Electronic Supplementary Information

Experimental section

Materials

$NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, and urea were purchased from Beijing Chemical Corp. KOH was purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) was purchased from Sigma-Aldrich. Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of $NiCo_2O_4$ nanowires array:

Typically, a piece of CC (3 cm × 2 cm) was cleaned by sonication sequentially in acetone, water and ethanol for 10 min each before use. The NiCo-precursor nanowires array was uniformly grown on the CC using a hydrothermal reaction, $NiCl_2 \cdot 6H_2O$ (4 mmol), $CoCl_2 \cdot 6H_2O$ (8 mmol) and urea (15 mmol) were dissolved in 75 mL water under vigorous stirring for 30 min. Then the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave in which a piece of CC was immersed into the solution. The autoclave was sealed and maintained at 120 °C for 6 h in an electric oven. After the autoclave cooled down at room temperature, the NiCo-precursor nanowires array was taken out and washed with water and ethanol several times, followed by drying at 60 ºC, and then annealed at 450 °C in air for 2 h to obtain the $NiCo_2O_4$ nanowires array.

Preparation of $NiCo_2S_4$ nanowires array:

To prepare $NiCo_2S_4$ nanowires array, the CC covered with $NiCo_2O_4$ nanowires was placed in the hot centre of a tube furnace, and an alumina boat containing 2g of S powder was placed at the farthest upstream position within the tube furnace. Subsequently, the two alumina boats were heated at 300 °C for 2 h with a heating speed of 8 ºC min^{-1} in Ar atmosphere, and then naturally cooled to ambient temperature under Ar. The loading for $NiCo_2S_4$ on CC was determined to be 4.0 mg cm^{-2}.

Characterizations

Powder X-ray diffraction (XRD) data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements

Electrochemical measurements are performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system, using $NiCo_2S_4$/CC as the working electrode, a graphite plate as the counter electrode and a SCE as the reference electrode. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). In 1.0 M KOH, E (RHE) = E (SCE) + 1.068 V.

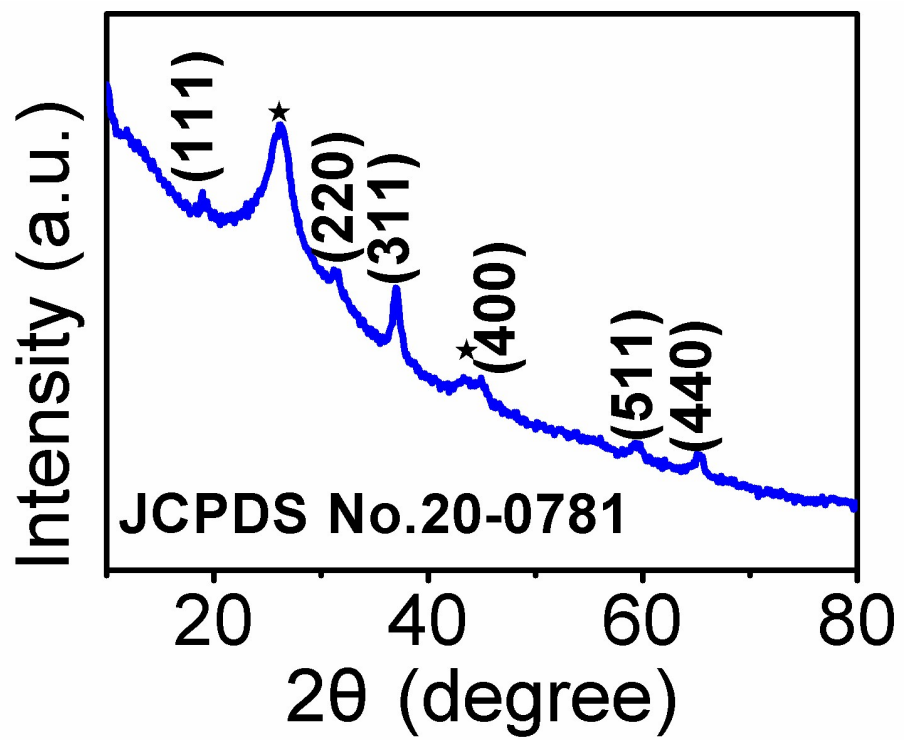

Fig. S1. XRD pattern of $NiCo_2O_4$ NA/CC.

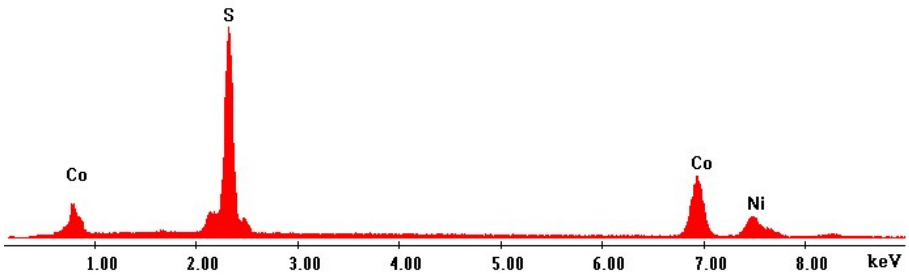

Fig. S2. EDX spectrum of $NiCo_2S_4$ NA/CC.

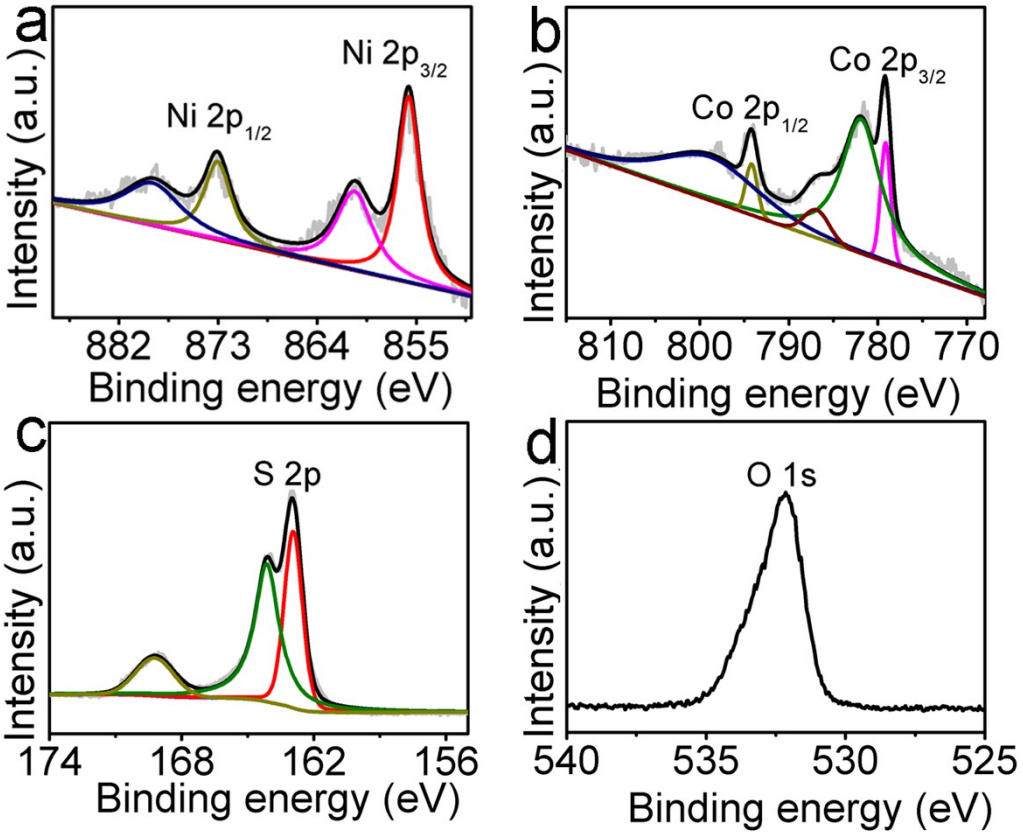

Fig. S3. XPS spectra in the (a) Ni 2p, (b) Co 2p, (c) S 2p and (d) O 1s for $NiCo_2S_4$ NA/CC.

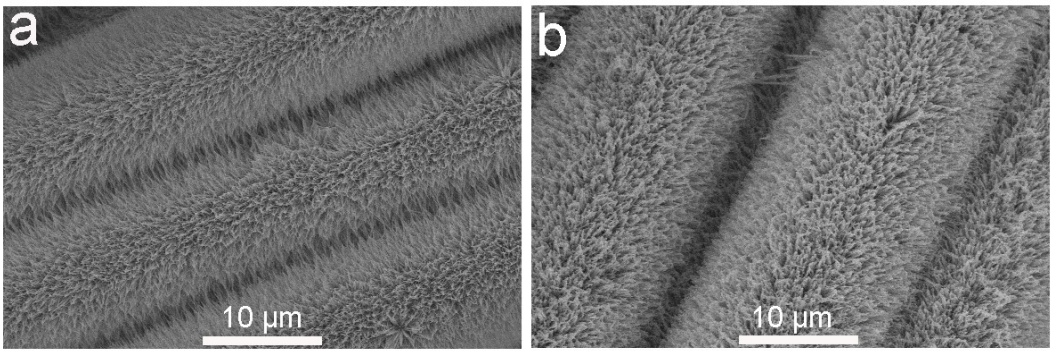

Fig. S4. SEM images of $NiCo_2S_4$ NA/CC after 500 CV cycling for (a) HER and (b) OER.

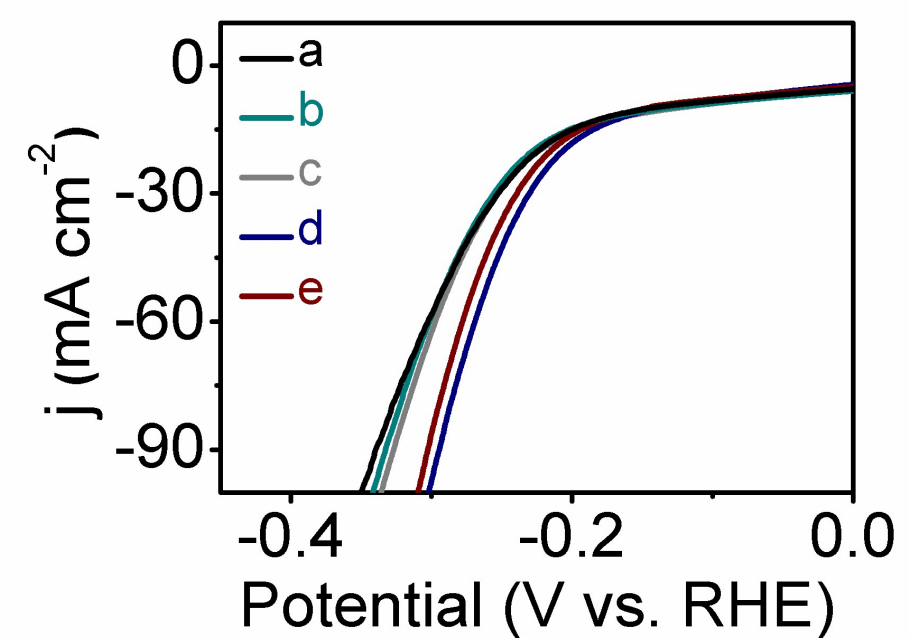

Fig. S5. Polarization curves of $NiCo_2S_4$ NA/CC with $NiCo_2S_4$ loading of (a) 0.43, (b) 0.97, (c) 1.42, (d) 2.35 and (e) 4.4 mg cm^{-2} in 1 M KOH with a scan rate of 2 mV s^{-1} for HER.

Table S1. Comparison of HER performance in alkaline electrolytes for $NiCo_2S_4$ NA/CC with some reported non-noble metal HER electrocatalysts.

Catalyst	Loading mass (mg cm^{-2})	Electrolyte	η@20 mA cm^{-2} (mV)	Ref.
$NiCo_2S_4$ NA/CC	0.43	1 M KOH	228	this work
Co-NRCNTs	0.28	1 M KOH	~360	1
Mo_2C	0.80	1 M KOH	~360	2
FeP NAs/CC	1.50	1 M KOH	~370	3
CoO_x@CN on GCE	0.42	1 M KOH	~393	4
PCPTF	0.10	1 M KOH	~807	5

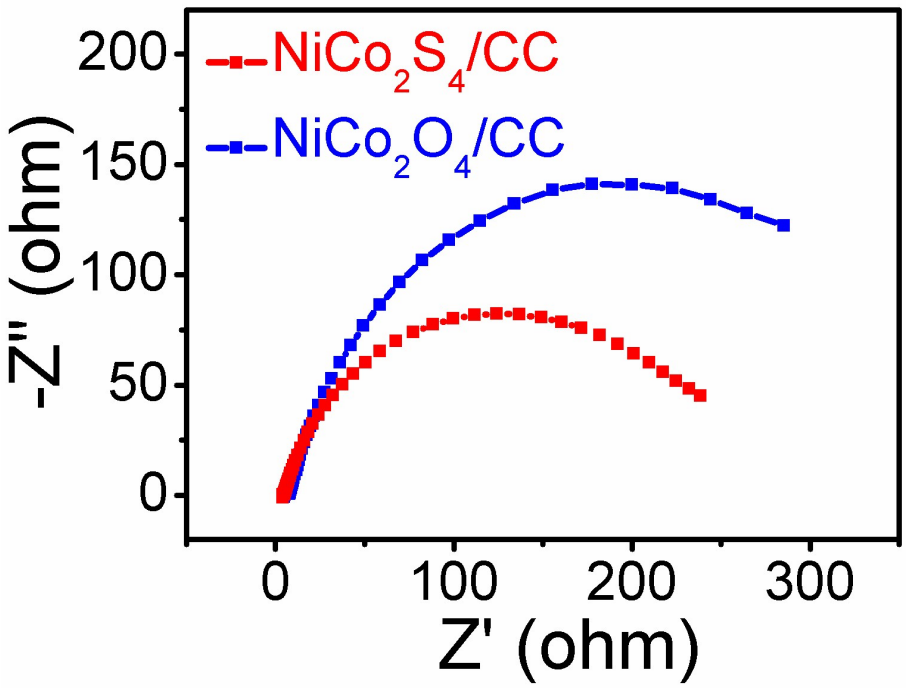

Fig. S6. Nyquist plots of $NiCo_2S_4$ NA/CC and $NiCo_2O_4$ NA/CC recorded in 1 M KOH solution.

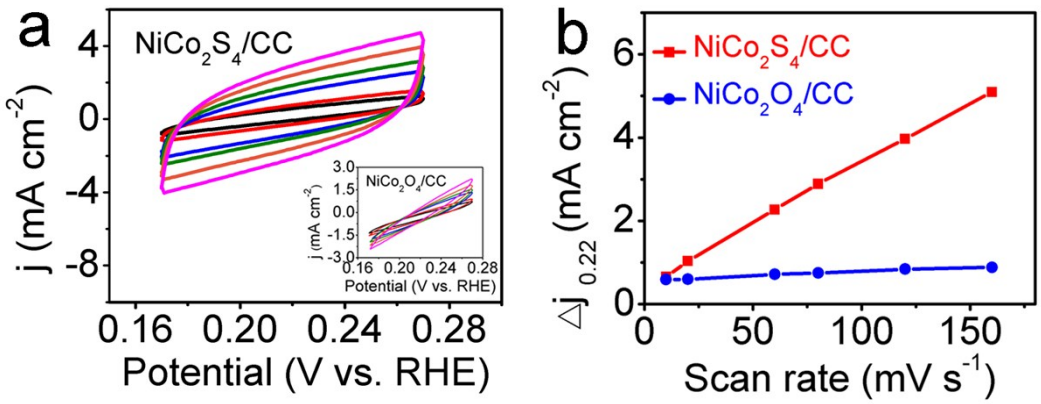

Fig. S7. (a) Cyclic voltammetrys for $NiCo_2S_4$ NA/CC and $NiCo_2O_4$ NA/CC (inset). (b) The capacitive currents at 0.22 V as a function of scan rate for $NiCo_2S_4$ NA/CC and $NiCo_2O_4$ NA/CC ($\Delta j_0 = j_a - j_c$).

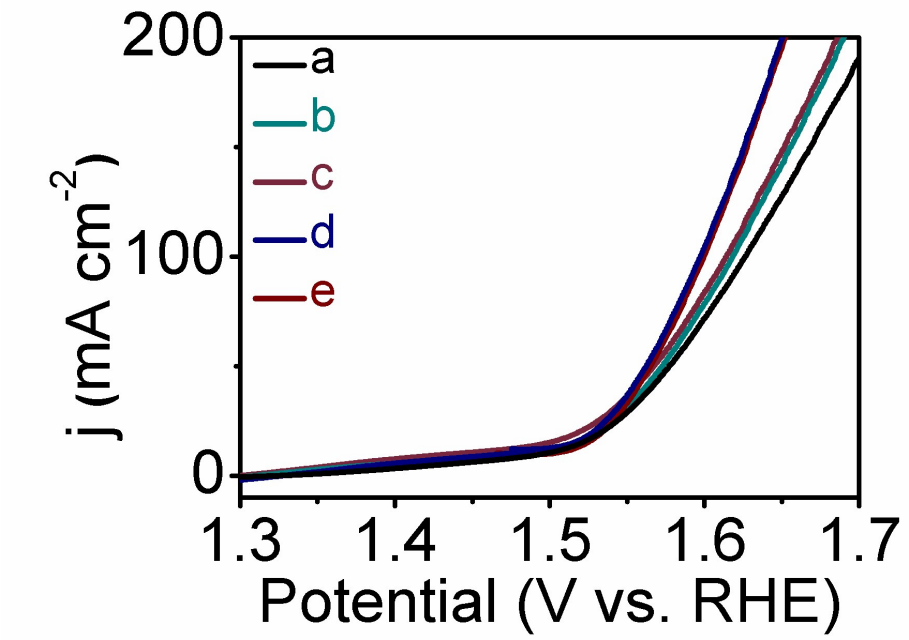

Fig. S8. Polarization curves of $NiCo_2S_4$ NA/CC with $NiCo_2S_4$ loading of (a) 0.43, (b) 0.97, (c) 1.42, (d) 2.35 and (e) 4.4 mg cm^{-2} in 1 M KOH with a scan rate of 2 mV s^{-1} for OER.

Table S2. Comparison of OER performance in alkaline electrolytes for $NiCo_2S_4$ NA/CC with some reported non-noble metal OER electrocatalysts.

Catalyst	Loading mass (mg cm^{-2})	Electrolyte	η@20mA cm^{-2} (mV)	Ref.
$NiCo_2S_4$ NA/CC	0.43	1 M KOH	336	this work
Co_3O_4 NCs	0.35	1 M KOH	~360	6
Co-P	1	1 M KOH	~370	7
NiCo LDH	0.23	1 M KOH	~393	8
$NiCo_2O_4$	~	1 M KOH	~391	9
$NiCo_2O_4$ NNs	0.53	1 M KOH	~807	10

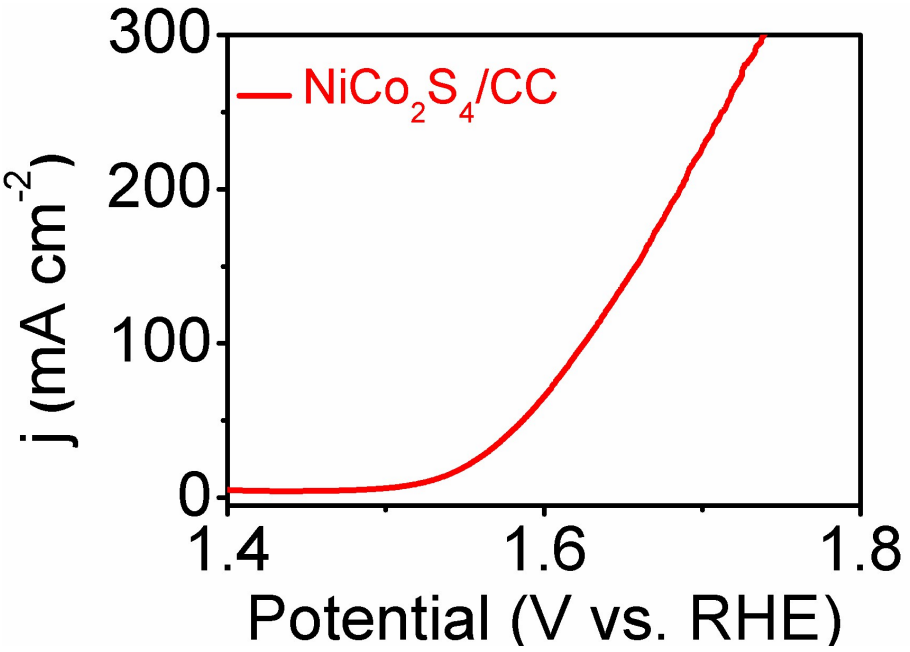

Fig. S9. LSV curves for $NiCo_2S_4$ NA/CC with a scan rate of 2 mV s^{-1} for OER in 0.1 M KOH.

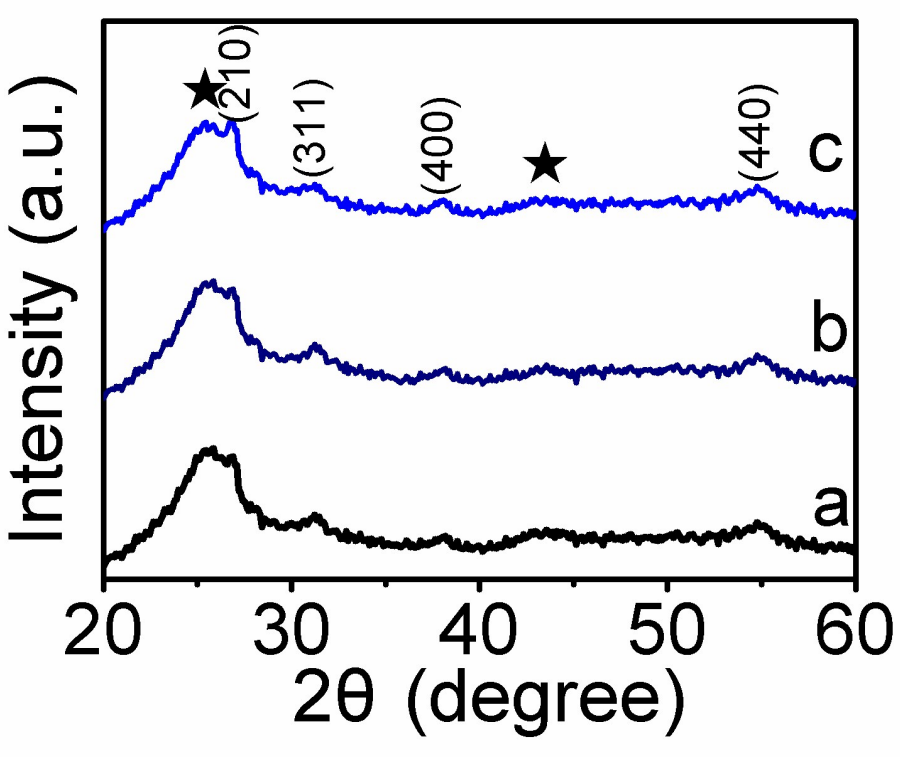

Fig. S10. XRD patterns $NiCo_2S_4$ NA/CC before (curve a) and after HER (curve b) and OER (curve c) electrolysis.

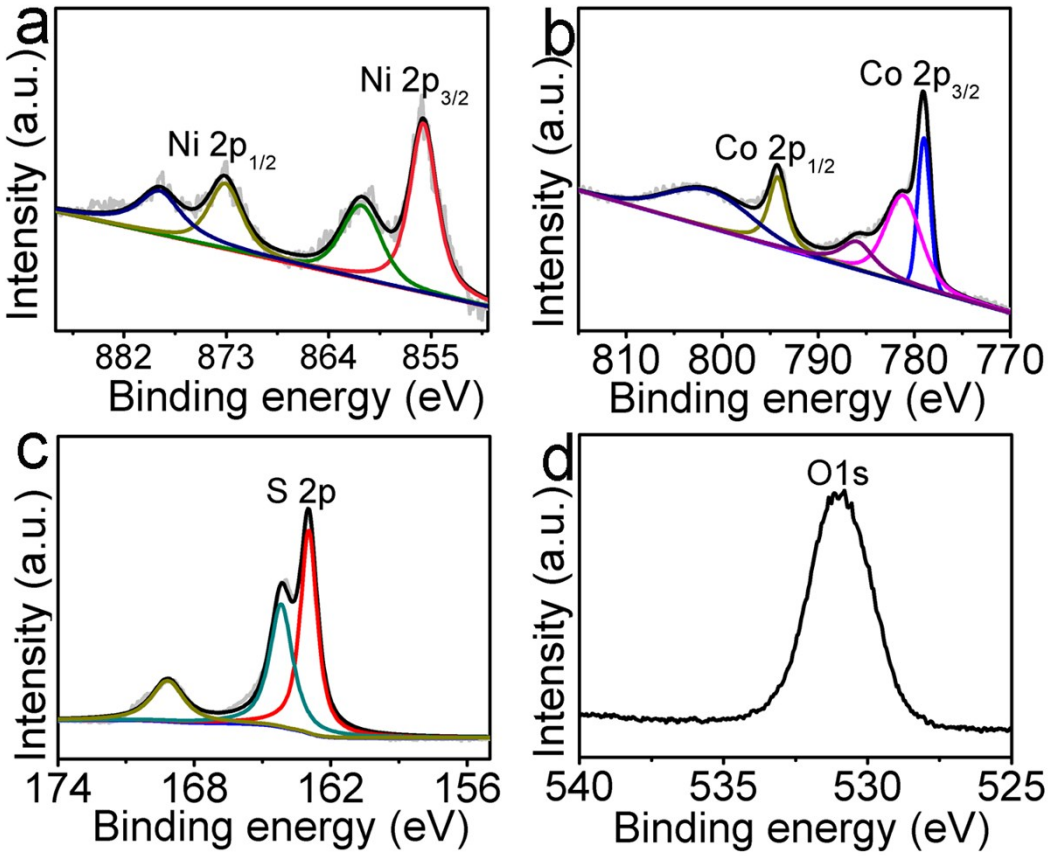

Fig. S11. XPS spectra in the (a) Ni 2p, (b) Co 2p, (c) S 2p and (d) O 1s regions for $NiCo_2S_4$ NA/CC after HER electrolysis in 1 M KOH

.

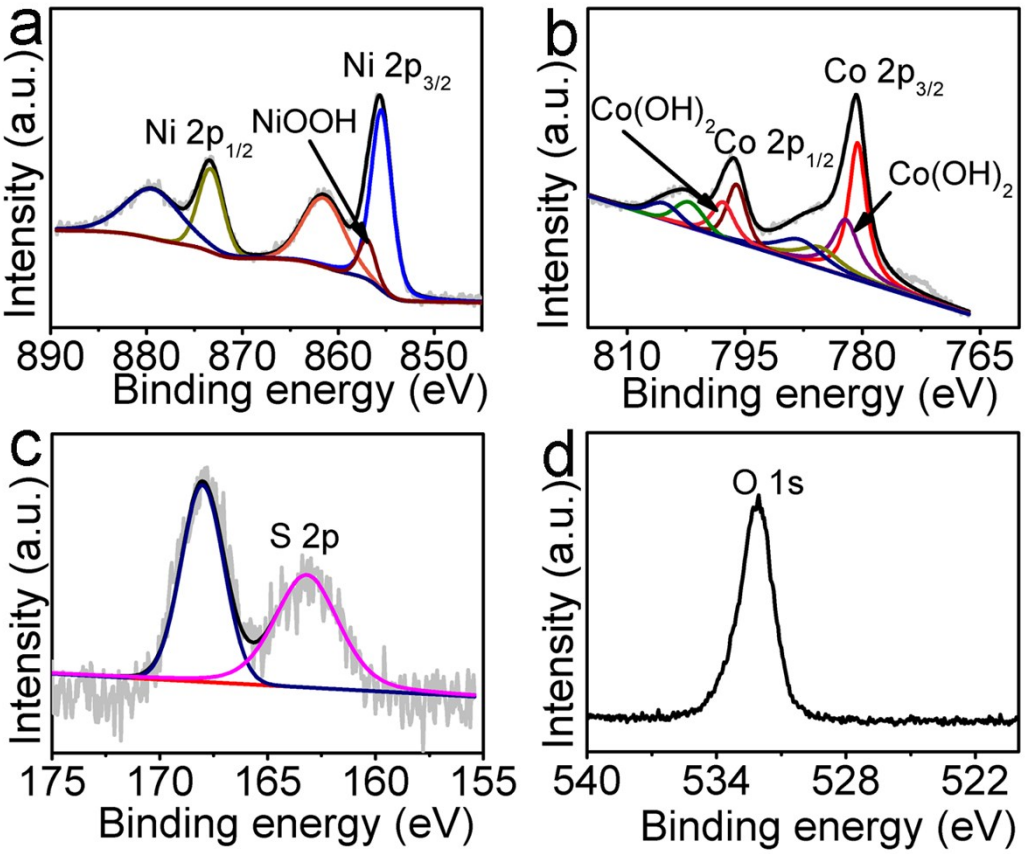

Fig. S12. XPS spectra in the (a) Ni 2p, (b) Co 2p, (c) S 2p and (d) O 1s regions for $NiCo_2S_4$ NA/CC after OER electrolysis in 1 M KOH.

References

1 X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková and A. Asefa, *Angew. Chem. Int. Ed.*, 2014, **53**, 4372.

2 H. Vrubel and X. Hu, *Angew. Chem. Int. Ed.*, 2012, **51**, 12703.

3 Y. Liang, Q. Liu, A. M. Asiri, X. Sun and Y. Luo, *ACS Catal.*, 2014, **4**, 4065.

4 H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**. 2688.

5 Y. Yang, H. Fei, G. Ruan and J. M. Tour, *Adv. Mater.*, 2015 **27**, 3175.

6 S. Du, Z. Ren, J. Zhang, J. Wu, W. Xi, J. Zhu and H. Fu, *Chem. Commun.*, 2015, **51**, 8066.

7 N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed.,* 2015, **54**, 6251.

8 H. Liang, F. Meng, C. A. Miguel, L. Li, A. Forticaux, L. Xiu, Z. Wang and S, Jin, *Nano. Lett.,* 2015, **15**, 1421.

9 Z. Peng, D. Jia, A. Al-Enizi, A. Elzatahry and G. Zheng, *Adv. Energy Mater.*, 2015, **5**, 1402031.

10 H. Shi and G. Zhao, *J. Phys. Chem. C,* 2014, **118**, 25939.