Electronic Supplementary Information

GO/CoMo₃S₁₃ chalcogel heterostructure with rich catalytic Mo-S-Co bridge site for hydrogen evolution reaction

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DFT Calculation

Models and Computational Methods: All the geometrical and energy-related calculations were carried out using density functional theory (DFT) approach within the generalized gradient approximation (GGA). The exchange-correlation energy was calculated using the Perdew, Burke, and Ernzerhof (PBE) gradient-corrected functional approach.¹ The double zeta basis plus polarization orbitals (DZP) was used for valence electrons. In contrast, core electrons were "frozen" in their atomic state using norm-conserving pseudo–potentials (NCP) in its fully nonlocal (Kleinman–Bylander) form.² The mesh cut-off was 250 Ryd. All the equilibrium structures were obtained using the Quasi-Newton algorithm, and all the forces acting on the dynamic atoms were smaller than 0.05 eV Å⁻¹. The DFT calculations were performed using the SIESTA code.³

We utilized a cluster model made up of three $Mo_3S_{13}^{2-}$ units and three Co^{2+} ions to explore the structure of $Mo_3S_{13}Co$ and optimize the computational costs. Edge effects are avoided or minimized in this model, thereby resulting in more accurate results than those obtained by the cluster model with one $[Mo_3S_{13}]^{2-}$ unit and one Co^{2+} ion.

Because of the numerous Co binding sites with $Mo_3S_{13}^{2-}$, determining the global minimum for $[Mo_3S_{13}]_3Co_3$ is relatively complex. Therefore, we used the artificial bee colony (ABC) algorithm combined with an accurate and broadly parametrized self-consistent tight-binding quantum chemical method GFN2–xTB for the preliminary generation of lower energy structures.^{4, 5} These structures were then fully refined through DFT calculations at a high level of theory to obtain the global minimum of $[Mo_3S_{13}]_3Co_3$.



Figure S1. Powder X-ray diffraction (PXRD) results of a) cobalt molybdenum sulfide aerogel in various $Co:Mo_3S_{13}$ ratios and b) $GO/CoMo_3S_{13}$ in different graphene oxide (GO) concentrations.

Figure S1 shows the PXRD patterns of cobalt molybdenum sulfide and GO/CoMo₃S₁₃ (1:1) chalcogel samples in different $Co^{2+}:[Mo_3S_{13}]^{2-}$ ratios and graphene oxide contents, respectively. These show the dominant amorphous phase composition exhibiting a porous structure of the aerogel materials.



Figure S2. Powder X-ray diffraction (PXRD) result of graphene oxide.



Figure S3. Raman spectroscopy result of graphene oxide (GO) including D and G bands.



Figure S4. Fourier-transform infrared spectroscopy (FT-IR) result of graphene oxide (GO).



Figure S5. XPS for O 1s of the graphene oxide (GO).



Figure S6. FE-SEM results of $CoMo_3S_{13}$ (1:1) chalcogel structure in different magnifications of a)50, b) 100, and c) 200 kX for determining the pore diameter distribution in range of meso-macropores (2-150 nm).



Figure S7. a-e) FE-SEM results of $Co_xMo_3S_{13}$ (x = a) 0.5, b) 1, c) 1.5, d) 2, and e) 3) chalcogel samples from left to right, respectively. Based on the briefly check the surface, the FE-SEM result of the ideal stoichiometric ratio of (b) $CoMo_3S_{13}$ (1:1) chalcogel shows the highest porosity with dominant meso-macro pore size range compared to other samples.



Figure S8. FE-SEM results of graphene oxide (GO) in different magnification of a) 50 and b) 100 kX.



Figure S9. a-d) FE-SEM results of $CoMo_3S_{13}$ (1:1) chalcogel samples with various GO contents of a) 20, b) 40, c) 60, and d) 80 %. The FE-SEM results of b) 40% GO/CoMo_3S_{13} (1:1) chalcogel material shows the tight and coherent heterostructure in GO-chalcogel, compared to incoherent GO-chalcogel connection in other samples.



Figure S10. a-f) FE-SEM results of (a, b, and c) 40% GO/CoMo₃S₁₃ (1:1) and (d, e, and f) 40% rGO/CoMo₃S₁₃ (1:1) chalcogel samples. Unlike tight connection in GO-chalcogel, the rGO/CoMo₃S₁₃ (1:1) chalcogel shows the poor connection between rGO and chalcogel with isolated particles of the reduced graphene oxide (rGO).



desorption pore distribution of $CoMo_3S_{13}$ (1:1) chalcogel sample.



Figure S12. a) Brunauer–Emmett–Teller (BET), and b) Barrett–Joyner–and Halenda (BJH) desorption pore distribution of graphene oxide (GO).



Figure S13. a,b) FE-SEM images of 40% GO/CoMo $_3S_{13}$ (1:1) chalcogel, which show the sandwich-like CoMo $_3S_{13}$ /GO/CoMo $_3S_{13}$ structure.



Figure S14. a) Polarization curves of $(NH_4)_2Mo_3S_{13}$, $CoMo_3S_{13}$ chalcogel samples with various ratios of Co/Mo₃S₁₃, and Pt/C catalysts at a scan rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ solution. b) Corresponding Tafel plots of materials.



Figure S15. a) Polarization curves of the $CoMo_3S_{13}(1:1)$ chalcogel and $GO/CoMo_3S_{13}(1:1)$ chalcogel with various contents of GO, and Pt/C catalysts at a scan rate of 5 mV s⁻¹ in 0.5 M H_2SO_4 solution. b) Corresponding Tafel plots of materials.



Figure S16. a-c) Cyclic voltammograms (0.1–0.2 V) of a) $(NH_4)_2Mo_3S_{13}$, b) $CoMo_3S_{13}(1:1)$ chalcogel, and c) 40% GO/CoMo₃S₁₃(1:1) chalcogel at various scan rates (25–175 mV s⁻¹) in 0.5 M H₂SO₄ solution.



Figure S17. a-c) FE-SEM of 40% GO/CoMo₃S₁₃ (1:1) chalcogel after long-term HER test (2000 cycles and 12 h operation).



Figure S18. EDS mapping of 40% GO/CoMo₃S₁₃ (1:1) chalcogel after long-term HER test (2000 cycles and 12 h operation) for various elements (C, O, Co, Mo and S).



Figure S19. XPS for a) Mo 3*d*, b) S 2*p* and c) Co 2*p* of the 40% GO/CoMo₃S₁₃ (1:1) heterostructure catalyst after long-term HER test (2000 cycles and 12 h operation).



Figure S20. a) Polarization curves of Ni foam (NF), $CoMo_3S_{13}$ (1:1)/NF, 40% GO/CoMo₃S₁₃ (1:1)/NF in 1 M KOH. b) Tafel slope of the materials



Figure S21. a) Optimized structures of $[Mo_3S_{13}]^{2-}$ and $[Mo_3S_{13}]_3Co_3$ clusters. b) Co–S distances (Å) in $[Mo_3S_{13}]_3Co_3$.



Figure S22. Adsorption of hydrogen on different sulfur sites in $[Mo_3S_{13}]^{2-}$: a) apical sulfide, b₁, b₂) terminal disulfides, and c₁, c₂) bridging disulfides. Notes 1 and 2 show the adsorbed hydrogen atom reaction on different orientation positions of sulfide.



Figure S23. Adsorption of hydrogen on different sulfur sites in $[Mo_3S_{13}]_3Co_3$: a) apical sulfide, b_1 and b_2) neighbor terminal disulfides of Mo-S-Co bridge, c_1 and c_2) bridging disulfides, d) terminal sulfide bridge Mo-S_t-Co and e) bridging sulfide bridge Mo-S_{br}-Co.

Table S1. Atomic ratio between Co and Mo in $CoMo_3S_{13}$ (1:1) aerogel from XPS analysis.

Chemical state	Co 2 <i>p</i>	Mo 3 <i>d</i>
Atomic (%)	0.68	2.07
Co:Mo ratio	1	:3

Samples	Rs	<i>R</i> ₁	R ₂
(NH ₄) ₂ Mo ₃ S ₁₃	13.6	20.2	8.2
CoMo ₃ S ₁₃ (1:1)	13.7	15.4	5.7
40% GO/CoMo ₃ S ₁₃ (1:1)	13.4	11.4	3.8

 Table S2. Comparison of resistance of various samples.

Samples	Overpotential (mV)	Tafel slope	C _{dl}	ECSA
	at 10 mA cm ⁻²	(mV dec⁻¹)	(mF cm⁻²)	(cm²)
(NH ₄) ₂ Mo ₃ S ₁₃	182	49.2	0.93	26.6
CoMo ₃ S ₁₃ (1:1)	155	45.5	3.18	90.9
40% GO/CoMo ₃ S ₁₃ (1:1)	130	40.1	4.25	121.4

Table S3. Comparison for the HER performance of various samples.

The calculation of the ECSA is based on double-layer capacitance (C_{dl}). The relationship between ECSA and C_{dl} is as follows:

$$ECSA = \frac{C_{dl}}{Cs \ cm_{ECSA}^{-2}},\tag{1}$$

where $C_s = 0.035 \text{ mF cm}^{-2}$ in an acidic solution, and C_{dl} is calculated from the slope of the plot of $\Delta j/2$ versus scan rate.

Table S4. XPS area ratio of Co 2p in 40%GO/CoMo₃S₁₃ (1:1) heterostructure catalyst before and after HER test, which exhibit a performance decay by cobalt loss in acidic electrolyte.

XPS peak of Co 2p	Before test (Area (P) CPS. eV)	After test (Area (P) CPS. eV)	
Narrow area peak value	53626.28	41283.15	
Area ratio	1:0.77		

Catalyst	Electrolyte	η for HER at corresponding (mV@mA/cm²)	Tafel slope (mV dec ⁻¹)	Reference
(NH ₄) ₂ Mo ₃ S ₁₃	0.5 M H ₂ SO ₄	182@10, 240@100, 255@200	49.2	This work
CoMo ₃ S ₁₃ (1:1) chalcogel	0.5 M H ₂ SO ₄	155@10, 215@100, 242@200	45.5	This work
40% GO/CoMo ₃ S ₁₃ (1:1) chalcogel	0.5 M H ₂ SO ₄	130@10, 201@100, 233@200	40.1	This work
CoMo ₃ S ₁₃ (1:1)/NF xerogels	1 M KOH	169@10, 317@100, 387@200	107.4	This work
40% GO/CoMo ₃ S ₁₃ (1:1)/NF	1 M KOH	132@10, 279@100, 352@200	98.1	This work
CoMoS _x /NF xerogel	$0.1 \text{ M H}_2\text{SO}_4$	118@10	85	C
	0.1 M KOH	129@10	113	0
CoMoS _x /NF xerogel	1 M KOH	89@10, 269@500	94	7
CNTs aerogel/MoS _x	0.5 M H ₂ SO ₄	150@10	62	8
H-2D/3D-MoS₂ -rGO aerogel	0.5 M H ₂ SO ₄	286@10	77	9
2H-MoS ₂ flakes	0.5 M H ₂ SO ₄	372@10	145	10
1T-MoS ₂ flakes	0.5 M H ₂ SO ₄	235@10	78	10
2H-WS ₂ nanosheets	0.5 M H ₂ SO ₄	360@10	85	11
1T-WS ₂ nanosheets	0.5 M H ₂ SO ₄	200@30	70	12

Table S5. Comparison of catalytic parameters of different HER catalyst systems such as

transition metal dichalcogenides (TMDs) and molybdenum sulfide aerogel catalysts.

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