Supporting Information

Dissecting reconstructed anions in sulfides as a role in urea oxidation to maximize assisted hydrogen production

Weiwei Bao[a,1], Mameng Yang[a,1], Taotao Ai[a,*], Jie Han[a,*], Zhifeng Deng[a], Xiangyu Zou[a], Peng Jiang[a], Junjun Zhang[b]

[a]National and Local Joint Engineering Laboratory for Slag Comprehensive Utilization and Environmental Technology, School of Materials Science and Engineering, Shaanxi University of Technology, Hanzhong 723000, Shaanxi, PR China.

[b]State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry & Chemical Engineering, Ningxia University, Yinchuan 750021, Ningxia, PR China.

[1] These authors contributed equally to this work

Corresponding author at: School of Materials Science and Engineering, Shaanxi University of Technology, No. 1 Dongyihuan, Hantai District, Hanzhong 723000, PR China, 18691612234 (T. Ai)

E-mail addresses: aitaotao0116@126.com (T. Ai); 805160700@qq.com (J. Han).

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Experimental Procedures

1. Treatment of Ni foam

The nickel foam (NF, 1×4 cm) was immersed in 2 M hydrochloric acid, ethanol and distilled water, respectively, for ultrasonic treatment over 12 min. which was dried at 60 °C for 8 h. After cooling to room temperature, it was obtained.

2. Chemicals and Reagents

Thioacetamide (C_2H_5NS) comes from Shanghai Macklin Biochemical Technology Co., Ltd. Sodium molybdate dehydrate ($Na_2MoO_4 \cdot 2H_2O$) is purchased from Sinopharm Chemical Reagent Co., Ltd. Nickel foam (NF) is used as substrate. All these chemicals are used without further purification.

3. Electrochemical measurements.

All the electrochemical measurements were conducted in a standard three-electrode setup on a CHI 660E electrochemical workstation (Chenhua Instruments, Shanghai, China). The fabricated self-supported electrodes ($1×4×0.1$ cm^{-2}) were directly employed as working electrodes, while a graphite rod and an Hg/HgO (filled in 1 M KOH) electrode as the counter electrode and the reference electrode, respectively. Before Multiple cyclic voltammetry (CV) scans were firstly performed at a scan rate of 5 mV s^{-1} until reached a stable state of electrodes. Then, linear sweep voltammetry (LSV) was conducted with a scan rate of 5 mV s^{-1} in 1 M KOH solution. The electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range of 100 kHz to 0.01 Hz with an amplitude of 10 mV. The long-term stability was measured by chronocurrent method. All the polarization curves were corrected using 85% iR compensation. Potentials were referenced to the reversible hydrogen electrode (RHE): E vs. RHE = E vs. Hg/HgO + 0.098 + 0.059 pH. The overpotential (η) was calculated according to the following equation: η = E vs. RHE - 1.23 V. In order to obtain the effective electrochemical active surface area (ECSA) of the electrocatalyst, a series of cyclic voltammetry (CV) measurements were performed at different scanning rates. Geometric double layer capacitance (C_{dl}) is calculated by plotting the difference between current density (J) and scan rate to build a linear trend.

4. In situ Raman spectroscopy.

The in-situ device was placed on a Renishaw Raman microscope, the potential was controlled by an electrochemical workstation, and the Raman spectra were recorded by 532 nm laser excitation. In situ device electrolytic cell is made of polytetrafluoroethylene, through the large pool, small pool, electrolyte and pump to form a closed loop, the top with a round quartz glass as a protective cover to protect the objective lens, the working electrode is facing the quartz glass, so that the laser is vertically incident, before the test should increase the pump rate, the circulation of bubbles clean, avoid blocking the light path, after stabilizing, reduce the speed for testing. The Hg/HgO electrode with 1.0 M KOH internal reference electrolyte was used as the reference electrode.

5. Theoretical calculations.

All the calculations were performed with the Vienna Ab initio Simulation Package (VASP) based on the density-functional theory (DFT). We use DFT to help understand the reaction mechanism. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional is used, and the long-range van der Waals interaction is considered using the DFT-D3 method, the cut off energy is 500 eV, and the K point is $3 \times 2 \times 1$. A 4×4 supercell model was constructed using $Ni(OH)_2$ (112) surfaces. A 15 Å vacuum is used along the z direction to avoid interaction between periodic images. The convergence criteria for electrons and ions are 10^{-7} eV energies and 0.05 eV A^{-1} forces to ensure adequate accuracy.

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Figure S2. SEM images of Mo_{31}-Ni_3S_2 (a, b), Mo_{65}-Ni_3S_2 (b, c) and Mo_{82}-Ni_3S_2 (e, f) at different magnifications.
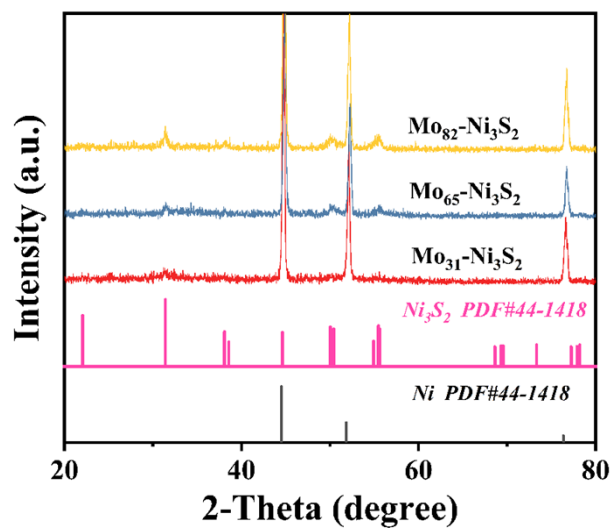
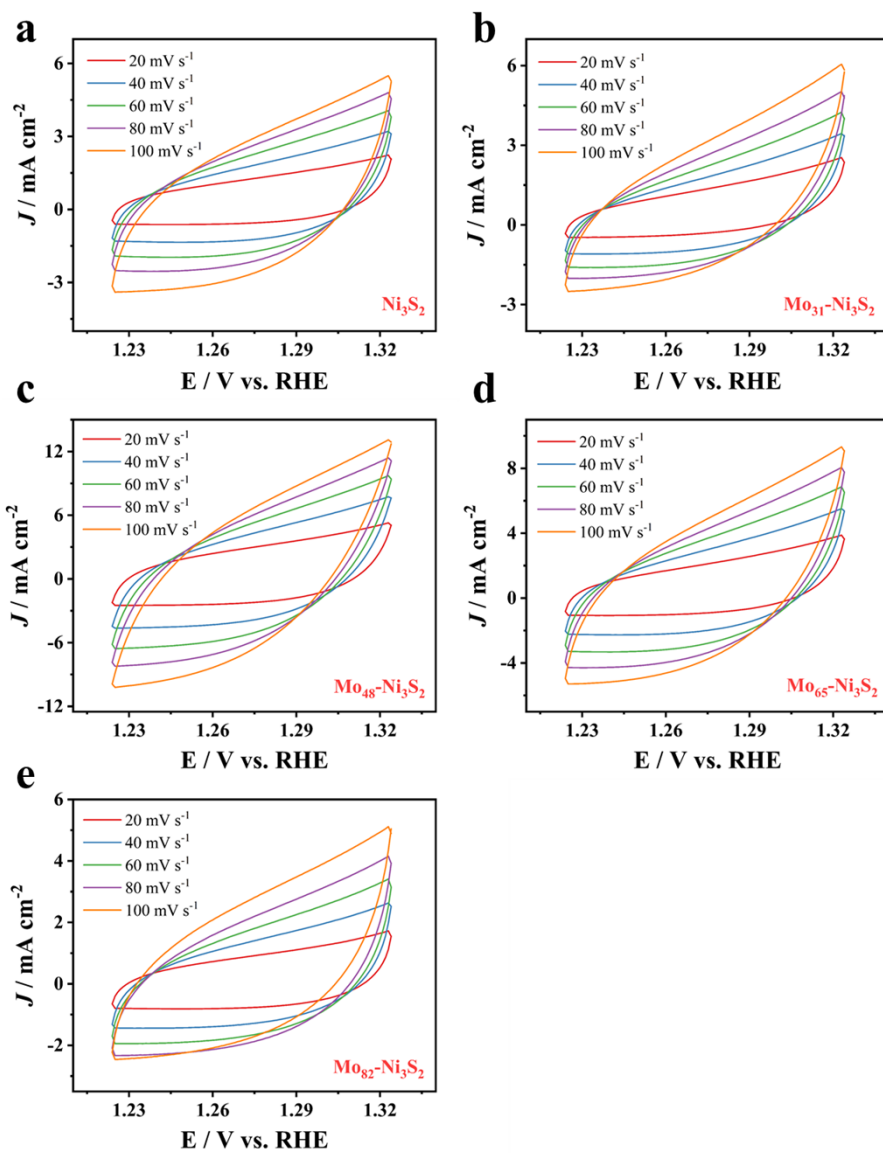**Figure S3.** XRD pattern of Mo_x-Ni_3S_2 samples with different doping ratios.

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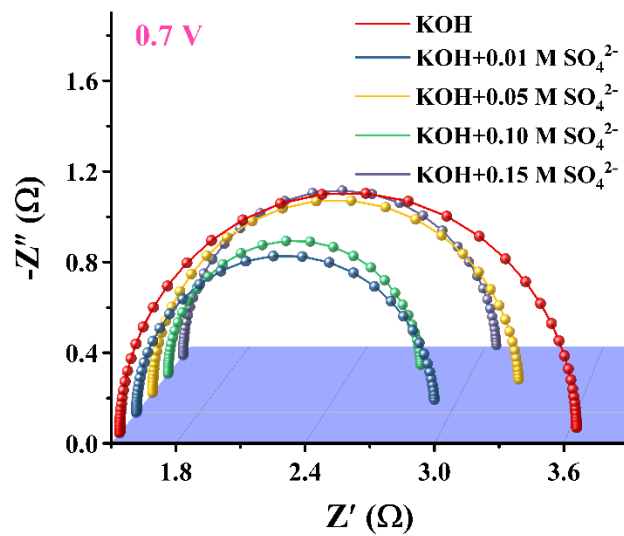**Figure S10.** Stability of $Ni(OH)_2$ in the presence of 0.1 M MoO_4^{2-} at the potential of 0.86 V.

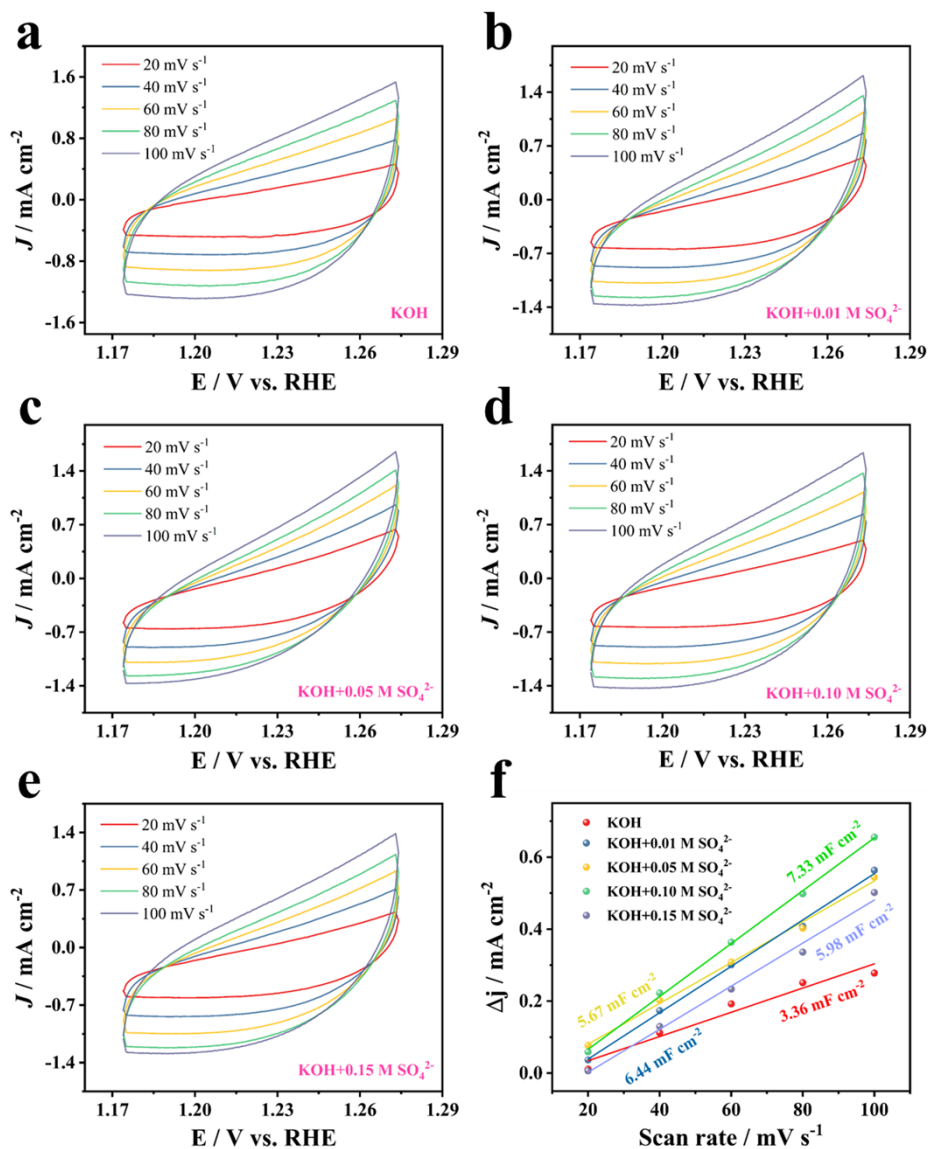**Figure S11.** EIS plots for different concentrations of SO_4^{2-} added to $Ni(OH)_2$.

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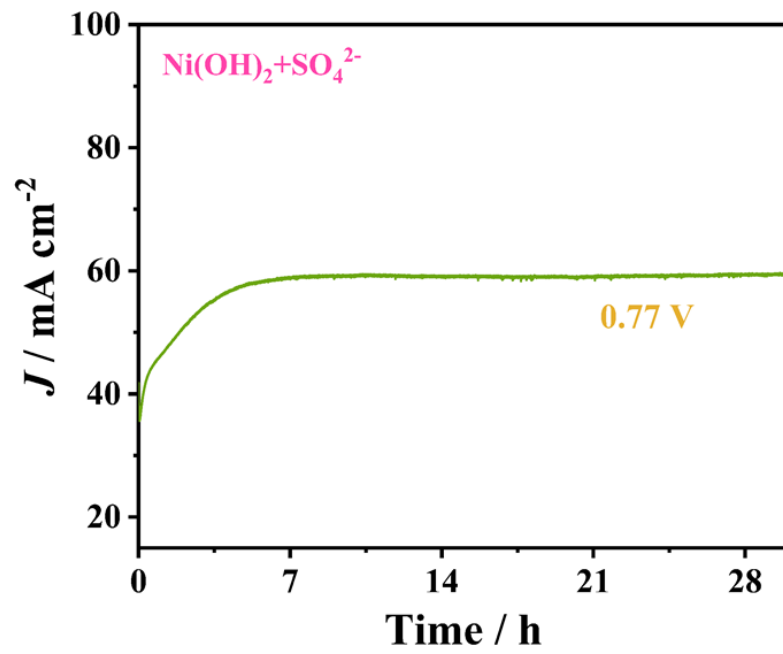
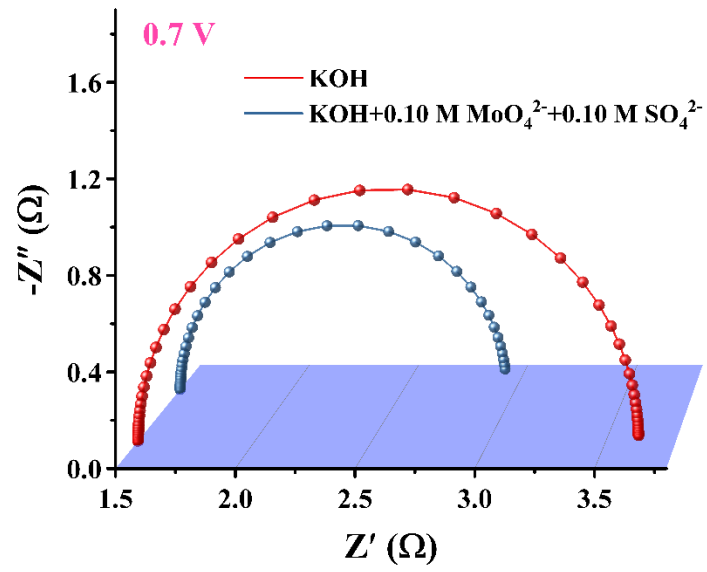**Figure S13.** Stability of Ni(OH)$_2$ in the presence of 0.1 M SO$_4^{2-}$ at the potential of 0.77 V.

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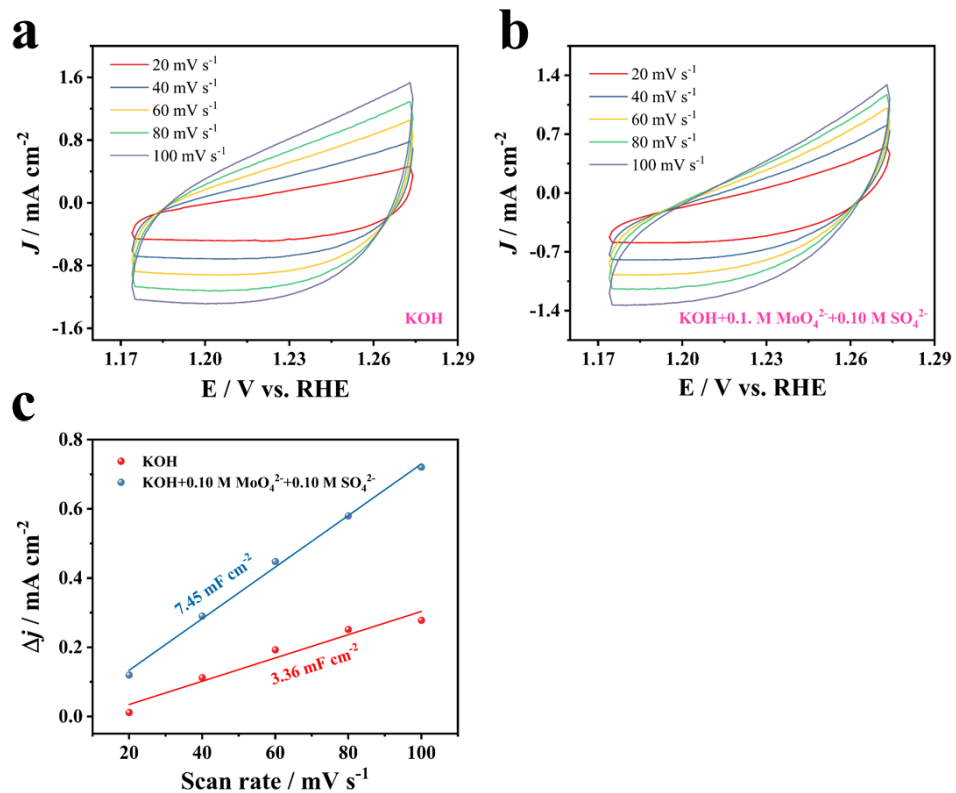
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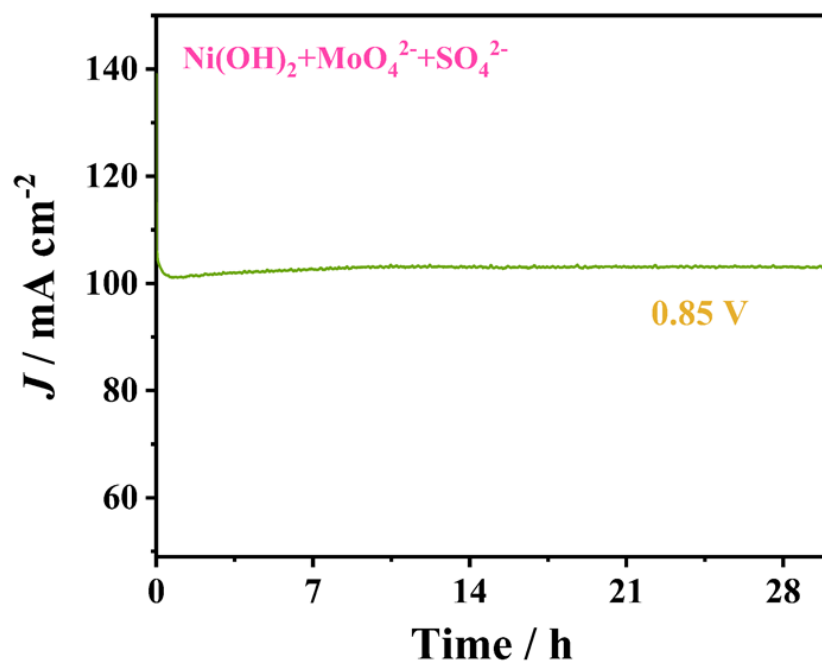
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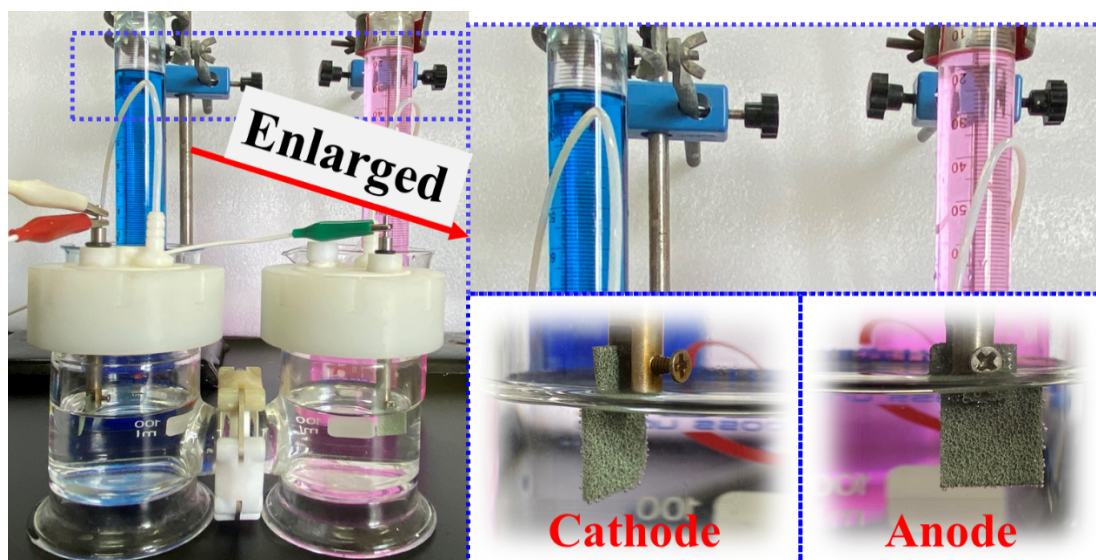
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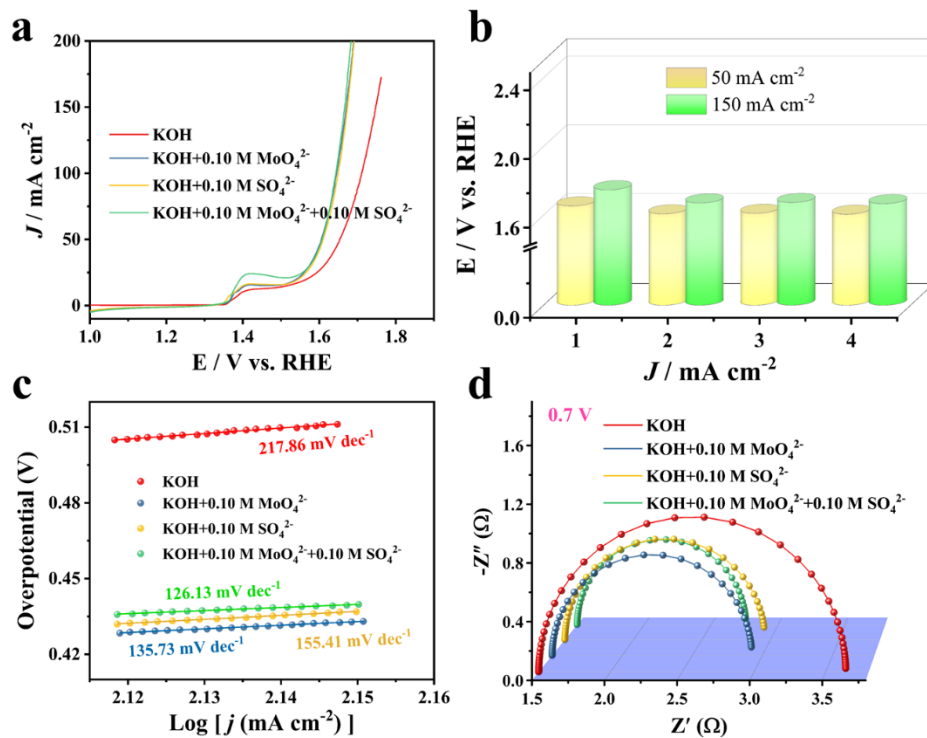
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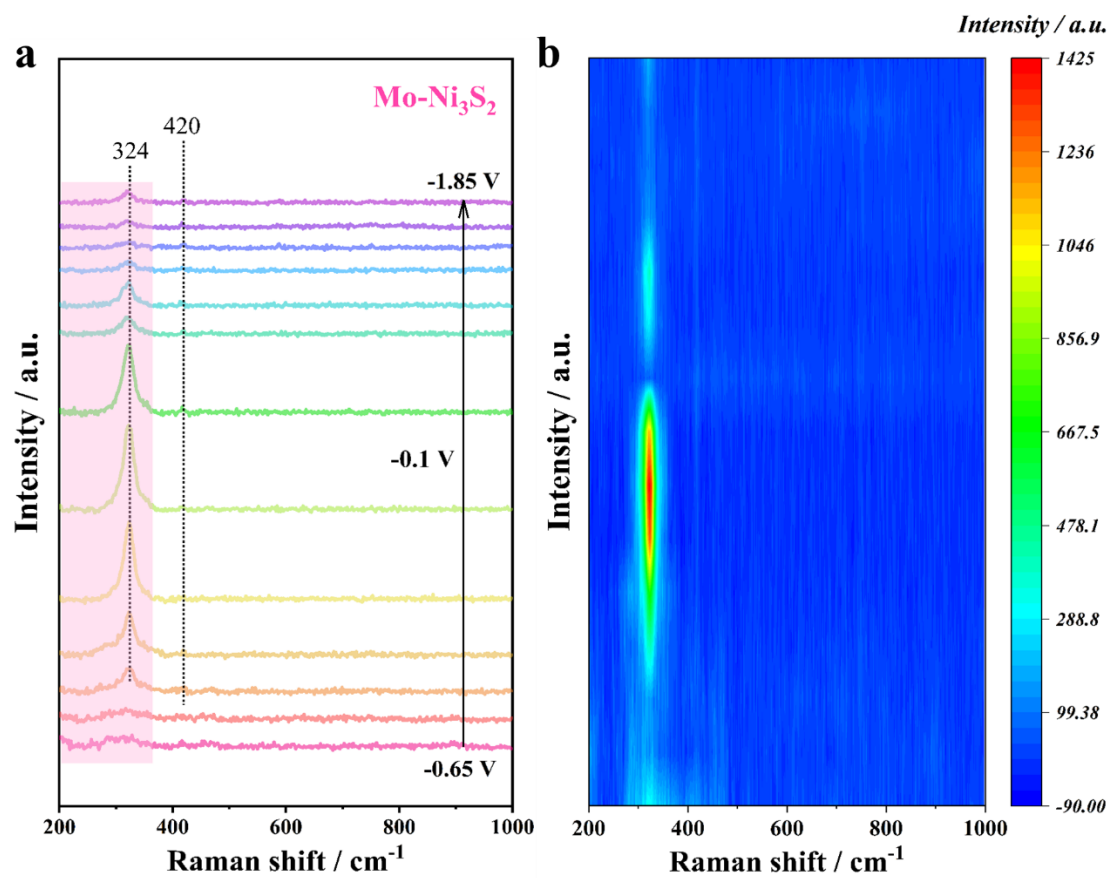
Figure S25. (a) in-situ Raman spectra of Mo_{48}-Ni_3S_2 in the HER process; (b) In situ Raman contour map.

Table S1. Comparison of UOR performances for Mo_{48}-Ni_3S_2 with various reported electrocatalysts in the alkaline media with urea.

electrocatalysts	electrolyte	Potential at 100 mA cm^{-2} (V)	Ref.
Fe-Ni_3S_2@FeNi$_3$-8	1.0 M KOH+ 0.33 M Urea	1.45	1
Ni_2P/Fe_2P/NF	1.0 M KOH+ 0.5 M Urea	1.46	2
NiS@Ni_3S_2@$NiMoO_4$	1.0 M KOH+ 0.5 M Urea	1.45	3
P-$CoNi_2S_4$	1.0 M KOH+ 0.5 M Urea	1.56	4
O-NiMoP/NF	1.0 M KOH+ 0.5 M Urea	1.41	5
NiS_2-MoS_2	1.0 M KOH+ 0.33 M Urea	1.54	6
Mn-Ni_3S_2/NF	1.0 M KOH+ 0.5 M Urea	1.4	7
Mo_{48}-Ni_3S_2	1.0 M KOH+ 0.5 M Urea	1.37	This work

Table S2. Measured pH of 1.0 M KOH with the addition of different concentrations of MoO_4^{2-}.

	KOH	+0.01 MoO_4^{2-}	+0.05 MoO_4^{2-}	+0.10 MoO_4^{2-}	+0.15 MoO_4^{2-}
1st	13.59	13.58	13.56	13.56	13.57
2nd	13.60	13.57	13.55	13.58	13.58
3rd	13.58	13.59	13.58	13.59	13.59
Average	13.59	13.58	13.56333	13.57667	13.58

Table S3. Measured pH of 1.0 M KOH with the addition of different concentrations of SO_4^{2-}.

	KOH	+0.01 SO_4^{2-}	+0.05 SO_4^{2-}	+0.10 SO_4^{2-}	+0.15 SO_4^{2-}
1st	13.56	13.54	13.56	13.57	13.53
2nd	13.55	13.57	13.58	13.54	13.54
3rd	13.58	13.58	13.54	13.56	13.55
Average	13.56333	13.56333	13.55667	13.55667	13.54

Table S4. Comparison of HER performances for Mo_{48}-Ni_3S_2 with various reported electrocatalysts in the alkaline media with urea.

electrocatalysts	electrolyte	Potential at 100 mA cm^{-2} (mV)	Ref.
$Ni_3S_2@Ni_9S_8$	1.0 M KOH	262	8
CoP-InNC@CNT	1.0 M KOH	293	9
Mo_2N-Mo_2C/NC-500	1.0 M KOH	165	10
1T-MoS_2/$Ni^{2+\delta}O_\delta(OH)^{2-\delta}$(1:1)	1.0 M KOH	175	11
Mo_2C@NPC	1.0 M KOH	178	12
VMS_2	1.0 M KOH	257	13
He_{1e13}-$MoSe_2$-A	1.0 M KOH	198	14
Mo_{48}-Ni_3S_2	1.0 M KOH	159.7	This work

Table S5. The potential required for a noble metal-based electrocatalyst in 0.5 M urea solution at 10 mA cm^{-2} has recently been reported.

electrocatalysts	electrolyte	Potential at 10 mA cm^{-2} (mV)	Ref.
Ni(OH)S/NF	0.5 M Urea	1.36	15
P-CoNi$_2$S$_4$	0.5 M Urea	1.4	4
NiS@Ni$_3$S$_2$/NiMoO$_4$	0.5 M Urea	1.41	3
Ni-Mo nanotube	0.5 M Urea	1.43	16
Ni-S-Se/NF	0.5 M Urea	1.47	17
Ni$_2$P/Fe$_2$P/NF	0.5 M Urea	1.48	2
Mo$_{48}$-Ni$_3$S$_2$	0.5 M Urea	1.34	This work

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sulfoselenide for efficient electrochemical urea-assisted hydrogen production in alkaline media, *Nano Energy*, 2021, **81**, 105605.