Supplementary Information

Experiment detail

Materials

Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and ammonium molybdate tetrahydrate $((NH_4)_6Mo_7O_{24}·4H_2O)$ were purchased from Aladdin Reagent Co., Ltd, Shanghai. Potassium hydroxide (KOH) and acetonitrile were obtained from FuChen Chemical Reagent Co., Ltd, Tianjin. Hydrochloric acid and ethyl alcohol were purchased from Beijing Chemical Reagent Co., Ltd. Nickel foam (NF) was purchased from LiZhiYuan Electronic Materials Co., Ltd.

Synthesis of NiMoO₄ precursor

First, nickel foam (NF, $4.0 \times 5.0 \text{ cm}^2$) was treated with ethanol, 1.0 M hydrochloric acid, and ultrapure water with ultrasonication, successively. Second, 40 mmol Ni(NO₃)₂·6H₂O and 70 mmol (NH₄)₆Mo₇O₂₄·4H₂O were dissolved in 80 mL of ultrapure water under stirring for 1 h. Subsequently, The cleaned NF was placed in a Teflon-lined stainless steel autoclave containing an 80 mL aqueous solution of Ni(NO₃)₂·6H₂O (40 mM) and (NH₄)₆Mo₇O₂₄·4H₂O (70 mM), and heated at 150 °C for 6 h. After cooling to room temperature, the NF was washed by ethanol and ultrapure water, and dried overnight in vacuum at 70°C to obtain NiMoO₄ precursor.

Synthesis of Ni₄Mo/MoO₂

The dried NiMoO₄ precursor was heated to 450°C at 3°C min⁻¹ and kept for 2 h in a H₂/Ar (5:95) atmosphere. The obtained sample was named as Ni₄Mo/MoO₂/NF.

Synthesis of NCNTs@Ni₄Mo/MoO₂

Firstly, the dried NiMoO₄ precursor was treated the same way as the preparation of Ni₄Mo/MoO₂. Then the introduction of hydrogen and argon was stopped and acetonitrile vapor was injected while the 450°C constant temperature continued to be kept for n minutes (n=5, 10, 20) to obtain the final product NCNTs@Ni₄Mo/MoO₂.

Characterizations

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS) elemental mapping characterization were carried out with a Zeiss SUPRA 55 electron microscopy. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8-Advance diffractometer with Cu Ka radiation (hv = 1486.6 eV) and a scanning rate of 5° min⁻¹. The high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with EDS elemental mapping and the high-resolution transmission electron microscopy (HRTEM) including SAED were performed on a LIBRA 200MC Cs scanning TEM (Carl Zeiss) with an acceleration voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra were collected using an ESCALAB250X with a monochromated Al Ka 150 W X-ray source. The Raman spectra were obtained on a Renishaw in Via Reflex with the 532 nm laser.

Electrochemical Tests

Electrochemical characterization of the prepared materials was carried out on a Correst 350 workstation. In conventional three-electrode tests, the prepared electrocatalyst was used as the working electrode (1x1 cm²), the nickel mesh as the counter electrode, and a saturated calomel electrode as the reference electrode. The test temperature was 27°C and no iR compensation was taken for all tests. The conversion equation for the measured potential into reversible hydrogen scale is $E(RHE) = E(SCE) + 0.05916 \times pH + 0.2412 V$. The linear sweep voltammetry (LSV) tests were conducted at the scan rate of 1 mV s⁻¹ after 3 cycles of cyclic voltammetry (CV) tests to stabilize the test system. Tafel plots were derived from LSV curves. Electrochemical impedance spectroscopy (EIS) spectra were recorded by setting an overpotential of -0.01 V and superimposing the AC signals with amplitude of 5 mV and frequencies ranging from 100 000 to 0.01 Hz. The double layer capacitance (Cdl), which is proportional to the ECSA, was measured by a typical cyclic voltammetry (CV) test at the scan rates changing from 5 to 10 mV s⁻¹.

To elucidate the temperature-dependent kinetics, linear sweep voltammetry (LSV) was systematically conducted across a thermal gradient (25-45°C, $\Delta T = 5^{\circ}$ C). The Arrhenius activation energy (Ea) at discrete overpotentials (η) was determined through linear regression of Arrhenius plots derived from the fundamental relationship:

$$In \, j = -\frac{E_a}{R} \left(\frac{1}{T}\right) + In \, A$$

where *j* denotes the current density (mA cm⁻²), *A* the pre-exponential factor (mA cm⁻²), E_a the apparent activation energy (kJ mol⁻¹), *R* the universal gas constant (8.314 J mol⁻¹ K⁻¹), and *T* the absolute temperature (K).

The Faraday efficiency (FE) was quantified as the percentage ratio between the experimentally determined hydrogen yield (n_{actual}) and its theoretical maximum ($n_{theoretical}$) derived from charge transfer analysis:

$$FE = \left(\frac{n_{actual}}{n_{theoretical}}\right) \times 100\%$$

The electrochemical measurements were conducted in a sealed H-type cell. The cathodic hydrogen stream was directed through hydrophobic PTFE tubing into a calibrated collection apparatus. Displaced deionized water was continuously weighed using a analytical balance (± 0.01 mg resolution) interfaced with LabVIEW-controlled data acquisition (1 Hz sampling).

The overall electrolysis process was switched in stages between room temperature and high temperature. During the day, the electrolyte pipeline was heated up to 80°C by means of an oil bath and electrolysis was carried out at a current density of 8000 A/m². At night, the electrolysis took place at room temperature, when the current density was set to 3000 A/m².



Fig. S1 SEM images of NiMoO₄.



Fig. S2 EDS mapping of NCNTs@Ni₄Mo/MoO₂.



Fig. S3 XRD patterns of NiMoO₄.



Fig. S4 XRD patterns of Ni₄Mo/MoO₂, NCNTs@Ni₄Mo/MoO₂-5, NCNTs@Ni₄Mo/MoO₂-

10 and NCNTs@Ni₄Mo/MoO₂-20.



Fig. S5 (a) TEM and (b) HRTEM of Ni₄Mo/MoO₂.



Fig. S6 HAADF-STEM and elemental mappings of NCNTs@Ni₄Mo/MoO₂-10.



Fig. S7 C 1s and XPS spectra of NCNTs@Ni₄Mo/MoO₂-10.

Table SI The area percent of N1 in	different valence states in the XPS spectra of Ni 2p.

Area Percent Electrocatalyst	Ni ⁰	Ni ²⁺	Satellite
NCNTs@Ni ₄ Mo/MoO ₂	26.8%	39.0%	34.2%
Ni ₄ Mo/MoO ₂	11.5%	52.3%	36.2%



Fig. S8 (a) the LCV curve, (b) Tafel slope and (c) C_{dl} of Ni_4Mo/MoO_2 obtained at 400°C, 450°C, 500°C, 550°C and 600°C.



Fig. S9 (a) C_{dl} and (b) EIS Nyquist plots of Ni₄Mo/MoO₂, NCNTs@Ni₄Mo/MoO₂-5, NCNTs@Ni₄Mo/MoO₂-10 and NCNTs@Ni₄Mo/MoO₂-20, NF, Pt/C.



Fig. S10 (a) LSV curve, (b) Cdl values and (c) EIS Nyquist plots of NiMoO₄.



Fig. S11 The volume of H₂ and FE of NCNTs@Ni₄Mo/MoO₂-10.



Fig. S12 Chrono-potentiometric curve of Ni₄Mo/MoO₂, NCNTs@Ni₄Mo/MoO₂-5, NCNTs@Ni₄Mo/MoO₂-10 and NCNTs@Ni₄Mo/MoO₂-20 for HER at a current density of 500 mA cm⁻² for 100 h in 30 wt.% KOH.



Fig. S13 Overpotential comparison of initial and after 100 h CP test of Ni₄Mo/MoO₂, NCNTs@Ni₄Mo/MoO₂-5, NCNTs@Ni₄Mo/MoO₂-10 and NCNTs@Ni₄Mo/MoO₂-20 at current densities of 10 and 100 mA cm⁻².



Fig. S14 LSV curves obtained at different temperature on (a) Ni₄Mo/MoO₂, (b) NCNTs@Ni₄Mo/MoO₂-5, (c) NCNTs@Ni₄Mo/MoO₂-10 and (d) NCNTs@Ni₄Mo/MoO₂-20. The semilogarithmic plots of *j vs.* η obtained at different temperature on I Ni₄Mo/MoO₂, (f) NCNTs@Ni₄Mo/MoO₂-5, (g) NCNTs@Ni₄Mo/MoO₂-10 and (h) NCNTs@Ni₄Mo/MoO₂-20.

The corresponding Arrhenius plots at different η on (i) Ni₄Mo/MoO₂, (j) NCNTs@Ni₄Mo/MoO₂-5, (k) NCNTs@Ni₄Mo/MoO₂-10 and (l) NCNTs@Ni₄Mo/MoO₂-20. The variation of E_a as a function of η on (m) Ni₄Mo/MoO₂, (n) NCNTs@Ni₄Mo/MoO₂-5, (o) NCNTs@Ni₄Mo/MoO₂-10 and (p) NCNTs@Ni₄Mo/MoO₂-20.



Fig. S15 Overall water splitting switch between current density of 3000 A m⁻² at room temperature and current density of 8000 A m⁻² at 80°C in 30 wt.% KOH for NiFeO_x(+)||Ni₄Mo/MoO₂(-).



Fig. S16 SEM images of NCNTs@Ni₄Mo/MoO₂ after overall water splitting.



Fig. S17 (a) Ni 2p and (b) Mo3d XPS spectra of NCNTs@Ni₄Mo/MoO₂ after overall water splitting.



Fig. S18 (a) Ni 2p and (b) Mo3d XPS spectra of Ni₄Mo/MoO₂ after overall water splitting.