

Supporting Information

Construction of self-supporting, hierarchically structured caterpillar-like NiCo₂S₄ arrays as an efficient trifunctional electrocatalyst for water and urea electrolysis

Wenjiao Song,^{†,a} Mingze Xu,^{†,a} Xue Teng,^a Yanli Niu,^a Shuaiqi Gong,^a Xuan Liu,^a

Xiaoming He,^b and Zuofeng Chen^{*,a}

^aShanghai Key Laboratory of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China;

^bSchool of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China.

* zfchen@tongji.edu.cn (Z.-F. C.)

† These authors contributed equally.

EXPERIMENTAL

Chemicals. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%), ammonium fluoride (NH₄F, 98%), urea (H₂NCONH₂, 99%), sodium sulfide (Na₂S, 98%), potassium hydroxide (KOH, 99%), concentrated nitric acid (HNO₃, 98%) and ethanol (C₂H₅OH, 99.5%) were obtained from Sigma Aldrich. The carbon cloth was obtained from Shanghai Hesen Electric Co.

(HCP330N, 32 cm × 16 cm, 0.32 mm). All reagents were analytical grade and used as received without further purification. Deionized water (18.0 MΩ cm) was used for preparing electrolyte solutions in all experiments.

Procedures. *Preparation of NiCo precursor arrays on carbon cloth.* Before being used, the carbon cloth (CC, ~2.5 × 3.5 cm) was cleaned with absolute ethanol, 10% nitric acid solution and distilled water under ultrasonication for 20 minutes to remove dust and oxides on the surface. The NiCo precursor arrays were synthesized according to the following procedure. Namely, 1.5 mmol Ni(NO₃)₂·6H₂O, 1.5 mmol Co(NO₃)₂·6H₂O, 6 mmol NH₄F and 15 mmol H₂NCONH₂ were dispersed into 35 mL deionized water under magnetic stirring to form a clear pink solution. Subsequently, the aqueous solution was transferred to a 50 mL Teflon-lined stainless steel autoclave with a piece of clean CC substrate vertically placed, which was kept in an oven at 100 °C for 8 h. After the reaction, the electrode was taken out, washed with distilled water and ethanol for several times and dried in an oven at 60 °C to obtain a light pink NiCo precursor/CC electrode.

Preparation of NiCo₂S₄ arrays on carbon cloth. To obtain corresponding sulfide, a piece of NiCo precursor/CC electrode was immersed into a solution (30 mL) containing Na₂S·9H₂O (3 mmol) and transferred to a 50 mL Teflon-lined stainless steel autoclave. The NiCo₂S₄/CC electrode was finally obtained after being heated in an electric oven at 160 °C for 8 h. After cooling to room temperature, the as-obtained black electrode was washed with distilled water and ethanol for several times and dried at 60 °C.

Preparation of NiS and Co₉S₈ arrays on carbon cloth. For comparison, the Ni precursor/CC and Co precursor/CC were prepared via a similar method without added Co(NO₃)₂ or Ni(NO₃)₂, and then transformed into NiS/CC and Co₉S₈/CC by the same sulfurization procedure.

Preparation of RuO₂ and Pt/C electrodes. To use RuO₂ as the benchmark, the catalyst ink was made up by dispersing 4 mg of the sample in 1 mL of 4:1 v/v water/ethanol with 80 μL of 5 wt% Nafion solution by at least 30 min sonication to form a homogeneous solution. Finally, 70 μL ink was loaded onto the CC electrode of 1×1 cm². The final loading for the RuO₂ electrocatalyst on the CC electrode is about 0.28 mg cm⁻². The 20 wt% Pt/C electrode was prepared in the same way.

Apparatus. X-ray diffraction (XRD) data was recorded on Bruker Foucs D8 via ceramic monochromatized Cu Kα radiation of 1.54178 Å with the operating voltage of 40 kV and current of 40 mA.

Scanning electron microscopy (SEM) images, energy dispersive X-ray spectroscopy (EDX) data and corresponding mapping images were acquired on a Hitachi S-4800 (Hitachi, Japan) equipped with an EDX instrumentation. Transmission electron microscopy (TEM) tests and the selected area electron diffraction (SAED) measurements were conducted on a JEM-2100, JEOL microscope.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. The binding energies were calibrated by taking the C 1s level of 284.6 eV as a reference.

The electrochemical measurements toward oxygen evolution reaction (OER),

hydrogen evolution reaction (HER) and urea oxidation reaction (UOR) were carried out in a three-electrode configuration on an electrochemical workstation (CHI660E), employing the as-prepared samples as the working electrode, saturated calomel electrode (SCE) as the reference electrode and carbon rod as the counter electrode. For overall water splitting and urea electrolysis, the measurements were conducted with the as-synthesized catalysts used as both cathode and anode in a two-electrode configuration.

During OER, HER and water electrolysis tests, the electrochemical activities were studied in 1 M KOH solution, while UOR and urea electrolysis tests were conducted in 1 M KOH solution containing 0.33 M urea. In water electrolysis measurements, the potentials reported were calculated with respect to the reversible hydrogen electrode (RHE), while in urea electrolysis tests, the potentials are calibrated with respect to the saturated calomel electrode (SCE). Linear sweep voltammetry (LSV) measurements were carried out at 2 mV s^{-1} for water splitting and 1 mV s^{-1} for urea electrolysis to minimize the capacitive current. Tafel slopes were acquired from polarization curves by plotting η vs. \log current density (j). Electrochemical impedance spectroscopy (EIS) tests were performed under a given overpotential over the frequency range 0.01 Hz to 100 kHz at the amplitude of the sinusoidal voltage of 5 mV.

Unless stated otherwise, all experiments were conducted at room temperature.

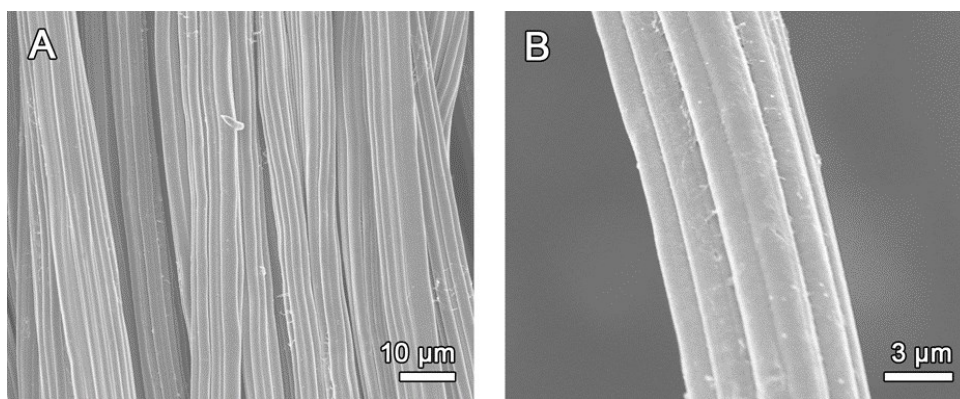


Figure S1. (A) Low- and (B) high-magnification SEM images of bare CC.

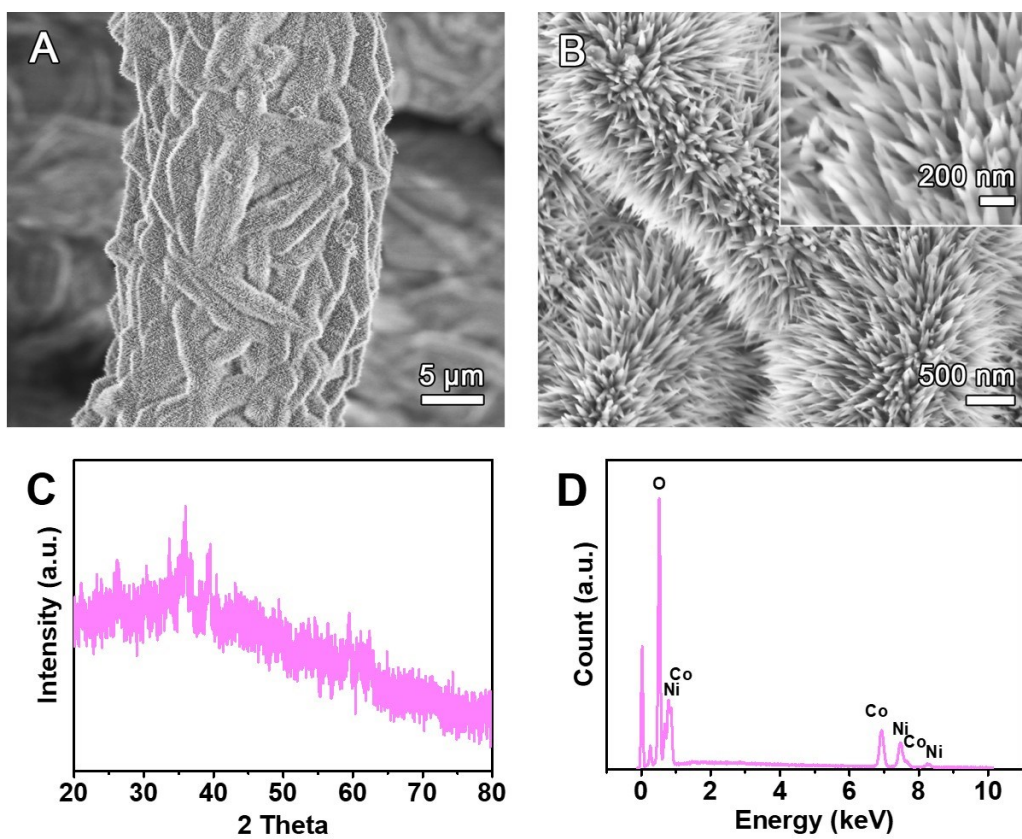


Figure S2. (A,B) SEM images of different magnifications, (C) XRD pattern and (D) EDX data of the NiCo precursor arrays.

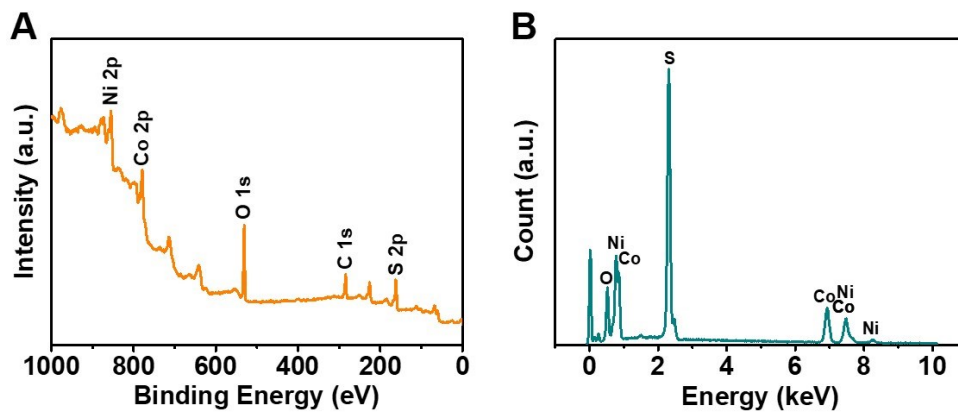


Figure S3. (A) XPS survey spectrum and (B) EDX data of the NiCo₂S₄/CC.

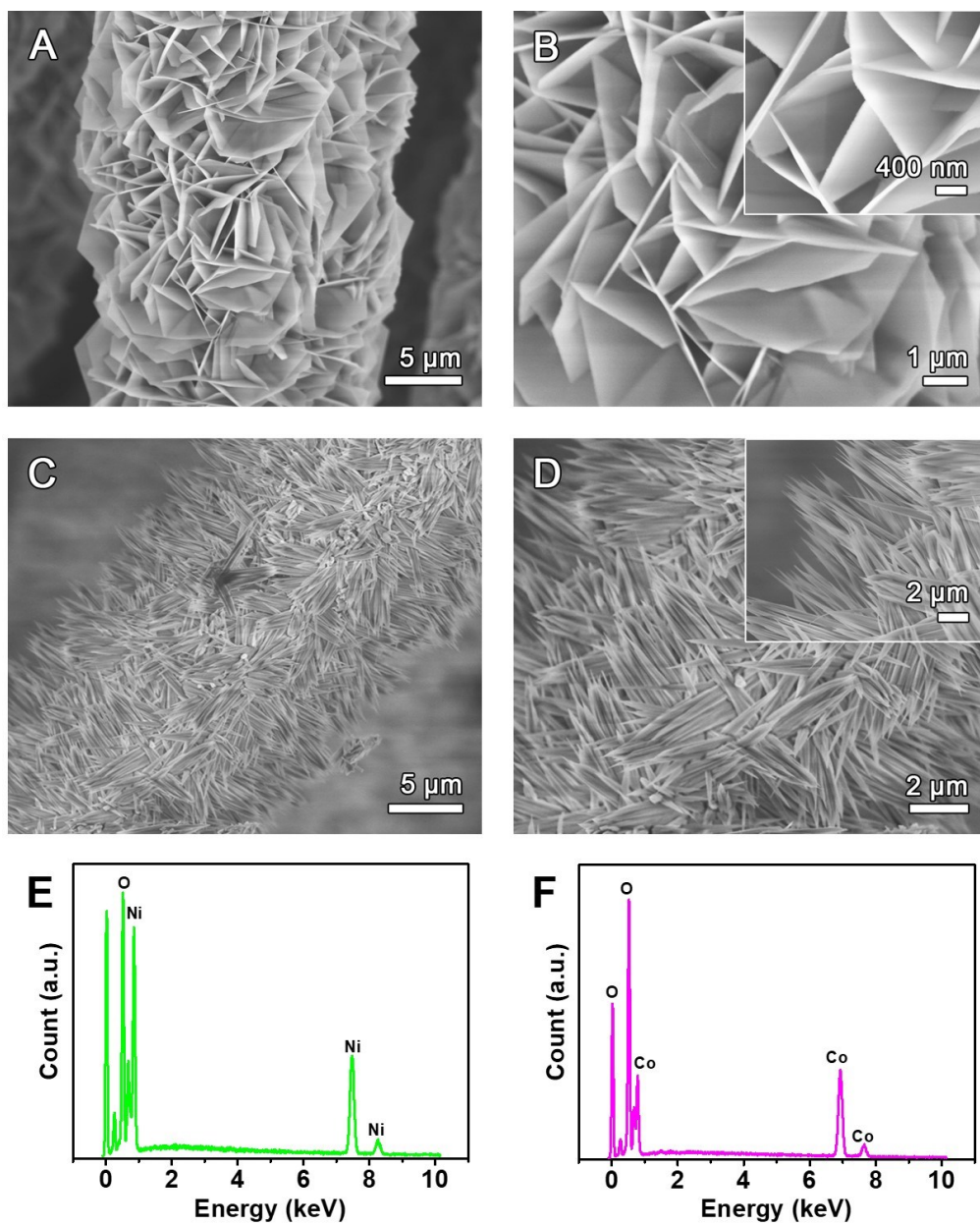


Figure S4. SEM images of (A,B) Ni precursor/CC and (C,D) Co precursor/CC; EDX data of (E) Ni precursor/CC and (F) Co precursor/CC.

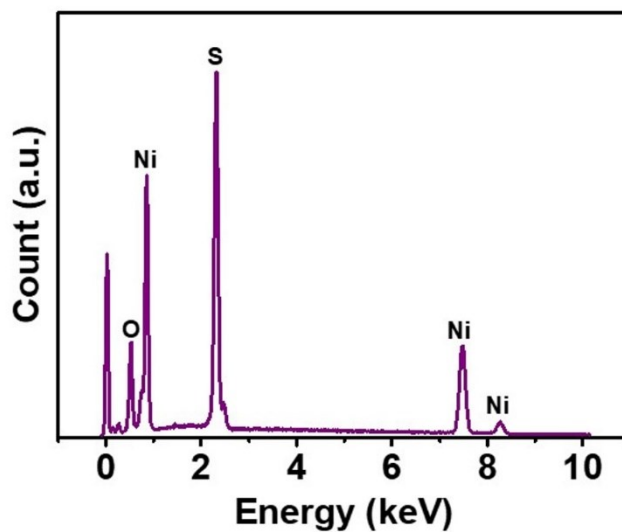


Figure S5. EDX data of the NiS/CC.

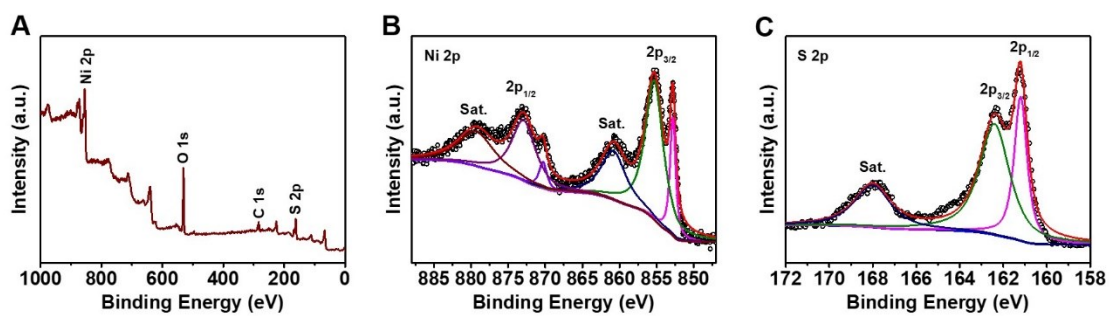


Figure S6. (A) XPS survey spectrum of the NiS/CC and high-resolution XPS spectra in (B) Ni 2p and (C) S 2p regions.

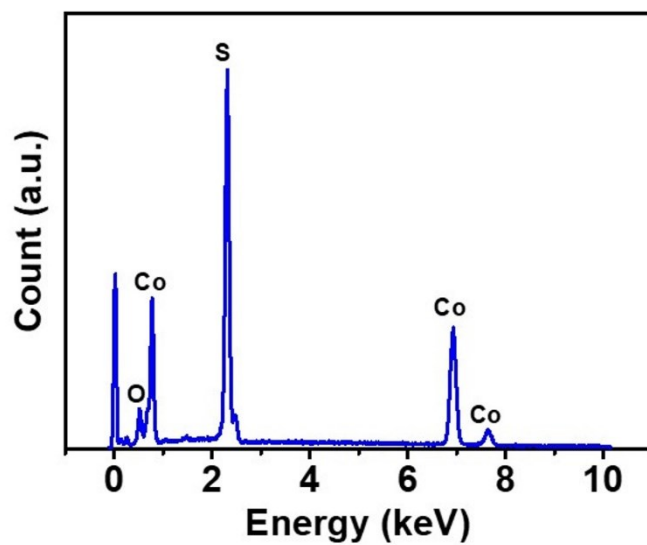


Figure S7. EDX data of the Co₉S₈/CC.

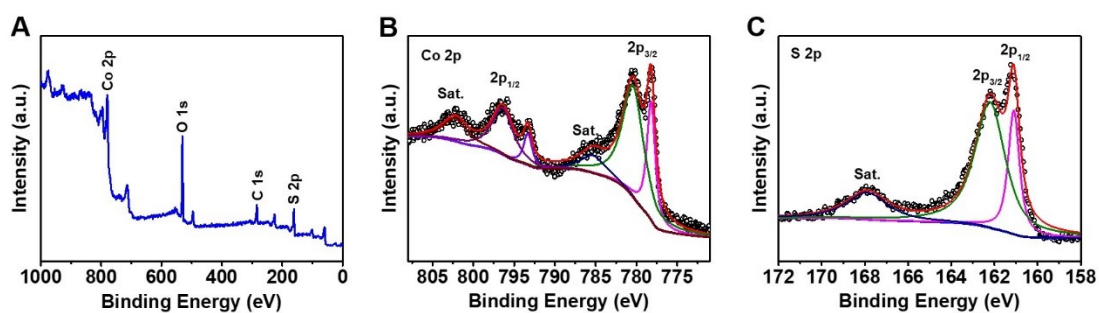


Figure S8. (A) XPS survey spectrum of the Co₉S₈/CC and high-resolution XPS spectra in (B) Co 2p and (C) S 2p regions.

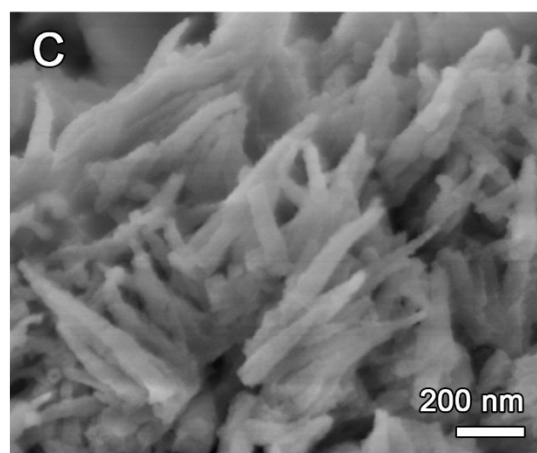
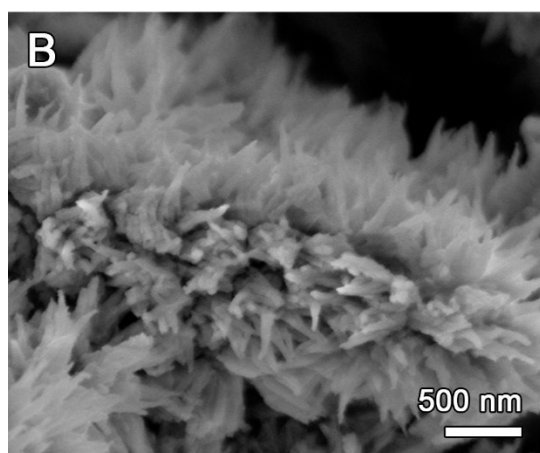
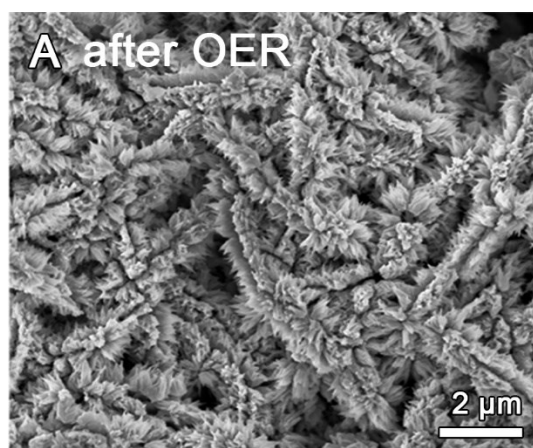


Figure S9. SEM images of different magnifications recorded for NiCo₂S₄/CC after long-term OER in 1.0 M KOH.

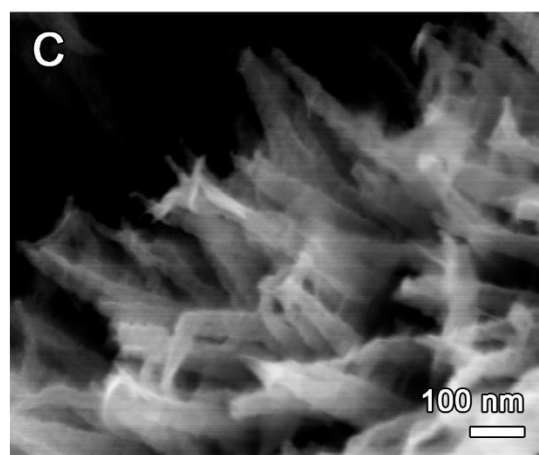
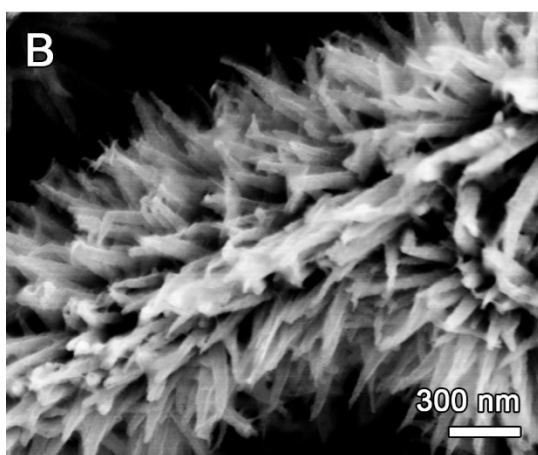
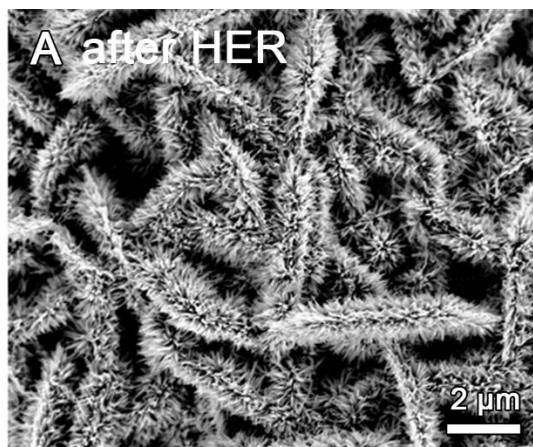


Figure S10. SEM images of different magnifications recorded for NiCo₂S₄/CC after long-term HER in 1.0 M KOH.

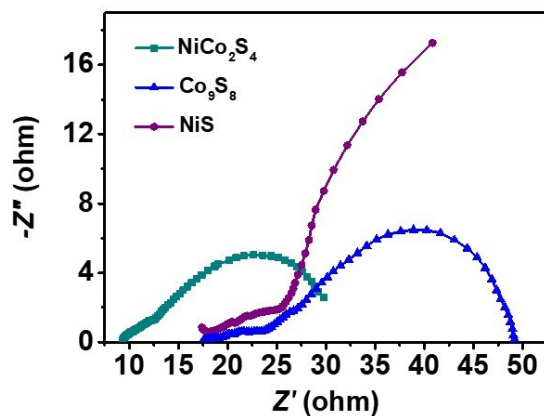


Figure S11. Nyquist plots of NiCo₂S₄/CC, Co₉S₈/CC and NiS/CC for UOR in 1.0 M KOH with 0.33 M added urea at 0.336 V vs. SCE.

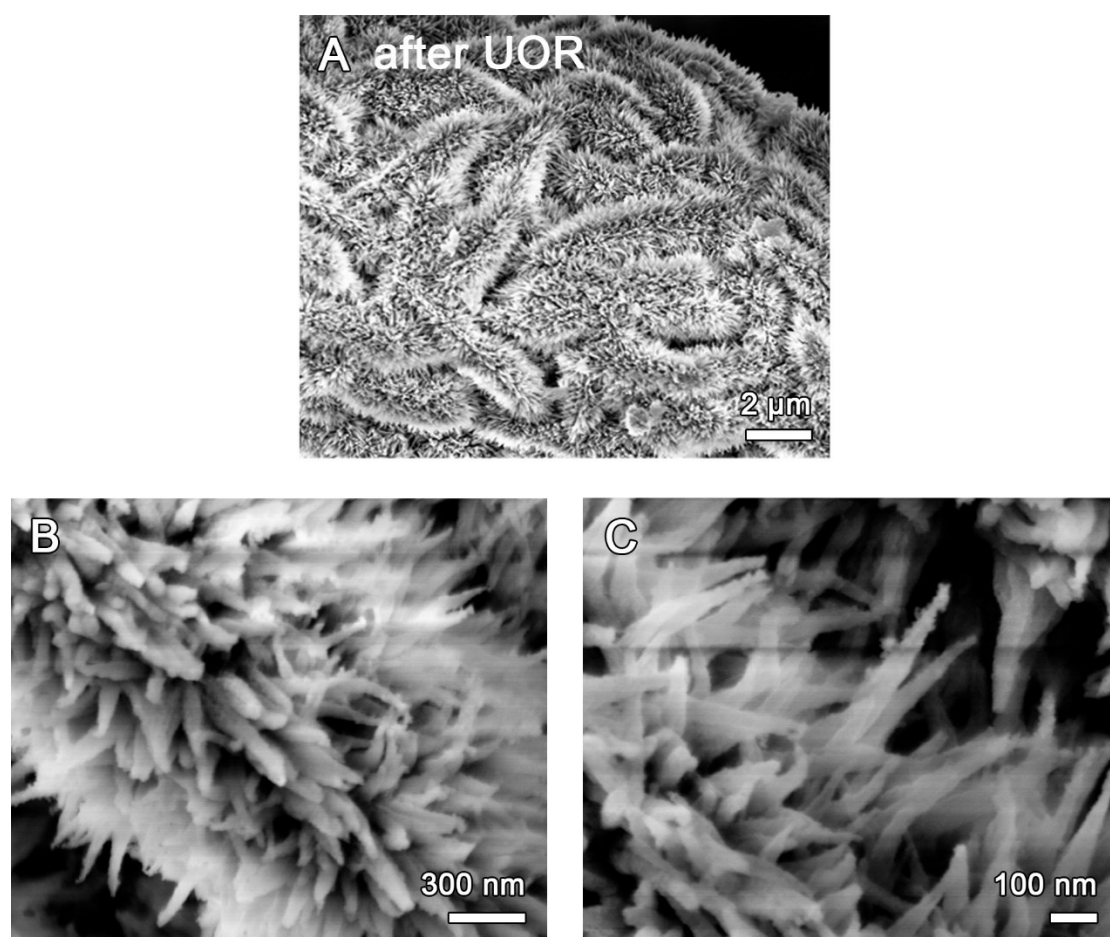


Figure S12. SEM images of different magnifications recorded for NiCo₂S₄/CC after long-term UOR in 1.0 M KOH with 0.33 M added urea.

Table S1. Comparison of the urea electrolysis performance for NiCo₂S₄/CC and other recently reported bifunctional electrocatalysts in 1.0 M KOH with 0.33 M urea.

Catalysts	substrate	Urea concentration (M)	Current density (mA cm ⁻²)	Voltage	Ref.
MoS ₂ /Ni ₃ S ₂	Nickel foam	0.33	20	1.45	1
Ni ₄ N/Cu ₃ N	Copper foam	0.5	10	1.48	2
NiMo alloy	Nickel foam	0.1	10	1.43	3
NiCo ₂ S ₄	Carbon cloth	0.33	10	1.45	4
NiMoS	Carbon cloth	0.5	10	1.59	5
NiCo₂S₄	Carbon cloth	0.33	10	1.45	This work

Supplementary References

1. F. Li, J. Chen, D. Zhang, W.-F. Fu, Y. Chen, Z. Wen and X.-J. Lv, *Chem. Commun.*, 2018, **54**, 5181-5184.
2. J. Li, C. Yao, X. Kong, Z. Li, M. Jiang, F. Zhang and X. Lei, *ACS Sustain. Chem. Eng.*, 2019, **7**, 13278-13285.
3. J.-Y. Zhang, T. He, M. Wang, R. Qi, Y. Yan, Z. Dong, H. Liu, H. Wang and B. Y. Xia, *Nano Energy*, 2019, **60**, 894-902.
4. W. Zhu, M. Ren, N. Hu, W. Zhang, Z. Luo, R. Wang, J. Wang, L. Huang, Y. Suo and J. Wang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 5011-5020.
5. X. Wang, J. Wang, X. Sun, S. Wei, L. Cui, W. Yang and J. Liu, *Nano Res.*, 2018, **11**, 988-996.