

## Supplementary Material

# Binary Ni-W metal sulfides with polyhedral nanostructures towards efficient hydrogen evolution

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## Experimental

Analytically pure ammonia solution was purchased from Xilong Scientific Co., Ltd. Nickel foam (NF, thickness of 1.2 mm) was provided by Shenzhen Poxon Machinery Technology Co., Ltd. All commercially available chemical reagents are of analytical grade and used in experiments without further purification.

### Synthesis of NiWO/NF and NiWO-S/NF

The synthesis of NiWO/NF catalyst is achieved through a simple one-step hydrothermal method. Prior to the synthesis, the NF was cut into small pieces of  $1 \times 2$  cm<sup>2</sup> and followed by consecutive sonication in 1.0 M hydrochloric acid, acetone and ethanol for 30 min, respectively. Then the clean NF pieces were dried at 60°C for at least 8 hours under vacuum. After that, 0.66 g of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and 0.58 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were weighed using an electronic balance and dissolved in two beakers containing 30 ml of deionized water. After thorough magnetic stirring, clear white and light green solutions were obtained. Then continue the stirring process and slowly add the nickel nitrate solution to the sodium tungstate solution using a dropper to ensure thorough mixing. Then, three pieces of pre-cleaned foam nickel mesh and the above solution were transferred to an autoclave and reacted at 120 °C for 12 h. Wait for the reaction to complete and cool naturally to room temperature. Rinse the prepared samples with deionized water and ethanol separately, and then dry them in a vacuum drying oven to obtain the NiWO/NF precursor. The obtained NiWO/NF precursor was placed in a tube furnace and sulfurized at 350 °C for 2 hours at a

heating rate of 3 °C min<sup>-1</sup> in an H<sub>2</sub>S/N<sub>2</sub> atmosphere (volume ratio of 1/9), to prepare the NiWO-S/NF catalyst. The loading capacity of NiWO and NiWO-S on the foam nickel mesh substrate is about 23.7 and 31.2 mg cm<sup>-2</sup>, respectively.

### **Synthesis of Ni<sub>3</sub>S<sub>2</sub>/NF**

As a comparison, the Ni<sub>3</sub>S<sub>2</sub>/NF material was prepared using NF alone in a tube furnace under the same gas-phase sulfurization conditions as NiWO-S/NF.

### **Characterization**

All the samples were tested using an X'Pert PRO MPD diffractometer (Cu K $\alpha$ ) and X-ray diffraction (XRD) patterns were recorded with a 2 $\theta$  range of 5° to 90°. The morphology of prepared samples was observed by scanning electron microscopy (SEM), and the instrument model was Hitachi S-4800. X-ray photoelectron spectra (XPS) were tested using a ThermoFisher Scientific II spectrometer with Al as the photo source.

### **Electrochemical measurements**

The electrocatalytic properties of the prepared samples were all measured using a three-electrode system connected to a computer and an electrochemical workstation (Gamry Reference 1010 Instruments, USA). In this experiment, all prepared samples were used as working electrodes, while the counter and reference electrodes were the carbon rod and saturated calomel electrode, respectively. All experimentally obtained electrochemical data were recorded using Gamry Framework Data Acquisition Software 6.11, and corrected for iR (current time resistance). Prior to testing, the

electrolyte (1.0 M KOH) was degassed with N<sub>2</sub> for 1 hour and continued to remain above the solution during the HER measurement. The LSV test was performed at a scan rate of 2 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was performed at -1.25 V (vs. SCE) from 105 to 0.1 Hz with an AC voltage of 5 mV. The electrochemical double layer capacitance C<sub>dl</sub> of the materials were obtained through a series of cyclic voltammetry(CV) measurements at various scan rates (40, 60, 80, 100 and 120 mV s<sup>-1</sup>) in the non-Faradaic potential region from 0.27 to 0.17 V vs. RHE. The derived linear slope was calculated as C<sub>dl</sub>. The stability tests were undertaken by CV from -1.0 to -1.4 V (vs. SCE) or chronoamperometry at -1.3 V (vs. SCE). The potential conversion between SCE and the reversible hydrogen electrode (RHE) is based on the equation as follows:

$$E \text{ (vs. RHE)} = E \text{ (vs. SCE)} + 0.244 \text{ V} + (0.059 \text{ V}) \text{ pH}$$

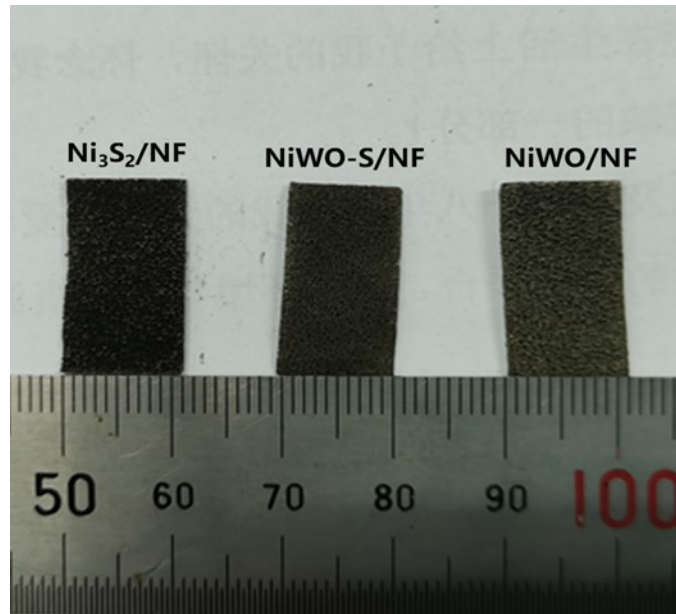
### **Calculation of electrochemically active surface area (ECSA)**

The values of ECSA can be calculated by the following equation:

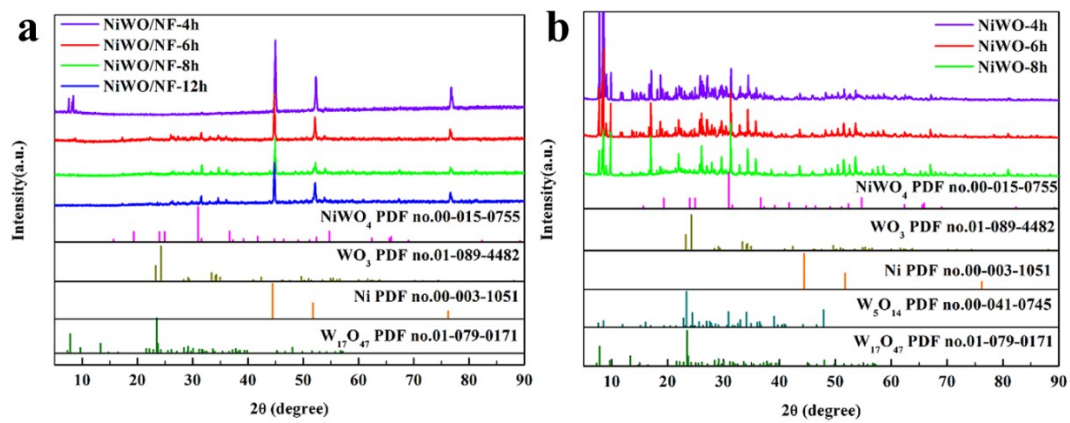
$$\text{ECSA} = C_{\text{dl}} / C_s$$

C<sub>dl</sub>: Double layer capacitance of catalyst measured in 1.0 M KOH (mF); geometric surface area of the working electrode is 2 cm<sup>-2</sup>;

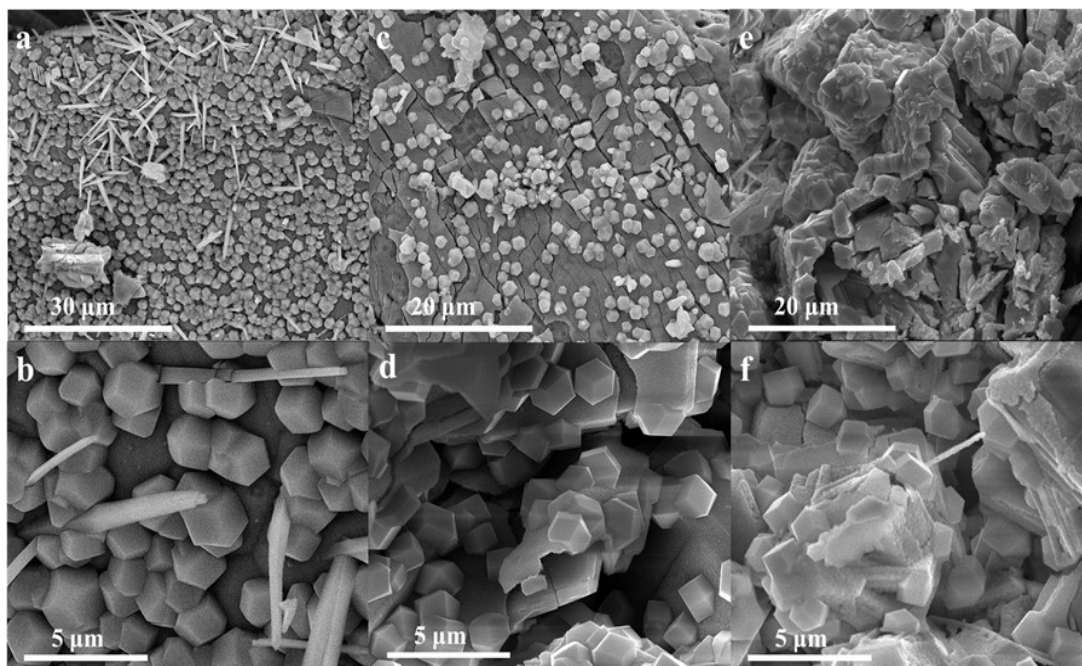
C<sub>s</sub>: Specific capacitance; the value of C<sub>s</sub> is 0.04 mF cm<sup>-2</sup> in 1.0 M KOH.



**Fig. S1** Photographs of the as-prepared samples.

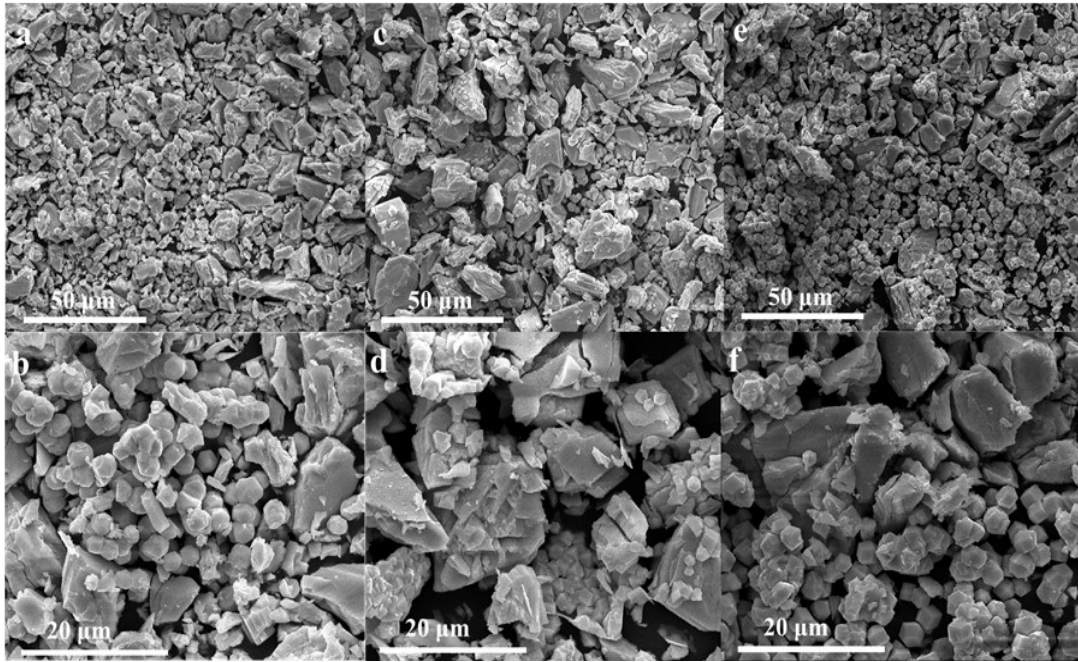


**Fig. S2** XRD patterns of (a) NiWO/NF-4h, NiWO/NF-6h, NiWO/NF-8h and NiWO/NF-12h. (b) NiWO-4h, NiWO-6h and NiWO-8h.



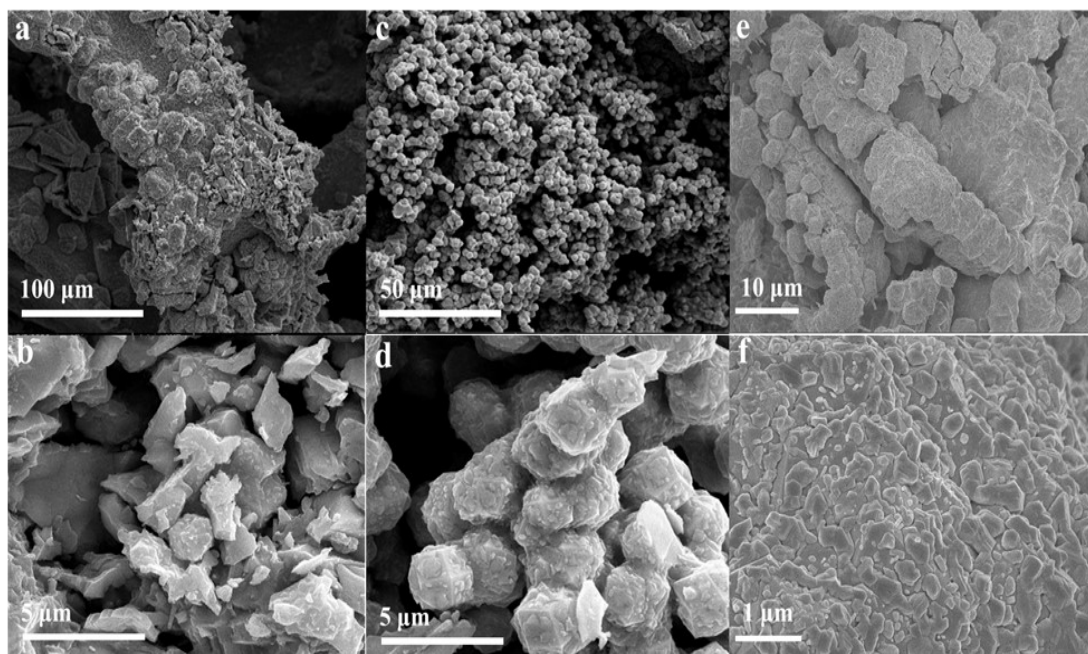
**Fig. S3** SEM images of (a–b) NiWO/NF-4h. (c–d) NiWO/NF-6h and (e–f)

NiWO/NF-8h.



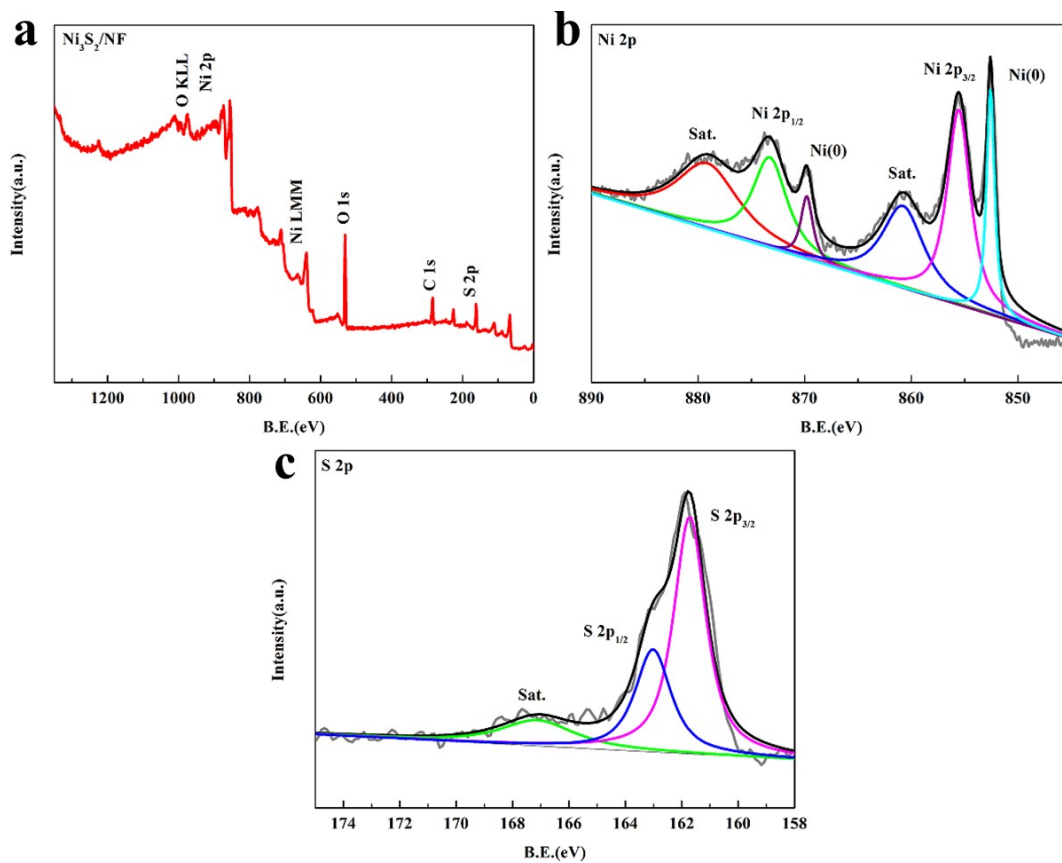
**Fig. S4** SEM images of (a–b) NiWO-4h. (c–d) NiWO-6h and (e–f) NiWO-8h.



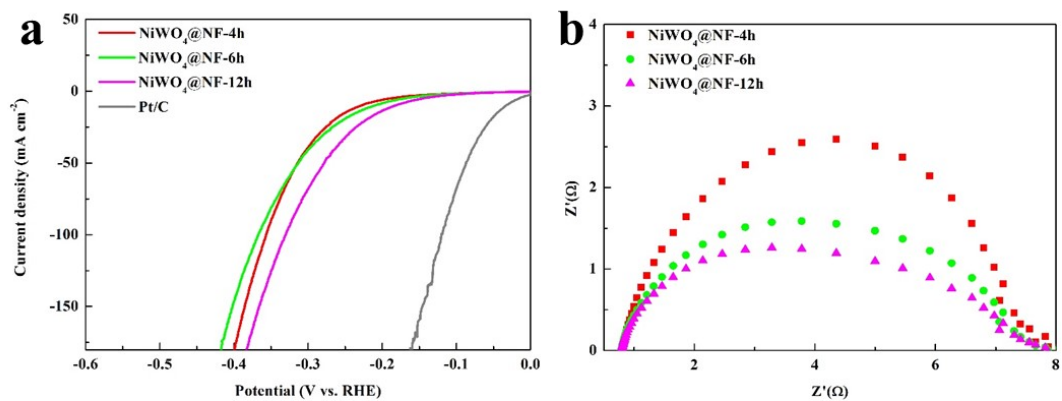


**Fig. S5** SEM images of (a-b) NiWO-S/NF-250°C. (c-d) NiWO-S/NF-300°C and (e-f)

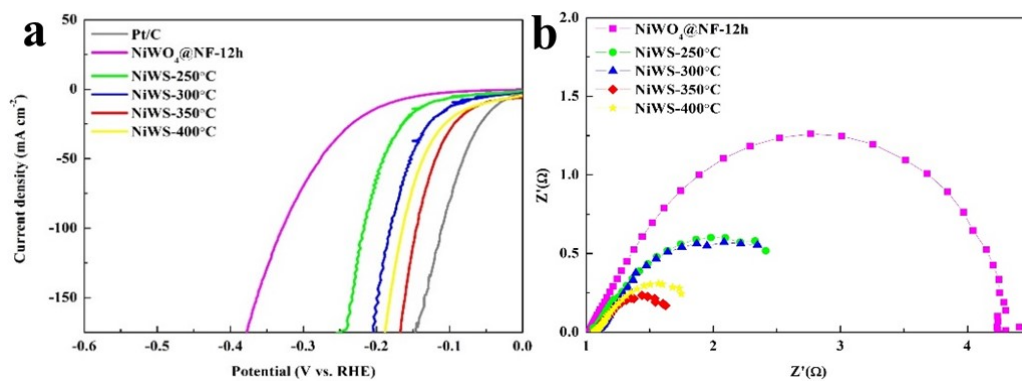
NiWO-S/NF-400°C.



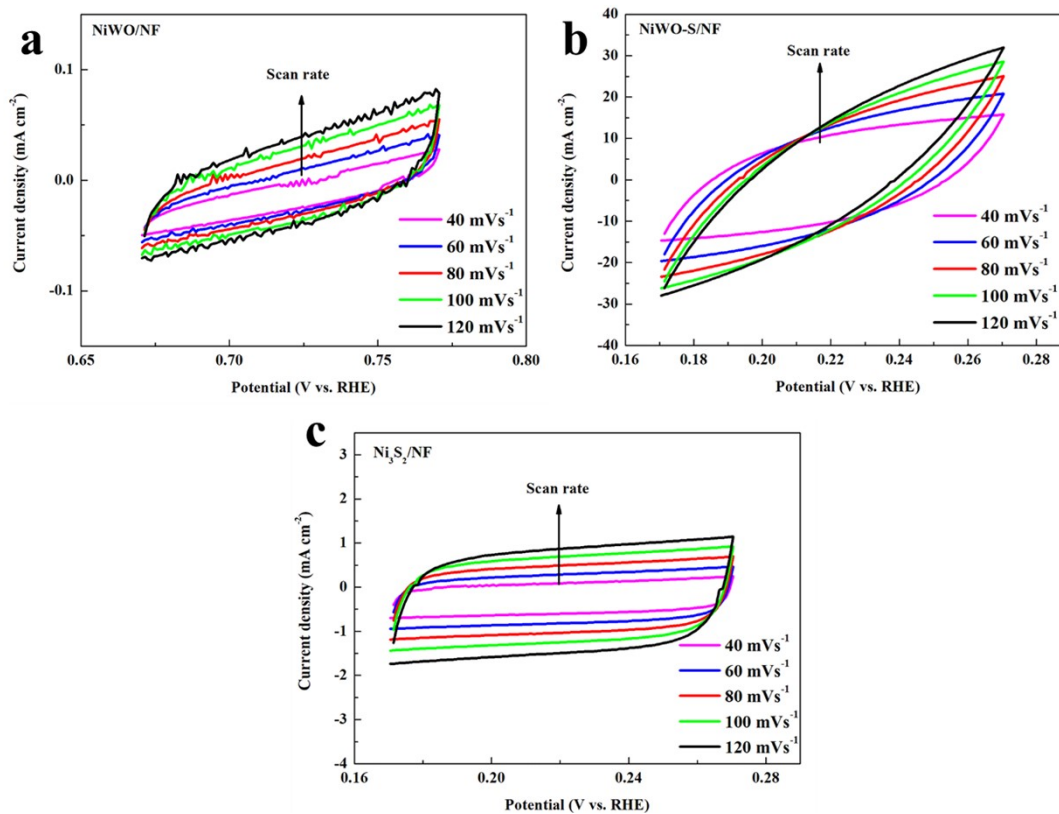
**Fig. S6** XPS spectra of  $\text{Ni}_3\text{S}_2$ . (a) Survey. (b) Ni 2p. (c) S 2p.



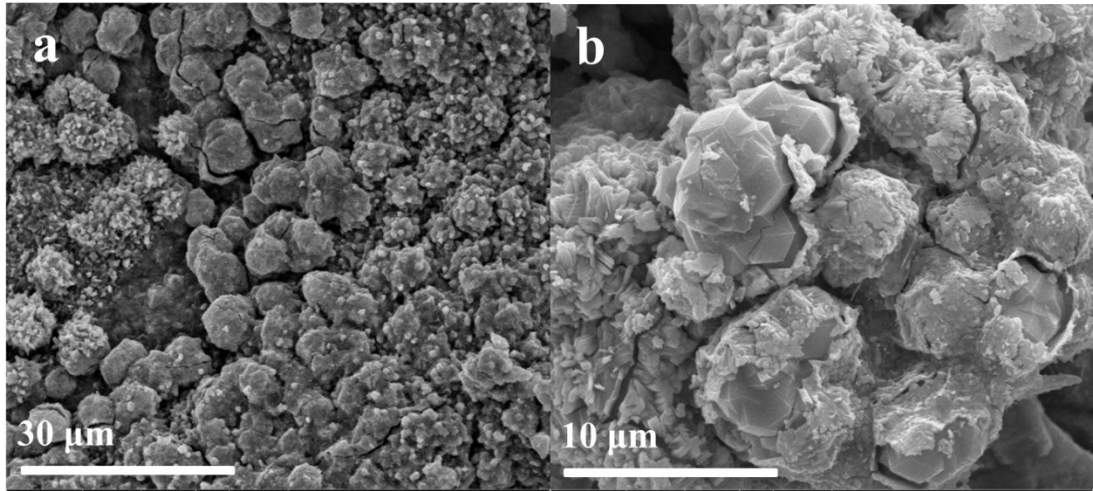
**Fig. S7** Electrocatalytic measurements of different NiWO<sub>4</sub>/NF samples. (a) Linear sweep voltammogram (LSV). (b) Electrochemical impedance spectroscopy (EIS).



**Fig. S8** Electrocatalytic measurements of different NiWO<sub>3</sub>-S/NF samples. (a) Linear sweep voltammogram (LSV). (b) Electrochemical impedance spectroscopy (EIS).



**Fig. S9** Cyclic voltammogram (CV) for ECSA of as-prepared samples. (a) NiWO/NF, (b) NiWO-S/NF, (c) Ni<sub>3</sub>S<sub>2</sub>/NF.



**Fig. S10** (a-b) SEM images of NiWO-S/NF after stability test.

**Table S1** Comparison of the electrocatalytic performance between the recently reported catalysts and as-prepared catalysts.

Electrocatalyst	Electrolyte	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Reference
NiWO-S/NF	1 M KOH	52	This work
Fe-CoMoS	1 M KOH	137	[1]
V-MoS <sub>2</sub>	1 M KOH	206	[2]
N-NiS/MoS <sub>2</sub> /NF	1 M KOH	71	[3]
Co-NiS <sub>2</sub> /NF	1 M KOH	80	[4]
2D MoP/Mo <sub>2</sub> N	1 M KOH	89	[5]
2D Ni-CoP	1 M KOH	88	[6]
P-NM-CF HNRs/NF	1 M KOH	100	[7]
Co <sub>2</sub> C	1 M KOH	181	[8]
Ni-Ni <sub>3</sub> C/CC	1 M KOH	98	[9]
Ru doped Ni(OH) <sub>2</sub> /TM-0.2	1 M KOH	135	[10]

**Table S2** Elemental values of fitted equivalent circuit related to EIS spectra.

Samples	$R_s/\Omega$	$R_{ct}/\Omega$
NiWO/NF	1.04	3.50
NiWO-S/NF	0.48	0.74
$N_3S_2$ /NF	1.18	30.1



**Table S3** The calculated ECSA values of N<sub>90</sub>-Ni(OH)<sub>2</sub>/NF, N<sub>130</sub>-Ni(OH)<sub>2</sub>/NF and N<sub>180</sub>-Ni(OH)<sub>2</sub>/NF.

Sample	$C_{dl}$ (mF)	$C_s$ (mF cm <sup>-2</sup> )	ECSA (cm <sup>2</sup> )
NiWO/NF	0.77	0.04	19.25
NiWO-S/NF	106.5	0.04	2662.5
N <sub>3</sub> S <sub>2</sub> /NF	20.9	0.04	522.5

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