Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Bimetallic doping Engineering into Ni_3S_2 Nanosheet Originated from NiFe Layered Double Hydroxide for Efficient Overall Water Splitting

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Experimental

Materials

$Ni(NO_3)_2\cdot 6H_2O$, $FeCl_2\cdot 4H_2O$, urea, NH_4F, Na_2MoO_4, Cysteine, N-Methyl pyrrolidone (NMP), and KOH are all purchased from Tianjin Fengchuan chemical reagent technology Ltd. IrO_2 is purchased from Aladdin. Pt/C(20ωt.%) is purchased from Johnson Matthey. Deionised water is used to prepare all solutions.

Preparation of NiFe-LDH/NF

Firstly, the Ni foam (2 cm×3 cm) used to be washed in 3 M HCl, deionized water, and ethanol with the assistance of ultrasonication each for 15 min. Then, $Ni(NO_3)_2\cdot 6H_2O$ (1 mmol), $FeSO_4\cdot 4H_2O$ (0.3 mmol), urea (5 mmol) and NH_4F (2 mmol) are added to a mixture of H_2O (11 mL) and ethanol (2 mL), and stir for 30 minutes at room temperature. The prepared NF is immersed into the above solution. The mixture is poured into a 20 mL autoclave and kept at 120 °C for 8 hours. The sample is rinsed with ethanol and deionized water after the hydrothermal reaction and dried in a vacuum oven at 60 °C.

Preparation of Fe-Ni_3S_2/NF

In general, 121.2 mg of cysteine and 15 mL of NMP is mixed by sonication for 30 minutes. The prepared NiFe-LDH/NF is immersed in the above solution. Then, the mixture is poured into a hydrothermal reactor with a capacity of 20 mL. The hydrothermal reactor is then placed in an oven at 200 °C for 20 hours. The sample is rinsed with ethanol and deionized water and dried in a vacuum oven at 60 °C.

Preparation of Fe, Mo-Ni_3S_2/NF

Fe, Mo-Ni_3S_2/NF is synthesized in a similar way to Fe-Ni_3S_2/NF. 121.2 mg of cysteine and 61 mg of Na_2MoO_4 are added to 15 mL of NMP and sonicated for 30 minutes. The prepared NiFe-LDH/NF is immersed in the above solution. Then, the mixture is poured into a hydrothermal reactor with a capacity of 20 mL. The hydrothermal reactor is then placed in an oven at 200 °C for 20 hours. The sample is rinsed with ethanol and deionized water and dried in a vacuum oven at 60 °C.

Preparation of Pt/C (20 ωt.%)/NF

The 5 mg of Pt/C (20 ωt.%) is added to a mixed solution of 20 microliters of Nafion (5%), 240 microliters of deionized water, and 240 microliters of anhydrous ethanol solution to form ink. Then the ink is evenly spread on the NF (Geometric Area: 1.0 cm^2).

Preparation of IrO_2/NF

The 5 mg of IrO_2 and 5 mg of graphene are added to a mixed solution of 20 microliters of Nafion (5%), 240 microliters of deionized water, and 240 microliters of anhydrous ethanol solution to form ink. Then the ink is evenly spread on the NF (Geometric Area: 1.0 cm^2).

Material characterization

The crystallinity and crystal structure of the synthesised catalysts are characterised by powder X-ray diffraction instrumentation. The instrument model used is the PAN analytical Empyrean XRD system. A high-resolution transmission electron microscope for characterisation the morphology, size, and element distribution of the synthesized catalyst. The instrument model is FEI Tecnai F20. X-ray photoelectron spectroscopy (XPS) is applied to characterize the element valence, surface composition, and relative content of each element of the synthesized catalyst. The instrument model used is XSAM800 photoelectron spectrometer. The Raman beam is detected on a Raman spectrometer (Renishaw in Via plus) with a 532 nm laser wavelength. The scanning electron microscopy (SEM) is performed on a JEOLJSM 6700-F scanning electron microscope. The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images are taken on the JEM-2010 transmission electron microscope system. The Park system is used for atomic force microscopy (AFM).

Electrochemical measurements

Electrochemistry is tested in a typical three-electrode system. The synthesized catalyst is used as the working electrode, the carbon rod is used as the counter electrode, and the Hg/HgO electrode is used as the reference electrode (CHI 760E, Inc. Shanghai). The electrocatalytic activity of OER, HER, and overall water splitting are tested by using linear scanning voltammetry (LSV) at room temperature at a scan rate of 5 $mV \cdot s^{-1}$ in 1.0 M KOH and corrected for the automatic iR compensation (90%). EIS data are recorded at open-circuit potentials. Stability is measured by cyclic voltammetry and amperometric i-t curve. The electrochemical double layer capacitance (C_{dl}) is also determined by cyclic voltammetry (CV). The electrochemically active surface area can be assessed by the slope of the charge current versus scan rate curve, which is proportional to C_{dl}. All potentials in the article have been converted to hydrogen electrodes ($E_{RHE} = 0.059*pH + E^0_{(Hg/HgO)} +$

$E_{(Hg/HgO)}$). The Faraday efficiency is measured by comparing the experimentally measured and theoretically calculated amount of gas. The Faraday yield is calculated from the total amount of oxygen produced (n_{O_2}: mmol) and the total amount of charge Q (C) passing through the cell. Suppose four electrons are required to produce O_2 molecule, the faradaic efficiency = 4F × $\frac{n_{O_2}}{Q}$ = 4F × n_{O_2}×10/t, where Q = t × 0.1 (C), F is the Faraday constant, and t represents the time (s) for the test time. The overall quantity of oxygen produced during the test is calculated by means of drainage.

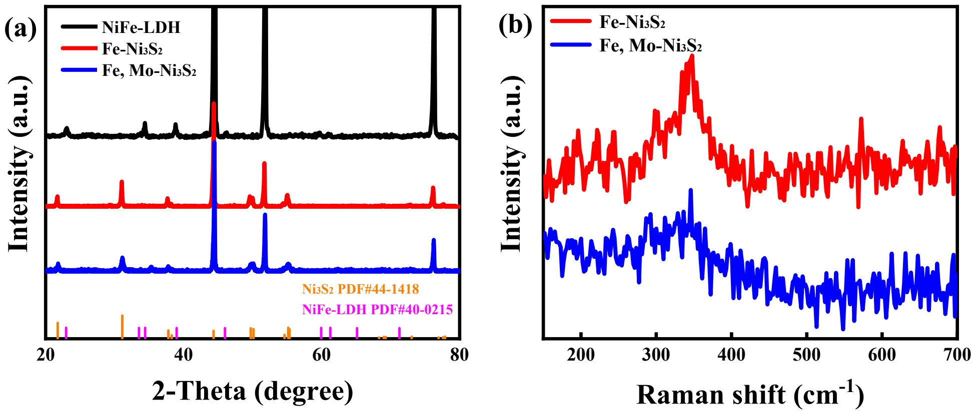

Fig. S1. (a) XRD and (b) Raman spectrum patterns of NiFe-LDH, Fe-Ni_3S_2, and Fe, Mo-Ni_3S_2 catalysts.

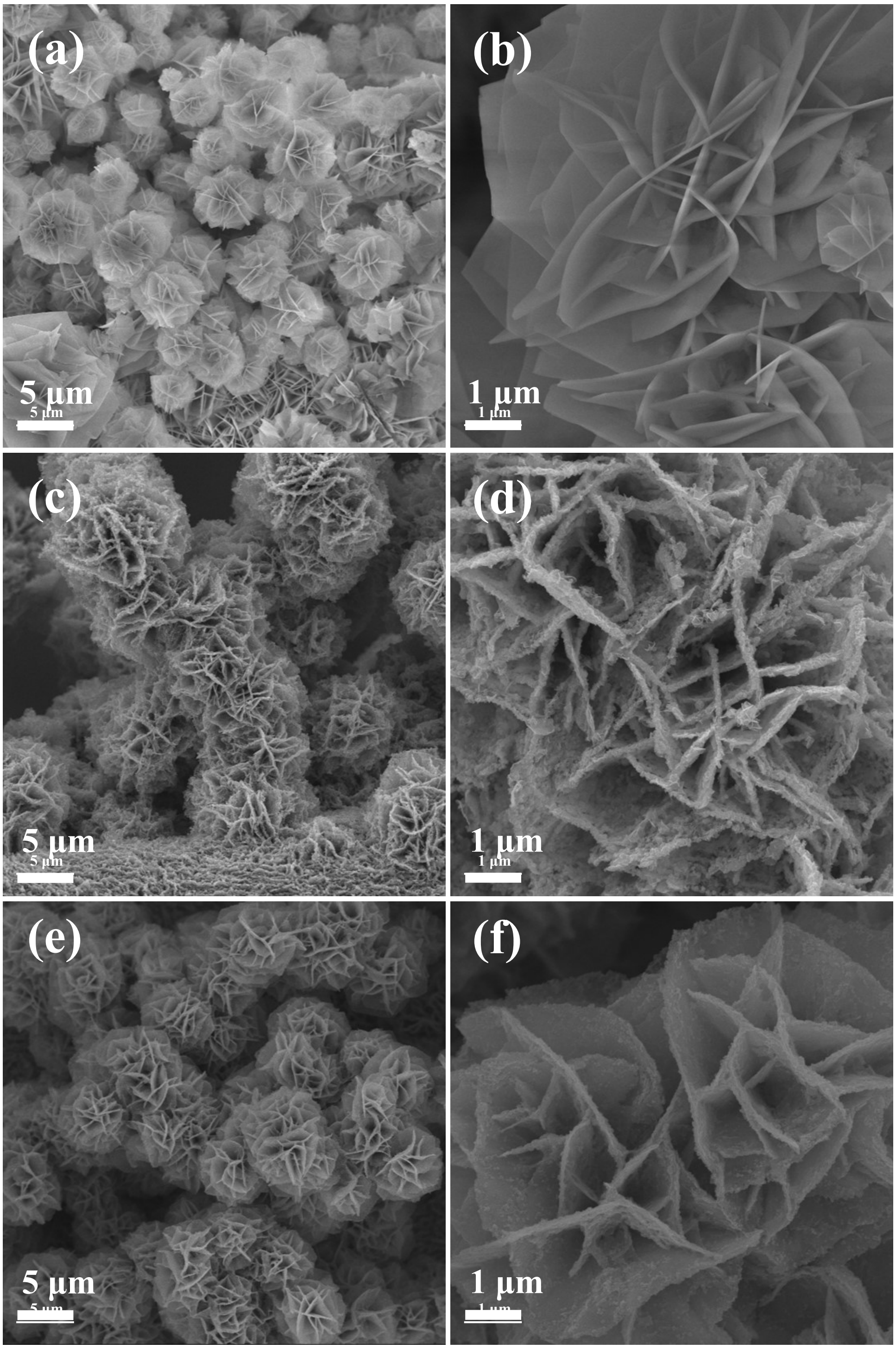

Fig. S2. SEM images with different magnifications of (a, b) NiFe-LDH, (c, d) Fe-Ni_3S_2, and (e, f) Fe, Mo-Ni_3S_2.

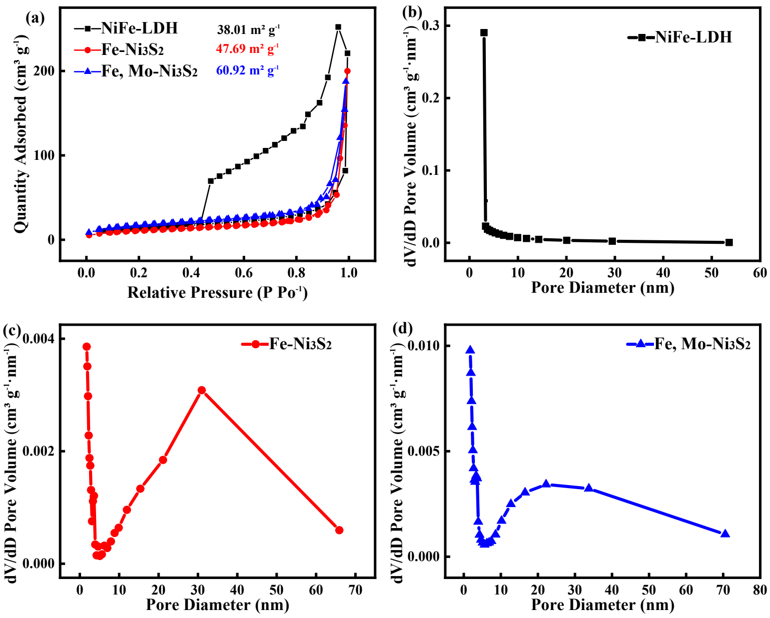

Fig. S3. (a) Nitrogen adsorption-desorption isotherms of different catalysts, pore size distribution of (b) NiFe-LDH, (c) Fe-Ni_3S_2, (d) Fe, Mo-Ni_3S_2.

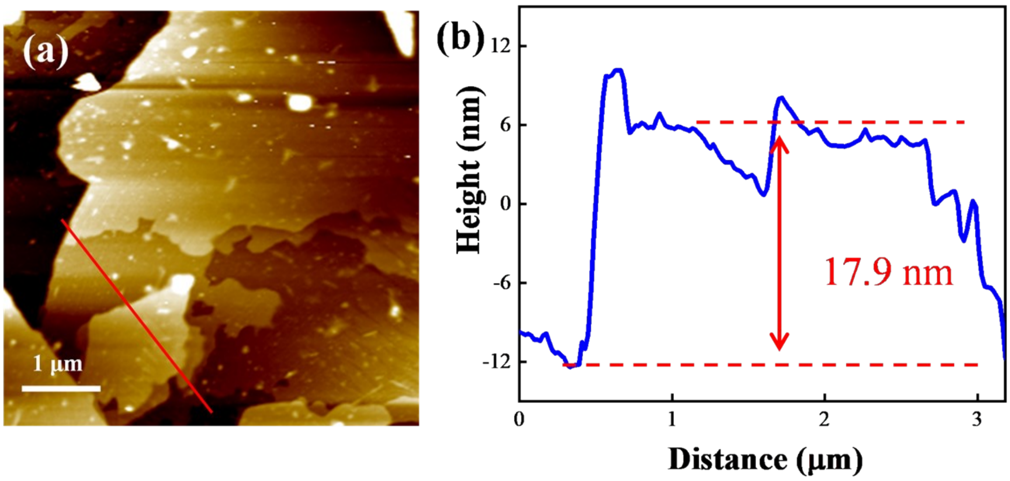

Fig. S4. AFM images of NiFe-LDH.

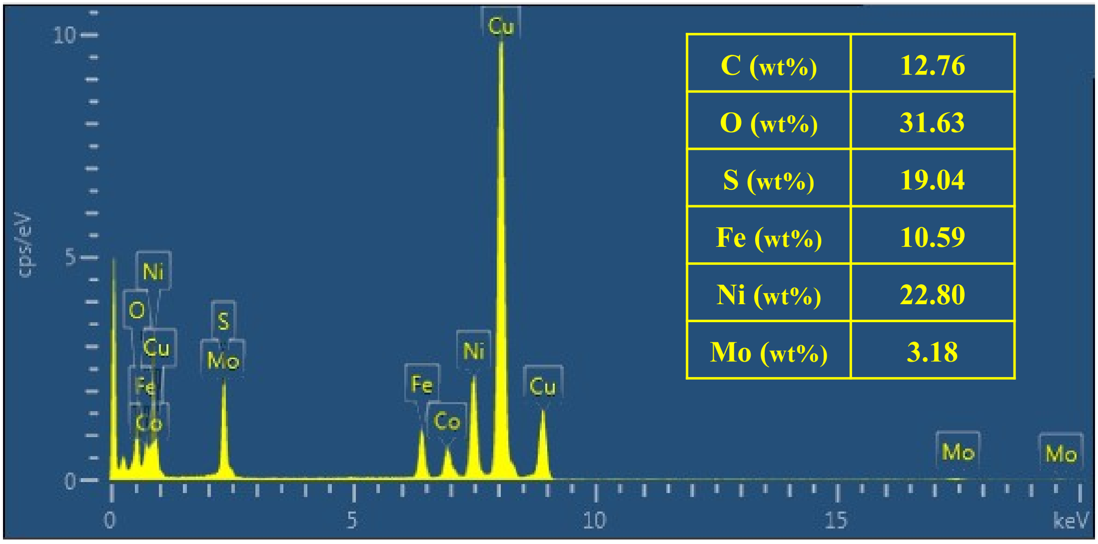

Fig. S5. EDS spectrum of Fe, Mo-Ni_3S_2 sample.

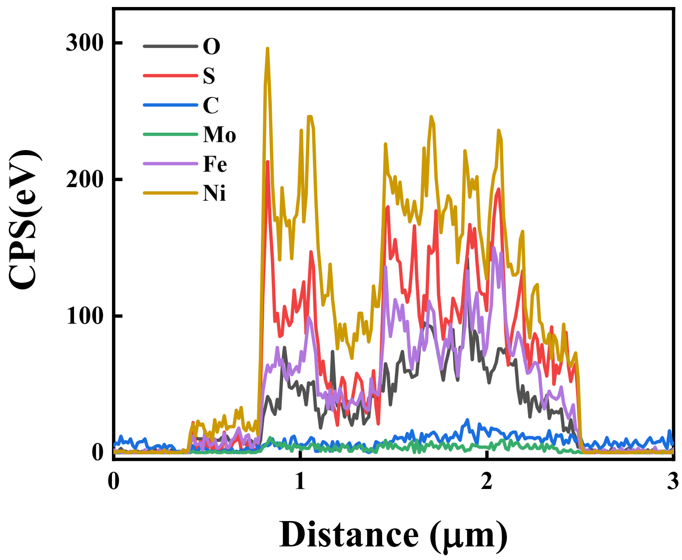

Fig. S6. EDS line scan profiles of Fe, Mo-Ni_3S_2.

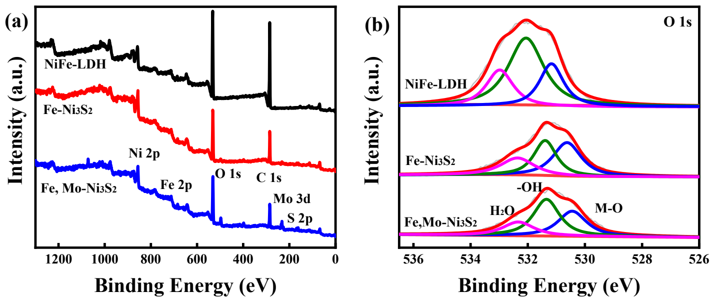

Fig. S7. XPS spectra of NiFe-LDH, Fe-Ni_3S_2, and Fe, Mo-Ni_3S_2 catalysts (a) full spectrum, (b) O 1s, and (c) C 1s.

Table S1. The atomic percentage of different elements in various catalysts.

	Ni (at.%)	Fe (at.%)	S (at.%)	O (at.%)	C (at.%)	Mo (at.%)
NiFe-LDH	4.05	1.51	0	27.83	66.61	0
Fe-Ni_3S_2	8.45	3.23	5.67	33.42	49.24	0
Fe, Mo-Ni_3S_2	8.03	3.4	7.45	36.05	42.96	2.12

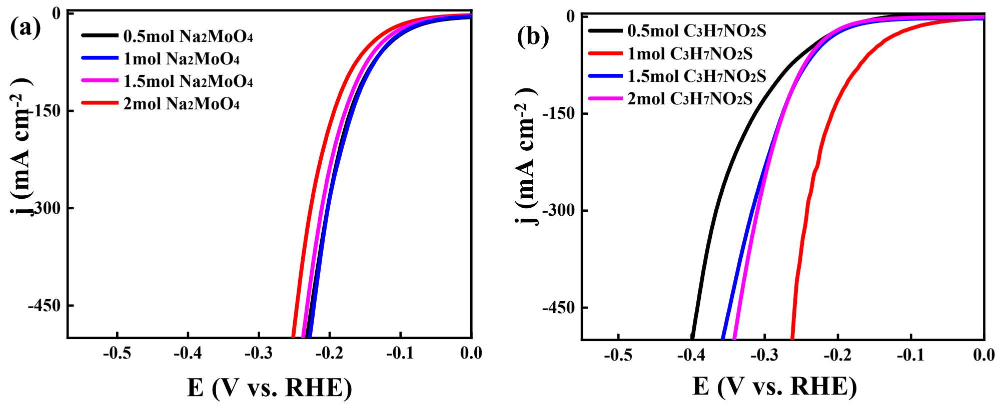

Fig. S8. HER polarization curves of catalysts prepared under different conditions.

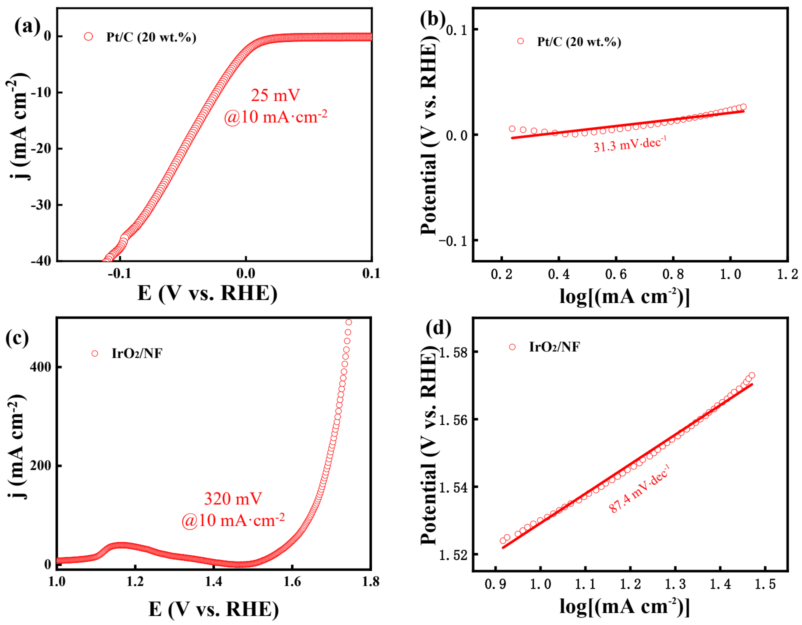

Fig. S9. (a) HER polarization curves of Pt/C/NF (20 wt.%) and (c) OER polarization curves of IrO_2/NF; (b, d) the corresponding Tafel slopes.

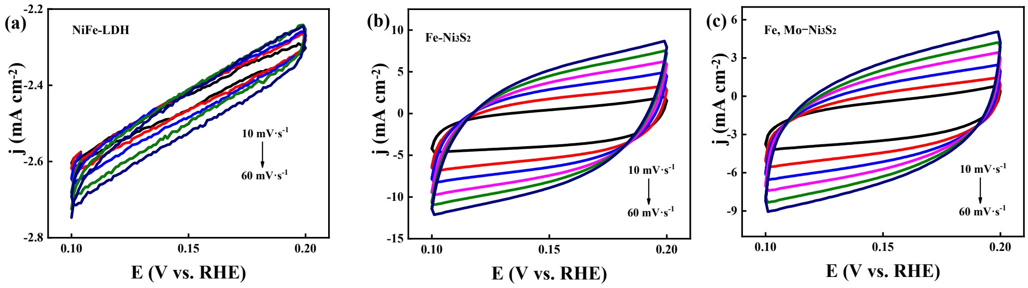

Fig. S10. (a-c) CV curves under different scanning speeds for NiFe-LDH, Fe-Ni_3S_2, and Fe, Mo-Ni_3S_2 in 1.0 M KOH solution of HER.

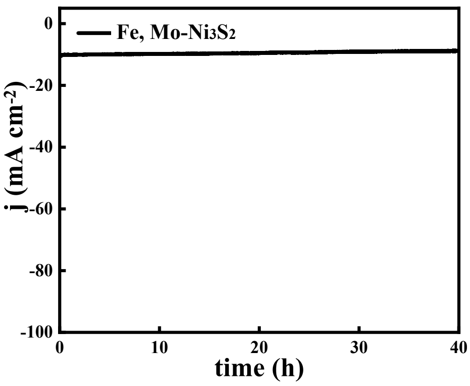

Fig. S11. I-t curves for the Fe, Mo-Ni_3S_2 in 1.0 M KOH solution of HER.

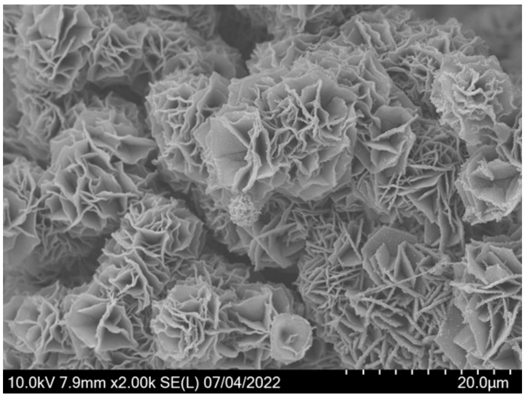

Fig. S12. SEM images of Fe, Mo-Ni_3S_2 catalysts after HER stability test.

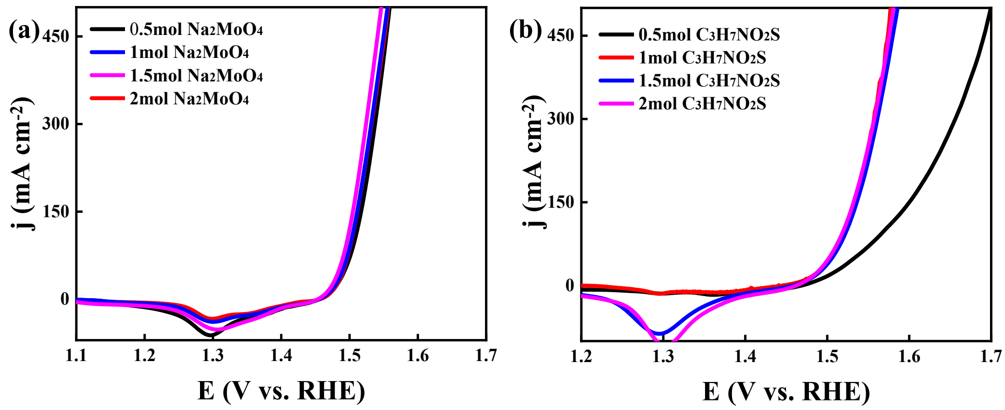

Fig. S13. OER polarization curves of catalysts prepared under different conditions.

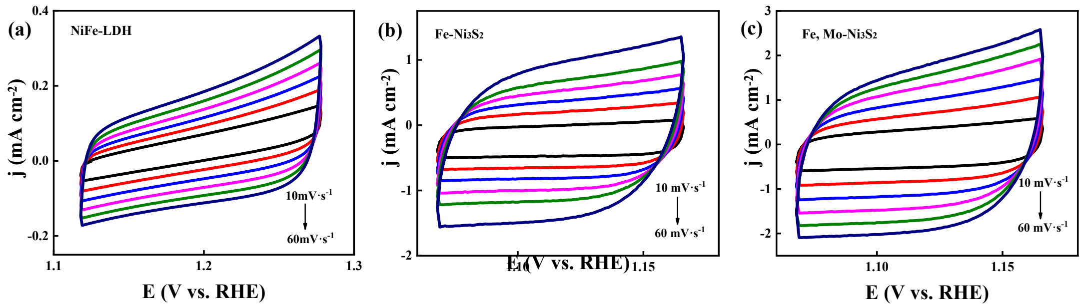

Fig. S14. (a-c) CV curves under different scanning speeds for NiFe-LDH, Fe-Ni_3S_2, and Fe, Mo-Ni_3S_2 in 1.0 M KOH solution of OER.

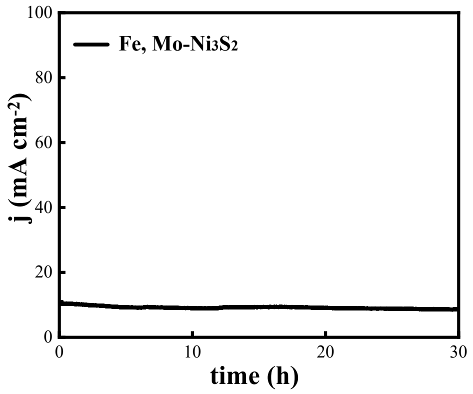

Fig. S15. I-t curves for the as-prepared samples in 1.0 M KOH solution of OER.

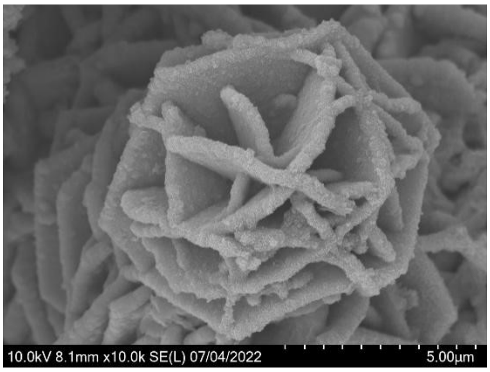

Fig. S16. SEM images of Fe, Mo-Ni_3S_2 catalysts after OER stability test.

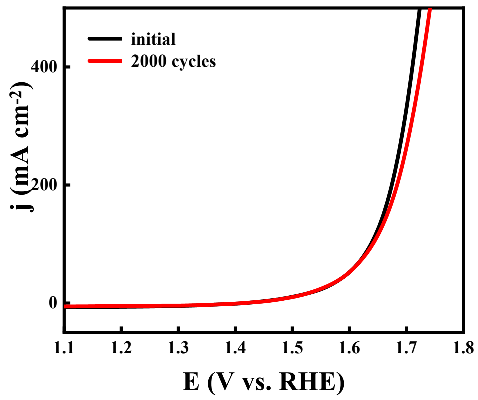

Fig. S17. The CV scanning of overall water splitting before and after 2000 cycles.

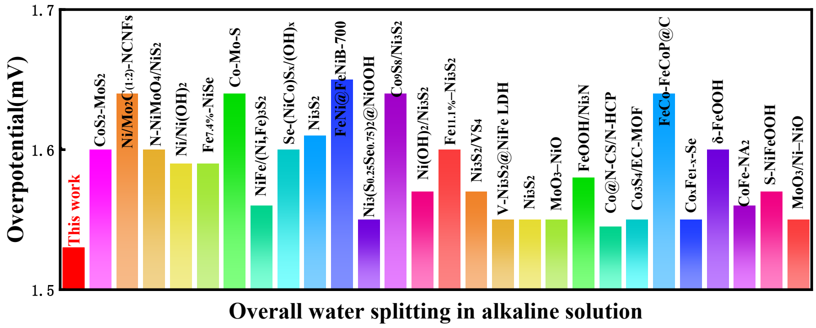

Fig. S18. Comparison of recently reported catalysts for overall water splitting.

Table S2. Summary of representative catalysts that have been recently reported in alkaline medium of HER in 1.0 M KOH.

Catalyst	**η (mV)@j (mA cm^{-2})**	**Substrate**	**Reference**
Fe, Mo-Ni_3S_2	67@10	Ni foam	This work
$NiCo_2S_4$	80@10	Ni foam	*Adv. Funct. Mater.,* **2019**, 29, 1807031
Se-$(NiCo)S_x/(OH)_x$	103@10	Ni foam	*Adv. Mater.,* **2018**, 30, 1705538
NiFe LDH@NiCoP	120@10	Ni foam	*Adv. Funct. Mater.,* **2018**, 28, 1706847
CoV/CF-CWs	118@10	Cu foam	*Adv. Funct. Mater.,* **2021**, 31, 2008822
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	92@10	Cu foam	*Adv. Mater.,* **2018**, 30, 1802121
CoP/NPC/TF	80@10	Ti foam	*Adv. Energy Mater*., **2019**, 1803970
Co-NiS_2 NSs	80@10	Ni foam	*Angew. Chem. Int. Ed.,* **2019,** 58, 18676-18682
Cu@NiFe LDH	116@10	Cu foam	*Energy Environ. Sci.*, **2017**, 10, 1820
CoNx@GDY NS	70@10	Ni foam	*Nano Energy*, **2019**, 59, 591-597
TiO_2@CoCH	96@20	carbon paper	*Nano Energy*, **2021,** 82, 105732
Ni_2P/Ni_3S_2	80@10	Ni foam	*Nano Energy*, **2018,** 51, 26
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	92@10	carbon cloth	*Adv. Mater.* **2018**, 30, 1802121
NFN-MOF/NF	87@10	Ni foam	*Adv. Energy Mater*. **2018**, 1801065
Co_3S_4/EC-MOF	84@10	carbon cloth	*Adv. Mater.* **2019**, 31, 1806672
δ-FeOOH	108@10	Ni foam	*Adv. Mater.* **2018**, 30, 1803144
CoMnCH/NF	180@10	Ni foam	*J. Am. Chem. Soc.*, **2017**, 139, 8320-

			8328
CoFe-NA$_2$/NF	73@10	Ni foam	*J. Energy Chem.*, **2022**, 65, 405-414
Co$_{0.9}$Fe$_{0.1}$-Se/NF	125@10	Ni foam	*J. Energy Chem.*, **2021**, 60, 194-201
NiCo-MoS$_2$	153@10	carbon cloth	*J. Energy Chem.*, **2021**, 57, 587-592
Ni-Ni(OH)$_2$	72@10	Ni foam	*J. Energy Chem.*, **2021**, 61, 236-242
(VO)$_2$P$_2$O$_7$-Ni$_2$P@NF	154@10	Ni foam	*J. Energy Chem.*, **2022**, 65, 674-680
MoS$_2$-AB/NF	77@10	Ni foam	*Nano Energy,* **2022**, 92, 106707

Table S3. Summary of representative catalysts that have been recently reported in alkaline medium of OER in 1.0 M KOH.

Catalyst	**η (mV)@j (mA cm^{-2})**	**Substrate**	**Reference**
Fe, Mo-Ni_3S_2	240@10	Ni foam	This work
LC-CoOOH NAs	290@10	carbon cloth	*ACS Catal.*, **2021**, 11, 6104-6112
Ni_3FeN	270@10	Ni foam	*ACS Nano*, **2018**, 12, 245-253
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	290@10	carbon cloth	*Adv. Mater.,* **2018**, 30, 1802121
a-$CoVO_x$	254@10	Ni foam	*ACS Catal.*, **2018**, 8, 644-650
$NiCo_2S_4$	243@10	Ni foam	*Adv. Funct. Mater.,* **2019**, 29, 1807031
Ni/Mo_2C-NCNFs	288@10	Ni foam	*Adv. Energy Mater.,* **2019**, 9, 1803185
$NiFe_xSn$@NiFe	260@10	carbon cloth	*Adv. Sci.,* **2020**, 7, 1903777
$(Ni_2Co_1)_{0.925}Fe_{0.075}$-MOF	257@10	Ni foam	*Adv. Mater.,* **2019**, 31, 1901139
NiFeCo-LDH	249@10	carbon fiber	*Small,* **2020**, 16, 2002426
CoNx@GDY NS	280@10	Ni foam	*Nano Energy*, **2019**, 59, 591-597
CoFe-PBA	256@10	Ni foam	*Nano Energy,* **2020**, 68, 104371
$Ni(Fe)(OH)_2$	275@10	Ni foam	*Nano Res.,* **2021**, 14, 4528-4533
NiFeSn@NiFe	260@10	carbon cloth	*Adv. Sci.* **2020**, 7, 1903777
Co@N-CS/N-HCP@CC	248@10	carbon cloth	*Adv. Energy Mater.*, **2019**, 1803918
Fe-Mn-O NS/CC	273@10	carbon cloth	*Adv. Funct. Mater.,* **2018**, 28, 1802463
NiFe LDH	260@10	Ni foam	*Adv. Mater.,* **2019**, 31, 1903909
δ-FeOOH	265@10	Ni foam	*Adv. Mater.,* **2018**, 30, 1803144

γ-FeOOH NAs	286@10	Ni foam	*Adv. Mater.,* **2021**, 33, 2005587
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	251@10	carbon cloth	*Adv. Mater.,* **2018**, 30, 1802121
$FeOOH/Ni_3N$	244@10	carbon cloth	*Appl. Catal. B,* **2020**, 269, 118600
CoN_x@GDY NS/NF	270@10	Ni foam	*Nano Energy,* **2019**, 59, 591-597
FeNiOOH(Se)	287@10	Fe foam	*J. Am. Chem. Soc.,* **2019**, 141, 7005-7013
DL-Co_3O_4/NF	256@20	Ni foam	*J. Energy Chem.*, **2020**, 47, 299-306
$Co_{0.9}Fe_{0.1}$-Se/NF	246@10	Ni foam	*J. Energy Chem.,* **2021**, 60, 194-201
CoFe-NA_2/NF	250@10	Ni foam	*J. Energy Chem.,* **2022**, 65, 405-414
$NH_4CoPO_4 \cdot H_2O$/Co	254@10	Co foil	*J. Energy Chem.,* **2020**, 51, 167-174
FCND	337@50	Ni foam	*J. Energy Chem.,* **2021**, 55, 10-16

Table S4. Summary of representative catalysts that have been recently reported in alkaline medium of overall water splitting in 1.0 M KOH.

Catalyst	**η (mV)@j (mA cm^{-2})**	**Substrate**	**Reference**
Fe, Mo-Ni_3S_2	1.53@10	Ni foam	This work
CoS_2-MoS_2	1.6@10	carbon cloth	*ACS Catal*., **2018**, 8, 4612-4621
Ni/$Mo_2C_{(1:2)}$-NCNFs	1.64@10	Ni foam	*Adv. Energy Mater*., **2019**, 1803185
N-$NiMoO_4$/NiS_2	1.6@10	carbon cloth	*Adv. Funct. Mater.,* **2019**, *29*, 1805298
Ni/$Ni(OH)_2$	1.59@10	carbon papers	*Adv. Mater.,* **2020**, 32, 1906915
$Fe_{7.4\%}$-NiSe	1.59@10	Ni foam	*J. Mater. Chem. A*, **2019**, 7, 2233
Co-Mo-S/CC	1.64@10	carbon cloth	*Nanoscale,* **2018**,10, 8404-8412
NiFe/$(Ni,Fe)_3S_2$	1.56@10	graphite plate	*Small Methods,* **2019**, 1900234
Se-$(NiCo)S_x/(OH)_x$	1.6@10	Ni foam	*Adv. Mater.,* **2018**, 30, 1705538
Ni_3S_2	1.61@10	Ni foil	*Appl. Catal. B*, **2019**, 243, 693-702
FeNi@FeNiB-700	1.65@10	FeNi foam	*J. Mater. Chem. A*, **2019**, 7, 19554
$Ni_3(S_{0.25}Se_{0.75})_2$@NiOOH	1.55@10	Ni foam	*Small,* **2018**, 14, 1803666
Co_9S_8/Ni_3S_2	1.64@10	Ni foam	*Appl. Catal. B*, **2019**, 253, 246-252
$Ni(OH)_2$/Ni_3S_2	1.57@10	Ni foam	*J. Mater. Chem. A*, **2018**, 6, 6938
$Fe_{11.1\%}$–Ni_3S_2	1.6@10	Ni foam	*J. Mater. Chem. A*, **2018**, 6, 4346
Ni_3S_2/VS_4	1.57@10	Ni foam	*Appl. Catal. B*, **2019**, 257, 117911

V-Ni_3S_2@NiFe LDH	1.55@10	Ni foam	*J. Mater. Chem. A*, **2019**, 7, 18118
Ni_3S_2	1.55@10	Ni foam	*J. Mater. Chem. A*, **2019**, 7, 18003
MoO_3-NiO	1.55@10	carbon cloth	*Adv. Mater.* **2020**, 32, 2003414
FeOOH/Ni_3N	1.58@10	carbon cloth	*Appl. Catal. B*, **2020**, 269, 118600
Co@N-CS/N-HCP	1.545@10	carbon cloth	*Adv. Energy Mater.*, **2019**, 1803918
Co_3S_4/EC-MOF	1.55@10	carbon cloth	*Adv. Mater.,* **2019**, 31, 1806672
FeCo-FeCoP@C	1.64@10	carbon cloth	*J. Energy Chem.*, **2021**, 53, 1-8
Co_xFe_{1-x}-Se	1.55@10	Ni foam	*J. Energy Chem.*, **2021**, 60, 194-201
δ-FeOOH	1.6@10	Ni foam	*Adv. Mater.,* **2018**, 30, 1803144
CoFe-NA_2	1.56@10	Ni foam	*J. Energy Chem.*, **2022**, 65, 405-414
S-NiFeOOH	1.57@10	Ni foam	J. Energy Chem., **2022**, 64, 364-371
MoO_3/Ni–NiO	1.55@10	carbon cloth	*Adv. Mater.,* **2020**, 32, 2003414