Supporting Information

Nickel nano-network facilitates short-path hydrogen spillover for

efficient alkaline hydrogen evolution with high-current-densities

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1. Experimental Dection

1.1 Materials

Ni foam was purchased from Suzhou Zhengtairong Ltd. (China). Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂, Aladdin, AR, 99%), nickel chloride hexahydrate (NiCl₂·6H₂O, Aladdin, AR, 99%), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Aladdin, AR, 99%), urea (CO(NH₂)₂, Aladdin, AR, 99%). Ruthenium(III) chloride hydrate (RuCl₃·xH₂O) was purchased from Shanghai Macklin Biochemical Co., Ltd. Commercial Pt/C (20 wt. % Pt loading on carbon) was purchased from TANAKA TKK. Nafion solution (5wt. %) was obtained from DUPONT. Potassium hydroxide(KOH), hydrochloric acid(HCl) and ethanol was purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used without further purification.

1.2 Synthesis of NiMoO₄·H₂O/NF

First, commercial nickel foam (3.5 cm \times 6 cm) was sequentially ultrasonically cleaned with 2 M HCl, ethanol, and deionized water to thoroughly remove surface oxides and impurities. Subsequently, 7 mmol of NiCl₂·6H₂O, 1 mmol of (NH₄)₆Mo₇O₂₄·4H₂O, and 13 mmol of urea were dissolved in 80 mL of deionized water under continuous stirring until complete dissolution was achieved. The cleaned nickel foam was immersed in the aforementioned solution and reacted in a water bath maintained at 90 °C for 5 hours. The material loading was optimized by adjusting the reaction time, which was found to be optimal within the range of 4 to 6 hours. At the conclusion of the reaction, the samples were extracted, rinsed with deionized water, and subsequently dried at 60 °C to yield the NiMoO₄·H₂O/NF precursor.

1.3 Synthesis of Ni-MoO₂/NF

The NiMoO₄-xH₂O/NF precursor was exposed to a H₂/Ar gas mixture (5% H₂) and heated to 500 °C at a rate of 5 °C/min, followed by holding at this temperature for 2 h. The material properties were systematically optimized by adjusting the annealing temperature in the range of 300-500 °C and the annealing time from 1 to 8 h. Ni-MoO₂/NF was synthesized through a process of annealing followed by natural cooling. **1.4 Synthesis of d-Ni-MoO₂/NF** The Ni-MoO₂/NF samples were immersed in a 1 M HCl solution for 2 hours. Afterward, they were removed, rinsed extensively with deionized water, and subsequently dried in an oven to yield the final d-Ni-MoO₂/NF.

1.5 Synthesis of NiMoO₄/NF

NiMoO₄/NF and Ni-MoO₂/NF are synthesized in the same steps, only the annealing atmospheres are different (Ar for NiMoO₄/NF, Ar/H₂ for Ni-MoO₂/NF).

1.6 Preparation of Pt/C Electrode

Commercial platinum carbon powder catalyst (20 wt.%) was loaded onto nickel foam substrates as a baseline hydrogenolysis reaction (HER) catalyst for performance comparison. Briefly, 10 mg of Pt/C powder was dispersed in a solution containing 50 μ L of Nafion and 950 μ L of ethanol, and the solution was sonicated to form a homogeneous catalyst ink. A 300- μ L drop of ink was placed on a clean nickel foam substrate (1.5 cm²) to achieve a loading of 2 mg·cm⁻², and then the nickel foam was dried in an oven.

1.7 Materials characterization

The X-ray diffraction (XRD) spectra were analyzed on a PANalytical 2Empyrean 2 X-ray diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5405$ Å) in the range of 2 θ =10-80°. The catalyst powder was sonicated from the NF for XRD analysis to reduce the contribution of Ni foam to the diffraction peaks. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images, elemental mapping images and selected area electron diffraction (SAED) images were obtained using a JEM-F200 at 200 kV. The morphology of the nanowire arrays of electrocatalysts was observed by field emission scanning electron microscopy (SEM, Hitachi Regulus8100, Hunan Navi New Mate-rials Technology). X-ray photoelectron spectroscopy (XPS) was performed with a thermos XPS spectrometer system using Al K α (1486.6 eV) radiation to investigate the surface compositions and valence states of the electrocatalysts. Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker EMXPLUS spectrometer from Germany.

1.8 Electrochemical measurements

All electrochemical tests were performed on a Gamry Interface 1010E electrochemical workstation equipped with standard three electrodes. In a typical threeelectrode electrolytic cell, the prepared catalyst (with a geometric surface area of 1 cm²), the carbon rod, and the Hg/HgO electrode were used as the working, counter, and reference electrodes, respectively. The catalyst performance was evaluated with 4.0 M KOH solution as the electrolyte. Polarization curves were obtained by linear scanning voltammetry (LSV) at a scan rate of 2 mV s⁻¹ and corrected by iR compensation. The reversible hydrogen electrode (RHE) potential (E_{RHE}) was converted using $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times pH$ at room temperature (298.15 K), and the pH of the 4 M KOH electrolyte was measured to be 14.50. The Tafel slope is calculated as $\eta = a + d$ blog(j), where η , a, b, and j are denoted as the overpotential, the Tafel constant, the Tafel slope, and the current density, respectively. Electrochemical impedance spectroscopy (EIS) was measured at a constant potential of -0.1 V vs. RHE (HER overpotential of 100 mV) from 100 kHz to 0.1 Hz with an AC voltage amplitude of 5 mV. Chronopotentiometry test was conducted at current density of 500 mA ·cm⁻² in 4M KOH electrolyte. The electrochemically active surface area (ECSA) of the catalysts was evaluated by the double layer capacitance method. Briefly, Cyclic Voltametric (CV) tests were performed in a non-Faraday potential window at different scanning rates of 20, 40, 60, 80, and 100 mV s⁻¹, and then half of the capacitance current was obtained as a function of the scanning rate. The ECSA was calculated as: ECSA = C_{dl}/C_s , where C_s is the specific capacitance for a flat surface (used here as 60 μ F cm⁻²).

1.9 Density Functional Theory (DFT) calculation

We have employed the VASP^{1, 2} to perform all the spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)³ formulation. We have chosen the projected augmented wave (PAW) potentials^{4, 5} to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 520eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The convergence criteria were set to 0.01 eV Å⁻¹ and 10⁻⁶ eV for the residual force and energy during structure relaxation.

The Brillouin zone was sampled by a $2 \times 2 \times 1$ k-points grid for the structure optimizations. In all calculations, van der Waals (vdW) interactions were accounted for at the D3 level⁶. Dipole correction was also applied throughout to avoid fictious charge interaction between neighboring images under the periodic boundary condition. And the differential charge is calculated by VASP.

The free energy change ($\triangle G$) of each elementary reaction was calculated as $\triangle G = \triangle E + \triangle E_{ZPE} - T \triangle S$, where $\triangle E$, $\triangle E_{ZPE}$, T, and S represent the reaction energy difference, zero-point energy, temperature, and entropy, respectively.



Figure S1. The SAED pattern of Ni-MoO₂/NF.



Figure S2. Nitrogen desorption curves of (a) NiMoO₄·H₂O/NF and (c) Ni-MoO₂/NF; Pore size distribution of (b) NiMoO₄·H₂O/NF NMO and (d) Ni-MoO₂/NF.

The adsorption and desorption isotherms of NiMoO₄·H₂O/NF catalysts indicated that the predominant internal pore size was 16.61 nm (Figures S2a and S2b). The Ni-MoO₂/NF catalyst exhibited a significantly higher abundance of 6.29 nm slit pores compared to the NiMoO₄·H₂O/NF catalyst (Figures S2c and S2d). According to the Brunauer-Emmett-Teller (BET) formula, the specific surface area of the Ni-MoO₂/NF catalyst was determined to be 107.37 m² g⁻¹, significantly exceeding that of the NiMoO₄·H₂O/NF catalyst (8.84 m² g⁻¹). Consequently, the Ni-MoO₂/NF catalyst exhibits markedly enhanced HER activity, in agreement with the EPR findings.



Figure S3. EDS elemental mappings of d-Ni-MoO₂ /NF.

Hydrochloric acid was employed to etch the Ni-MoO₂/NF catalyst, disrupting the densely packed nano-network of Ni particles on surface, resulting in the formation of the d-Ni-MoO₂/NF catalyst. As illustrated in Figure S3, the Ni particles on the surface of the d-Ni-MoO₂/NF catalyst no longer exhibited a network-like distribution, instead becoming isolated and dispersed. Notably, the Ni-MoO₂/NF catalyst demonstrated a significantly higher HER activity compared to the d-Ni-MoO₂/NF catalyst, highlighting the enhanced performance attributed to the unique Ni nano-network structure.



Figure S4. (a) The XRD pattern of NiMoO₄/NF catalyst; (b) LSV curves of NiMoO₄/NF and Ni-MoO₂/NF catalysts.

We prepared NiMoO₄/NF by annealing the NiMoO₄·H₂O/NF catalyst at an identical temperature under a non-reducing atmosphere (Ar) to prevent the formation of Ni nanoparticles (Figure S4a). The NiMoO₄/NF catalyst demonstrates a significantly high overpotential, suggesting that the pure oxide substrate exhibits negligible catalytic activity toward HER (Figure S4b).



Figure S5. (a) The EIS patterns for different catalysts; (b) Equivalent circuit models for EIS analysis.



Figure S6. The R_{ct} value of different catalysts.

The electrochemical impedance spectra (EIS) of various catalysts were measured to compare their electron transfer kinetics during the HER process (Figure S5a). The EIS results were derived from fitting the equivalent circuit model shown in Figure S5b. In this model, R_s denotes the solution's internal resistance, while R_{ct} signifies the charge transfer impedance at the electrolyte/catalyst interface. Evidently, the Ni-MoO₂/NF catalysts exhibit the smallest charge transfer impedance (R_{ct}) value (0.35 Ω), which indicates the most rapid electron transfer rate (Figure S6).



Figure S7. The CV curves of different catalysts with the scan rate ranging from 20 to 100 mV s⁻¹ in 4 M KOH: (a) Ni-MoO₂/NF, (b) d-Ni-MoO₂/NF, (c) NiMoO₄·H₂O/NF, and (d) Pt/C.



Figure S8. The ECSA values for different catalysts.



Figure S9. The SEM images of the Ni-MoO₂/NF catalysts at different water-bath times: (a-c) 4 h, (d-f) 5 h, and (g-i) 6 h.



Figure S10. (a) HER performance and (b) Tafel slope of Ni-MoO₂/NF catalysts obtained at different water bath times.

As illustrated in Figure S9, the density of fluffy structure on the surface of the Ni-MoO₂/NF catalyst progressively increased with the extension of water-bath time. However, the HER performance of the Ni-MoO₂/NF catalysts exhibited an initial enhancement followed by a subsequent decline as the fluffy structure density increased.



Figure S11. The SEM images of the Ni-MoO₂/NF catalysts at different annealing temperatures: (a-c) 400 °C, (d-f) 500 °C, and (g-i) 600 °C.



Figure S12. (a) HER performance and (b) Tafel slopes of Ni-MoO₂/NF catalysts obtained at different annealing temperatures.



Figure S13. The SEM images of the Ni-MoO₂/NF catalysts at different annealing times: (a-c) 1 h, (d-f) 2 h, and (g-i) 4 h.



Figure S14. (a) HER performance and (b) Tafel slopes of Ni-MoO₂/NF catalysts obtained at different annealing times.

The Ni-MoO₂/NF catalyst exhibited the highest HER activity when the water-bath time was 5 hours (Figures S9 and S10). In addition, the optimal annealing conditions were determined to be 2 hours at a temperature of 500 °C (Figures S11-S14).



Figure S15. (a) The CV curves of Ni-MoO₂/NF catalysts for 500 cycles between $0.05 \sim -0.3$ V; (b) The comparison of HER performance of Ni-MoO₂/NF catalysts before and after 500 CV cycles.

The Ni-MoO₂/NF catalyst exhibited negligible performance degradation after 500 cycles of CV testing (Figure S15), which meets the demand for catalysts used in renewable energy hydrogen production equipment very well.



Figure S16. The XRD pattern of Ni-MoO₂/NF catalyst after HER stability tests.

As illustrated in Figure S16, the phase composition of the Ni-MoO $_2$ /NF catalyst exhibited negligible changes following the stability test.



Figure S17. The SEM images of Ni-MoO₂/NF catalyst after HER stability tests.

The SEM images revealed that the Ni-MoO₂/NF catalyst retained its original microstructure intact after the stability test (Figure S17).



Figure S18. High-resolution XPS spectrum of (a) Ni 2p; (b) Mo 3d; (c) O 1s for Ni-MoO₂/NF catalyst after HER stability tests.

XPS spectra revealed that the valence states of the elements in the Ni-MoO₂/NF catalysts remained largely unchanged after the stability tests (Figure S18).



Figure S19. (a) The TEM images of Ni-MoO₂/NF catalyst after HER stability tests; (b) EDS elemental mappings of Ni-MoO₂/NF catalyst after HER stability tests.

TEM images further demonstrated that the MoO₂-supported Ni nano-network structure exhibited remarkable stability under prolonged high-current-density testing (Figure S19).



Figure S20. The EPR spectra for Ni-MoO₂/NF catalyst before and after HER stability tests.

The EPR results indicated that a significant concentration of oxygen vacancies remained on the surface of the Ni-MoO₂/NF catalyst even after the stability test, which can be attributed to its exceptional structural stability (Figure S20).



Figure S21. Capacitance contribution of NiMoO₄·H₂O/NF catalysts at different scan rates: (a) 1 mV s⁻¹, (b) 2 mV s⁻¹, (c) 3 mV s⁻¹, (d) 4 mV s⁻¹, and (e) 5 mV s⁻¹; (f) The percentage of capacitance contribution of NiMoO₄·H₂O/NF catalysts at different scan rates.



Figure S22. Capacitance contribution of Ni-MoO₂/NF catalysts at different scan rates: (a) 1 mV s⁻¹, (b) 2 mV s⁻¹, (c) 3 mV s⁻¹, (d) 4 mV s⁻¹, and (e) 5 mV s⁻¹; (f) The percentage of capacitance contribution of Ni-MoO₂/NF catalysts at different scan rates.



Figure S23. Analysis of b value for adsorption peaks of different catalysts.

This can be further substantiated by calculating the gravimetric capacitance of various catalysts (Figures S21 and S22). Based on the equation $i = av^b$, the *b* value of 0.5 signifies diffusion-limited dynamics, while the *b* value of 1.0 denotes ideal capacitive behaviour (Figure S23)⁷. Clearly, the HER kinetics at the surface of Ni-MoO₂/NF catalysts are predominantly governed by capacity control. This indicates that the pseudocapacitive behavior associated with hydrogen extraction/insertion is the predominant factor influencing the HER kinetics on the surface of Ni-MoO₂/NF catalysts.



Figure S24. The DFT calculation model for MoO₂ and Ni-MoO₂ (The red, cyan and yellow spheres represent O, Mo and Ni atoms, respectively.).

According to density functional theory (DFT), we constructed two models based on the MoO_2 (-211) facet: one for MoO_2 and the other for Ni-MoO₂ (Figure S24).



Figure S25. The differential charge diagram for Ni-MoO₂ (yellow for electron accumulation, blue for electron depletion).

The differential charge results for Ni-MoO₂ indicate significant electronic interactions at the interface between the Ni nanonetwork and MoO₂, aligning well with the experimental observations (Figure S25).



Figure S26. The modeling of H adsorption at different sites on the Ni-MoO₂ surface: (a) Ni site; (b) Mo site; (c) O site; The modeling of H adsorption at different sites on the MoO₂ surface: (d) O site; (e) Mo site.

The free energy changes associated with hydrogen evolution processes at various sites in both MoO_2 and $Ni-MoO_2$ models were calculated, as shown in Figure S26 and Figure 4d. As expected, the Ni site in $Ni-MoO_2$ emerges as the thermodynamically most favorable site for hydrogen evolution. This can primarily be attributed to the short-path hydrogen spillover effect and the efficient electron transfer capability of the surface Ni nanonetwork.

Catalyst	Overpotential	Tafel slope	Reference
	(j=100 mA cm ⁻²)	(mV dec ⁻¹)	
HW-NiMoN-2h	34	28.3	8
Ni-MoN	61	35.5	9
MoNi ₄ /MoO _{3-x}	52	36	10
Co ₂ P-Ni ₃ S ₂ /NF	110	114.2	11
Ni(OH) _x /Ni ₃ S ₂ /NF	126	67	12
PBSCF-Ni ₃ S ₂	137	24	13
Ni _{0.96} Co _{0.04} P	90.4	49.6	14
F-Co ₂ P/Fe ₂ P/IF	151.8	115	15
Ni _{2(1-x)} Mo _{2x} P	162	46.6	16
FeS ₂ /Fe-Ni ₃ S ₂	228	103	17
A-NiCo LDH/NF	151	57	18
MCu _{0.10} -BNiMo	255	40.4	19
Ni-MoO ₂ /NF	41	28.5	This work

Table S1. Comparison of the performance of most alkaline HER catalysts reported in the current literature.

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