

Supporting Information

Boosting the Efficiency and Stability of CoMoS₄ by N Incorporation for Electrocatalytic Hydrogen Evolution

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Experimental section

1.1 Materials synthesis

All the chemicals are analytical grade and used as received without further purification. The CoMoO_4 precursor was firstly synthesized on Ni foam by a hydrothermal method. In atypical synthesis process, 1.5 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.5 mmol $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 15 ml DI water to form a transparent pink colored solution. As formed solution was then transferred to 25 ml Teflon-lined stainless steel autoclave with the pre-cleaned Ni foam placed perpendicularly into the solution, and heated to 180 °C for 12 h. After reaction, the Ni foam was washed with DI water and ethanol for several times, and then dried at 60 °C. For synthesis of N incorporated CoMoS_4 , the Ni foam coated with CoMoO_4 was further reacted with 1.5 mmol thioacetamide in 15 ml ethanol at 120°C for another 8 h. The mass loading of the catalyst is weighted to be about 3.4 mg/cm² (N-CoMoS). As references, CoMoS_4 with different N doping amount was obtained using anhydrous sodium sulfide and thioacetamide (TAA) as sulfurization agents with total amount of 1.5 mmol.

1.2 Characterization

X-ray diffraction (XRD) patterns were performed on a SHIMADZU XRD-7000 X-ray diffractometer using Cu K α radiation with the 2 θ range from 10 to 90°. Scanning electron microscopy (SEM) conducted on Hitachi S4800N was used to observe the morphologies of obtained samples. Transmission electron microscopy (TEM) images and elemental mapping were recorded on a JEM-2010 electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were performed an AXIS-HSi spectroscope (XPS ESCALAB 250Xi) using a monochromatic Al K α X-ray source. The Co and Mo ions concentrations in electrolyte after stability test were investigated by Horiba Ultima-2 Inductively Coupled Plasma Spectroscopy, and total S amount was analyzed by chemical method as follows: the electrolyte was first reacted with perchloric acid to oxide the all possible S ion to +6 state, then Ion Chromatography was adopted to determine the overall S concentrations in the electrolyte.

1.3 Electrochemical measurements

The electrochemical measurements were carried out on a Bio-logic VMP3 electrochemical workstation using typical three-electrode system in 1.0 M KOH aqueous solution. As prepared catalysts on NF were directly used as working electrode, while Ag/AgCl electrode and a carbon rod were used as the reference electrode and the counter electrode, respectively. Electrocatalytic hydrogen evolution were performed at the scan rate of 5 mV s⁻¹. The electrochemical doublelayer capacitance tests were

estimated by cyclic voltammograms (CVs) at the scan rates of 20, 40, 60, and 80 mV s⁻¹, respectively. The electrochemical impedance spectroscopy was recorded at the frequency from 0.1Hz to 100KHz.

1.4 Density functional theory (DFT) calculation

DFT calculation is done on Vienna Ab-initio Simulation Package (VASP) using the PAW pseudopotential and the GGA exchange-correlation functional¹. The calculations consider 9 valence electrons for Co (3d⁷4s²), 14 for Mo (4p⁶4d⁵5s¹), 6 for S (2s²2p⁴) and 5 for N (2s²2p³). In all calculations, the stopping criterion for electron relaxation is 10⁻⁴ eV between consecutive steps; for ionic relaxation the stopping criterion is when all forces decrease to below 0.001 eV/Å. The precession setting of “PREC = Accurate” is used; the energy cutoff is set to be 400 eV for all structures. For calculation of a charged system, the number of electrons is directly specified in the INCAR by the NELECT parameter. For N substitution calculation, one S atom on the surface is substituted by N and the absorption is made near the N atom.

The amorphous structure is constructed by the following steps: 72 atoms (12 CoMoS₄ molecules) are added randomly to a cubic box of 11.3 Å in length so that the atomic volume is 20 Å³/atom. This number is believed to be sufficiently large so that the box will not explode under relaxation. Then the system is initially relaxed with low accuracy and fixed volume and only atomic positions are allowed to change. After equilibrium is achieved, the system is subjected to full relaxation of both box volume and atomic positions with high accuracy. The final relaxed atomic volume is calculated to be 17.8 Å³ and cohesive energy is -5.94 eV/atom.

Surface structures are constructed by creating a vacuum of 15 Å in the c direction of the relaxed structure to create an amorphous surface. The structure is then relaxed for atomic coordinates (ISIF=2) with fixing the atoms in the bottom 2 Å. Some extent of surface relaxation is expected. The N-doped surface is created by substituting one S atom close to the surface for an N atom in a relaxed surface structure. The doped structure is then relaxed again for atomic coordinates. The relaxed pure and doped surfaces will be used in the absorption calculation.

The reaction energy ΔG for a particular reaction with j products and k is calculated as:

$$\Delta G = \sum_j E_j^{pro} - \sum_k E_k^{rea}$$

where E_j^{pro} is the cohesive energy of the j-th products, E_k^{rea} is the cohesive energy of k-th reactants.

For calculation of transition states, the climbing-image nudged elastic band (CI-NEB) method is

used with 7 images², the spring constant between images is 5 eV/Å².

References

- [1] G. Kresse and D. Joubert, *Phy. Rev. B*, 1999, **59**, 1758-1775.
- [2] G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901-9904.

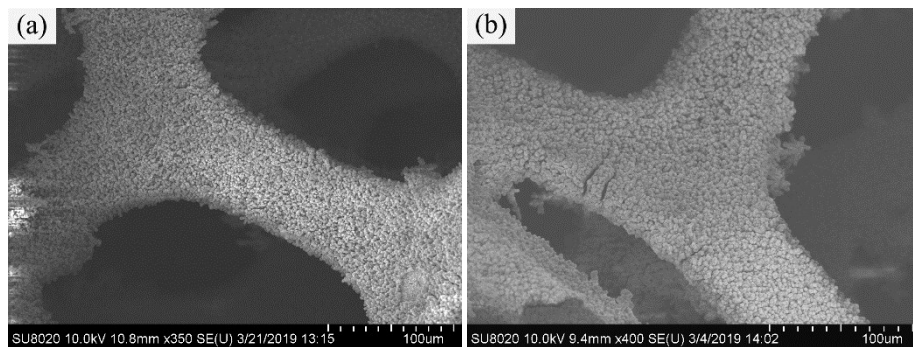


Figure S1 Low magnified SEM images of (a) CoMoO_4 and (b) N- CoMoS_4

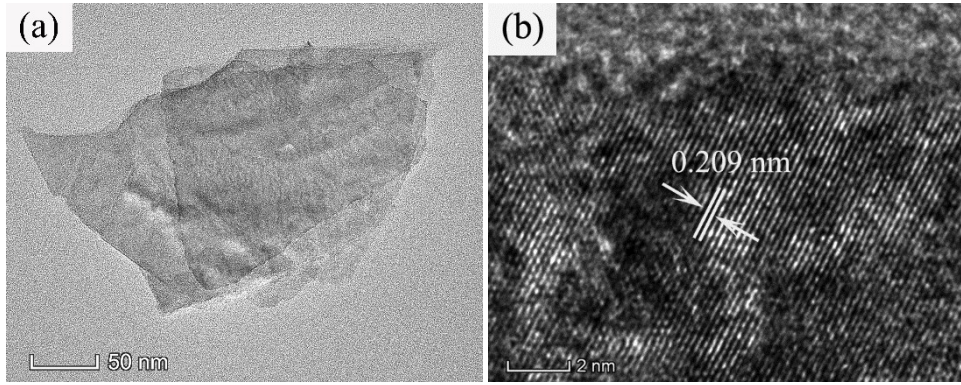


Figure S2 (a) TEM and (b) HRTEM images of CoMoO₄ nanosheet.

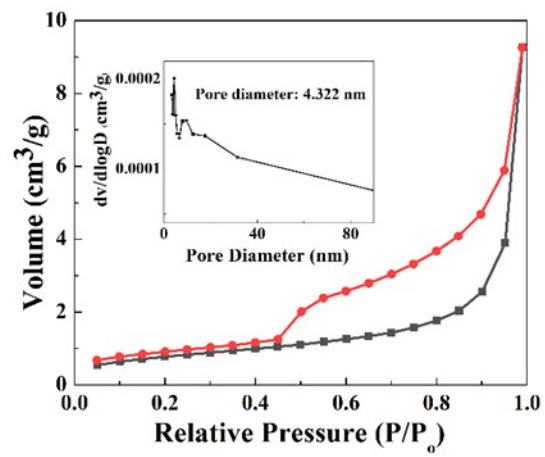


Figure S3 Nitrogen adsorption-desorption isotherm and pore size distribution curve of obtained N-COMoS₄.

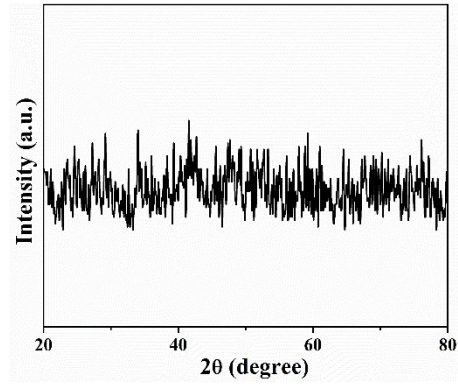


Figure S4 XRD pattern of N-CoMoS₄ obtained by the same procedure without using Ni foam.

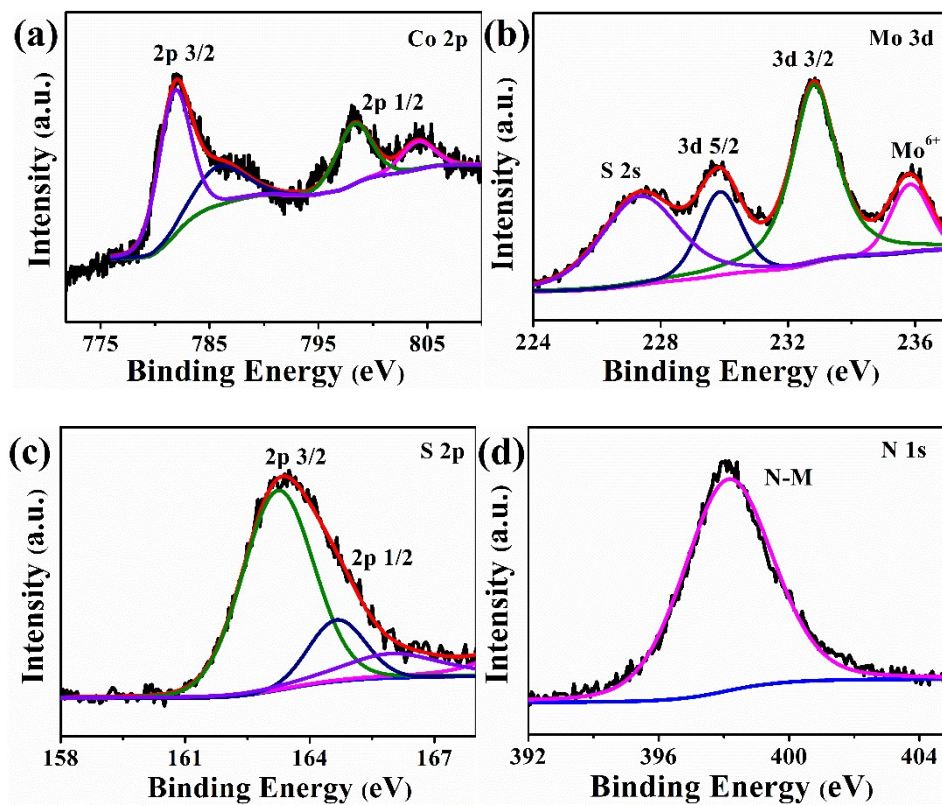


Figure S5 The deconvoluted core-level XPS spectra of (a) Co 2p, (b) Mo 3d, (c) S 2p and (d) N 1s in

N-CoMoS₄.

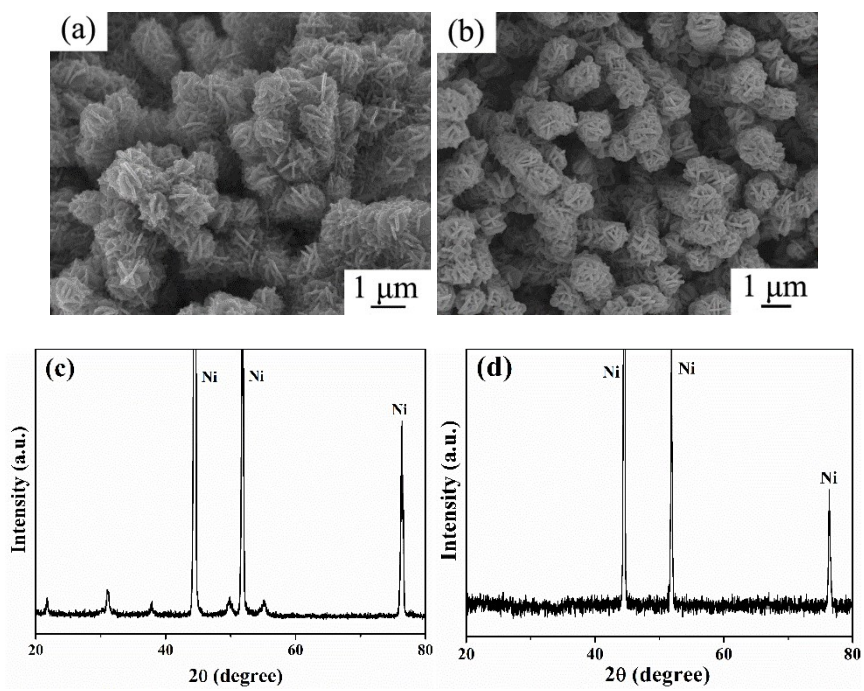


Figure S6 SEM images of (a) N-CoMoO₄ and (b) CoMoS₄ and corresponding XRD pattern in (c) and (d).

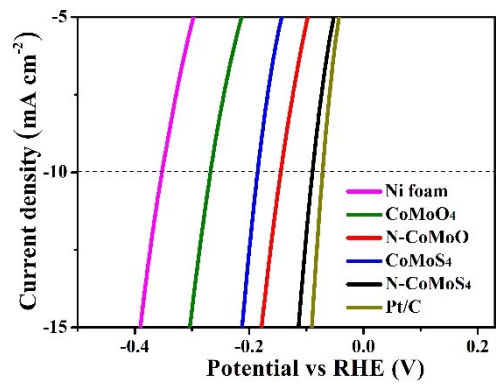


Figure S7 LSV curves of different electrocatalysts at the current density from -5 to -15 mA cm⁻².

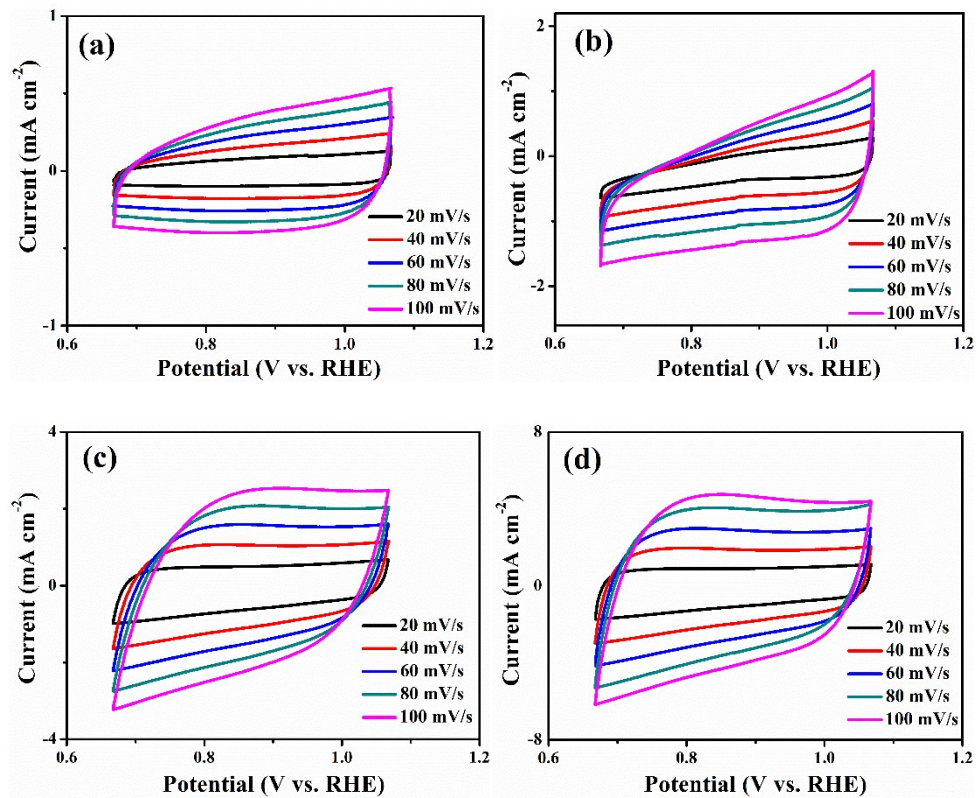


Figure S8 The cyclic voltammograms of (a) CoMoO₄, (b) N-CoMoO₄, (c) CoMoS₄ and (d) N-CoMoS₄.

Table S1 A comparative summary of HER activities of various electrocatalysts in 1 M KOH.

Materials	Overpotential At 10 mA cm ⁻²	Stability	Reference
Ni/N-CoMoS ₄			
hierarchical nanoarrays	95 mV	~85.0 % after 120 h	This work
Ni/CoMoS ₄			
hierarchical nanoarrays	146 mV	~44.3 % after 120 h	
C/CoMoS ₃			J. Mater. Chem. A,
Nanotubes	133 mV	~89.8. % after 10 h	2017, 5, 11309
Ni/Ni ₃ S ₂ /CoMoS ₄			J. Power. Sources
Nanosheet arrays	158 mV	~7.1 % after 10 h	2019, 416, 95
Ti/CoMoS ₄			J. Mater. Chem. A,
Nanosheet arrays	138 mV	---	2017,5, 16585
C/NiMoS ₄			Electrochim. Acta,
nanoparticles	191 mV	---	2016, 213, 236
C/CoMoS ₄			Nanoscale,
nanoparticles	143 mV	---	2016, 45, 18887
Ni/NiCo ₂ S ₄			Adv. Funct. Mater.
Nanowire arrays	210 mV	~13 % after 50 h	2016, 26, 4661
Ni/N-Ni ₃ S ₂ @C			Catal. Sci. Technol.
	113 mV	~94.5 % after 10 h	2019,9, 3099
Ni/N-Ni ₃ S ₂			Adv. Energ. Mater.
	155 mV	---	2018, 8, 1703538
CNT/P-CoFeS			Electrochimica Acta
	130 mV	~88 % after 50 h	2019, 318, 892

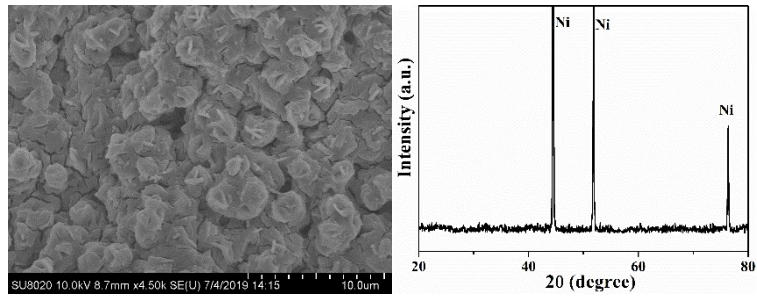


Figure S9 SEM image and XRD pattern of N-CoMoS₄ after stability test.

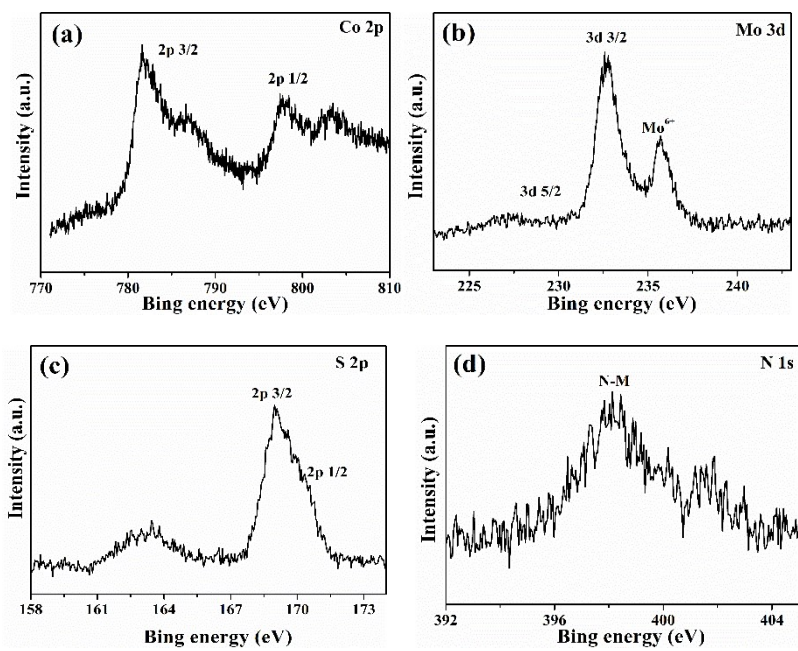


Figure S10 XPS spectra of N-CoMoS₄ after stability test.

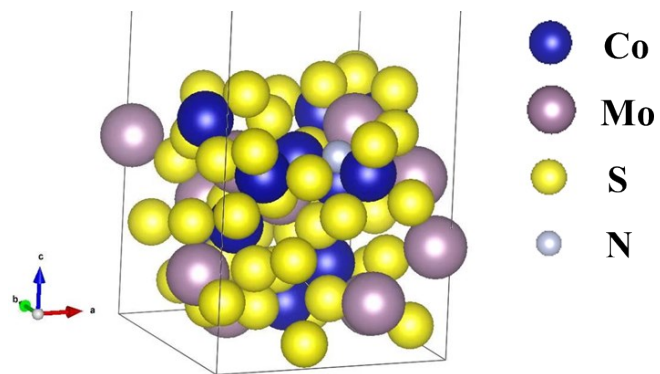


Figure S11 The side-view of the slab model of N-CoMoS₄.

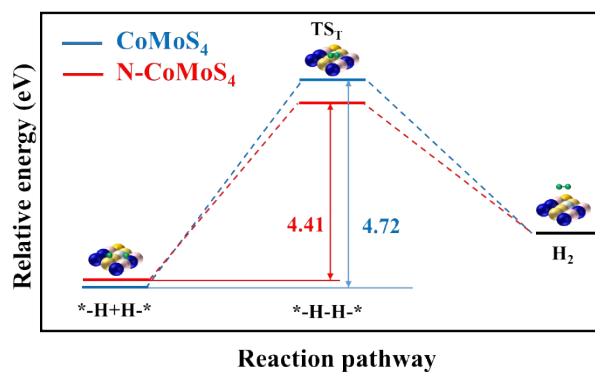


Figure S12 Energy barrier and the simplified surface structures of the Tafel process.

Recently work reveals that Mo-edges and Co-bonded S-edges are available active sites of CoMoS₄ for HER,^{1,2} thus the sluggish H* desorption behaviour from the metal edges is responsible for the unsatisfactory catalytic activity, which is also illustrated by the high energy barrier of H* desorption shown in Fig. 4. Because of the higher electronegativity of N, electrons are transport from metal to N from formed metal–N bonds, and decreases the electron density of nearby metal by electron redistribution, which has been confirmed by the positive shifts of their binding energies in Fig. 2. Since the electronic structure is critical to the adsorption strength of the intermediates that determine the reaction efficiency, decreased localized electron densities of metal sites weaken the interaction of adsorbed H (H*), and in turn facilitates the hydrogen desorption with increased HER efficiency.

[1] J. Bonde, P. G. Moses, T. F. Jaramillo, J. K. Nørskov and I. Chorkendorff, *Faraday Discussions*, 2009, **140**, 219-231.

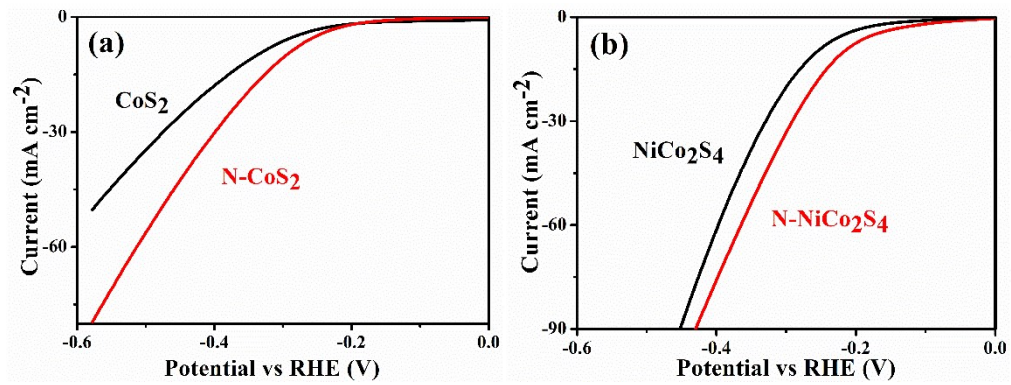


Figure S13 The LSV curves of (a) CoS₂ and N-CoS₂, (b) NiCo₂S₄ and N-NiCo₂S₄ towards HER in 1.0 M KOH solution at the scan rate of 5 mV s⁻¹.

Table S2 Compositional comparison of the electrolyte after HER reaction with different catalysts.

	Mo	Co	S
N-CoMoS ₄	1.270 mg/l	0.014 mg/l	2.23 mg/l
CoMoS ₄	5.363 mg/l	0.038 mg/l	2.60 mg/l