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## Supporting Information

#### Construction of S and Fe co-regulated metal Ni electrocatalyst for

## efficient alkaline overall water splitting

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#### **Experimental Section**

Synthesis of the S-Fe-Ni/NF. The S-Fe-Ni/NF catalyst was prepared by a one-step electrodeposition process using a two-electrode configuration, in which nickel foam (NF, 2 cm  $\times$  3 cm) and carbon paper (CP, 2 cm  $\times$  3 cm) were served as cathode and anode, respectively. The NF was washed by 3.0 M HCl, water and ethanol, and carbon paper was also washed by water and ethanol. For preparing S-Fe-Ni/NF catalyst, 50 mM NiCl<sub>2</sub>·6H<sub>2</sub>O, 9 mM FeCl<sub>3</sub>·6H<sub>2</sub>O, 2.5 M CS(NH<sub>2</sub>)<sub>2</sub> and 1.0 M NH<sub>4</sub>F were added into 50 mL water to form an electrolyte. The synthesis process was performed on a digital control DC power supply with 3.5 V for 30 min at ambient temperature. Then the S-Fe-Ni/NF catalyst was washed by water and ethanol to remove the remaining ions. The catalyst loading is about 20 mg cm<sup>-2</sup>. The effects of deposition potentials, thiourea and Fe<sup>3+</sup> ion concentrations on catalytic performance were also explored. Moreover, all the electrodeposition was performed at room temperature and the distance between cathode and anode electrodes was maintained at 3 cm.

Synthesis of the S-Ni/NF, Fe-Ni/NF and Ni/NF. Comparison samples of S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts were prepared with the similar method. In detail, the S-Ni/NF catalyst was prepared at 3.5 V for 30 min in 50 mL electrolyte containing 50 mM NiCl<sub>2</sub>· $6H_2O$ , 2.5 M CS(NH<sub>2</sub>)<sub>2</sub> and 1.0 M NH<sub>4</sub>F, and the catalyst loading is about 20 mg cm<sup>-2</sup>. The Fe-Ni/NF catalyst was prepared in 50 mL electrolyte containing 50 mM NiCl<sub>2</sub>· $6H_2O$ , 9 mM FeCl<sub>3</sub>· $6H_2O$  and 1.0 M NH<sub>4</sub>F under 3.5 V for 30 min, while the catalyst loading is about 13 mg cm<sup>-2</sup>. The Ni/NF was prepared with 3.5 V for 30

min in 50 mL electrolyte containing 50 mM NiCl<sub>2</sub>· $6H_2O$  and 1.0 M NH<sub>4</sub>F, and the catalyst loading is about 16 mg cm<sup>-2</sup>.

**Preparation of the Pt/C/NF and RuO<sub>2</sub>/C/NF.** The Pt/C/NF catalyst ink was prepared by dispersing 5 mg commercial Pt/C (20%) in 720  $\mu$ L deionized water, 250  $\mu$ L isopropanol and 30  $\mu$ L Nafion, then it was sonicated for 30 min and 50  $\mu$ L ink was dropped on NF (1 cm × 1 cm). RuO<sub>2</sub>/C electrode ink was prepared in the same method, except that 5 mg Pt/C was replaced with 2 mg RuO<sub>2</sub> and 3 mg carbon black. **Synthesis of the Ni<sub>3</sub>S<sub>2</sub>.** The Ni<sub>3</sub>S<sub>2</sub> was prepared through a typical solvothermal process. Specifically, 0.4362 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.2283 g CS(NH<sub>2</sub>)<sub>2</sub>, 0.1 g cetyl trimethyl ammonium bromide (CTAB) were dissolved in 25 mL ethanol, stirred for 15 min, and transferred into a 30 mL Teflon-lined stainless-steel autoclave with a piece of cleaned NF (1 cm × 2 cm). The autoclave was sealed and heated at 140 °C for 9 h. After cooling to room temperature, the Ni<sub>3</sub>S<sub>2</sub> was washed with water and ethanol, and dried in the air.

**Materials characterizations.** X-ray power diffraction (XRD) patterns were collected on a Bruker D8 Discover with Cu Kα radiation. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed on Quanta 450 FEG. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 instrument at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250Xi. All XPS spectra were corrected using the C 1s line at 284.6 eV. Raman spectra were collected on a laser Raman spectrometer (Renishaw inVia Reflex) with an excitation laser of 532 nm. In addition, only SEM measurements of all catalysts were conducted on the nickel foam carrier, other characterization was conducted with powder catalysts. In order to obtain powder catalysts, S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF were ultrasonically treated in deionized water for 10 min and then the supernatant was freeze-dried.

Electrochemical measurements. The electrochemical measurements were conducted with CHI750E in a three-electrode system using a 1 cm  $\times$  1 cm NF loaded with catalysts as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode. The OER and HER activities were evaluated in O<sub>2</sub>-saturated or N<sub>2</sub>-saturated 1.0 M KOH electrolyte. The measured potentials were converted to the reversible hydrogen electrode (RHE) according to the formula  $E_{RHE} = E_{SCE} + 0.244 + 0.059 \times pH$ . Linear sweep voltammetry (LSV) was collected at a scan rate of 5 mV s<sup>-1</sup>. All the polarization curves were corrected with 95% iR compensation according to the equation:  $E_{corr}$  =  $E_{mea}$  – 0.95 × I × R<sub>s</sub>, where  $E_{corr}$  is the compensated potential,  $E_{mea}$  is the measured potentials, I is the current and R<sub>s</sub> is measured through CHI750E, except the twoelectrode water splitting polarization curves. Electrochemical impedance spectroscopy (EIS) was performed at an overpotential of 150 mV for HER and 250 mV for OER between 1000 kHz and 0.1 Hz. Electrochemical active surface area (ECSA) was estimated based on cyclic voltammetry (CV) scan at different rates of 5, 10, 15, 20, 25, 30 mV s<sup>-1</sup> in a non-Faradaic region from 0.337 to 0.437 V (vs. RHE) for HER and from 1.137 to 1.187 V (vs. RHE) for OER. The double layer capacitance (C<sub>dl</sub>) can be

calculated through fitting the slope of plotting the halves of the anodic and cathodic current density against scan rates, which is positively proportional to the ECSA. Faradaic efficiency (FE) of overall water splitting was evaluated according to the formula:  $FE = V_r/V_t \times 100\%$ , where  $V_r$  is the actual measured volumes and  $V_t$  is the theoretical volumes. The  $V_r$  can be obtained through the equation:  $V_r = (I \times t) / (n \times F)$  $\times V_m$ , where I is current (mA), t is running time (s), n is transferred electrons number (two for HER and four for OER), F is Faradaic constant (96485 C mol<sup>-1</sup>) and  $V_m$  is the gas molar volume (22.4 L mol<sup>-1</sup>). The turnover frequency (TOF) was calculated from the equation:  $TOF(s^{-1}) = \frac{j \times S}{n \times F \times N}(s^{-1})$ , where j, S, n, F and N are the current density (mA cm<sup>-2</sup>), the surface area of the electrode (1 cm<sup>-2</sup>), the number of electrons involved (2 for HER and 4 for OER), Faradaic constant (96485 C mol<sup>-1</sup>) and the number of metal atoms on the electrode (mol), respectively. All the metal atoms loaded on the electrode were considered as active sites and the calculated value is a lower limit of TOF.

**Computational Methods.** All spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the projector-augmented wave (PAW) pseudopotentials.<sup>1-3</sup> The exchange–correlation interactions were treated within the generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) function.<sup>4</sup> For the expansion of wavefunctions over the plane-wave basis set, a converged cutoff was set to 450 eV. The Ni (111) model is constructed as  $4 \times 4$  periodic supercell (a = b = 9.85 Å), which contains four atomic layers with two bottom layers fixed and the

other atoms fully relaxed. A vacuum space of 15 Å was applied to all periodic slabs calculations to avoid interactions between periodic images. In geometry optimizations, the convergence threshold for energy change and structural optimization were set to be  $10^{-5}$  eV and 0.03 eV/Å. The Brillouin zone was sampled by  $(3 \times 3 \times 1)$  Monkhorst–Pack k-point mesh. For density of state and Bader charge calculations, the k-points were set to be  $7 \times 7 \times 1$ . The adsorption energies were calculated by  $\Delta E_{ads} = E_{ads+slab} - E_{slab} - E_{ads}$ , where  $E_{ads+slab}$ ,  $E_{slab}$  and  $E_{ads}$  represent total energies of the adsorbate-slab, slab and the adsorbate in the structure, respectively. The Gibbs free energies for the adsorption of H atoms were calculated by  $\Delta G_{H} = \Delta E_{H} + \Delta E_{ZPE} - T\Delta S_{H}$ , where  $\Delta E_{H}$  is the H adsorption energy,  $\Delta E_{ZPE}$  is the change in zero-point energies, T is the temperature (T = 298.15 K) and  $\Delta S_{H}$  is the entropy changes.



Fig. S1. (a) XRD pattern and (b) Raman spectrum of the  $Ni_3S_2$ .



Fig. S2. The SEM images of S-Fe-Ni/NF at (a) low magnification, (b) high magnification, and (c) the corresponding EDS result.



**Fig. S3.** The SEM images of S-Ni/NF at (a) low magnification, (b) high magnification, and (c) the corresponding EDS result.



**Fig. S4.** The SEM images of Fe-Ni/NF at (a) low magnification, (b) high magnification, and (c) the corresponding EDS result.



**Fig. S5.** The SEM images of Ni/NF at (a) low magnification, (b) high magnification, and (c) the corresponding EDS result.



Fig. S6. XPS spectra and fitting curves of O 1s for S-Fe-Ni, S-Ni, Fe-Ni and Ni catalysts.



**Fig. S7.** The equivalent circuit of (a) S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF, (b) Pt/C/NF for HER.



**Fig. S8.** The HER performance in 1.0 M KOH for S-Fe-Ni/NF catalysts prepared with different potentials. (a) Polarization curves with a scan rate of 5 mV s<sup>-1</sup>, (b) corresponding comparison of overpotentials at 10 mA cm<sup>-2</sup>, (c) Tafel plots, (d) EIS curves.



**Fig. S9.** The HER performance in 1.0 M KOH for S-Fe-Ni/NF catalysts prepared at different thiourea concentrations. (a) Polarization curves with a scan rate of 5 mV s<sup>-1</sup>, (b) corresponding comparison of overpotentials at 10 mA cm<sup>-2</sup>, (c) Tafel plots, (d) EIS curves.



**Fig. S10.** The HER performance in 1.0 M KOH for S-Fe-Ni/NF catalysts prepared with different Fe<sup>3+</sup> concentrations. (a) Polarization curves with a scan rate of 5 mV s<sup>-1</sup>, (b) corresponding comparison of overpotentials at 10 mA cm<sup>-2</sup>, (c) Tafel plots, (d) EIS curves.



Fig. S11. CV curves of (a) S-Fe-Ni/NF, (b) S-Ni/NF, (c) Fe-Ni/NF and (d) Ni/NF

recorded in N<sub>2</sub> saturated 1.0 M KOH solution with different scan rates.



Fig. S12. The HER polarization curves normalized by ECSA for S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts.



**Fig. S13.** The HER polarization curves normalized by mass for S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts.



Fig. S14. The TOF values of S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts for

HER.



Fig. S15. Multi-current process of S-Fe-Ni/NF. The current density started at 20 mA  $cm^{-2}$  and with an increment of 20 mA  $cm^{-2}$  per 500 s without iR correction, and finished at 20 mA  $cm^{-2}$ .



Fig. S16. (a) I-t curves of S-Ni/NF, Fe-Ni/NF, Ni/NF and Pt/C/NF at -0.146 V, -0.305 V, -0.355 V and -0.067 V for 50 h, (b) polarization curves of S-Fe-Ni/NF before and after i-t test at -0.086 V for 50 h.



Fig. S17. XRD patterns of the S-Fe-Ni catalyst after HER and OER i-t test at 20 mA  $cm^{-2}$  for 50 h.



Fig. S18. The SEM images of S-Fe-Ni/NF after HER i-t test at 20 mA cm<sup>-2</sup> for 50 h.
(a) low magnification, (b) high magnification, and (c) the corresponding EDS result.



Fig. S19. (a) TEM and (b) HRTEM images of S-Fe-Ni catalyst after HER i-t test at 20 mA cm<sup>-2</sup> for 50 h.



Fig. S20. CV curves of S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF, Ni/NF and  $RuO_2/C/NF$ 

catalysts in 1.0 M KOH with a scan rate of 50 mV s<sup>-1</sup>.



Fig. S21. The OER performance in 1.0 M KOH for S-Fe-Ni/NF catalysts prepared with different potentials. (a) Polarization curves with a scan rate of 5 mV s<sup>-1</sup>, (b) corresponding comparison of overpotentials at 10 mA cm<sup>-2</sup>, (c) Tafel plots, (d) EIS curves.



Fig. S22. The OER performance in 1.0 M KOH for S-Fe-Ni/NF catalysts prepared with different thiourea concentrations. (a) Polarization curves with a scan rate of 5 mV s<sup>-1</sup>, (b) corresponding comparison of overpotentials at 10 mA cm<sup>-2</sup>, (c) Tafel plots, (d) EIS curves.



**Fig. S23.** The OER performance in 1.0 M KOH for S-Fe-Ni/NF catalysts prepared with different Fe<sup>3+</sup> concentrations. (a) Polarization curves with a scan rate of 5 mV s<sup>-1</sup>, (b) corresponding comparison of overpotentials at 10 mA cm<sup>-2</sup>, (c) Tafel plots, (d) EIS curves.



Fig. S24. CV curves of (a) S-Fe-Ni/NF, (b) S-Ni/NF, (c) Fe-Ni/NF and (d) Ni/NF

recorded in O<sub>2</sub> saturated 1.0 M KOH solution with different scan rates.



Fig. S25. The OER polarization curves normalized by ECSA for S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts.



**Fig. S26.** The OER polarization curves normalized by mass for S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts.



Fig. S27. The TOF values of S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF and Ni/NF catalysts for

OER.



Fig. S28. Multi-current process of S-Fe-Ni/NF. The current density started at 20 mA  $cm^{-2}$  and with an increment of 20 mA  $cm^{-2}$  per 500 s without iR correction, and finished at 20 mA  $cm^{-2}$ .



Fig. S29. (a) I-t curves of S-Ni/NF, Fe-Ni/NF, Ni/NF and  $RuO_2/C/NF$  at 1.590 V, 1.530 V, 1.670 V and 1.610 V for 50 h, (b) polarization curves of S-Fe-Ni before and after i-t test at 1.476 V for 50 h.



Fig. S30. The SEM images of S-Fe-Ni/NF after OER i-t test at 20 mA cm<sup>-2</sup> for 50 h.
(a) low magnification, (b) high magnification, and (c) the corresponding EDS result.



Fig. S31. (a) TEM and (b) HRTEM images of S-Fe-Ni catalyst after OER i-t test at 20 mA cm<sup>-2</sup> for 50 h.



**Fig. S32.** The polarization curves of Fe-Ni/NF and Ni/NF after immersed in 2.5 M TU solution for 30 min for (a) HER and (b) OER.



Fig. S33. Anodic scans showing the oxidative adsorption of  $OH^-$  in 1.0 M N<sub>2</sub>-saturated KOH solution for S-Fe-Ni/NF, Fe-Ni/NF, S-Ni/NF and Ni/NF catalysts.



**Fig. S34.** (a) The model of Ni (111) surface, (b) the model of S-Fe-Ni. Color code : gray, Ni; brown, Fe; yellow, S.



Fig. S35. Bader charge numbers of S atom in (a) S-Fe-Ni and (b) H<sub>2</sub>O adsorbed S-Fe-

Ni. Color code: gray, Ni; brown, Fe; yellow, S; red, O; white, H.



**Fig. S36.** Models of H adsorption at different sites. (a) H adsorption at fcc hollow of Ni (111), (b-d) H adsorption at different hollows of S-Fe-Ni, (e) H adsorption at S site (The S-H bond is perpendicular to the S-Fe-Ni surface), (f) H adsorption at S site (The angle between S-H bond and S-Fe Ni surface is 45 °, and it is parallel to S-Fe Ni surface after structure optimization). Color code: gray, Ni; brown, Fe; yellow, S; white, H.



**Fig. S37.** The percentage of Ni<sup>3+</sup>, Ni<sup>2+</sup> and Ni<sup>0</sup>, Fe<sup>3+</sup> and Fe<sup>0</sup> in S-Fe-Ni catalyst before and after HER, OER long-term durability at 20 mA cm<sup>-2</sup> for 50 h.



Fig. S38. The Raman spectra of S-Fe-Ni catalyst before and after HER, OER long-term durability at 20 mA cm<sup>-2</sup> for 50 h.



Fig. S39. (a) Device of drainage gas collection method, (b)  $H_2$  and  $O_2$  collected at 0, 200, 400, 600, 800 and 1000 s.



Fig. S40. (a) I-t curve of  $Pt/C ||RuO_2/C/NF$  at 1.67 V for 50 h, (b) polarization curves of S-Fe-Ni before and after i-t test at 1.59 V for 50 h.

Table S1. Elemental contents of different catalysts obtained from SEM-EDS

measurement.

Catalyst	Ni (At%/W%)	Fe (At%/W%)	S (At%/W%)	O (At%/W%)
S-Fe-Ni/NF	64.6%/76.6%	8.3%/9.4%	16.1%/10.4%	11.0%/3.6%
S-Ni/NF	84.1%/91.8%	/	11.9%/7.0%	4.0%/1.2%
Fe-Ni/NF	79.9%/86.2%	10.7%/11.0 %	/	9.4%/2.8%
Ni/NF	92.1%/97.7%	/	/	7.9%/2.3%
S-Fe-Ni/NF after HER	57.5%/73.5%	7.6%/9.2%	14.6%/10.2%	20.3%/7.1%
S-Fe-Ni/NF after OER	60.0%/74.9%	8.1%/9.6%	13.6%/9.3%	18.3%/6.2%

Catalyst	Ni (At%)	Fe (At%)	S (At%)	O (At%)	C (At%)
S-Fe-Ni/NF	15.88%	3.58%	10.02%	42.64%	27.88%
S-Ni/NF	21.69%	/	9.20%	42.48%	26.63%
Fe-Ni/NF	9.43%	1.82%	/	33.52%	55.23%
Ni/NF	5.62%	/	/	22.81%	71.57%
S-Fe-Ni/NF	14 010/	2.940/	5 5 40/	50 ((0)	25.05%
after HER	14.91%	3.84%	5.54%	50.66%	25.05%
S-Fe-Ni/NF	17 210/	2.590/	0.420/	54 660/	24 120/
after OER	1/.21%	3.38%	0.42%	34.00%	24.13%

 Table S2. Elemental contents of different catalysts obtained from XPS measurement.

Table S3. Comparison of HER activity of S-Fe-Ni/NF with reported Ni-based

	J (mA	Overpotential	Tafel slope	Stability		
Catalysts	cm <sup>-2</sup> )	(mV)	$(mV dec^{-1})$	test	Kelerences	
S-Fe-Ni/NF	10 100	25 89	41.1	50 h	This work	
N-P-Ni	10	25.8	34	50 h	5	
Ni <sub>3</sub> Fe@N-C NT/NFs	10	72	98	40000 s	6	
Ni <sub>3</sub> S <sub>2</sub> /Ni/NF	10	45	54	140000 s	7	
Mn-hcp Ni/C	10	80	68	10 h	8	
Ni/MoC	10	70	68.9	20 h	9	
Co@NC-CNTs@NiFe-LDH	10	160	116	1000 cycles	10	
Ni/TiO <sub>2</sub>	10	88	78	17 h	11	
Ni/Ni(OH) <sub>2</sub>	10	77	53	10 h	12	
Ni–Co–P HNBs	10	107	46	20 h	13	
O-NiCu	10	23	34.1	100 h	14	
Ni <sub>SA</sub> Fe <sub>SA</sub> -Ni <sub>50</sub> Fe/CNT	10	64	48.1	72 h	15	
W-NiCo	10	109.2	110.3	10 h	16	
Cr-Ni	10	75	72	12 h	17	
MoS <sub>2</sub> /NiFe LDH	10	98	95	24 h	18	
Ni-N <sub>0.19</sub>	10	42	125	20 h	19	
NiFe-CS	10	33	68	100 h	20	
NCNT-Ni@NF	10	96.1	84.8	100 h	21	
H-CoS <sub>x</sub> @NiFe LDH/NF	10	95	90	100 h	22	
Ni-Ni <sub>3</sub> C	10	98	88.5	35 h	23	
Ni/WC@NC	10	77	68.6	24 h	24	

electrocatalysts in 1.0 M KOH solution.

Table S4. EIS fitting results of S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF, Ni/NF and Pt/C/NF

for HER.

Catalysts	Solution series resistances $R_s$	Charge transfer resistance $R_{ct}$		
	$(\Omega)$	$(\Omega)$		
S-Fe-Ni/NF	1.38	0.93		
S-Ni/NF	1.34	1.54		
Fe-Ni/NF	1.49	62.0		
Ni/NF	1.47	62.6		
Pt/C/NF	1.32	1.04		

**Table S5.** Comparison of OER activity of S-Fe-Ni/NF catalyst with reported Ni-basedelectrocatalysts in 1.0 M KOH solution.

	J (mA	Overpotential	Tafel slope	Stability	D. (	
Catalysts	$cm^{-2})$	(mV)	$(mV dec^{-1})$	test	Keterences	
S-Fa Ni/NF	10	200	31 /	50 h	This work	
5-1'C-11//11	100	235	51.4	<b>30 II</b>	i niş wurk	
Ni <sub>0.8</sub> Fe <sub>0.2</sub> -AHNA	10	190	34.7	120 h	25	
Ni/MoC	10	219	49.5	20 h	9	
Ni/Ni(OH) <sub>2</sub>	10	270	70	10 h	12	
Ni <sub>SA</sub> Fe <sub>SA</sub> -Ni <sub>50</sub> Fe/CNT	10	227	41.8	65 h	15	
NiFe-CS	10	191	42	100 h	20	
Ni <sub>83</sub> Fe <sub>17</sub> -ONCAs	10	190	39	120 h	26	
Ni-Co-P HNBs	10	270	76	20 h	13	
NCNT-Ni@NF	10	240	30.7	55000 s	21	
Ni-Ni <sub>3</sub> C	20	299	64.5	15 h	23	
Ni/Mo <sub>2</sub> C	10	288	78.4	100 h	27	
Ni <sub>3</sub> FeN/Ni <sub>3</sub> Fe	10	250	51	2000 cycles	28	
Co@NC-CNTs@NiFe-	10	240	96	1000 cycles	10	
Ni/Fe <sub>3</sub> O <sub>4</sub>	10	210	44	100 h	29	
MoS <sub>2</sub> /NiFe LDH	10	257	59	24 h	18	
Fe-Ni <sub>3</sub> S <sub>2</sub>	100	252	64	24 h	30	
NiFeP/MXene	10	286	35	12 h	31	
H-CoS <sub>x</sub> @NiFe LDH/NF	10	250	49	100 h	22	
$N-NiS_2$	10	270	/	40 h	32	
NiP <sub>2</sub> /NiSe <sub>2</sub>	10	250	71.65	30 h	33	
Fe-NiO/NiS <sub>2</sub>	10	270	40	10 h	34	

Table S6. EIS fitting results of S-Fe-Ni/NF, S-Ni/NF, Fe-Ni/NF, Ni/NF and  $RuO_2/C/NF$  for OER.

Catalysts	Solution series resistances $R_s$	Charge transfer resistance $R_{ct}$	
	$(\Omega)$	$(\Omega)$	
S-Fe-Ni/NF	1.38	0.74	
S-Ni/NF	1.34	3.06	
Fe-Ni/NF	1.60	2.11	
Ni/NF	1.48	73.72	
RuO <sub>2</sub> /C/NF	1.37	8.92	

**Table S7.** Comparison of water splitting performance of S-Fe-Ni/NF with reportedNi-based electrocatalysts in 1.0 M KOH solution.

Catalysts	J (mA cm <sup>-2</sup> )	Voltage (V)	Stability test	References
S-Fe-Ni/NF	10	1.49	50 h	This work
Ni/MoC	10	1.535	30 h	9
Ni/Ni(OH) <sub>2</sub>	10	1.59	20 h	12
Ni <sub>SA</sub> Fe <sub>SA</sub> -Ni <sub>50</sub> Fe/CNT	10	1.49	30 h	15
NCNT-Ni@NF	10	1.54	150 h	21
Ni-Ni <sub>3</sub> C	10	1.64	20 h	23
Co@NC-CNTs@NiFe-	10	1.66	120 h	10
Ni/Mo <sub>2</sub> C	10	1.64	100 h	27
Ni <sub>3</sub> FeN/Ni <sub>3</sub> Fe	10	1.61	90 h	28
Fe-Ni <sub>3</sub> S <sub>2</sub>	10	1.51	100 h	30
MoS <sub>2</sub> /NiFe LDH	10	1.61	24 h	18
NiP/NiFeP/C	10	1.53	20 h	35
NiP <sub>2</sub> /NiSe <sub>2</sub>	10	1.56	30 h	33
FeOOH/Ni <sub>3</sub> S <sub>2</sub>	10	1.525	24 h	36
H-CoS <sub>x</sub> @NiFe LDH/NF	10	1.59	100 h	22
MoO <sub>3</sub> /Ni-NiO	10	1.55	20 h	37
NiFe(OH) <sub>x</sub> /FeS/IF	10	1.50	70 h	38
Ni–Co–P HNBs	10	1.62	20 h	13
FeOOH/Ni <sub>3</sub> N	10	1.58	40 h	39
V-Ni <sub>3</sub> S <sub>2</sub> @NiFe LDH	10	1.55	24 h	40
Ni <sub>3</sub> S <sub>2</sub> /VS <sub>4</sub>	10	1.57	70 h	41

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