S3S4S2S7	0.32
S3	0.28	S7S1	0.60	S6S8S8	0.92	S6S8S4S1	0.62	S6S8S3S4S7	0.80	S6S8S3S4S5S5	-0.08
S4	-0.23	S8S8	0.57	S6S8S7	0.88	S6S8S4S7	0.47	S6S8S4S5S5	0.77	S6S8S3S4S5S2	-0.12
S5	0.17	S8S5	0.53	S6S8S1	0.77	S6S8S4S4	0.17	S6S8S3S4S1	0.76	S6S8S3S4S3S5	-0.43
S6	-0.29	S6S5	0.51	S6S8S5	0.55	S6S8S3S2	-0.11	S6S8S3S4S4	0.70		
S7	0.26	S2S2	0.50	S6S8S2	0.54	S6S8S4S2	-0.12	S6S8S4S5S2	0.64		
S8	0.50	S6S2	0.47	S6S4S4	0.53	S6S8S3S3	-0.17	S6S8S3S4S2	0.43		
S9	1.29	S4S4	0.41	S6S3S4	0.53	S6S8S4S5	-0.32	S6S8S3S4S3	0.41		
Mo1	0.65	S8S2	0.40	S6S2S3	0.46	S6S8S3S4	-0.43				
Mo2	0.65	S8S3	0.38	S8S3S4	0.41						
Mo3	0.60	S4S2	0.23	S6S3S3	0.33						
		S8S4	-0.20	S6S8S4	0.31						
		S6S4	-0.26	S6S2S2	0.29						
		S6S8	-0.29	S6S8S3	0.28						

Table S1: Adsorption energy for different numbers of hydrogen atoms adsorbed on Mo_3S_9 . The next hydrogen atom positions were explored after the most stable position found in the previous step. For instance, if the first hydrogen sticks best to site S6, then the next one will likely go to S6Sx, followed by S6S8Sx, and so on.

S2.2 Hydrogen adsorption on Mo₃S₉

These results correspond to the calculation of hydrogen adsorption energies before symmetrization of the various structures.

As for Mo₃S₉ without support, we proceed here to the adsorption of hydrogen on the different sites of Mo₃S₉ on graphite. We started with the first hydrogen and tested different positions. The most promising position is the one with ΔG_H equal to -0.32 eV. Starting from this most stable structure, we added the second hydrogen and we tried several positions as well. In this case, the most stable site has ΔG_H equal to -0.11 eV. We moved to the adsorption of the third hydrogen atom at different sites. The most promising is with ΔG_H very close to 0 eV. Starting from this structure, we proceed to the adsorption of the fourth hydrogen. We observe that the most stable position leads to the formation of H₂S. Fig. S3 summarizes the most promising sites for the adsorption of hydrogen until the formation of H₂S, which gives a new structure, Mo₃S₈ with two hydrogen atoms.

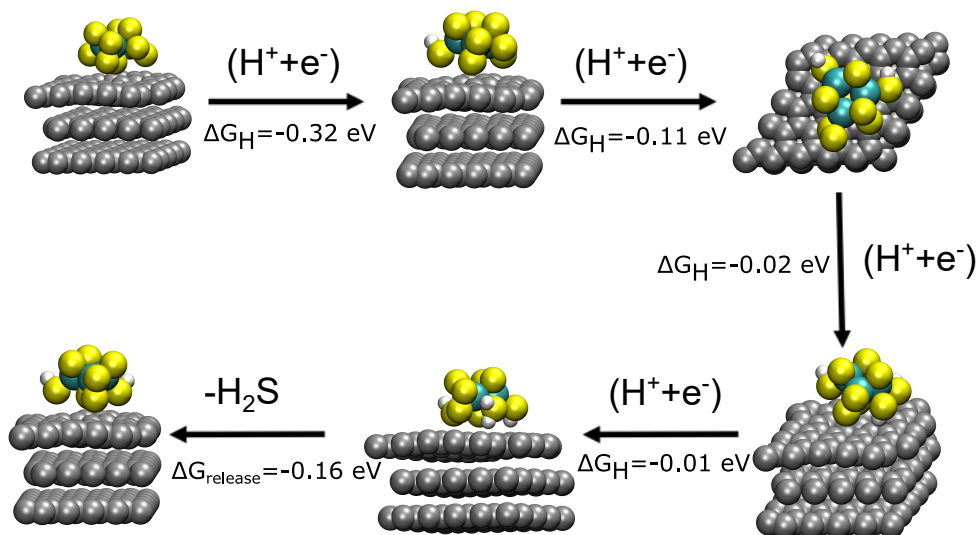


Figure S3: Summary of the most promising sites for the adsorption of hydrogen on Mo₃S₉ until the formation of H₂S and the final structure obtained is Mo₃S₈ with two hydrogen atoms.

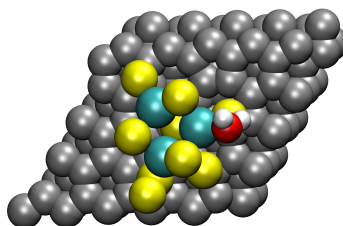
S2.3 H, OH and H₂O adsorption on Mo₃S₉

The hydrogen evolution reaction is a process that occurs in an aqueous medium, and as demonstrated in our previous studies, consideration of the adsorption of other species present, such as OH and H₂O, is crucial. Fig. S4 illustrates the adsorption of H₂O and OH on Mo₃S₉ on graphite. After trying different orientations of the water molecule, we find that two H₂O molecules bind to the unsaturated Mo sites. Unlike water, OH could not adsorb.

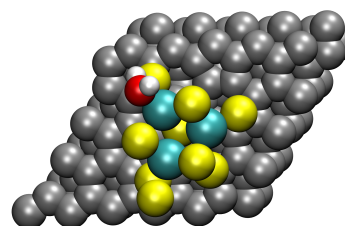
To capture the hydrogen adsorption in the presence of water, we start with Mo₃S₉ with the two adsorbed water molecules and test again the different positions. We find that the same positions for the different hydrogen atoms are maintained without considering water, but ΔG_H changes (see Fig. S5). Fig. S5 shows that H₂S is also released with water, which converts Mo₃S₉ to Mo₃S₈ with two adsorbed water and two hydrogen atoms.

Adsorbate	Adsorption energy (eV)
H2O 1-1	-0.22
H2O 1-2	-0.24
H2O 1-3	0.35
H2O 2	-0.17
OH 1-1	0.35
OH 1-2	0.63
OH 1-3	1.13

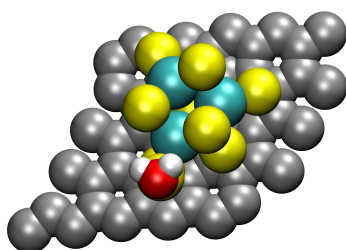
(a) Adsorption energies



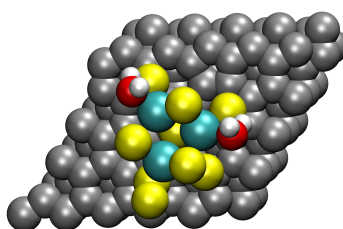
(b) H₂O 1-1 on Mo



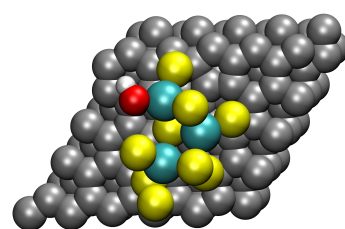
(c) H₂O 1-2 on Mo



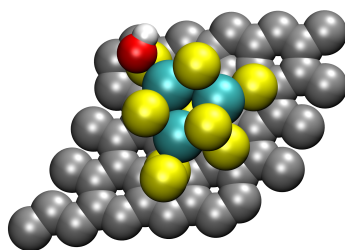
(d) H₂O 1-3 on S



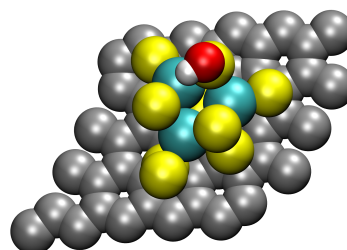
(e) H₂O 2 on Mo



(f) OH 1-1 on Mo



(g) OH 1-2 on S



(h) OH 1-3 on S

Figure S4: (a) Table presenting the adsorption energies of the different species on Mo₃S₉ on graphite, (b), (c), (d), (e), (f), (g) and (h) the different structures mentioned in the table. The figure shows that H₂O is adsorbed on the unsaturated-Mo sites while it could not bind on S. A second H₂O could also be adsorbed on Mo. For OH, it could not bind on Mo and S. Note that not all the sites are reported but the same result is found for the other Mo and S sites. The color code for atoms is white for H; red for O; silver for C; yellow for S and greenish for Mo.

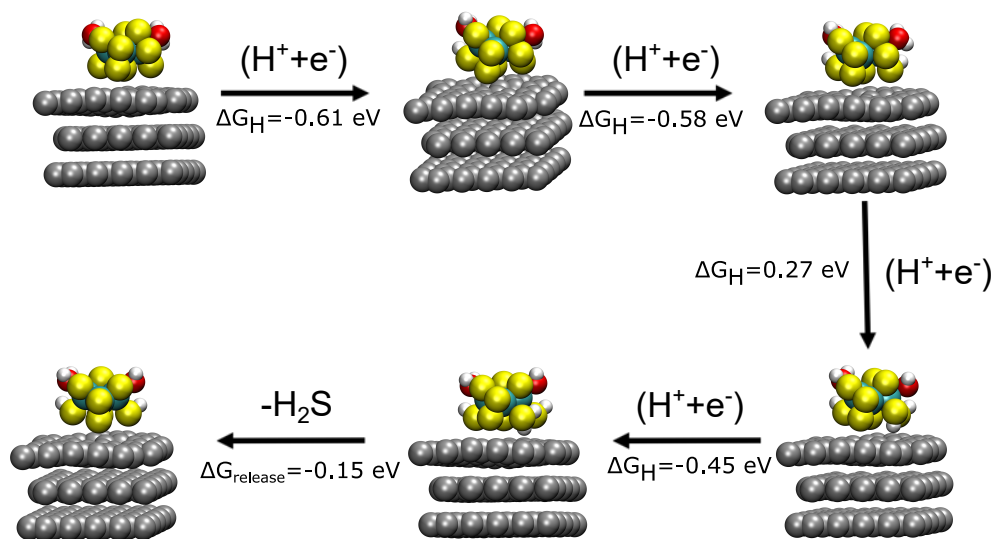


Figure S5: The most promising sites for the adsorption of hydrogen on Mo_3S_9 with presence of water adsorption until the formation of H_2S and the final structure obtained is Mo_3S_8 with two hydrogen atoms and two adsorbed water molecules.

S2.4 Hydrogen adsorption on Mo_3S_8

The same study is now performed for the new structure from the previous section, Mo_3S_8 . Fig. S6 shows that we start with two hydrogen atoms already adsorbed and we added another hydrogen trying all the possible positions. The structures shown in the figure present only the most stable site for each hydrogen until another H_2S molecule is formed again leading to the loss of another sulfur atom to obtain Mo_3S_7 with three adsorbed hydrogen atoms.

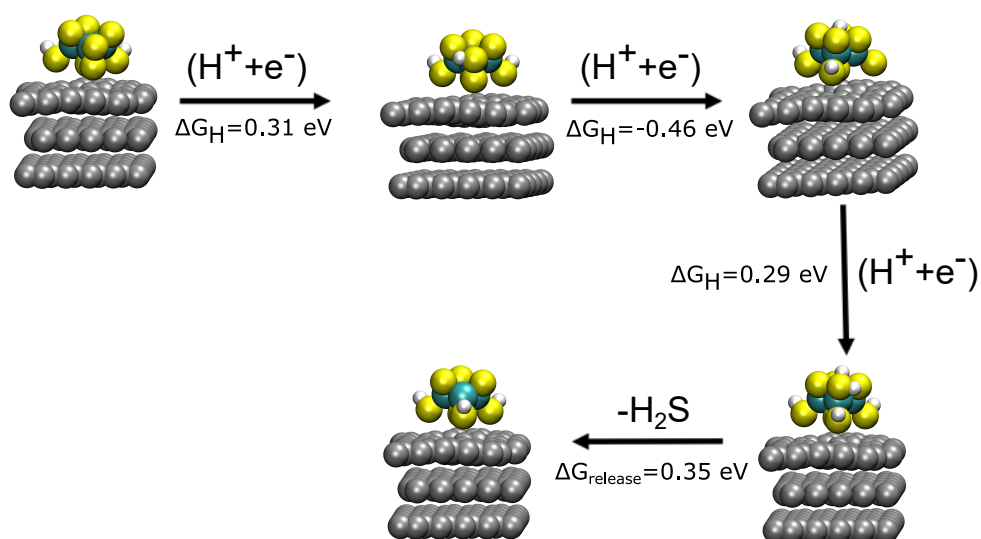


Figure S6: The most promising sites for the adsorption of hydrogen on Mo_3S_8 until the formation of H_2S and the final structure obtained is Mo_3S_7 with three hydrogen atoms.

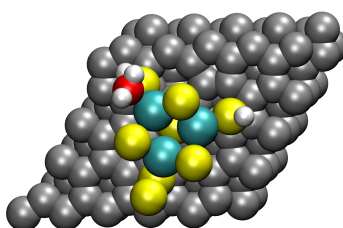
S2.5 H, OH and H₂O adsorption on Mo₃S₈

To evaluate the water effect, we adsorb OH and H₂O onto Mo₃S₈ with two hydrogen atoms. We observe that both OH and H₂O are adsorbed, but the water binding is much stronger. Therefore, the Mo-sites are covered by H₂O.

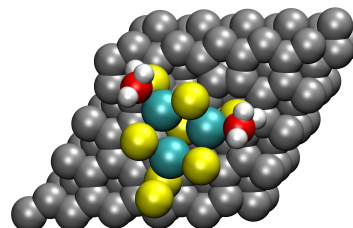
As in the above section, we now proceed to the structure with explicit water molecules. We start with Mo₃S₈ with two water molecules and two hydrogens (structure in Fig. S7). Again, the positions of the hydrogen molecules are the same as without water, but the difference is in the ΔG_H values (see Fig. S8).

Adsorbate	Adsorption energy (eV)
H2O 1	-0.68
H2O 2	-0.62
OH 1	0.00
OH 2	0.21

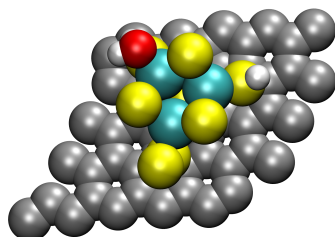
(a) Adsorption energies



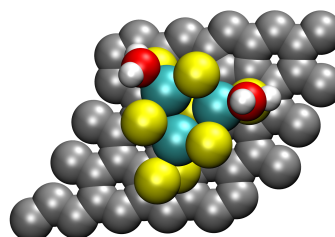
(b) H₂O 1 on Mo



(c) H₂O 2 on Mo



(d) OH 1 on Mo



(e) OH 2 on Mo

Figure S7: (a) Table presenting the adsorption energies of the different species on Mo₃S₈ on graphite with two adsorbed hydrogen, (b), (c), (d) and (e) the different structures mentioned in the table. The figure shows that H₂O is strongly adsorbed on the unsaturated-Mo sites compared to OH. The color code for atoms is white for H; red for O; silver for C; yellow for S and greenish for Mo.

Fig. S8 shows that the last adsorbed hydrogen molecule forms a H₂S molecule that could be released with $\Delta G_{release}$ equal to 0.09 eV (value at $P_{H_2S} = 1$ bar, at $P_{H_2S} = 10^{-5}$ bar, H₂S energy is equal to -0.21 eV), and we obtain Mo₃S₇ with two water molecules and three hydrogen atoms.

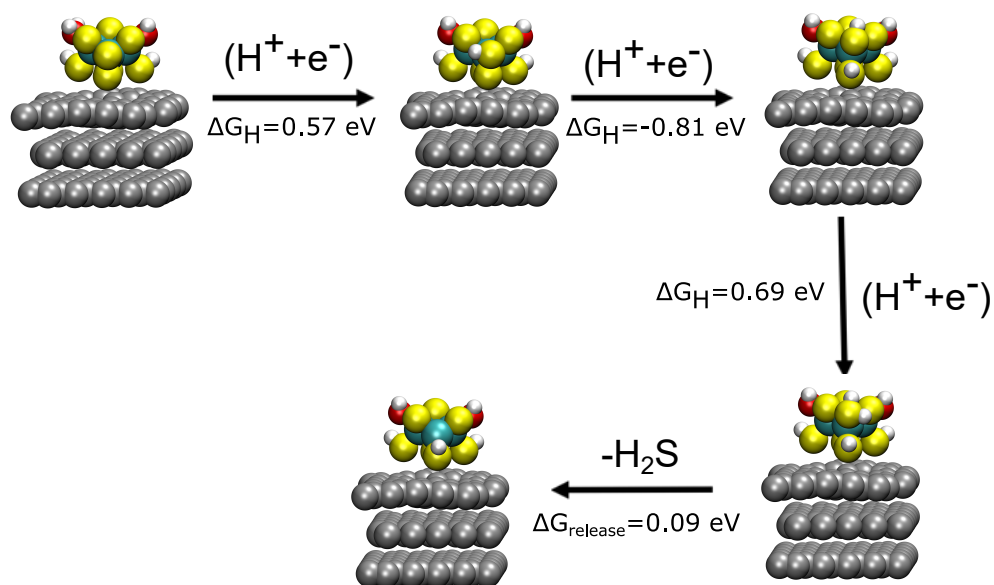


Figure S8: The most promising sites for the adsorption of hydrogen on Mo_3S_8 with presence of water adsorption until the formation of H_2S and the final structure obtained is Mo_3S_7 with three hydrogen atoms and two adsorbed water molecules.

S2.6 H, OH and H₂O adsorption on Mo₃S₇

At this level, we directly consider the structure of Mo₃S₇ with the adsorbed water molecules and hydrogen atoms. We observe that a new Mo site is available. We tested the adsorption of H, OH and H₂O at this site. We find that the adsorption of water and OH is more favorable than that of hydrogen (see Fig. S9).

Adsorbate	Adsorption energy (eV)
H ₂ O	-0.44
OH	-0.70
H	-0.39

(a) Adsorption energies

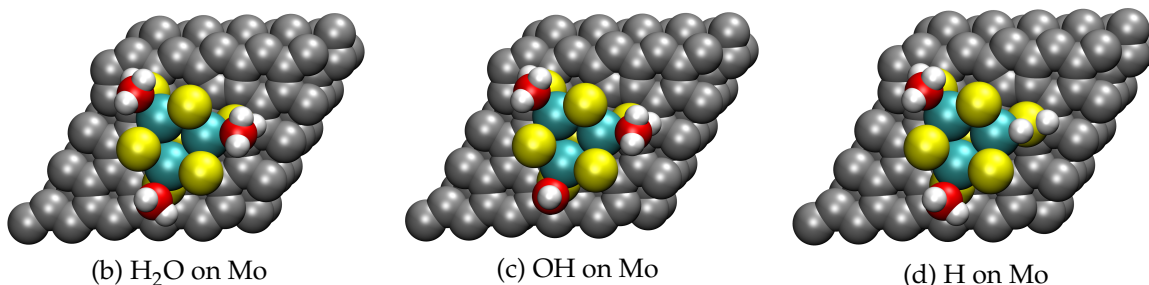


Figure S9: (a) Table presenting the adsorption energies of the different H, OH and H₂O on Mo₃S₇ on graphite with two water molecules and three hydrogen atoms strongly adsorbed, (b), (c) and (d) the different structures mentioned in the table. The figure shows that all the species could be adsorbed on the unsaturated-Mo but the most strong binding is with OH. The color code for atoms is white for H; red for O; silver for C; yellow for S and greenish for Mo.

The hydrogen atoms at the terminal S are strongly adsorbed, with ΔG_H equal to about -1 eV. Therefore, we turn to the adsorbed water molecules to see if we can have a cycle between water and OH to produce H₂. Fig. S10 shows that only one water molecule can be dissociated to OH and H to release H₂ via the Heyrovsky mechanism. The second cycle is not possible as ΔG_2 is very positive. This means that the site is definitely blocked by H₂O. In summary, Mo₃S₇ on graphite is a stable structure formed from Mo₃S₉ on graphite after the loss of two sulfur atoms by the release of H₂S. To assess its catalytic activity, we

proved that we should consider not only hydrogen adsorption but also OH and water. We found that only three sulfur atoms are promising for hydrogen adsorption, but ΔG_H is very strong. Therefore, their participation in the production of H_2 is not possible. The molybdenum sites are covered by water, and only one H_2O could dissociate to $OH + H$, and after a Heyrovsky step we can produce H_2 .

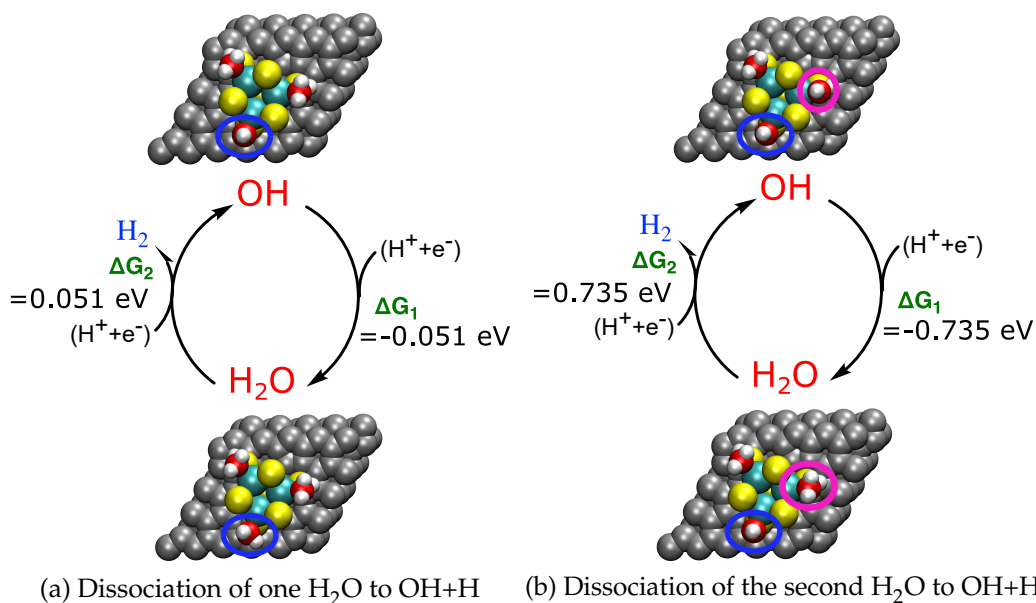


Figure S10: The production of H_2 from H_2O . ΔG_1 is a Volmer step and ΔG_2 is a Heyrovsky step. The cycle is feasible when ΔG_1 and ΔG_2 are both close to 0 eV.

S3 Calculations with implicit solvent and explicit electrochemical potential

S3.1 Hydrogen adsorption on symmetric Mo_3S_9

Fig. S11 shows the energy profile at 0 V considering only hydrogen as adsorbate. The first hydrogen is adsorbed at one of the top S with ΔG_H equal to -0.34 eV to form $\text{Mo}_3\text{S}_9\text{-H}$. The second hydrogen is adsorbed at the other top S with ΔG_H equal to 0.02 eV. Then, the third and fourth hydrogen atoms are adsorbed on the Bridge S_2 with ΔG_H equal to -0.15 eV and 0.13 eV, respectively. Once four hydrogens are adsorbed, the S-S bond is broken and the release of H_2S occurs by -0.16 eV at $P_{\text{H}_2\text{S}} = 1$ bar. Considering HER conditions, H_2S pressure is much lower ($P_{\text{H}_2\text{S}} = 10^{-5}$) and the energy at this pressure decreases to reach -0.46 eV. Thus, This the conversion of Mo_3S_9 into Mo_3S_8 is very exergonic. In other words, HER is unlikely on Mo_3S_9 , but HER conditions lead to the release of H_2S and the conversion of Mo_3S_9 to Mo_3S_8 .

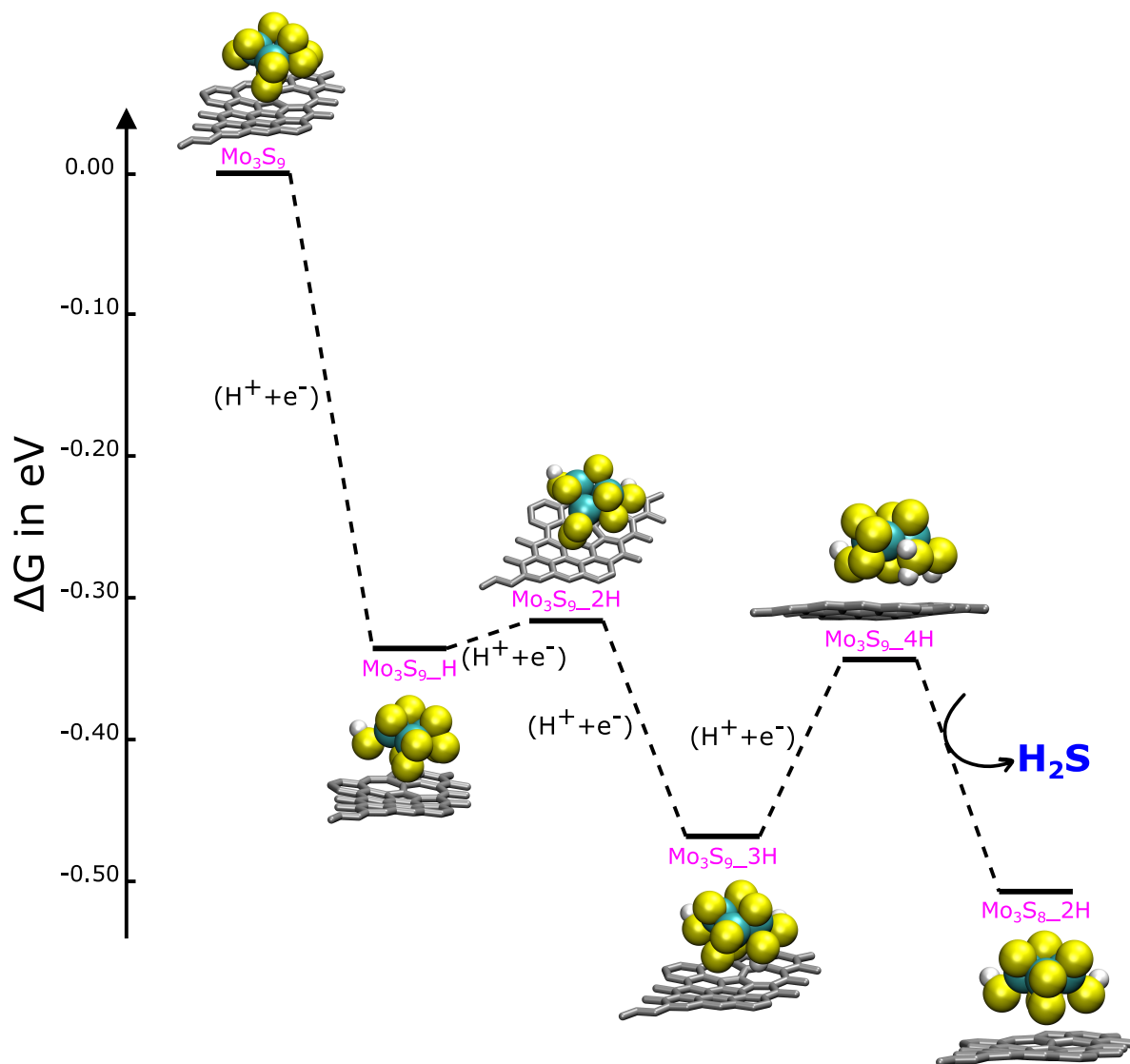


Figure S11: Reaction energy profile on Mo₃S₉ at 0 V. The first four steps correspond to hydrogen adsorption and the last step is the release of H₂S. The color code for atoms is white for H; yellow for S and greenish for Mo.

S3.2 Hydrogen adsorption on symmetric Mo_3S_8

We now proceed with the study of $\text{Mo}_3\text{S}_8\text{-2H}$ obtained in the last step of the energy profile of Mo_3S_9 . We consider the hydrogen adsorption without water. Fig. S12 shows the energy profile of hydrogen adsorption starting from $\text{Mo}_3\text{S}_8\text{-2H}$ with the two hydrogen atoms adsorbed on terminal S at 0 V. The next hydrogen is adsorbed onto the other S of Bridge S_2 with ΔG_H equal to 0.28 eV. The S-S bond is broken and another H is strongly adsorbed onto the other sulfur with ΔG_H equal to -0.45 eV. At this level, we observe that hydrogen production is possible by a Tafel step, and we again obtain $\text{Mo}_3\text{S}_8\text{-2H}$ with a release energy at 0 V equal to 0.17 eV. This competes with the formation of H_2S after adsorption of another hydrogen on sulfur with ΔG_H equal to 0.25 eV. From this structure, we can either release H_2 this time via the Heyrovsky step and return to $\text{Mo}_3\text{S}_8\text{-4H}$ with energy equal to -0.25 eV or by Tafel with energy equal to 0.2 eV to form again $\text{Mo}_3\text{S}_8\text{-3H}$ or as shown in the profile, a release of H_2S to go from $\text{Mo}_3\text{S}_8\text{-5H}$ to $\text{Mo}_3\text{S}_7\text{-3H}$. This last scenario is endergonic considering $P_{\text{H}_2\text{S}} = 1$ bar with energy equal to 0.39 eV. However, as we mentioned before under HER conditions we assume $P_{\text{H}_2\text{S}} = 10^{-5}$ which decreases the energy to release H_2S to 0.1 eV.

To conclude, the adsorbed hydrogen atoms on Mo_3S_8 could lead either to the release of H_2 via Tafel or Heyrovsky steps, as explained above, or to the release of H_2S and the reconstruction of Mo_3S_8 to give Mo_3S_7 with three adsorbed hydrogen atoms. The most favorable scenario is the Heyrovsky mechanism, then the H_2S release and the less probable is the Tafel mechanism.

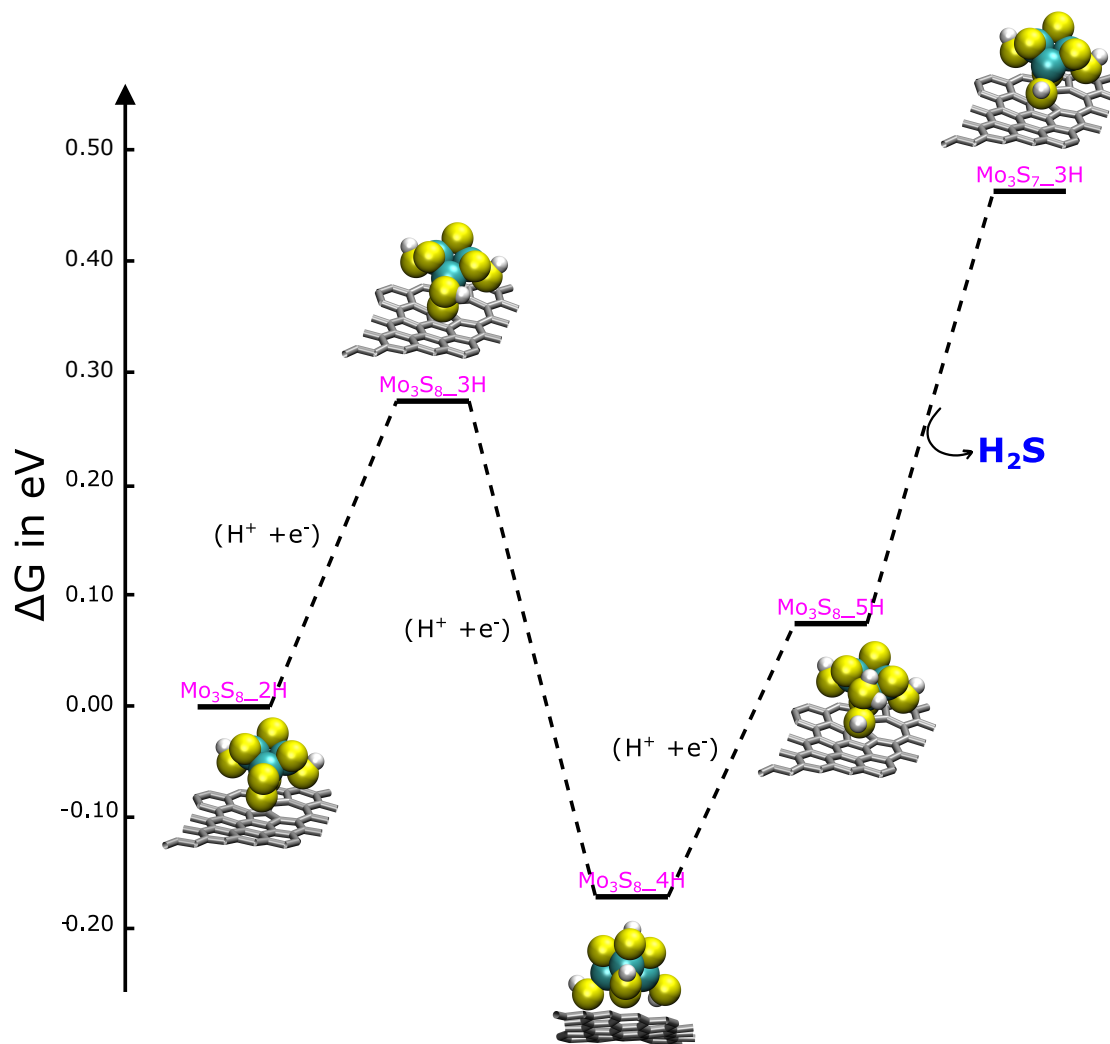


Figure S12: Hydrogen adsorption profile on Mo₃S₈ at 0 V. The color code for atoms is white for H; yellow for S and greenish for Mo.

S4 Summary of electronic energies of H adsorption and H₂S release with and without water: Comparison between vacuum, 0 charge and 0 potential

Table S2: Electronic energies for different systems

System	Process	Species	Vacuum (eV)	0 Charge (eV)	0 Potential (eV)	
Mo ₃ S ₉	H Adsorption	H1	-0.52	-0.51	-0.54	
		H2	-0.31	-0.40	-0.18	
		H3	-0.22	-0.10	-0.35	
		H4	-0.21	-0.32	-0.08	
	H ₂ S Release	H ₂ S	0.48	0.47	0.47	
		H1	-0.81	-0.80	-0.81	
	H Adsorption in presence of water	H2	-0.78	-0.78	-0.80	
		H3	0.07	0.08	0.08	
		H4	-0.65	-0.66	-0.65	
		H ₂ S	0.49	0.50	0.48	
Mo ₃ S ₈	H Adsorption	H1	-0.73	-0.67	-0.51	
		H2	-0.04	-0.26	-0.04	
		H3	0.11	0.12	0.08	
		H4	-0.66	-0.66	-0.65	
		H5	0.09	0.10	0.05	
	H ₂ S Release	H ₂ S	0.99	0.96	1.03	
		H1	-0.78	-0.77	-0.79	
	H Adsorption in presence of water	H2	-0.78	-0.78	-0.79	
		H3	0.37	0.56	-0.08	
		H4	-1.01	-1.20	-0.57	
		H5	0.49	0.72	-0.07	
		H ₂ S	0.72	0.58	1.05	
	Mo ₃ S ₇	OH Adsorption in presence of water and hydrogen	OH 1	-0.78	-0.85	-0.55
		H ₂ O Adsorption in presence of water and hydrogen	H ₂ O 3	-0.73	-0.55	-1.17

S5 Charge Injection

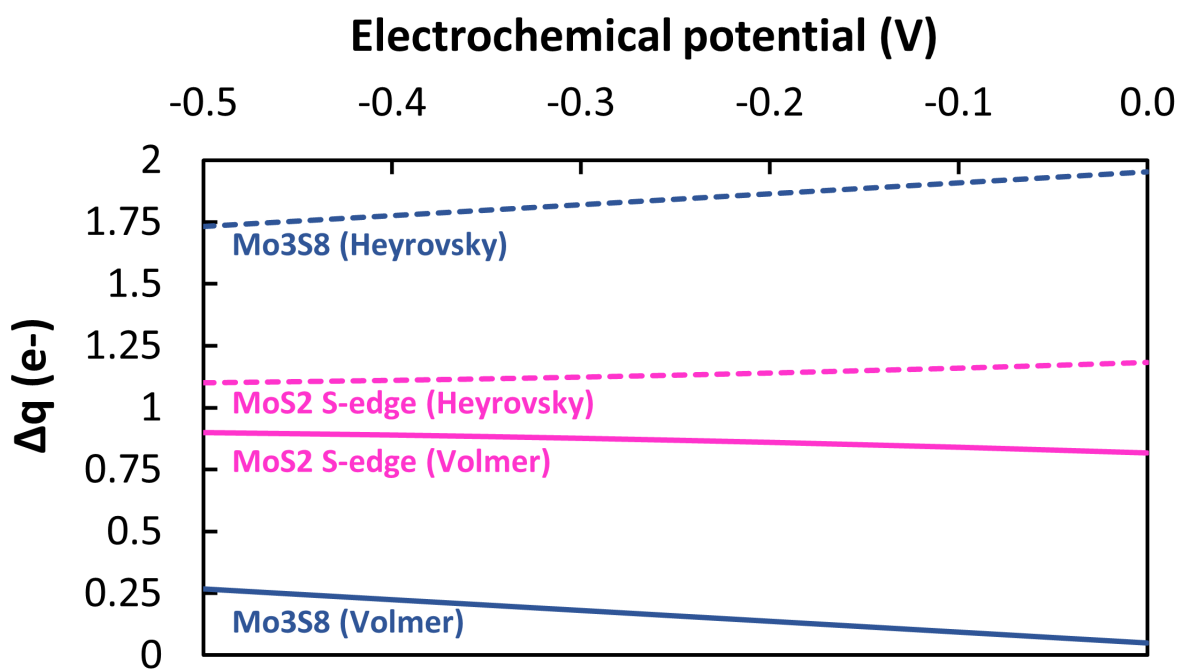


Figure S13: Variation of Δq , for the Volmer and Heyrovsky step as a function of the electrochemical potential for MoS₂ S-edge and Mo₃S₈. Δq would be 1.0 for a strictly proton coupled electron transfer. A value close to zero corresponds to a protonation step.

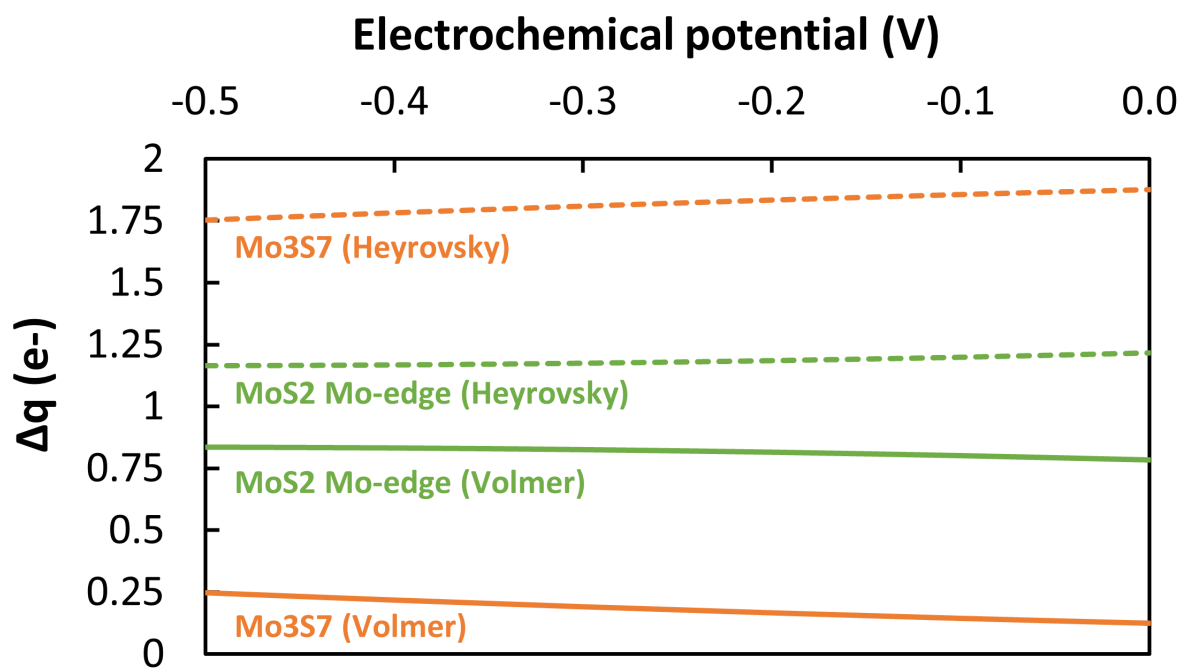


Figure S14: Variation of Δq , for the Volmer and Heyrovsky step as a function of the electrochemical potential for MoS₂ Mo-edge and Mo₃S₇. Δq would be 1.0 for a strictly proton coupled electron transfer. A value close to zero corresponds to a protonation step.