

## Supporting Information

# **Anchoring $\text{Co}_3\text{S}_4$ nanowires on $\text{NiCo}_2\text{O}_4$ nanosheet arrays as high-performance electrocatalyst for hydrogen and oxygen evolution**

Hongfang Jiu<sup>\*a</sup>, Hao Wei<sup>a</sup>, Sicong Che<sup>a</sup>, Congli Wang<sup>a</sup>, Zhixin Guo<sup>a</sup>, Yuxin Han<sup>a</sup>, Yaqi Qin<sup>a</sup>,  
Lixin Zhang<sup>\*a,b</sup>

<sup>a</sup> *School of Chemistry and Chemical Engineering, North University of China, Taiyuan 030051*

<sup>b</sup> *Shanxi Key Laboratory of High Performance Battery Materials and Devices, North University of China, Taiyuan, 030051, People's Republic of China*

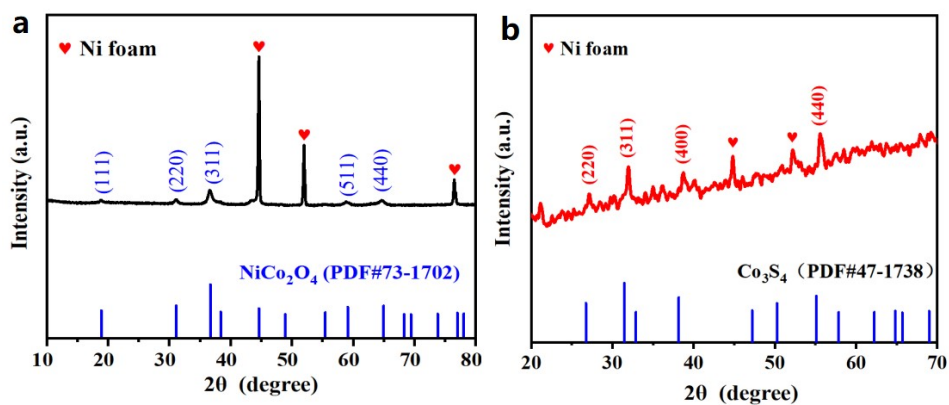


Fig. S1 XRD patterns of (a) NiCo<sub>2</sub>O<sub>4</sub>/NF and (b) Co<sub>3</sub>S<sub>4</sub>/NF

The structure composition and purity of Ni/NiCo<sub>2</sub>O<sub>4</sub> and Ni/Co<sub>3</sub>S<sub>4</sub> was characterized by X-ray diffraction (XRD). The XRD pattern of NiCo<sub>2</sub>O<sub>4</sub>/NF is shown in Fig. S1a. It is obvious that the three characteristic peaks at 44.6°, 52.0° and 76.4° be assigned to Ni foam. The diffraction peaks located at 18.9°, 31.1°, 36.6°, 58.8° and 64.8° correspond to the (111), (220), (311), (511) and (440) planes of NiCo<sub>2</sub>O<sub>4</sub> (JCPDS PDF#73-1702). This result proves that we have successfully synthesized NiCo<sub>2</sub>O<sub>4</sub>/NF.

The XRD patterns of Co<sub>3</sub>S<sub>4</sub>/NF are shown in Fig. S1b. The peaks at 27.2°, 31.9°, 38.7° and 55.6° were detected, which were well indexed to (220), (311), (400) and (440) planes of Co<sub>3</sub>S<sub>4</sub> (PDF#47-1738), respectively. The two peaks at 44.8° and 52.1° were well matched the (111) and (200) planes of Ni foam substrate.

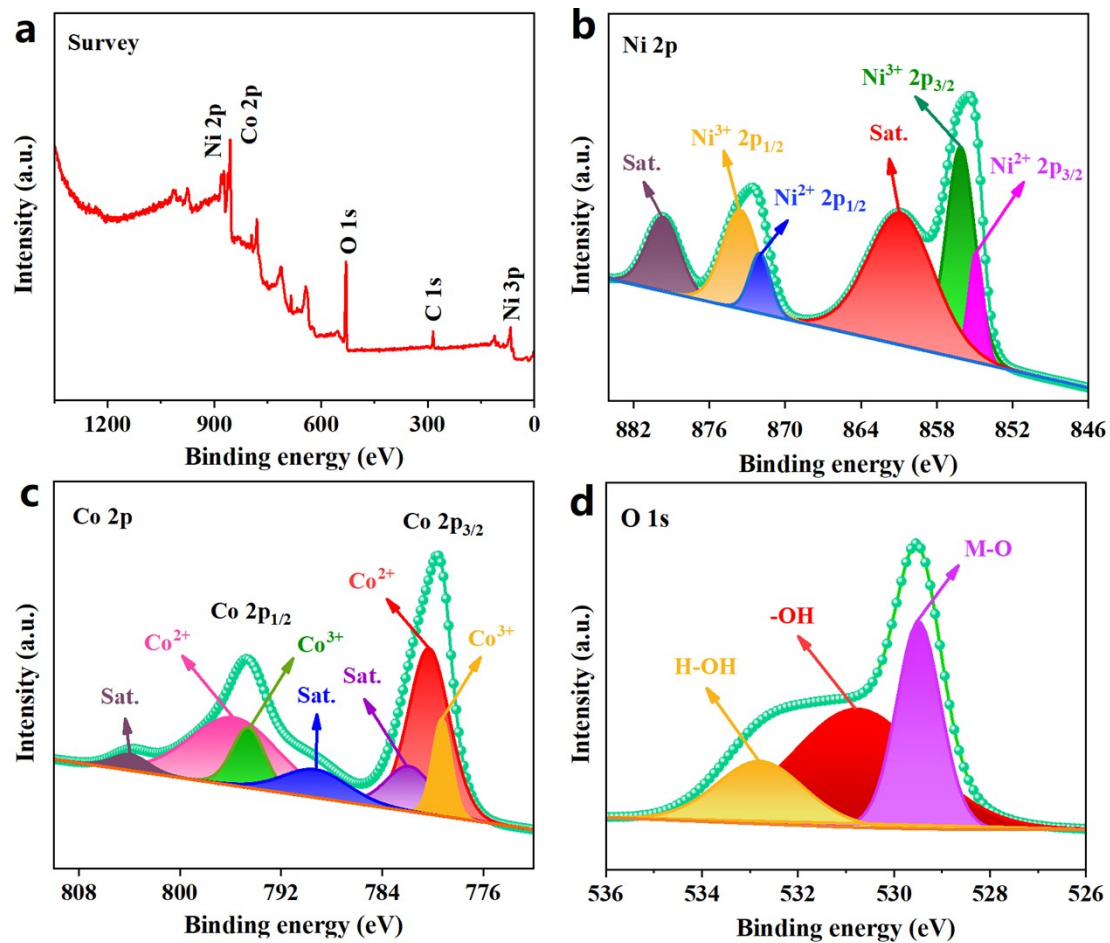


Fig.S2 The high-resolution spectra of NiCo<sub>2</sub>O<sub>4</sub>/NF (a) Survey (b) Ni 2p, (c) Co 2p, (d) O 1s.

The elemental surface properties and oxidation states of NiCo<sub>2</sub>O<sub>4</sub>/NF catalysts were deep researched by X-ray photoelectron spectroscopy (XPS). It is Fig. S2a that shows the XPS survey spectrum, we can clearly see the presence of Co, Ni and O from which. The Ni 2p spectrum (Fig.S2b) consists of Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub>, which are further divided by the Ni<sup>2+</sup> peak and Ni<sup>3+</sup> peak. The Ni<sup>2+</sup> peak is located at 854.5, 872.0eV, and the Ni<sup>3+</sup> peak at 856.1 and 873.6 eV, respectively. In addition, the satellite peaks of Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> are observed at 861.1 eV and 879.7 eV, respectively. The Co 2p spectra is shown in Fig. S2c, two main peaks for Co 2p<sub>3/2</sub> are observed at 779.6 and 780.3 eV, and Co 2p<sub>1/2</sub> is observed at 794.6 and 795.9 eV. They both have two shakeup satellite peak (identified as "Sat."). It is worth pointing out that the two peaks with binding energies of 781.9 eV and 804.0 eV are assigned to Co2p. The fine spectrum of O 1s is presented in Fig. S2d. The three peaks located at 529.4, 530.8 and 532.8 eV correspond to the M-O, -OH and H-OH bonds, respectively. The above results prove that we have successfully synthesized NiCo<sub>2</sub>O<sub>4</sub>/NF.

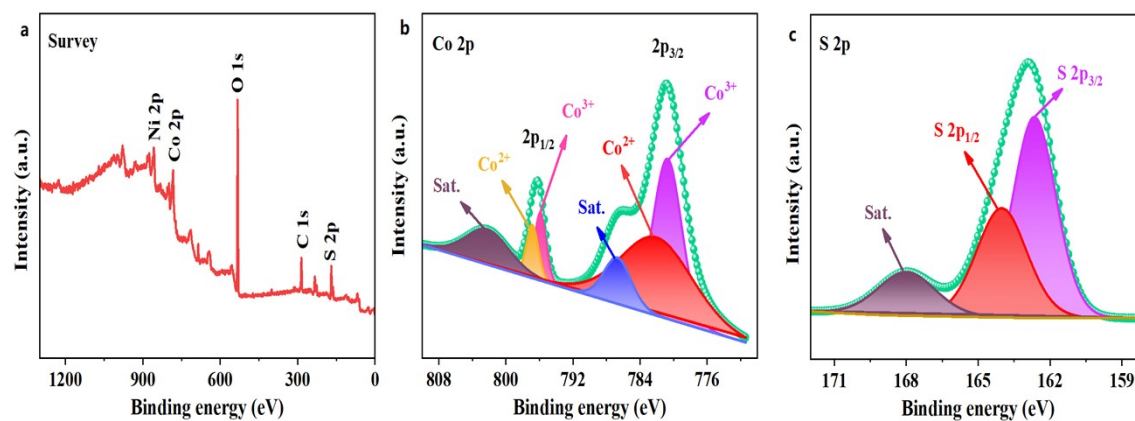
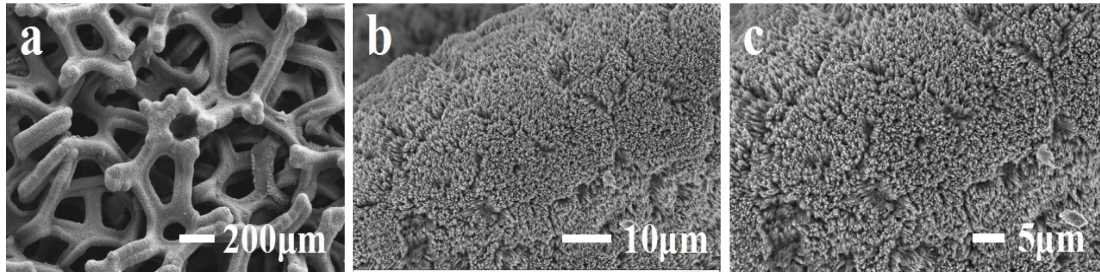


Fig.S3 The high-resolution spectra of NF/Co<sub>3</sub>S<sub>4</sub> (a) Survey, (b) Co 2p and (c) S 2p

XPS analysis was performed to examine the composition and chemical binding environments of each catalyst. Fig. S3a shows a survey XPS spectrum of Co<sub>3</sub>S<sub>4</sub>/NF, indicating the presence of Co and S. The Co 2p XPS spectrum of Co<sub>3</sub>S<sub>4</sub>/NF is shown in Fig. S3b. Co2p spectrum was de-convoluted into six components at 780.8 eV, 782.5eV, 786.8eV, 795.2 eV, 794.4eV and 797.4eV. The peaks at 780.8 and 795.2 eV were assigned to Co<sup>3+</sup> species, while the two peaks located at 782.5eV and 784.4 eV corresponded to Co<sup>2+</sup> ones. Besides, the satellite peaks were detected at 786.8 eV and 797.4 eV. Furthermore, distinct peaks were observed at 162.72 eV and 164.0 eV in the S 2p spectrum, and a satellite peak at 168.02 eV can be seen in Fig. S3c. These findings verified that Co<sub>3</sub>S<sub>4</sub> had formed on the surface of Ni Foam.



*Fig.S4 The SEM images of  $\text{Co}_3\text{S}_4/\text{NF}$*

*It can clearly be seen that  $\text{NiCo}_2\text{O}_4$  nanosheet covers the surface of Ni foam, and  $\text{NiCo}_2\text{O}_4/\text{NF}$  has a dandelion-like microstructure made of nanowire. The surface morphologies of as-obtained  $\text{Co}_3\text{S}_4/\text{NF}$  are studied by scanning electron microscopy (SEM), which is displayed in Fig.S4. Obviously, a large amount of  $\text{Co}_3\text{S}_4$  nanowires were grown on the surface of Ni foam, which look like cluttered grass.*

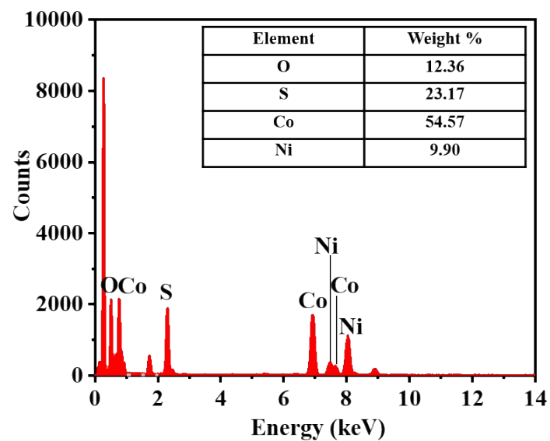


Fig. S5 The energy dispersive X-ray spectrum of NF/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub>.

Furthermore, the energy dispersive X-ray spectrum (EDX) of NF/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub> revealed that its weight percentage ratio of Ni/Co/O/S is 9.90:54.57:12.36:23.17.

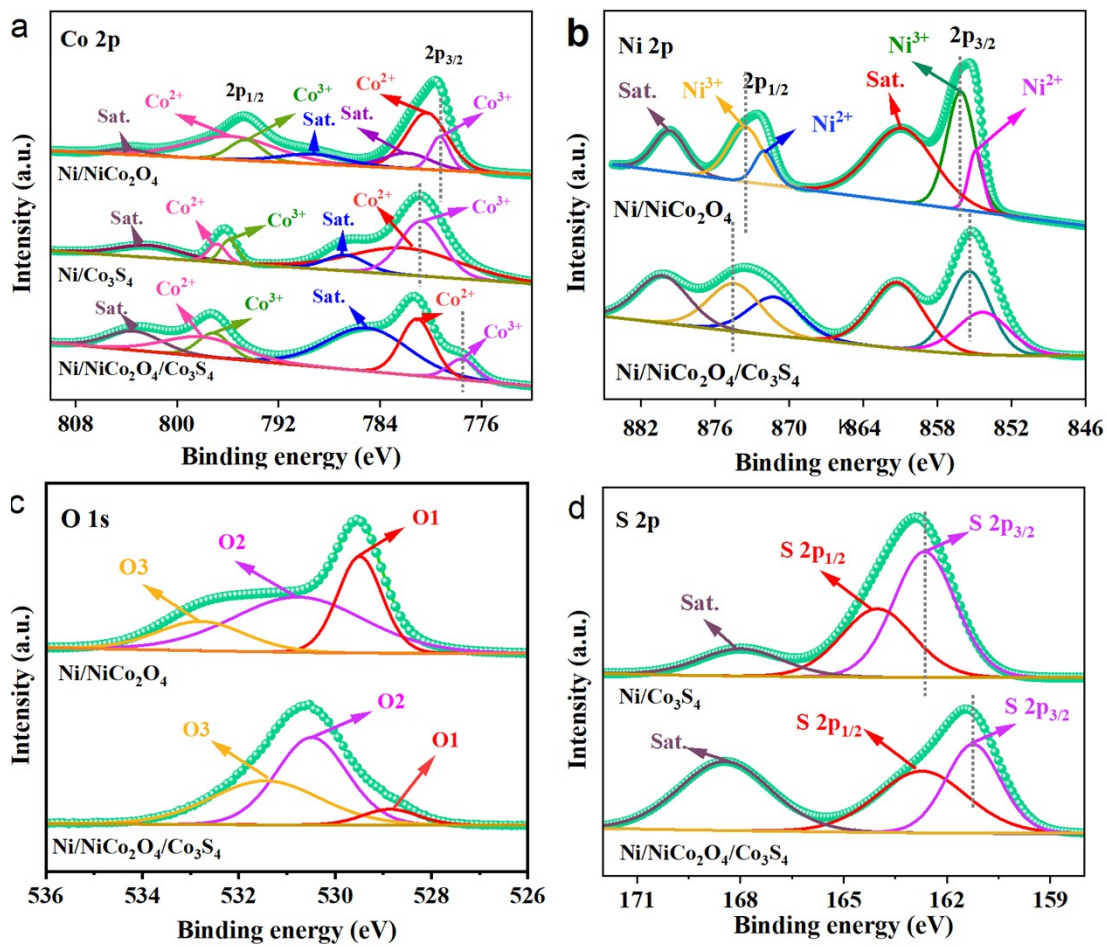
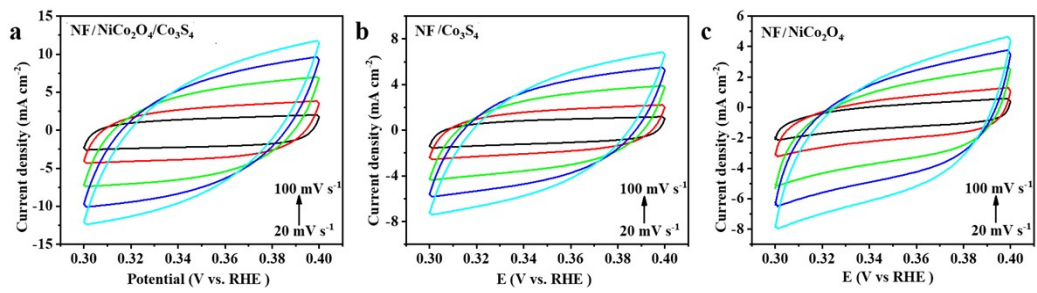
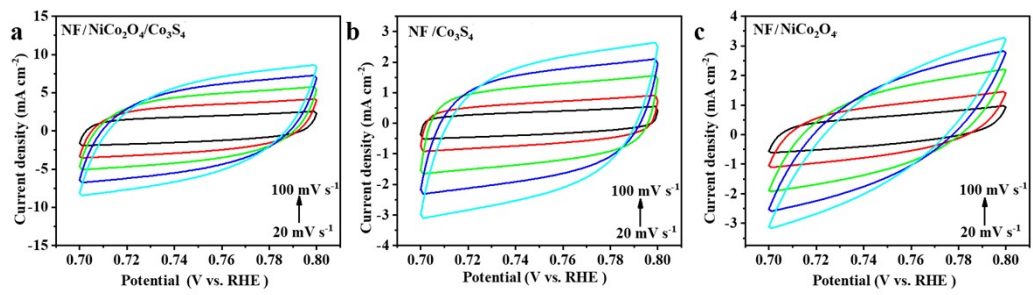


Fig.S6 High-resolution XPS spectra of Ni/NiCo<sub>2</sub>O<sub>4</sub>, Ni/Co<sub>3</sub>S<sub>4</sub> and Ni/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub> electrodes: a) Co 2p, b) Ni 2p, c) O 1s, and d) S 2p.



**Fig. S7** Cyclic voltammograms of (a) NF/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub>, (b) NF/Co<sub>3</sub>S<sub>4</sub> (c) NF/NiCo<sub>2</sub>O<sub>4</sub> at the different scan rates varying from 20 to 100 mV s<sup>-1</sup> in HER.





**Fig. S8.** Cyclic voltammograms of (a) NF/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub>, (b) NF/Co<sub>3</sub>S<sub>4</sub> (c) NF/NiCo<sub>2</sub>O<sub>4</sub> at the different scan rates varying from 20 to 100  $\text{mV s}^{-1}$  in OER.

**Table. S1.** The HER activity of the NF/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub> compared with other recently reported catalysts in the alkaline (1M KOH) medium.

Catalysts	$\eta_{10}$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
NF/NiCo <sub>2</sub> O <sub>4</sub> /Co <sub>3</sub> S <sub>4</sub>	71	120	This work
Ni <sub>3</sub> S <sub>2</sub> -FeS-CoS	82	68	1
CoNi <sub>2</sub> S <sub>4</sub> /WS <sub>2</sub> /Co <sub>9</sub> S <sub>8</sub>	70	112	2
NiCo <sub>2</sub> O <sub>4</sub> /CF-P	158	85	3
NiCo <sub>2</sub> S <sub>4</sub> @NiFe LDH	200	101.1	4
Cu-Ni <sub>3</sub> S <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub>	79	50.4	5
Co(OH) <sub>2</sub> @NCNTs@NF	170	-	6
Ni <sub>0.33</sub> Co <sub>0.67</sub> S <sub>2</sub>	192.1	93.64	7
NiCo <sub>2</sub> O <sub>4</sub>	106.5	52	8

**Table. S2.** The OER activity of the NF/NiCo<sub>2</sub>O<sub>4</sub>/Co<sub>3</sub>S<sub>4</sub> compared with other recently reported catalysts in the alkaline (1M KOH) medium

Catalysts	$\eta_{10}$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
NF/NiCo <sub>2</sub> O <sub>4</sub> /Co <sub>3</sub> S <sub>4</sub>	170	79	This work
Ni <sub>3</sub> S <sub>2</sub> -FeS-CoS	170	76	1
NiCo <sub>2</sub> O <sub>4</sub> /CF-P	191	83	3
Cu-Ni <sub>3</sub> S <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub>	160(50mV)	59.7	5
NiO/NiS	209(40mV)	60	9
MCNTs@CoS <sub>x</sub> @MoS <sub>2</sub> ,	285	76	10
Ni <sub>3</sub> S <sub>4</sub>	257	67	11
MoS <sub>2</sub> /Co <sub>9</sub> S <sub>8</sub> /Ni <sub>3</sub> S <sub>2</sub> /Ni	166	58	12
Fe-NiCoP/PBA	290	70	13

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