

Electronic Supporting Information

Multiple regulation towards all-in-one NiCuMo/MoO_x heterostructure for boosting alkaline hydrogen oxidation

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Experimental section

Materials: All chemicals used in this work were as received without any further purification. Nickel Sulphate Hexahydrate (NiSO₄ · 6H₂O, ≥ 98.5%, Greagent), Sodium Molybdate Dihydrate (Na₂MoO₄ · 2H₂O, ≥ 99%, Adamas), Copper Sulphate Pentahydrate (CuSO₄ · 5H₂O, ≥ 98.5%, Greagent), Sodium citrate tribasic dihydrate (C₆H₅Na₃O₇ · 2H₂O, ≥ 99.0%, Adamas). Ammonium hydroxide solution (NH₄OH, ≥ 28%, Greagent), Hydrogen (H₂, 99.999%) and Argon (Ar, 99.999%). All reagents were analytically pure and used without further purification.

Synthesis of NiCuMo/MoO_x: The electrode is prepared by electrodeposition. Typically, nickel foam (1 cm × 1 cm) was pretreated by sonication in ethanol, deionized water, 3M HCl for 30 min, to clean the surface of the nickel foam. Transfer the cleaned foam nickel to the alkaline electroplating containing 4 mmol NiSO₄ · 6H₂O, 7 mmol Na₂MoO₄ · 2H₂O, 1 mmol CuSO₄ · 5H₂O and 12 mmol C₆H₅Na₃O₇ · 2H₂O. Then adjust the pH of the plating solution to about 9 with NH₄OH and deposition of NiCuMo/MoO_x on nickel foam by galvanostatic method. During this period, the temperature was maintained at 40°C, the current is maintained at 300 mA and the total electrodeposition time is 30 min. The synthesis of NiCu were the same as

NiCuMo/MoO_x, except that Na₂MoO₄ · 2H₂O was not added, respectively. The synthesis of NiMo/MoO_x were the same as NiCuMo/MoO_x, except that CuSO₄ · 5H₂O was not added, respectively. The synthesis of CuMo/MoO_x were the same as NiCuMo/MoO_x, except that NiSO₄ · 6H₂O was not added, respectively.

Preparation of Pt/C electrode: 1.5mg 20 wt% Pt/C was dispersed in a mixed solution of alcohol (960 μL) and 5 wt% Nafion (40μL), followed by ultrasonication for 30 min to obtain a uniform catalyst ink. Pipette was used to transfer the catalyst ink onto a pre-cleaned nickel foam (1cm × 1 cm) to obtain a mass load of 1.5 mg cm⁻².

Physicochemical characterization

X-Ray Diffraction (XRD) measurements were used a Rigaku D/Max-2550 V X-ray diffractometer with Cu-Kα radiation target (40 kV, 40 mA, λ = 1.5418 Å). Scanning Electron Microscopy (SEM) was collected from a Hitachi S-4800 scanning electron microscope and the accelerating voltage was 3 kV. Transition Electron Microscopy (TEM) and Energy Dispersive X-Ray Spectroscopy (EDS) were performed with a JEOL-2010F electron microscope operated at 200 kV. X-ray Photoelectron Spectroscopy (XPS) results were obtained from a Thermo Fisher Scientific, ESCALAB250Xi instrument using monochromatic Mg Ka X-rays at 1253.6 eV operated at 150 W, and the internal reference for spectrum was the C 1s electron peak (BE = 284.8 eV). Inductively coupled plasma (ICP) atomic emission spectroscopy data were performed on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The Raman spectra were conducted with a LabRAM HR 800 system at 785 nm laser.

Electrochemical measurements

Three electrode system is applied to HOR performance test. The MoO_x/NiCu@NF was directly used as working electrode. An Ag/AgCl electrode with saturated AgCl solution and a graphite were the reference electrode and the counter electrode, respectively. LSV and CV curves were recorded using Gamry electrochemical workstation. The reversible hydrogen electrode (RHE) is reference of the potentials existed in this work. Before HOR test, inject hydrogen into the solution for 30 min until it is saturated. Before LSV test, CV is circulated at -0.1 V ~ 0.5 V vs. RHE until the curve is stable. LSV results were acquired in H₂-saturated electrolyte with a scan rate of 1 mV s⁻¹ from -0.05 V to 0.2 V vs. RHE. ADT was performed by CV scanning for 1000, 3000, 500 cycles, 200 mV s⁻¹ from -0.1 V to 0.1 V vs. RHE in 0.1 M KOH, respectively. Electrochemical impedance spectroscopy (EIS) tests were performed using the Potentiostatic EIS function of the Gamry electrochemical workstation after each LSV measurement, during which hydrogen gas on was maintained. The frequency range was 100 kHz to 0.01 Hz, the overpotential was 30 mV, and the voltage

perturbation was 5 mV. The conversion between the measured potential and the reversible hydrogen electrode is recorded according to the following equation:

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 + 0.0592 \times \text{pH}$$

All LSV polarization curves for HOR were iR-corrected and obtained by scanning from negative to positive potential. Correct according to the following equation:

$$E_{\text{corrected}} = E_{\text{measured}} - iRs$$

In situ electrochemical Raman measurements

In situ SHINERS measurements were carried out using a LabRAM HR 800 system. The excitation wavelength of Raman device is 785 nm, and a 50× microscope for all Raman measurements. In situ electrochemical Raman experiments were performed in a homemade Raman cell with nickel foam deposited with NiCuMo/MoO_x as the working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode (filled with 3.5 M KCl) as the reference electrode (**Fig.S1**). A Gamry electrochemical workstation was used to control the potential. The acquisition time of each spectrum is 10 seconds, and the chronoamperometric measurement is performed at 65mV, 165 mV, 265 mV, 365 mV, 465 mV respectively. The Raman spectrum of the in-situ sample is obtained together with the chronoamperometric measurement All electrolytes are saturated with hydrogen before injection into the spectroelectrochemical cell.

Micro-polarization method

In a small potential window of the micro-polarization region near the equilibrium potential (± 10 mV vs. RHE), j_k approximately equals to the measured current j . In this case, the Butler–Volmer equation can be expanded by Taylor’s formula and simplified as:

$$j_0 = \frac{j}{\eta} \frac{RT}{F}$$

where j is the measured current density, η is the overpotential, R is the universal gas constant, T is the temperature, and F is Faraday’s constant. Therefore, j_0 can be obtained from the slope of the linear fitting in the micro-polarization region. The exchange current density (j_0) was normalized by the electrochemically active surface area (ECSA).

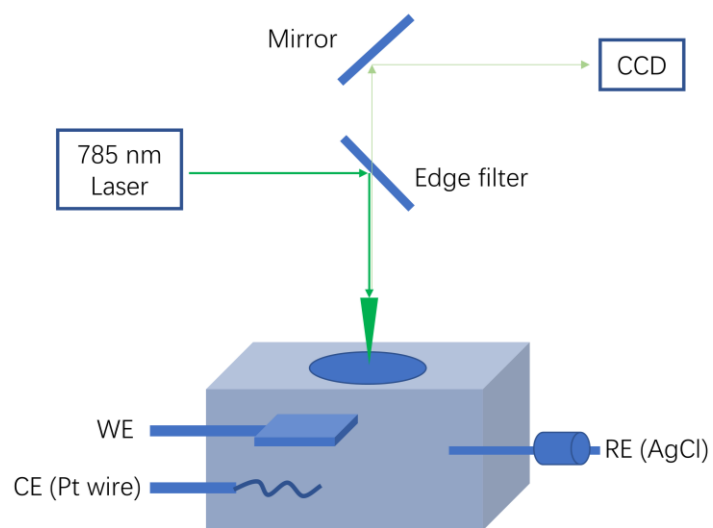


Fig. S1 Schematic diagram of the in-situ Raman spectroscopy combined with electrochemical tests.

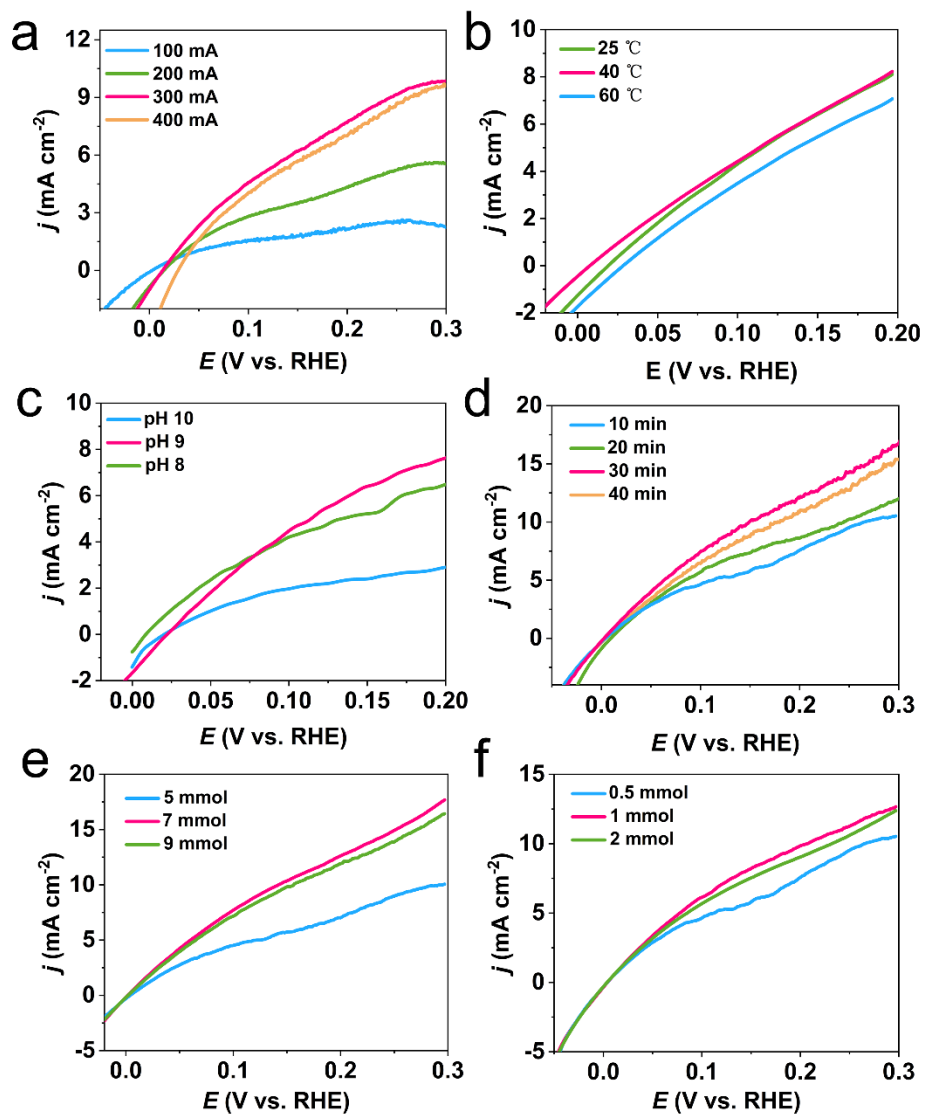


Fig. S2 LSV results of catalytic materials changing the preparation process parameters (Scan rate: 5 mV s^{-1}). Effects of (a) electro-deposition current (100 mA, 200 mA, 300 mA, 400 mA); (b) temperature of electroplating solution (25°C, 40°C, 60°C); (c) pH of electroplating solution (pH 8, pH 9, pH 10); (d) electro-deposition time (10 min, 20 min, 30 min, 40 min); (e) Mo Concentration of electroplating solution (5 mmol, 7 mmol, 9 mmol); (f) Cu Concentration of electroplating solution (0.5 mmol, 1 mmol, 2 mmol).

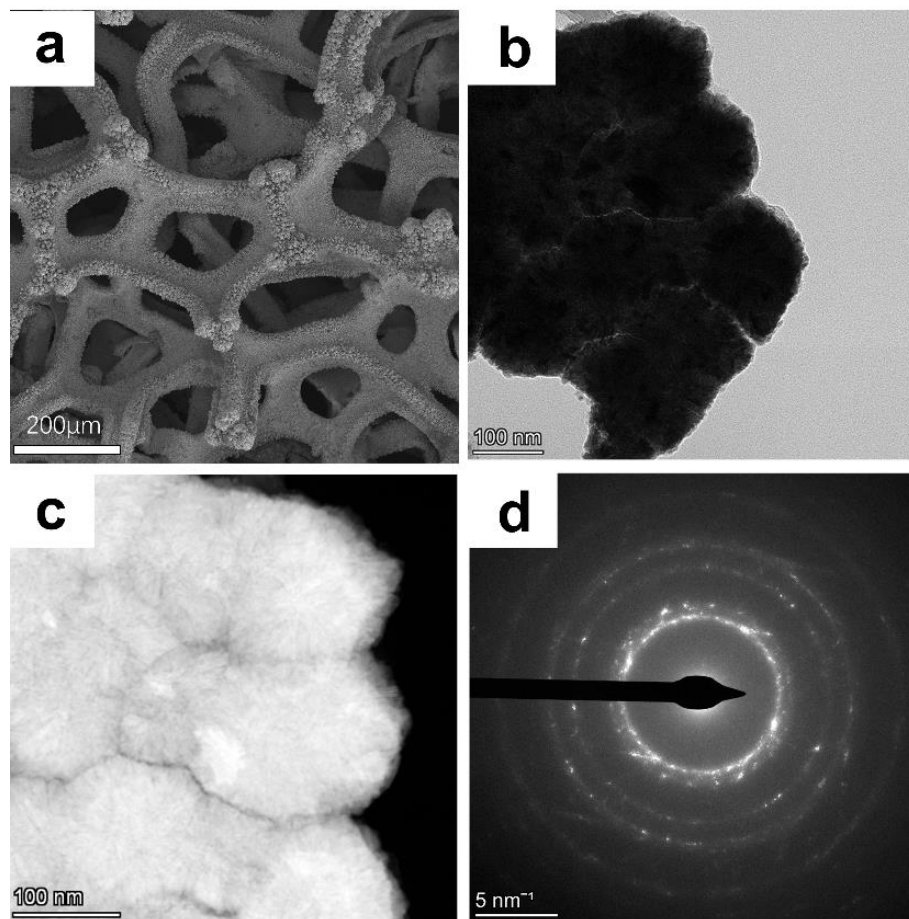


Fig. S3 (a) SEM images of NiCuMo/MoO_x samples. (b) HAADF-STEM images of NiCuMo/MoO_x samples. (c) HAADF-STEM images of NiCuMo/MoO_x samples and (d) The SAED pattern.

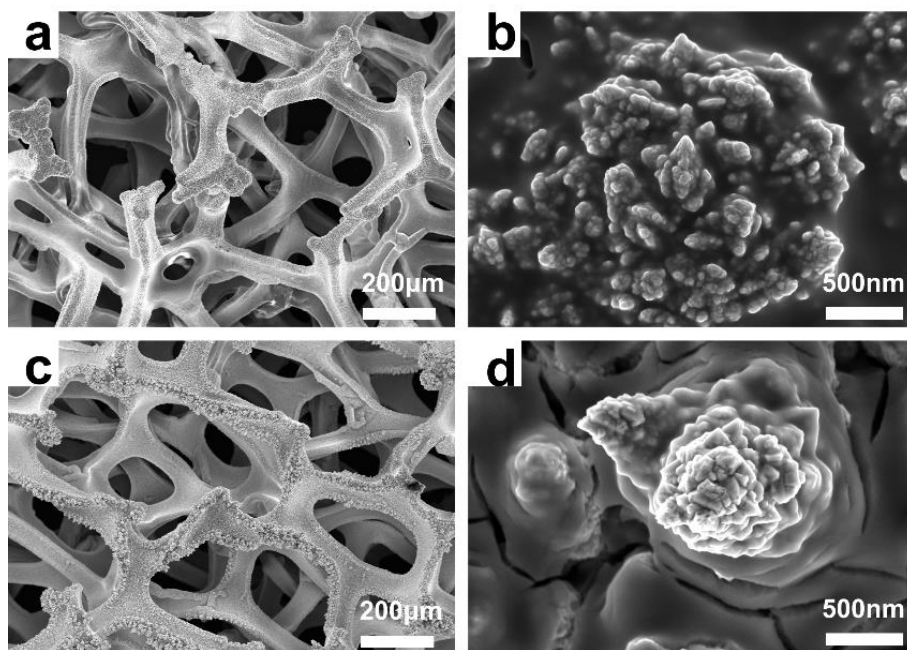


Fig. S4 Scanning electron microscopy (SEM) images of (a) NiCuMo/MoO_x, (b) NiCuMo/MoO_x, (c) NiCu and (d) NiCu.

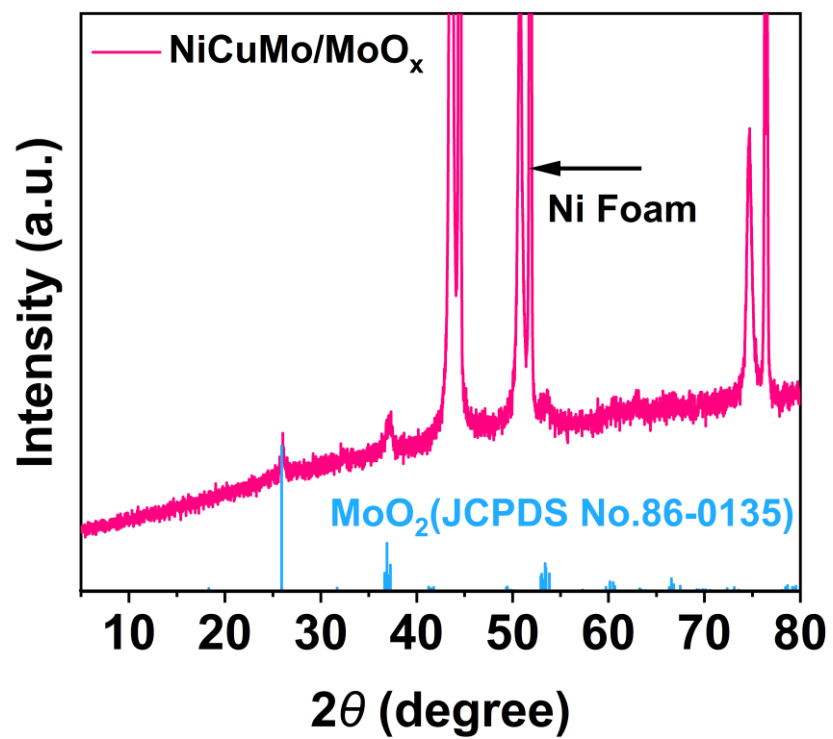


Fig. S5 XRD patterns of NiCuMo/MoO_x samples after Ar annealing. (The three sharp peaks are Ni foam)

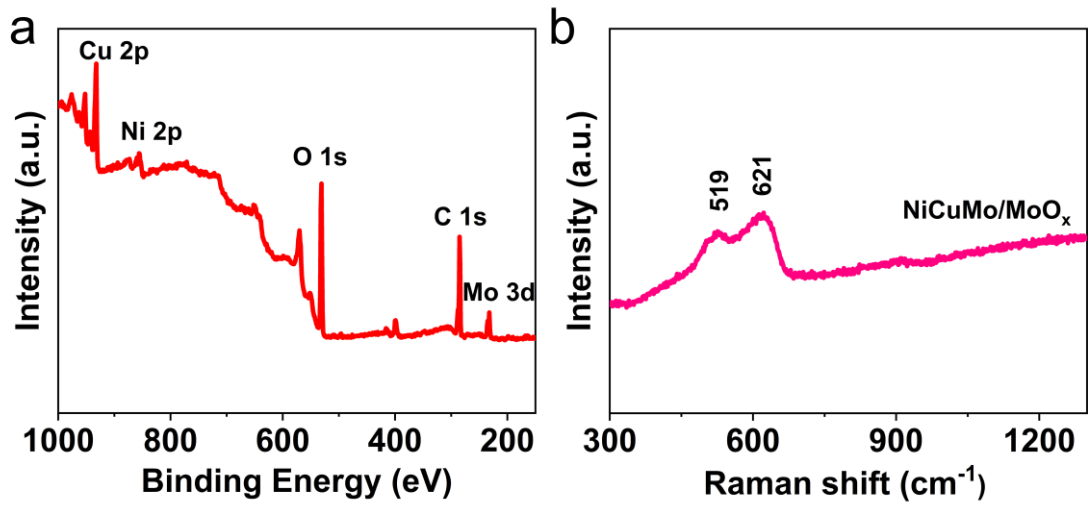


Fig. S6 (a) XPS survey spectra of NiCuMo/MoO_x nanosheets. (b) Raman spectra of NiCuMo/MoO_x samples.

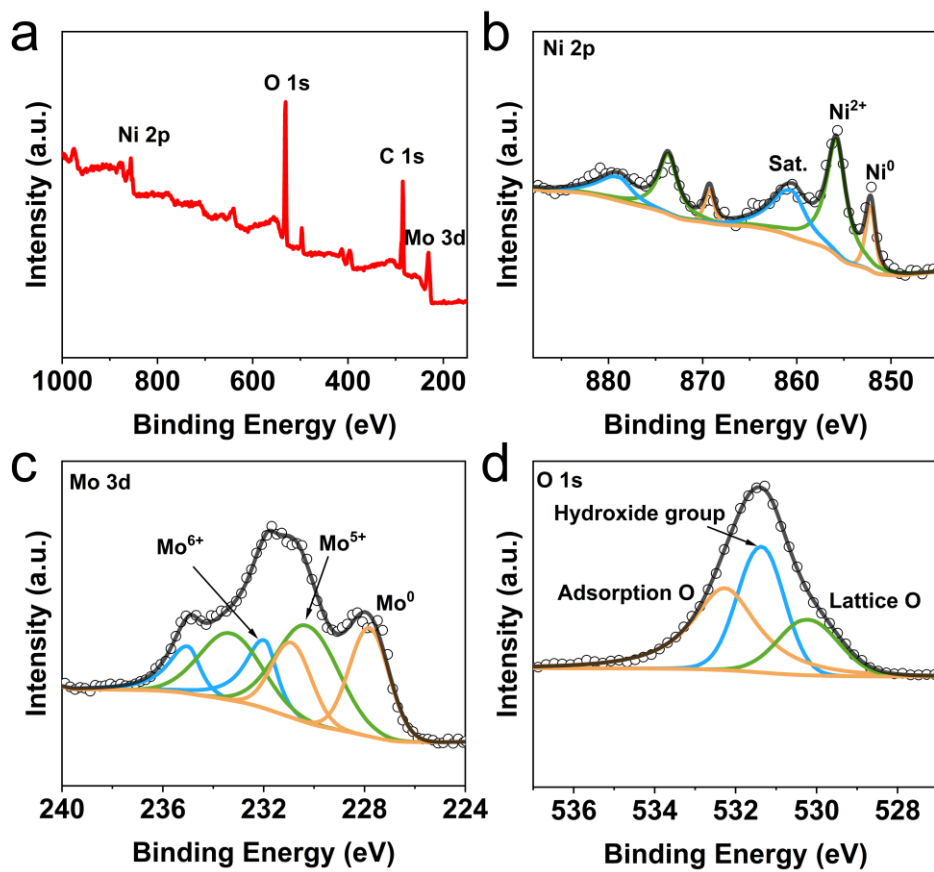


Fig. S7 (a) XPS survey spectrum of NiMo/MoO_x. XPS survey spectra of (b) Ni 2p; (c) Mo 3d and (d) O 1s.

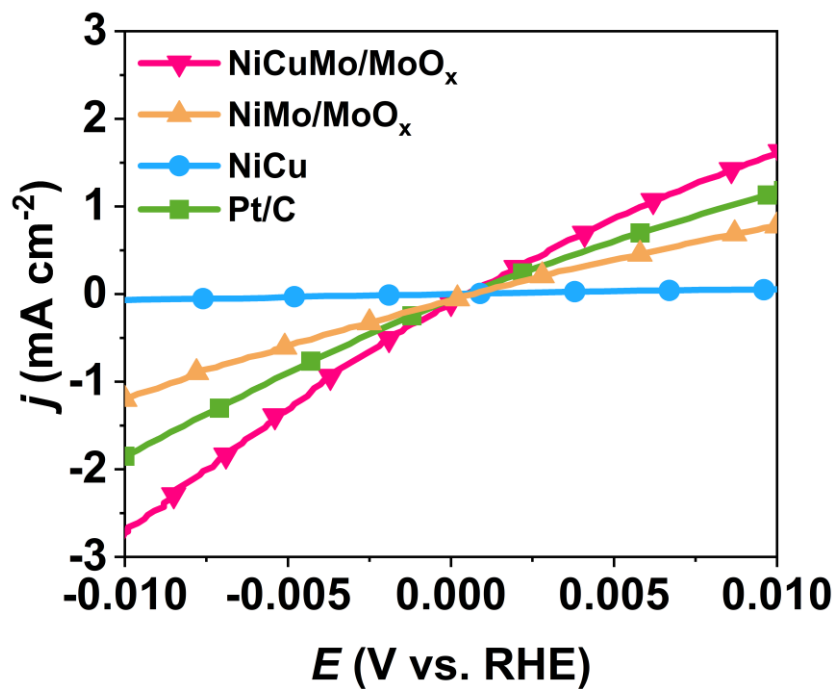


Fig. S8 Micro-polarization region (-10 to 10 mV vs. RHE) of NiCuMo/MoO_x, NiCu, NiMo/MoO_x and Pt/C, respectively.

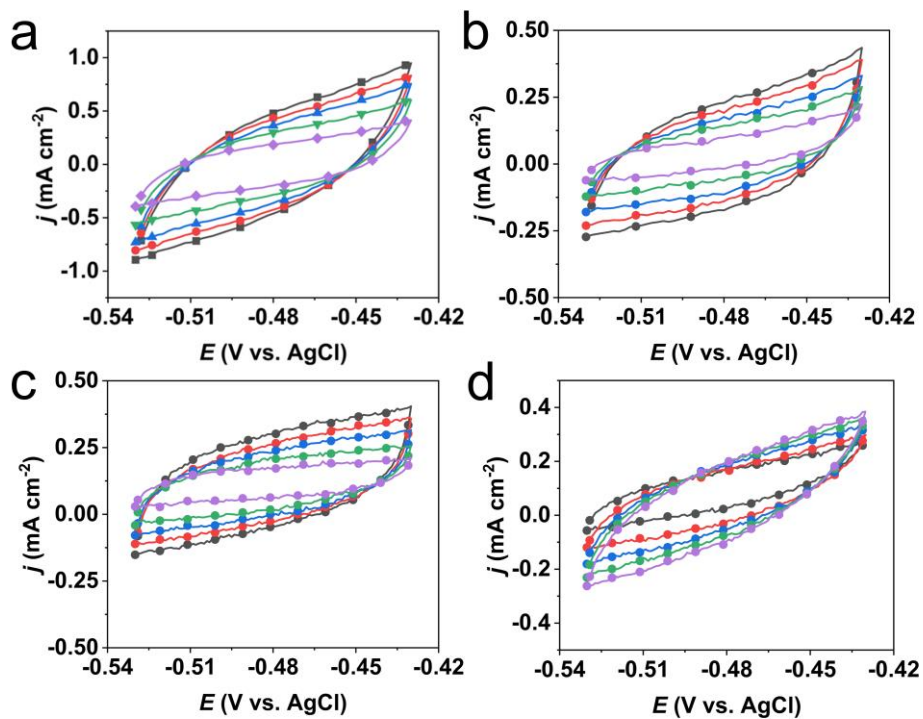


Fig. S9 CV curves of (a) NiCuMo/MoO_x, (b) NiCu, (c) Pt/C and (d) NiMo/MoO_x samples collected at various scan rates ranging from 5 to 25 mV s⁻¹ in 0.1 M KOH.

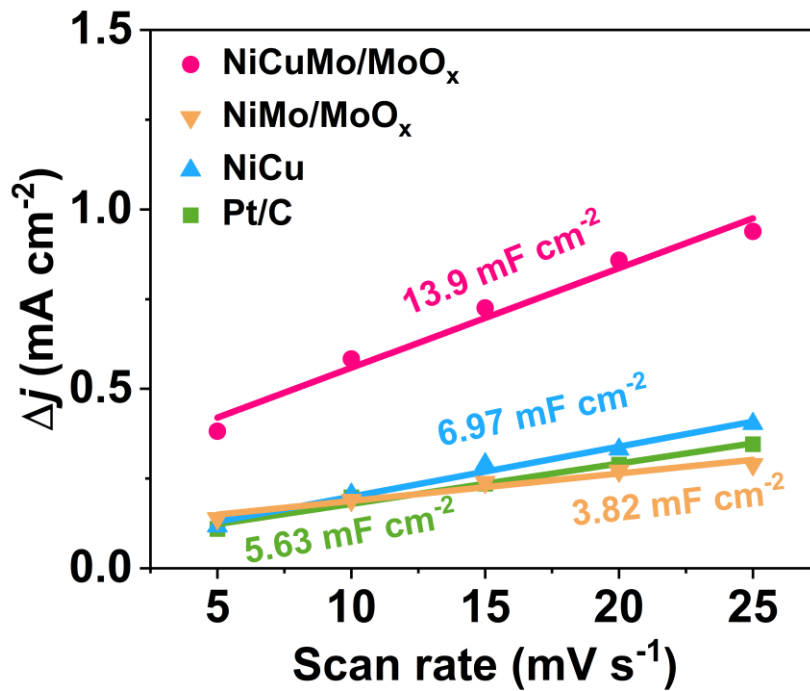


Fig. S10 The linear fitting of scan rate versus difference between the anodic and cathodic current for various NiCuMo/MoO_x samples.

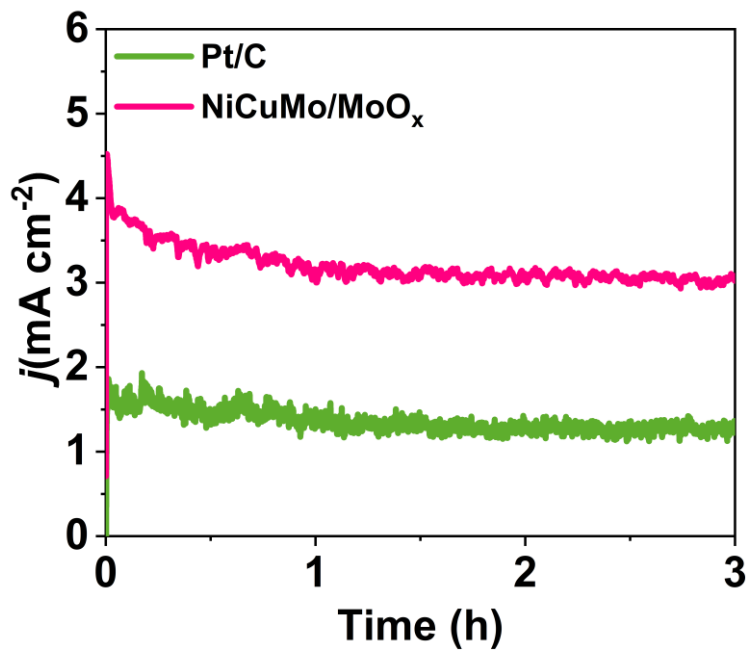


Fig. S11 Chronoamperometry ($j - t$) responses recorded on NiCuMo/MoO_x and Pt/C catalyst at a 150 mV overpotential in H₂-saturated 0.1 M KOH at room temperature.

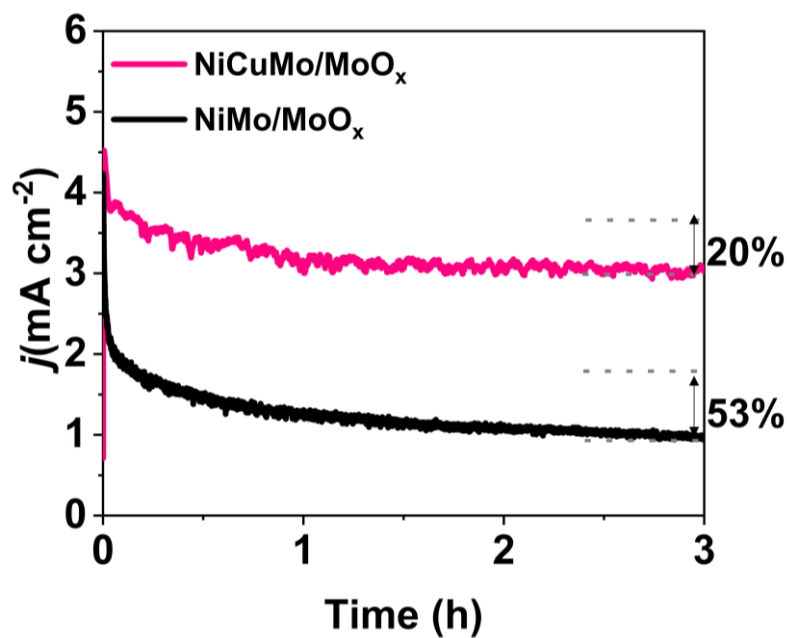


Fig. S12 Chronoamperometry (j - t) responses recorded on NiCuMo/MoO_x and NiMo/MoO_x catalyst at a 150 mV overpotential in H₂-saturated 0.1 M KOH at room temperature.

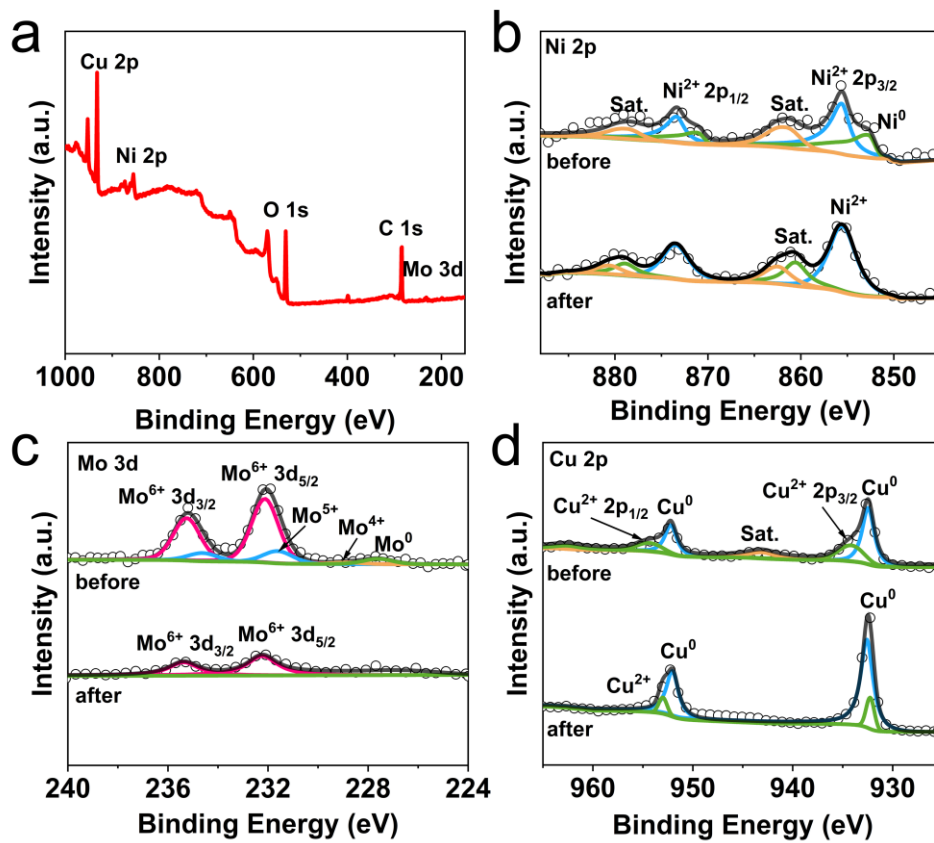


Fig. S13 (a) XPS survey spectrum of NiCuMo/MoO_x nanosheets after HOR test. XPS survey spectra of (b) Ni 2p; (c) Mo 3d and (d) Cu 2p before and after long-time stability test.

Table S1. Atomic ratios of Ni-based alloys by ICP-OES results

Element	Sample elemental content W	Atomic ratio after subtraction of Ni foam
Cu	25.6089%	17
Mo	2.2915%	1
Ni	71.4295%	12

The Ni content of the nickel foam substrate was included in the ICP-OES test, and this part of the mass was subtracted from the actual calculation.

Table S2. Comparison of HOR performance for NiCuMo/MoO_x with recently reported electrocatalysts in 0.1 M KOH.

Catalysts	$j_{0.05V \text{ vs. RHE}}$ (mA cm ⁻²)	j_{0ESCA} (mA cm ⁻²)	Reference
NiCuMo/MoO _x	4.63	0.016	This work
Pt/C	3.56	0.027	This work
Ni/N-CNT	1.3	0.028	<i>Nat. Commun.</i> 2016 , 7, 1
Ni _{5.2} WCu _{2.2}	11	0.014	<i>Nat. Commun.</i> 2021 , 12, 1.
CoNiMo	1.9	0.015	<i>Energy Environ. Sci.</i> 2014 , 7, 1719.
NiCu/KB	0.6	0.025	<i>Sustain. Energ. Fuels.</i> 2018 , 2, 2268.
Ni ₃ @h-(BN) ₁ /C	1.2	0.022	<i>Chem. Sci.</i> 2017 , 8, 5728.
Ni/Ni ₃ N/NF	5.0	0.003	<i>Nat. Commun.</i> 2018 , 9, 1.
NiMo/C	0.8	0.027	<i>J. Mater. Chem. A.</i> 2017 , 5, 24433.
Ni/CeO ₂ /C	1.2	0.038	<i>Angew. Chem.-Int. Edit.</i> 2019 , 58, 14179.
Ni/NiO/C	0.85	0.026	<i>Angew. Chem.-Int. Edit.</i> 2019 , 58, 10644.
Ni ₃ N-Ni (OH) ₂ /NF	1.5	-	<i>Appl. Catal. B-Environ.</i> 2022 , 309,121279.
Ni _{0.95} Cu _{0.05} /C	-	0.014	<i>J. Electroanal. Chem.</i> 2016 , 783, 146.

Table S3. ICP-OES results of Ni element and Mo element dissolved amounts in the electrolyte after reaction

Element	NiCuMo/MoO_x(μ g g⁻¹)	NiMo/MoO_x(μ g g⁻¹)
Cu	0.25	-
Mo	1.98	5.43
Ni	0.67	1.97

Table S4. Mass load of each sample.

Sample	Mass loading (mg)
NiCuMo/MoO_x	7.3
NiMo/MoO_x	1.5
CuMo/MoO_x	9.2
NiCu	13.1
Pt/C	1.5

The mass load is obtained by weighing the quality difference of nickel foam before and after electrodeposition.