Supporting Information for

Strongly coupled Fe-doped NiS$_2$/MoS$_2$ composite for high-efficiency water splitting

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S1. Experimental section

S1.1 Chemicals and reagents

Molybdenum (V) chloride ($MoCl_5$, A.R. grade) and nafion solution (5.0 wt.%, Dupont) were bought from Shanghai Macklin Biochemical Co., Ltd. Ferrous chloride ($FeCl_2$, A.R. grade), nickel dichloride ($NiCl_2$, A.R. grade) were bought from Shanghai Aladdin Bio-Chem Technology Co. Ltd. Formamide (CH_3NO, purity>99%) was brought from Tianjin Damao Chemical Factory. Sulfur powder and absolute ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. Commercial Pt/C (20.0 wt.%) was bought from Tanaka Kikinzoku Kogyo K.K. Commercial RuO_2 was bought from Suzhou Sinero Technology Co., Ltd. Carbon black (BP2000) was purchased from Nanjing Xianfeng Nanomaterial Technology Co., Ltd. All reagents were used as received without further purification.

S1.2 Preparation of Fe-NiS$_2$/MoS$_2$ material

Fe-NiS$_2$/MoS$_2$ material was prepared by a stepwise method, which includes solvothermal treatment of $Ni^{2+}/Fe^{2+}/Mo^{5+}$/formamide solution, followed by inert annealing of the NiFeMo-NC precursor in S vapor. Generally, 1.2 mmol $NiCl_2$, 1.2 mmol $FeCl_2$, and 0.9 mmol $MoCl_5$ (Ni/Fe molar ratio = 1) are dissolved in 30.0 mL of formamide and sonicated for 30 minutes to form a homogeneous solution. Then, the solution was transferred to a 50 mL autoclave, kept at 180 ℃ for 12 h, and naturally cooled to room temperature. The slurry product was washed 3 times with water, 1 time with absolute ethanol, and dried at 80 °C for 6 h to obtain a NiFeMo-NC precursor. Next, 0.1 g of the obtained NiFeMo-NC precursor was placed in the center of the quartz tube furnace. Place sulfur powder (1.0 g) in the upstream area of the quartz tube, 10 cm from the precursor. After purging with N_2 for 30 min, the tube furnace was heated from room temperature to 600 ℃ at a rate of 5 ℃ min^{-1}, kept for 1 h, and naturally cooled to room temperature. The resulting sample is named Fe-NiS$_2$/MoS$_2$. The control samples of MoS$_2$ and NiFe$_2$S$_4$ were synthesized without $NiCl_2$ and $FeCl_2$ or without $MoCl_5$, respectively.The rest steps were the same as those for the synthesis of Fe-NiS$_2$/MoS$_2$..

S1.3 Materials characterizations

Powder X-ray diffraction (XRD) was performed on a Brüker D8 Advance diffractometer at 40 kV and 40 mA using Cu Kα radiation (λ=0.15406 nm). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a JEOL 2100 high-resolution transmission electron microscope. Raman spectra was recorded with a LabRAM Aramis Raman spectrometer (HORIBA

Jobin Yvon, 500-3000 cm^{-1}) with 532 nm line of Ar laser as excitation source. X-ray photoelectron spectrum (XPS) analysis was performed on a PHI 5000 Versaprobe system using monochromatic Al Kα radiation (1486.6 eV). Elemental analysis of Ni, Fe, and Mo in the Fe-NiS$_2$/MoS$_2$ was detected by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720es).

S1.4 Electrochemical measurements

The HER and OER measurements were performed on a typical three-electrode system using a CHI 760e electrochemical station (Shanghai Chenhua Instrument Co., Ltd) at room temperature. The 5 mm diameter glassy carbon electrode (GCE), saturated calomel electrode (SCE) and graphite rod electrode were used as working electrode, reference electrode and counter electrode, respectively. The working electrode was prepared as follows: by dispersing 5.0 mg of catalyst and 1.0 mg of carbon black into a mixed solution including 10 μL of Nafion solution and 0.5 mL of ethanol solution.The homogeneous catalyst ink was formed by ultrasonic treatment for at least 1 h. Then, the well-dispersed catalyst ink was casted on the glassy carbon electrode to generate a load of ~0.25 mg cm^{-2} for all samples, and then the modified GCE electrode was dried with an infrared lamp for the following electrochemical tests. The manufacturing method of the carbon paper coated electrode is as follows: When using two electrodes to test the water splitting of the powdered catalyst, the catalyst ink was prepared like above and coated on the carbon paper for testing. Then, the well-dispersed catalyst ink was drop-cast on 1×1 cm^2 hydrophilic carbon paper to generate ~0.25 mg cm^{-2} load for all samples.

Before collecting data, all working electrodes were pre-processed by repeated cyclic voltammetry scanning to fully activate the accessible surface of the electrode material. Linear sweep voltammetry (LSV) polarization curves were obtained in 1.0 M KOH solution at a sweep rate of 5.0 mV s^{-1}. In order to compare our work with other documents, all the current densities in this work are normalized by the geometric area of the electrode. According to the equation of $E_{RHE}=E_{SCE}+0.241$ V+pH×0.059 V, all potentials were converted into potentials relative to the reversible hydrogen electrode (RHE). All the LSV curves are not iR-corrected. Electrochemical Impedance Spectroscopy (EIS) measurement was carried out in 1.0 M KOH solution. The frequency was 10 mHz to 100 kHz and the amplitude was 5 mV. According to the literature, the electrochemically active surface area of the sample was estimated by using cyclic voltammograms with different scan rates (20-120 mV s^{-1}) in the 0-0.2 V vs RHE region to ensure that there is no Faraday current in the selected voltage window. The long-term stability test was recorded by acquiring the chronoamperometric curve under a constant overpotential.
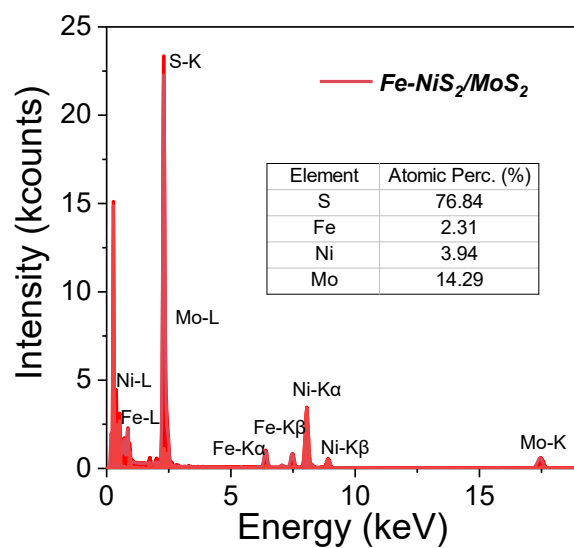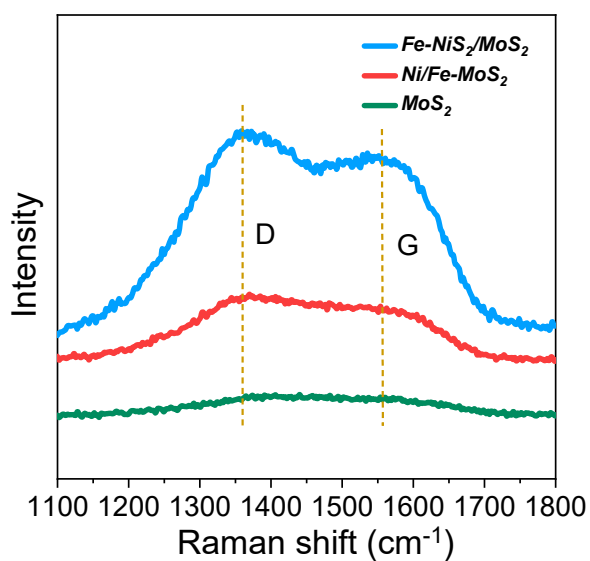
S2. Figures and Tables
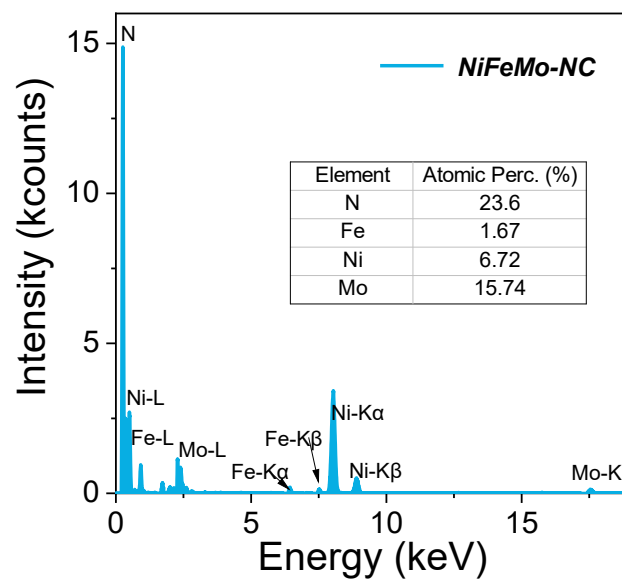
Figure S1. EDS spectra of NiFeMo-NC precursor. Inset shows the element content of NiFeMo-NC precursor measured by EDS analysis.
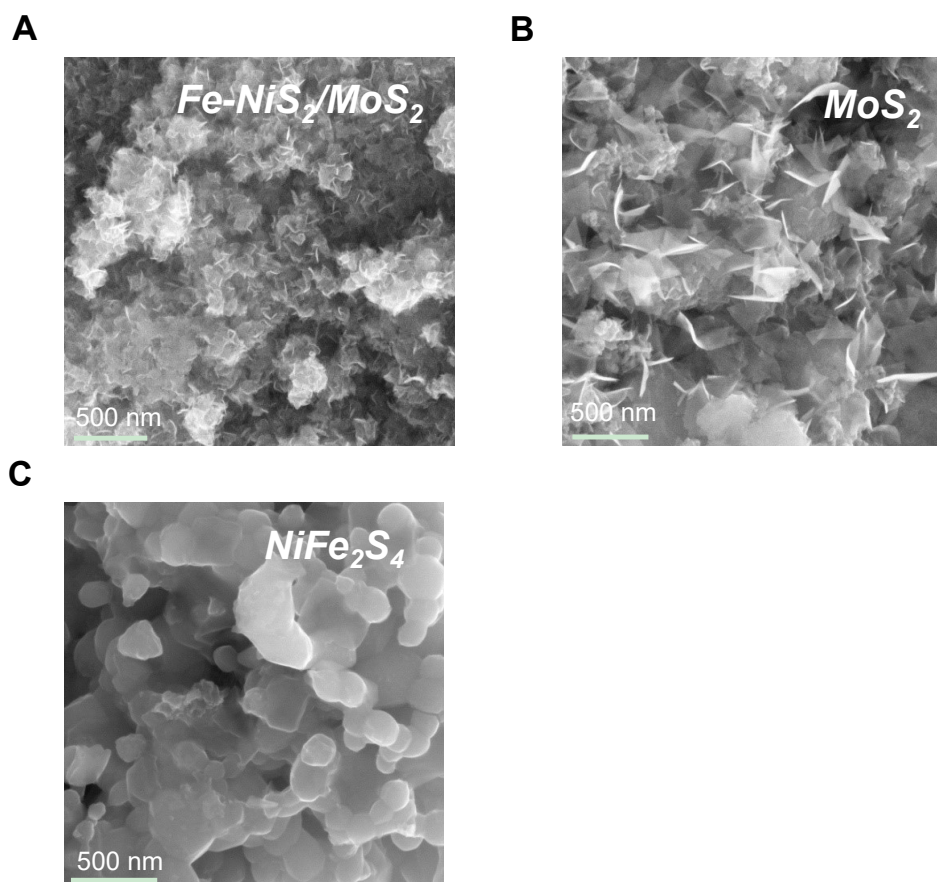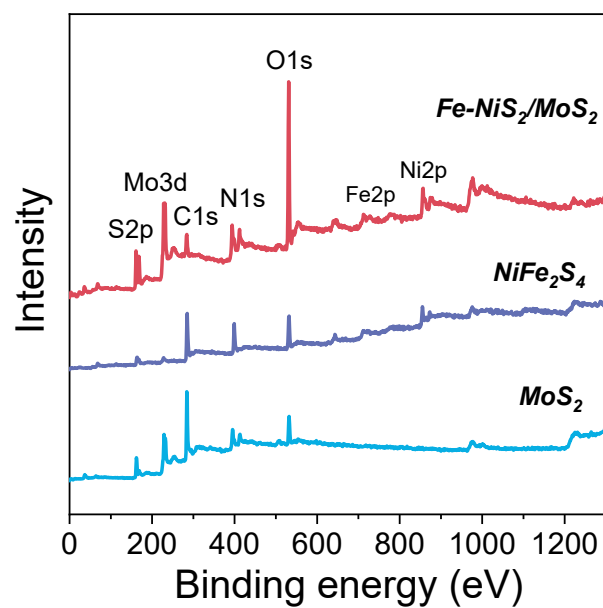

Figure S2. SEM images of (A) Fe-NiS$_2$/MoS$_2$, (B) MoS$_2$, and (C) NiFe$_2$S$_4$.
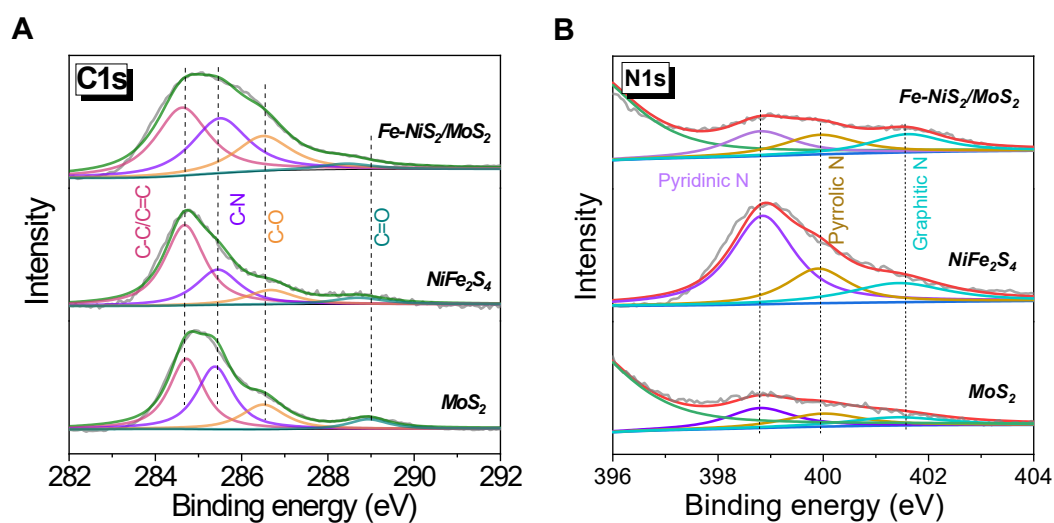
Figure S3. EDS spectra of Fe-NiS$_2$/MoS$_2$, inset shows the element content of Fe-NiS$_2$/MoS$_2$ measured by EDS analysis.
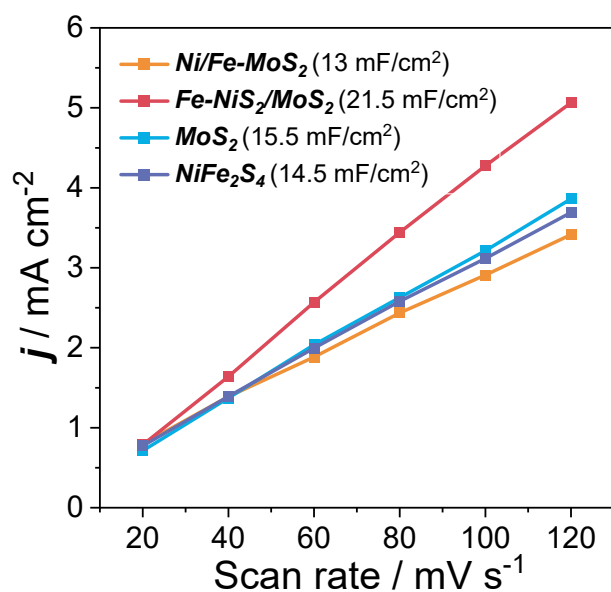

Figure S4. Raman spectra of Fe-NiS$_2$/MoS$_2$, Ni/Fe-MoS$_2$, and MoS$_2$.
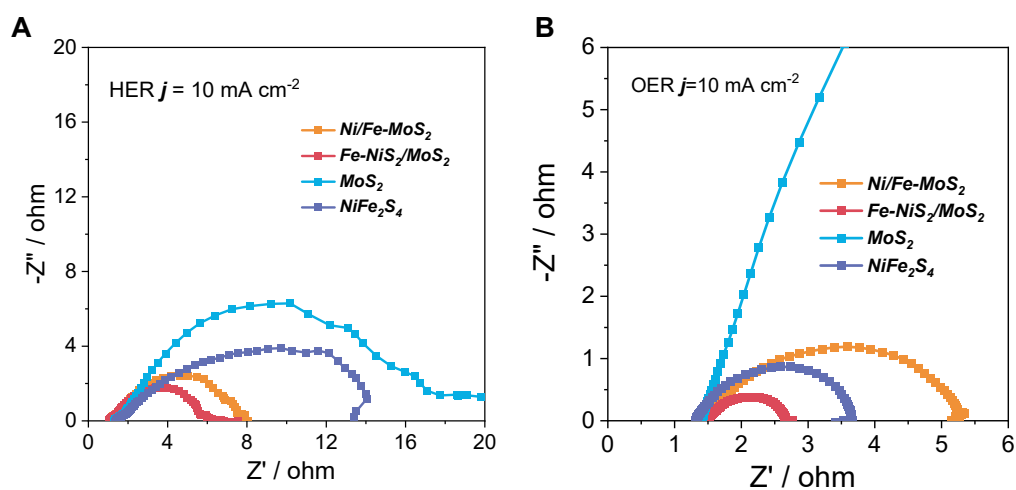
**Figure S5.** XPS element survey of Fe-NiS$_2$/MoS$_2$, MoS$_2$, and NiFe$_2$S$_4$.

Figure S6. (A) XPS C1s spectra and (B) N1s spectra of Fe-NiS$_2$/MoS$_2$, MoS$_2$, and NiFe$_2$S$_4$.
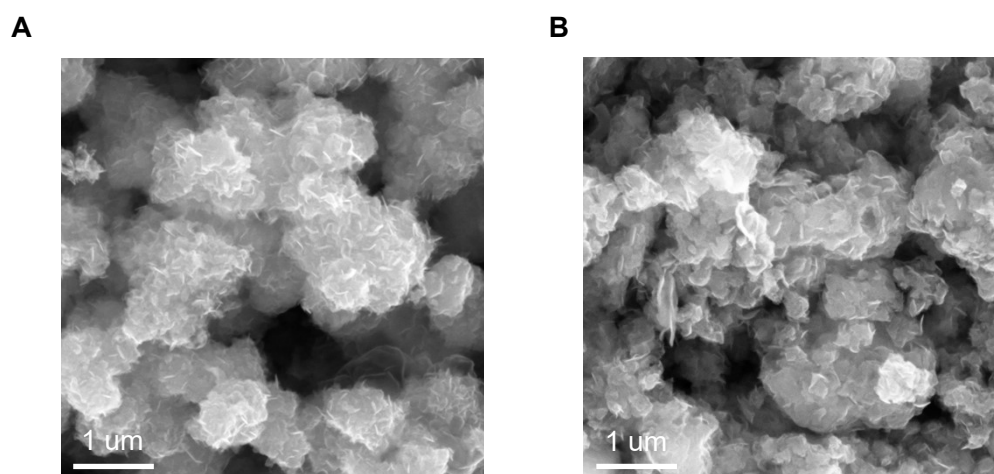
Figure S7. Electrochemical accessible surface area measurements of Fe-NiS$_2$/MoS$_2$, Ni/Fe-MoS$_2$, MoS$_2$, and NiFe$_2$S$_4$.

Figure S8. EIS curves of Fe-NiS$_2$/MoS$_2$, Ni/Fe-MoS$_2$, MoS$_2$, and NiFe$_2$S$_4$ measured at potentials of (A) HER and (B) OER current density reaching 10 mA cm^{-2}.
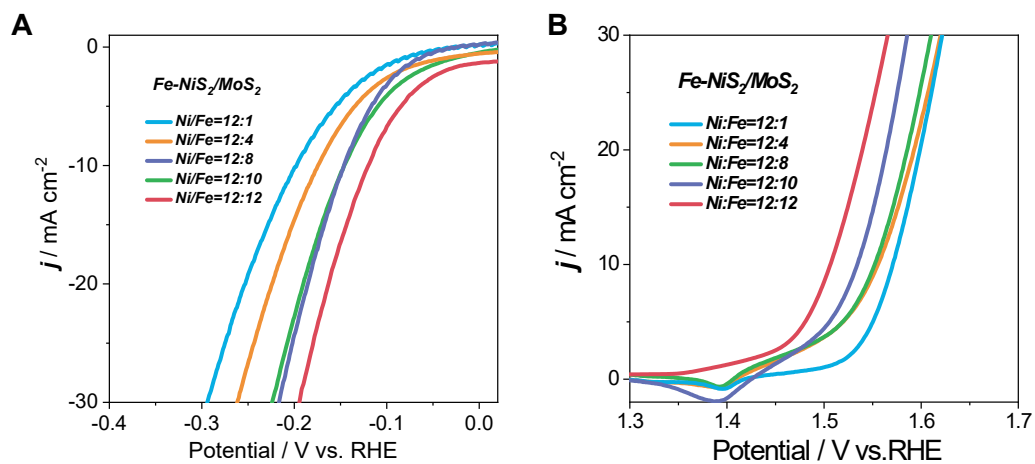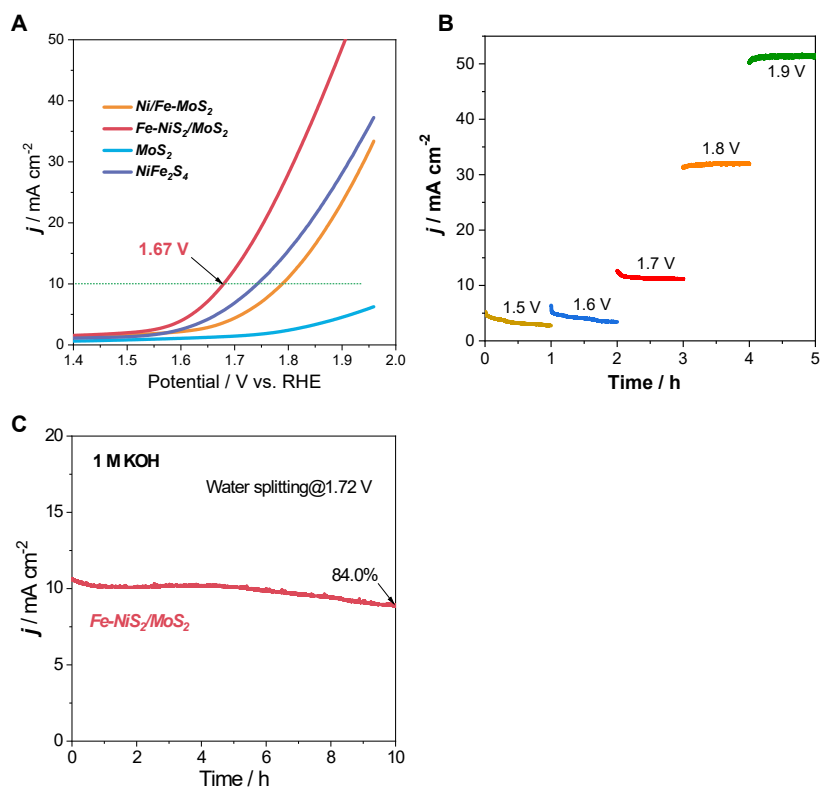
Figure S9. (A) HER and (B) OER polarization curves of as-prepared Fe-NiS$_2$/MoS$_2$ samples with different Ni:Fe ratios.

Figure S10. Fe-NiS$_2$/MoS$_2$ catalyst after 24-h long working for (A) HER and (B) OER.

Figure S11. (A) Overall water splitting measurements of Fe-NiS$_2$/MoS$_2$, Ni/Fe-MoS$_2$, NiFe$_2$S$_4$, and MoS$_2$. (B) Current responses at different potentials, measured using chronoamperometry methods. (C) Long-term stability measurement of Fe-NiS$_2$/MoS$_2$ for overall water splitting at current density of 10 mA cm^{-2}.

Table S1. Contents of Ni, Fe, and Mo in Fe-NiS$_2$/MoS$_2$, measured by ICP.

Elements	ICP			XPS		
	Ni	**Fe**	**Mo**	**Ni**	**Fe**	**Mo**
Weight percentage (%)	8.92	1.35	24.74	10.91	2.25	21.64
Atomic percentage (%)	-	-	-	4.59	1.03	5.96

Table S2. Element contents of Fe-NiS$_2$/MoS$_2$, MoS$_2$, and NiFe$_2$S$_4$, measured by XPS.

Sample	C (at.%)	O (at.%)	N (at.%)	Ni (at.%)	Fe (at.%)	Mo (at.%)	S (at.%)
Fe-NiS$_2$/MoS$_2$	43.98	17.90	2.73	4.59	1.03	5.96	23.81
NiFe$_2$S$_4$	56.58	15.52	18.76	2.27	0.65	-	6.41
MoS$_2$	73.00	10.00	1.26	-	-	4.76	10.98

Table S3. Summary of E_{10} (potential at current density of 10 mA cm^{-2}) of our made bifunctional HER/OER catalysts with comparison to currently reported values.

Catalyst	Testing media	HER E_{10} (V)	OER E_{10} (V)	Overall water splitting E_{10} (V)	Source
Fe-NiS$_2$/MoS$_2$	1 M KOH	-0.12	1.51	1.67	This work
Ni/Fe-MoS$_2$	1 M KOH	-0.23	1.60	1.79	This work
MoS$_2$	1 M KOH	-0.24	-	2.07	This work
NiFe$_2$S$_4$	1 M KOH	-0.23	1.55	1.74	This work
(Ni, Fe)S$_2$@MoS$_2$	1 M KOH	-0.13	1.50	1.56	Appl. Catal. B: Environ., 2019, 247, 107
Fe-(NiS$_2$/MoS$_2$)/CNT	1 M KOH	-0.09	1.47	1.51	J. Mater. Chem. A, 2020, 8, 17527
(2)NiS$_2$/MoS$_2$-CC	1 M KOH	-0.09	1.53	1.61	Electrochimica Acta, 2019, 326, 134983
NiS$_2$ NWs/CFP	1 M KOH	-0.17	1.48	1.59	Int. J. Hydrogen Energy, 2017, 42(27), 17038
h-Co$_{0.34}$Fe$_{0.33}$Ni$_{0.33}$-LDH	1 M KOH	-0. 07	1.43	1.49	Adv. Mater. 2020, 32, 2006784
Ni-Fe-selenide	1 M KOH	-0.06	1.43	1.46	Appl. Catal. B: Environ., 2020, 277: 119220
MoS$_2$/LDH	1 M KOH	-0.11	1.44	1.57	Nano lett., 2019, 19(7): 4518
NiFe-LDH/MXene/NF	1 M KOH	-0.13	1.55	1.65	Nano Energy, 2019, 63: 103880