Supporting Information

Engineering Water Dissociation Sites in MoS₂ Nanosheets for Accelerated Electrocatalytic Hydrogen Production

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Electrocatalytic HER mechanisms in acidic and alkaline solutions:

HER in acidic solution:

$H^+ + e^- + cat \rightarrow H^*$ -cat	Volmer step
$2H^*\text{-cat} \rightarrow \uparrow H_2$	Tafel step
$H^*\text{-}cat + H^+ + e^- \rightarrow cat + \uparrow H_2$	Heyrovsky step

HER in alkaline solution:

$H_2O + e^- + cat \rightarrow H^*-cat + OH$	Volmer step
$2H^*\text{-cat} \rightarrow \uparrow H_2$	Tafel step
$H^*-cat + H_2O + e^- \rightarrow cat + {}^{-}OH + \uparrow H_2$	Heyrovsky step

DFT calculations

Method: All calculations were conducted using the plane-wave based periodic density functional theory (DFT) method as implemented in the Vienna ab initio simulation package (VASP).¹ The electron ion interaction was described with the projector augmented wave (PAW)

method.² The electron exchange and correlation energy was treated within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof formalism (PBE).³ Spinpolarization was included for MoS₂, Ni-MoS₂, Fe-MoS₂, and Co-MoS₂ models to correctly account for their magnetic properties. An energy cut-off of 400 eV and a second-order Methfessel-Paxton electron smearing with $\sigma = 0.2$ eV were employed to ensure accurate energies with errors less than 1 meV per atom.⁴ The geometry optimization was carried out when the forces became smaller than 0.02 eV/Å and the energy difference was lower than $1 \times$ 10^{-4} eV. Adsorption energy (E_{ads}) was calculated by subtracting the energies of gas phase species and the clean surface from the total energy of the adsorbed system; E_{ads} = E(adsorbate/slab) - [E(adsorbate) + E(slab)], and a more negative E_{ads} indicates a more stable adsorption. To evaluate the energy barrier, the transitional state (TS) was located using the nudged elastic band (NEB) method.⁵ The TS configurations were verified by vibration analysis, and in all cases, only one imaginary frequency was found. The barrier (E_a) and reaction energy $(\triangle E_r)$ were calculated according to $E_a = E_{TS} - E_{IS}$ and $\triangle E_r = E_{FS} - E_{IS}$, where E_{IS} , E_{FS} , and E_{TS} were the energies of the corresponding initial state (IS), final state (FS), and transition state (TS), respectively.

DFT Models: The bulk MoS₂ has a hexagonal crystal lattice with a R₃M symmetry group. The calculated lattice parameters are a = b = 3.19 Å, c = 20.44 Å. The (002) plane of MoS₂ is widely considered as the active surface.⁶ As shown in Supplementary Fig. S1, a MoS₂ with 25% S coverage on the (002) surface was used as the model. It is commonly considered that promoter atoms (such as Fe, Co and Ni) are located at the MoS₂ edges, which results in a significant decrease of the metal–sulfur bonding energies and eventually affects the catalytic properties of MoS₂.⁷ All the calculated adsorption Gibbs free energies (G) of H₂O, H, and OH as well as energy barriers ($\triangle G$) of H₂O dissociation on different catalysts are listed in Table S1.

Experimental section

Preparation of electrocatalysts: Commercial carbon cloth (thickness: 0.36 mm, density: $0.160-0.180 \text{ g cm}^{-2}$, HESEN) was first treated overnight in concentrated nitric acid at 100 °C and then washed with deionized water. A hydrothermal approach was utilized for synthesizing the MoS₂, Ni-MoS₂, Fe-MoS₂, and Co-MoS₂ catalysts on carbon cloth. The hydrophilic carbon cloth (1 × 3 cm^2) was immersed in 15 mL aqueous solution containing Na₂MoO₄·2H₂O (0.5 mmol), NiSO₄·6H₂O (0.5 mmol), and L-cysteine (2.5 mmol) and was then heated for 24 h at 200 °C. After rinsing with 1 M H₂SO₄ aqueous solution and deionized water, the Ni-MoS₂ catalysts coated on the carbon cloth were obtained. The loading weight of the Ni-MoS₂ catalysts on the carbon cloth were approximately 0.89 mg cm⁻². The molar content of nickel in Ni-MoS₂ catalysts can be tuned from 6.3 to ~19.1% by adjusting the dosage of NiSO₄·6H₂O (0.17 mmol, 0.25 mmol, 0.5 mmol, 1.0 mmol, and 1.5 mmol, respectively). Under the same hydrothermal conditions, the Co-MoS₂ and Fe-MoS₂ catalysts on carbon cloth were further prepared with CoSO₄·7H₂O and FeSO₄·7H₂O as Co and Fe sources, respectively. For comparison, pristine MoS₂ catalysts on the carbon cloth were synthesized through the same process without involving NiSO₄·6H₂O.

Electrochemical tests: All electrochemical tests were performed at room temperature. The electrochemical HER tests were carried out in a three-electrode system. A standard Hg/HgO electrode and a graphite rod were used as the reference and counter electrodes, respectively. The Hg/HgO electrode was calibrated by bubbling H₂ gas on the Pt coil electrode. Potentials were referred to the standard RHE by adding 0.901 V (0.099 + 0.059 × pH) in 1 M KOH aqueous solution (pH = 13.6). The impedance spectra of the catalysts in a three-electrode setup were recorded at -0.1 V versus the RHE in 1 M KOH aqueous solution. All potentials were corrected by eliminating electrolyte resistances unless noted. The polarization curves were acquired at a scanning rate of 1 mV s⁻¹.

Calculation of TOF: The TOF (in s⁻¹) were calculated with the following equation:

TOF = I/(2NF)

I: current (in A) during the linear sweep measurement.

The factor ¹/₂ arrives by taking into account that two electrons are required to form one hydrogen

molecule from two protons.

N: number of active sites (in mol): cyclic voltammetry measurements were conducted from -0.87 V to -0.77 V at 1 mV/s in 1 M KOH solution. The absolute components of the voltammetric charges (cathodic and anodic) tested during one CV cycle were calculated. Assuming a one electron redox process, this absolute charge was divided by two. The obtained value was then divided by the Faraday constant to get the number of active sites of the catalysts.

F: Faraday constant (in C/mol).



Fig. S1. The structural models of the $M-MoS_2$ (M = Mo, Ni, Co, and Fe) catalysts.

Table S1. Gibbs free energies (G, eV) of adsorbed H_2O , H, and OH on the catalysts; the energy barriers ($\triangle G$, eV) of H_2O dissociation step (Volmer step) and combination of H* into molecular hydrogen (Tafel step) on different catalyst models. Adsorption energy of H is referred to gas phase H_2 .

Catalysts	G(H ₂ O)	G(H)	G(OH)	$\triangle G(H_2O)$	$\triangle G(H)$
MoS ₂	-1.17	-0.60	-4.95	1.17	0.60
<mark>Ni-MoS</mark> 2	<mark>-0.45</mark>	<mark>0.07</mark>	<mark>-3.36</mark>	<mark>0.66</mark>	<mark>-0.07</mark>
Co-MoS ₂	-0.69	-0.13	-3.46	0.76	0.13
Fe-MoS ₂	<mark>-0.52</mark>	<mark>0.11</mark>	<mark>-3.46</mark>	<mark>0.96</mark>	<mark>-0.11</mark>



Fig. S2. The synthesis scheme of the MoS₂ and Ni-MoS₂ nanosheets on the carbon cloth.



Fig. S3. The XRD pattern of the catalysts. The diffraction peaks indexed to (002), (004), (100), (103) and (110) facets of MoS₂ appear at $2\theta = 8.5^{\circ}$, 17.1°, 32.2°, 43.2° and 56.9°, respectively. The layered (002) lattice plane of carbon cloth shows a signal at $2\theta = 25.1^{\circ}$.



Fig. S4. SEM and HRTEM images of the Ni-MoS₂ catalysts.



Fig. S5. a) SEM and the corresponding mapping images of the Ni-MoS₂ catalysts on the carbon cloth: c) Ni, d) Mo and e) S elements; f) the corresponding EDS spectrum.



Fig. S6. a) SEM and the corresponding mapping images of the MoS₂ catalysts on carbon cloth: (c) Mo and (d) S elements.



Fig. S7. SEM (a) and the corresponding mapping images of Co (c), Mo (d), and S (e) elements, and the EDS spectrum (f) of the Co-MoS₂ catalysts on the carbon cloth. The chemical composition of Co-MoS₂ catalysts is $Co_{0.03}Mo_{0.97}S_2$.



Fig. S8. SEM (a) and the corresponding mapping images of Fe (c), Mo (d), and S (e) elements, and the EDS spectrum (f) of the Fe-MoS₂ catalysts on the carbon cloth. The chemical composition of Fe-MoS₂ catalysts is $Fe_{0.12}Mo_{0.88}S_2$.



Fig. S9. a) The XPS survey spectrum of the Ni-MoS₂ catalysts and high resolution spectrum of S 2p in (b) MoS₂ and (c) Ni-MoS₂ catalysts.



Fig. S10. a) The XPS survey spectrum of the $Co-MoS_2$ catalysts and corresponding high-resolution spectrum of (b) Co 2p, (c) Mo 3d, and (d) S 2p.



Fig. S11. a) The XPS survey spectrum of the Fe-MoS₂ catalysts and corresponding high-resolution spectrum of (b) Fe 2p, (c) Mo 3d, and (d) S 2p.



Fig. S12. The Raman spectrum of the MoS_2 and $Ni-MoS_2$ catalysts.



Fig. S13. A three-electrode configuration in an Ar-saturated 1 M KOH aqueous solution.



Fig. S14. a) Polarization curve and (b) corresponding Tafel plot of a Pt coil in $0.5 \text{ M H}_2\text{SO}_4$ (pH = 0.607). The standard potential (vs. RHE) of Hg/HgO reference electrode is approximately 0.99 mV.

 Table S2. The HER activities of the as-prepared Ni-MoS₂ and the reported MoS₂-based catalysts.

 Catalysts
 Overpotential (mV)
 Tafel slope
 TOF (s⁻¹)
 Exchange current
 Electrolyte

Catalysts	Overpotential (mV) at 10 mA/cm ²	Tafel slope (mV/decade)	TOF (s ⁻¹)	Exchange current density (mA/cm ²)	Electrolyte
Ni-MoS ₂ (this work)	98	60	0.32 s ⁻¹ (150 mV)	0.98	1 М КОН
Amorphous MoS film ⁸	540 mV at 4 mA/cm ²	_	_	_	0.1 M KOH
Anorphous Moo _x min	200 mV at 14 mA/cm ²	40	_	_	1 M H ₂ SO ₄
Amorphous Ni-MoS _x film ⁹	215 mV at 1 mA/cm ²	96	_	0.01	Phosphate buffer (pH = 7)
CoS./MoS2 chalcogels ¹⁰	210 mV at 5 mA/cm ²	—	_	—	0.1 M KOH
	235 mV at 5 mA/cm ²	_	_	_	0.1 M HClO ₄
Double-gyroid mesoporous MoS ₂ film ¹¹	235	50	_	0.69 × 10 ⁻³	0.5 M H ₂ SO ₄
Metallic MoS ₂ nanosheets ¹²	187	43	_	_	0.5 M H ₂ SO ₄
Defect-rich MoS ₂ nanosheets ¹³	190	50	0.725 s ⁻¹ (300 mV)	8.91 × 10 ⁻³	0.5 M H ₂ SO ₄
Li-MoS ₂ film ¹⁴	168	44	—	0.19 × 10 ⁻³	0.5 M H ₂ SO ₄
Strained MoS ₂ nanosheets ¹⁵	170	60	0.08-0.31 s ⁻¹		0.5 M H ₂ SO ₄
MoS ₂ /N-doped CNT	110	40	3.5 s ⁻¹ at 200	33.11 × 10 ⁻³	0.5 M H ₂ SO ₄

forest ¹⁶			mV		
Edge-terminated MoS ₂ nanosheets ¹⁷	149	49	_	9.62 × 10 ⁻³	$0.5 \mathrm{~M~H_2SO_4}$
MoS ₂ nanoparticles/ Graphene ¹⁸	155	41	_		0.5 M H ₂ SO ₄
Dimeric [Mo ₃ S ₁₃] ²⁻ clusters ¹⁹	180	40	1 s ⁻¹ per Mo at 100 mV		$0.5 \mathrm{~M~H_2SO_4}$
MoS ₂ /mesoporous graphene ²⁰	140	42			$0.5 \mathrm{~M~H_2SO_4}$
Metallic phase MoS ₂ nanosheets ²¹	175	41		0.1	0.5 M H ₂ SO ₄

Table S3. The HER activities of the as-achieved N1-MoS ₂ and the reported catalyst
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Catalysts	Overpotential (mV) at 10 mA/cm ²	Tafel slope (mV/decade)	TOF (s ⁻¹)	Exchange current density (mA/cm ²)	Electrolyte
Ni-MoS ₂ (this work)	98	60	0.32 s ⁻¹ (150 mV)	0.98	1 М КОН
$MoS_{2(1-x)}P_x$ solid solution ²²	150	57	0.83 s ⁻¹ (100 mV)	_	0.5 M H ₂ SO ₄
cobalt-sulfide (Co–S) film ²³	180	93	_	_	Phosphate buffer (pH = 7)
MoP nanoparticles ²⁴	140	54	—	3.4 × 10 ⁻²	0.5 M H ₂ SO ₄
wor nanoparticles	130	48		4.6 × 10 ⁻²	1 M KOH
Porous MoC _x nano-	142	53	_	2.3 × 10 ⁻²	0.5 M H ₂ SO ₄
octahedrons ²⁵	151	59		2.9 × 10 ⁻²	1 M KOH
Cobalt-doped FeS ₂ nanosheets–carbon nanotubes ²⁶	120 mV at 20 mA/cm ⁻²	46	_	_	0.5 M H ₂ SO ₄
Ni-S/MOF electrocatalysts ²⁷	238	111	34 s ⁻¹	_	0.1 M HCl
Ni ₂ P nanoparticles ²⁸	130 mV at 20 mA/cm ⁻²	46	0.50 s ⁻¹ (200 mV)	3.3 × 10 ⁻²	0.5 M H ₂ SO ₄
MoB nanonarticles ²⁹	190	55	—	1.4 × 10 ⁻³	0.5 M H ₂ SO ₄
MOB hanoparticles.	212	59	—	2.0 × 10 ⁻³	1 M KOH
Ni-Mo nanopowders ³⁰	70 mV at 20 mA/cm ⁻²	_	_	_	2 M KOH
NiO/Ni heterostructures ³¹	80	82	—		1 M KOH
CoP nanowires/carbon	209	129	—	—	1 M KOH

cloth ³²					
CoO/Co/N-doped carbon ³³	232	115	—	_	1 M KOH
Cobalt-embedded					
nitrogen-rich carbon	380	—	—	—	1 M KOH
nanotubes ³⁴					
CoNx/carbon catalyst ³⁵	170	75	—	—	1 M KOH



Fig. S15. The exchange current densities of the MoS₂, Ni-MoS₂, Co-MoS₂, Fe-MoS₂, and Pt catalysts.



Fig. S16. The calculated turnover frequencies for the MoS_2 and $Ni-MoS_2$ catalysts.⁸



Fig. S17. Electrochemical impedance spectroscopy (EIS) analyses of the catalysts. EIS measurements were recorded in Ar-saturated 1 M KOH aqueous solution at -0.1 V vs. RHE with 10 mV AC potential from 10 kHz to 0.01 Hz. The measured impedances were presented in the form of imaginary (Im) vs. real (Re) parts at various frequencies. It has been recognized that the high frequency interception of the Re-axis represents the resistance of the electrodes and that the width of the semicircle on the Re-axis corresponds to the charge-transfer resistances and indicates the overall kinetic effects. Clearly, all catalysts exhibited almost the similar intrinsic resistance, while the charge-transfer resistance of the Ni-MoS₂ catalysts was much lower than those of the MoS₂, Co-MoS₂, and Fe-MoS₂ catalysts, suggesting a faster HER kinetic process on the Ni-MoS₂ catalysts.



Fig. S18. SEM images of the Ni-MoS₂ catalysts after a 100-h durability test.



Fig. S19. SEM (a) and the corresponding mapping images of Ni (c), Mo (d), and S (e) elements, and the EDS spectrum (f) of the Ni-MoS₂ catalysts on the carbon cloth after a 100-h durability test.



Fig. S20. a) The XPS survey spectrum of the Ni-MoS₂ catalysts and corresponding high-resolution spectrum of (b) Ni 2p, (c) Mo 3d, and (d) S 2p after a 100-h stability test.



Fig. S21. The Cps of the MoS₂, Ni-MoS₂, Co-MoS₂, and Fe-MoS₂ catalysts were estimated utilizing a series of cyclic voltammetry (CV) circles at different scan rates. Cyclic voltammograms at different scan rates in the region between -870 and -770 mV (vs. the Hg/HgO) were recorded: a) MoS₂, b) Ni-MoS₂, c) Co-MoS₂, and d) Fe-MoS₂ catalysts. e) The differences in current densities ($\Delta J = Ja - Jc$) at 0 mV (vs. Hg/HgO) plotted against the scan rates fit to a linear regression and the slope is twice Cp.¹²



Fig. S22. SEM images of the Ni-MoS₂ catalysts with different molar contents of Ni: a and b) 6.2%, c and d) 10.3%, e and f) 16.8%, and g and h) 19.1%.



Fig. S23. a) Polarization curves of the as-prepared Ni-MoS₂ catalysts and b) the HER overpotentials of the corresponding Ni-MoS₂ catalysts at 10 mA cm⁻². Electrolyte: 1 M KOH aqueous solution; scan rate: 1 mV s⁻¹.

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