Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.


Supplementary Information

# Hierarchical $Cu_2S$ hollow nanowire arrays for highly efficient hydrogen evolution reaction

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## 1. Experimental Section

### *1.1. Chemical and Materials*

Methanol ($CH_3OH$, A.R.), acetone ($C_3H_6O$, A.R.), potassium hydroxide (KOH, A.R.), sodium hydroxide (NaOH, A.R.), ethanol ($C_2H_5OH$, A.R.), thiourea ($H_2NCSNH_2$, A.R.), thioacetamide ($CH_3CSNH_2$, A.R.), ammonium persulfate ($(NH_4)_2S_2O_8$, A.R.), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), A.R.), hydrochloric acid (HCl, A.R.), tetrahydrofuran (THF, 99%) and sodium diethyldithiocarbarnate trihydrate ($(C_2H_5)_2NCS_2Na \cdot 3H_2O$, A.R.) were bought from Sinopharm Chemical Reagent Co., Ltd. Cu Foam were purchased from Suzhou Zhengtai Rong New Materials Co., Ltd. The deionized water (18.2 MΩ $cm^{-1}$) used in all tests was generated by passing through an ultra-pure purified water system.

### *1.2. Synthesis of $Cu(OH)_2$ NAs-CF*

Firstly, the CF (2.5 cm × 2.0 cm) was treated with acetone and diluted hydrochloric acid (2 M), rinsed with ethanol and deionized water in sequence. Secondly, NaOH (40 mmol, 1.60 g) and $(NH_4)_2S_2O_8$ (2 mmol, 0.46 g) aqueous solution with 30 mL were prepared. To make the reaction more uniform, the pretreated CF was stood in above solution at room temperature for 30 minutes. Finally, the foam materials were taken out and rinsed with deionized water for three times, then dried in a vacuum oven at room temperature for 10 h, noted as $Cu(OH)_2$ NAs-CF.

### *1.3. Synthesis of hierarchical $Cu_2S$ HNAs-CF*

Firstly, $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ was added to a Teflon-lined stainless autoclave containing 40 mL methanol, and then ultrasonically treated until the solution becomes clear. Secondly, the as-prepared $Cu(OH)_2$ NAs-CF was threaded by a wire and submerged in the Teflon-lined stainless autoclave at 120 °C for 18 h. Finally, the hierarchical $Cu_2S$ HNAs-CF were taken out and rinsed with deionized water for three times, then dried in a vacuum oven at 40 °C for 10 h.

*1.4. Synthesis of compared samples*

The compared samples were synthesized with the similar procedures with $Cu_2S$ HNAs-CF, except that thiourea (named as $Cu_2S_{TU}$ NAs-CF) and thioacetamide (named as $Cu_2S_{TAA}$ NAs-CF) were used instead of sodium diethyldithiocarbarnate trihydrate.

*1.5. Preparation of PtC/CF*

PtC ink with 5.0 mg was added in a 2.0 mL centrifuge tube consisting of $H_2O$ (700 μL), ethanol (200 μL) and Nafion (100 μL). After ultrasonic treated for 30 min, 535 μL of the homogeneous ink was dropped on the CF with the size of 1.0 × 1.0 $cm^2$ and dried naturally at room temperature.

*1.6. Preparation of $RuO_2$/CF*

$RuO_2$/CF was prepared with the similar procedures for PtC/CF.

*1.7. Preparation of OMS-$RuO_2$/CF*

The OMS-$RuO_2$ samples were synthesized according to the previous work of our group. OMS-$RuO_2$/CF was prepared with the similar procedures for PtC/CF.

*1.8. Characterizations*

The powder X-ray diffraction (PXRD) measurements were conducted on a Benchtop X-ray diffractometer (Miniflex 600) at 40 kV and 40 mA with Cu Kα radiation to investigate crystal phases of the as-prepared samples. The scanning electron microscopy (SEM) images were carried out on a Zeiss Sigma 300 instrument with the accelerating voltage of 5 kV. The high-resolution transmission electron microscope (HRTEM) and TEM images were performed on the Tecnai F20 instrument with the accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) with monochromatized Al $K_\alpha$ Radiation data was recorded on a Thermo Fischer ESCALAB 250Xi X-ray photoelectron spectrometer (E = 1486.2 eV), using the C 1s peak located at Binding energy = 284.8 eV as the reference line.

*1.9. Electrocatalytic measurements*

The electrochemical measurements were carried out on a CHI 760E

electrochemical workstation (Shanghai CH Instrument) with a typical three-electrode electrochemical cell system in 1.0 M KOH alkaline electrolyte. All samples for testing were cut into 1.0 × 1.0 $cm^2$. As-synthesized $Cu_2S$ NAs-CF, Carbon rod and Saturated Calomel Electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. All electrochemical measurements of potentials were calibrated to the following equation: $E_{RHE} = E_{SCE} + 0.245 + 0.059 \times pH$ (V). The LSV+ curves were obtained at a scanning rate of 5 mV with 95% iR-compensation until the CV curves were stable. The ECSAs were conducted by CV tests from 15 mV $s^{-1}$ to 40 mV $s^{-1}$ in the non-faradaic region between 0.04 and −0.01 V versus RHE. The Tafel curves were recorded by potential against log current density from the LSV plots. The EIS was obtained in frequency ranging from 0.01 to $10^5$ Hz with an AC amplitude of 5 mV.

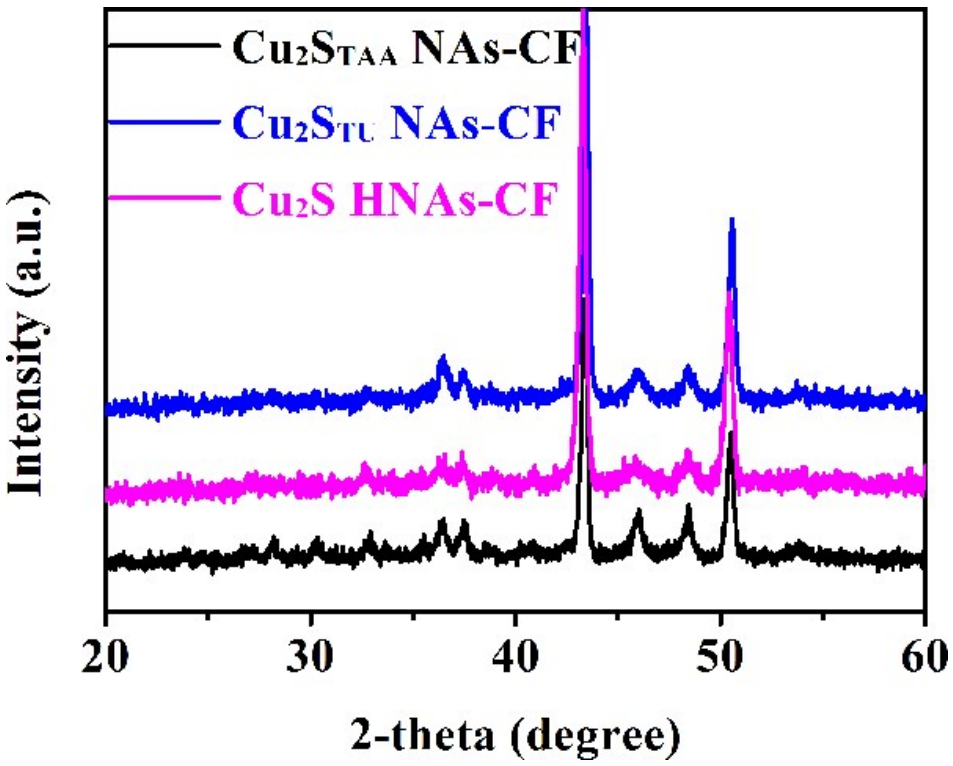


**Fig. S1** PXRD patterns of $Cu_2S$ NAs-CF with different sulfur sources.

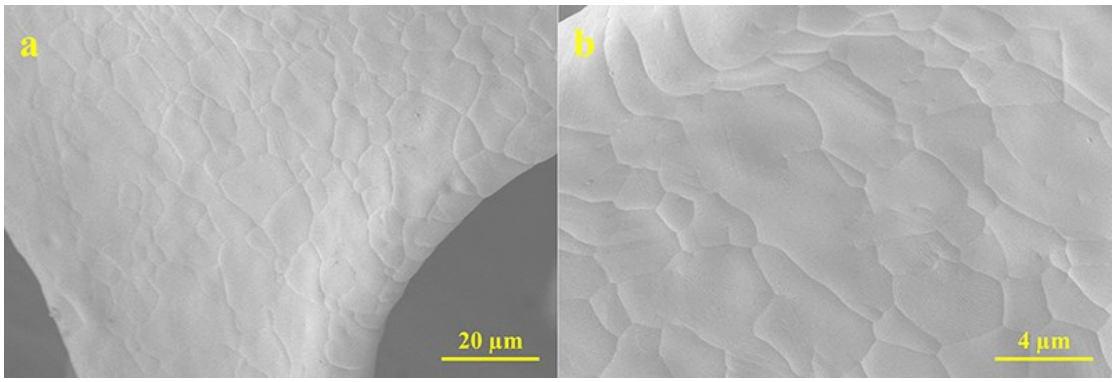


**Fig. S2** SEM images of CF (a-b).

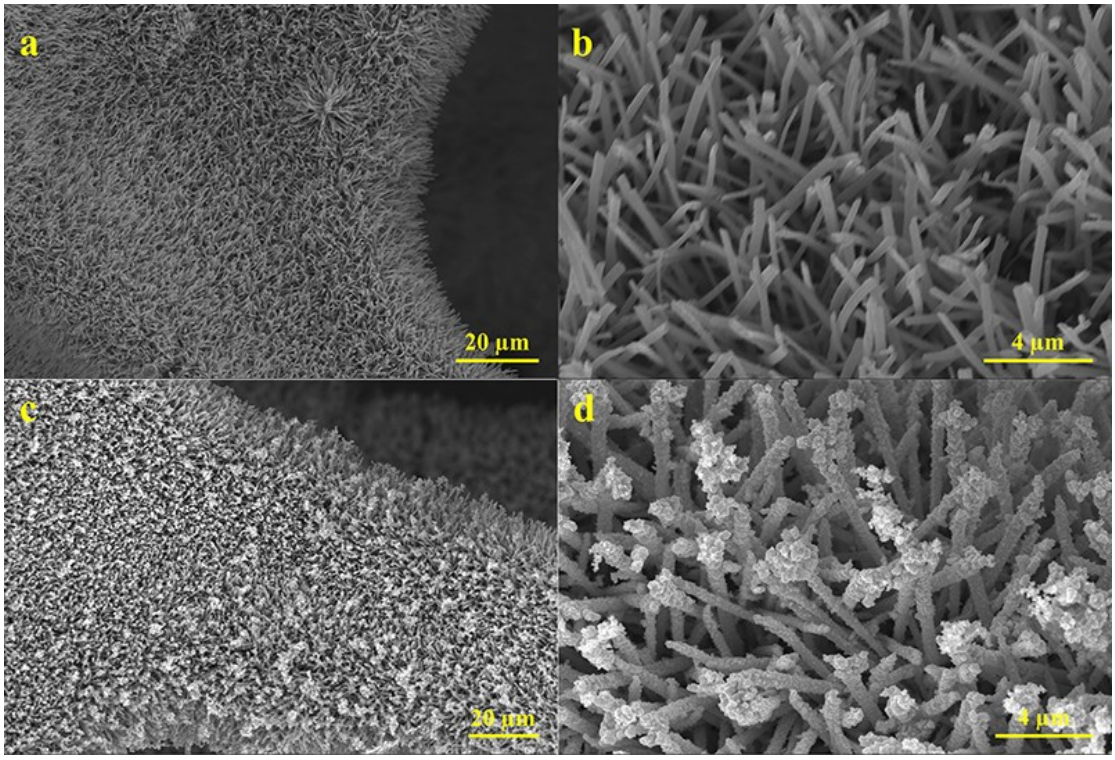


**Fig. S3** SEM images of $Cu(OH)_2$ NAs-CF (a-b) and hierarchical $Cu_2S$ HNAs-CF (c-d).

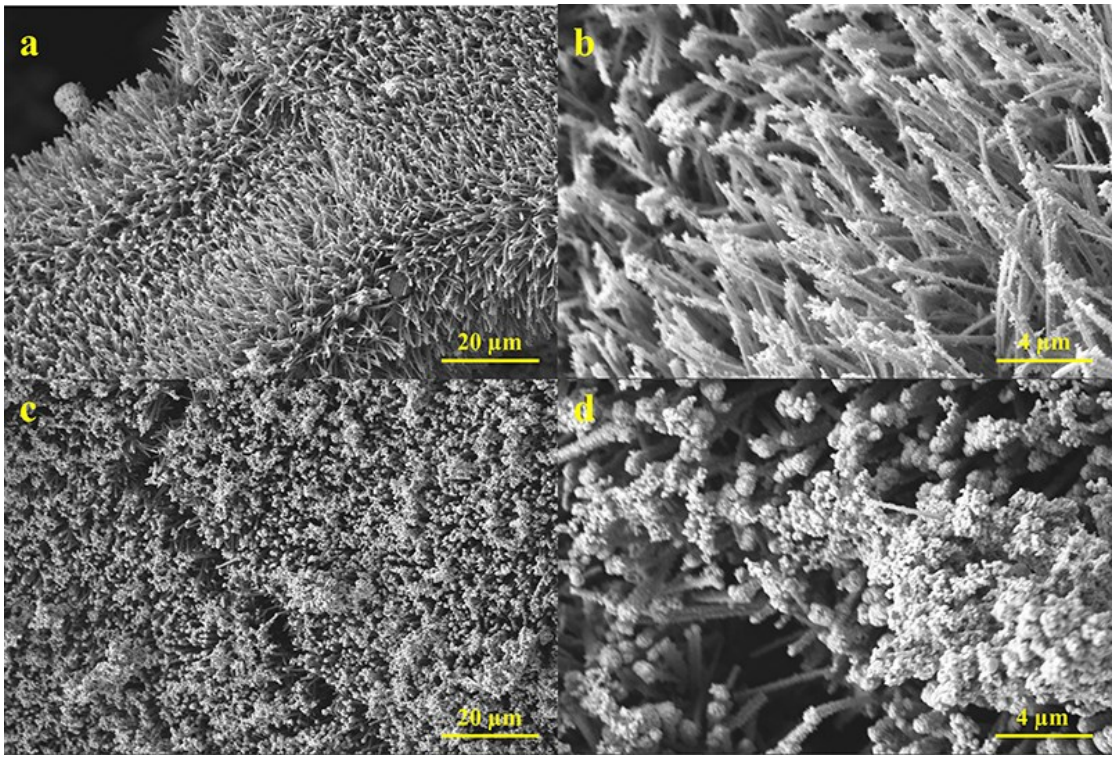


**Fig. S4** SEM images of hierarchical $Cu_2S$ HNAs-CF prepared at 90 °C (a-b) and 150 °C (c-d).

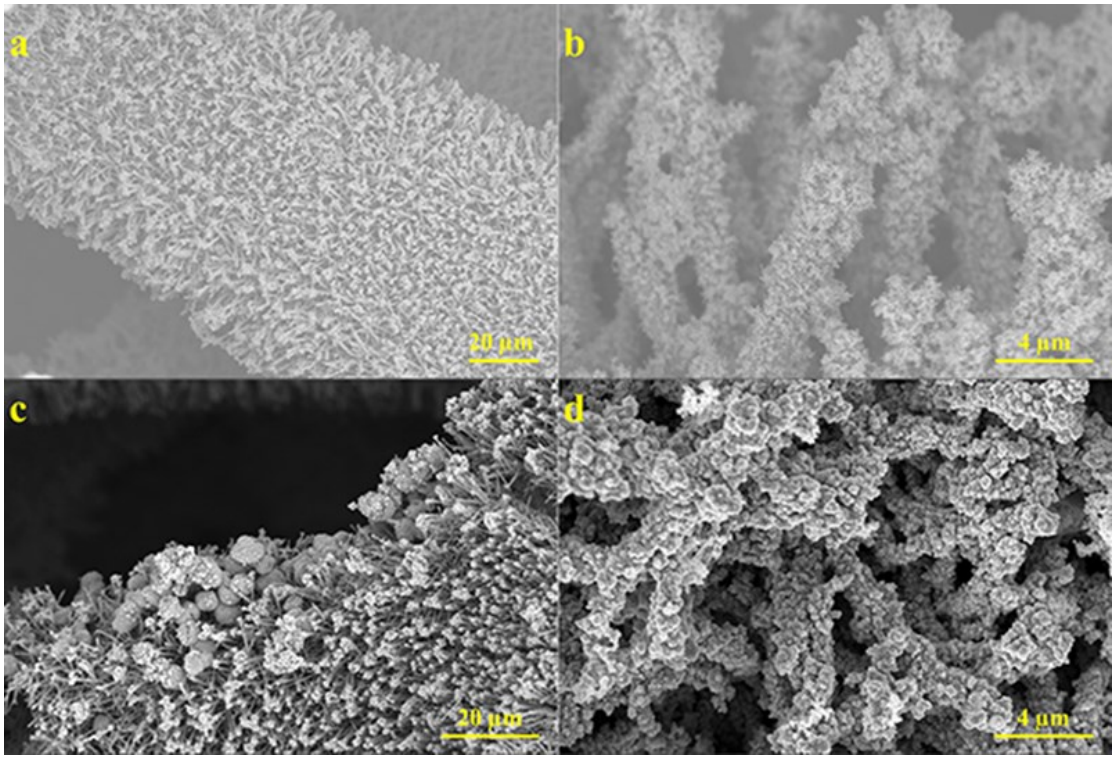


**Fig. S5** SEM images of hierarchical $Cu_2S$ HNAs-CF prepared with different reaction times of 12 h (a-b) and 24 h (c-d).

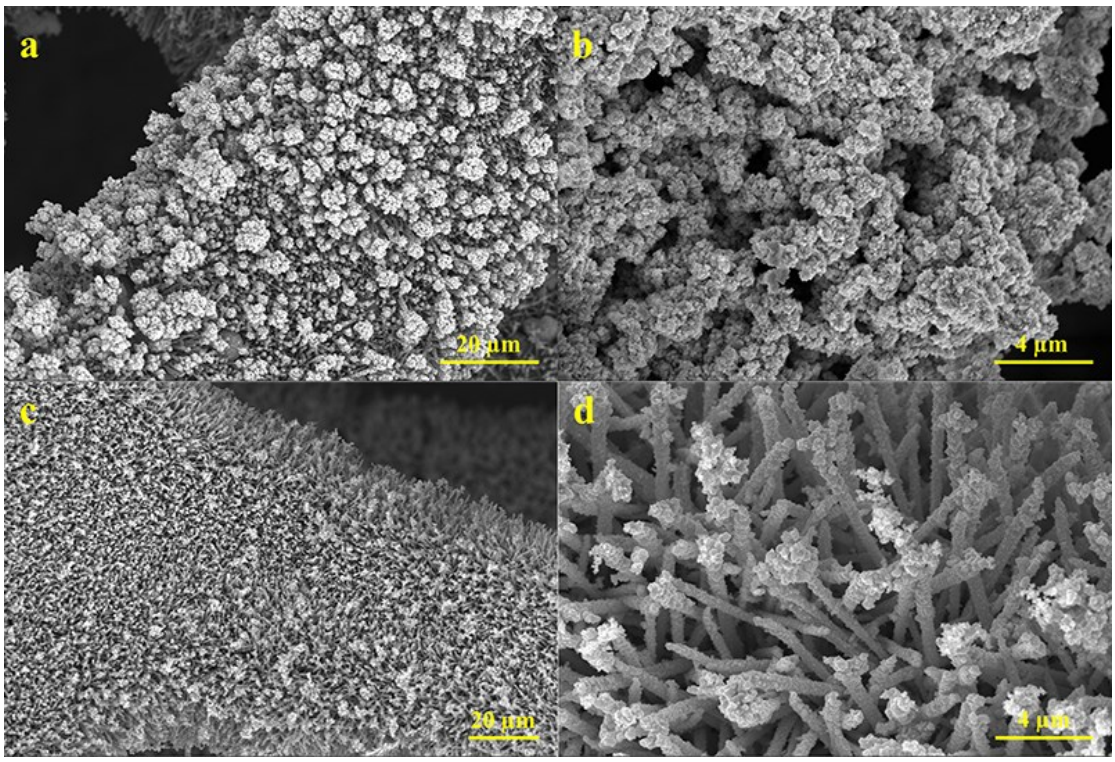


**Fig. S6** SEM images of hierarchical $Cu_2S$ HNAs-CF prepared with different reactants of 150 mg (a-b) and 100 mg (c-d).

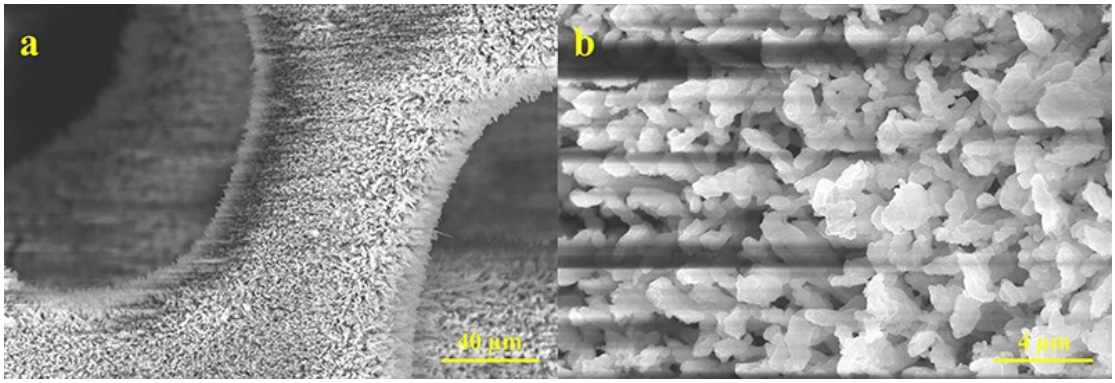


**Fig. S7** SEM images of hierarchical $Cu_2S$ HNAs-CF prepared with water as the solvent.

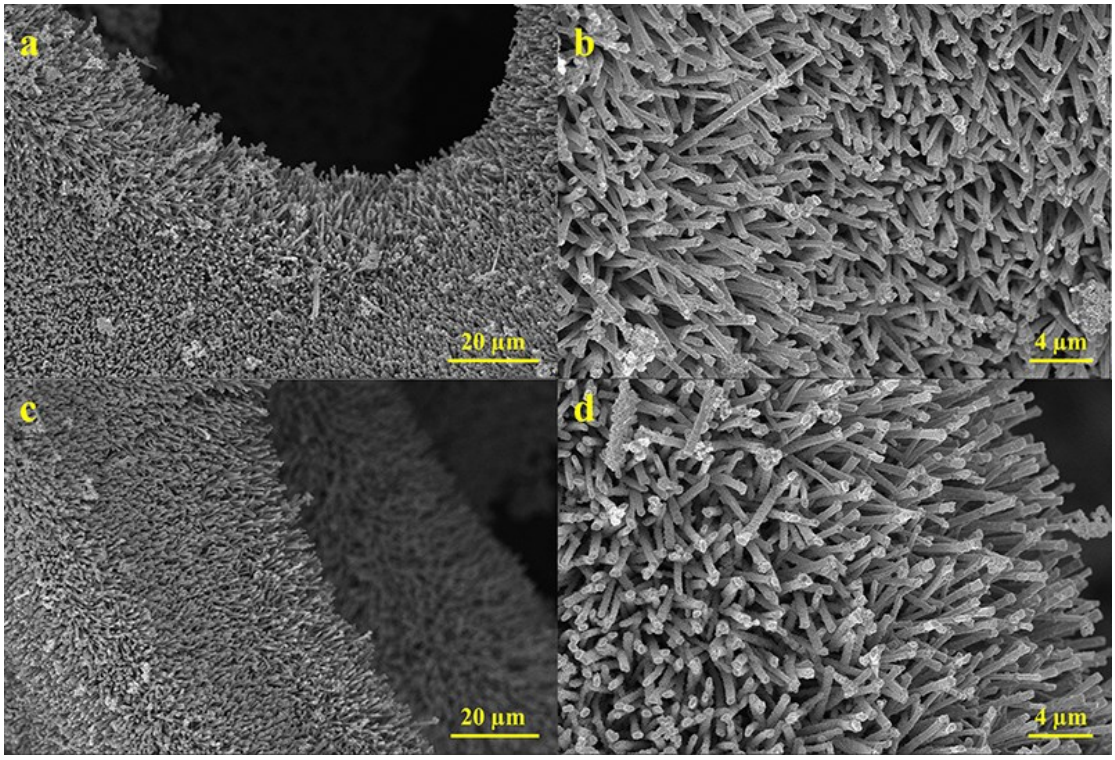


**Fig. S8** TEM images of $Cu_2S$ NAs-CF prepared with different sulfur sources: a) thiourea, b) thioacetamide, respectively.

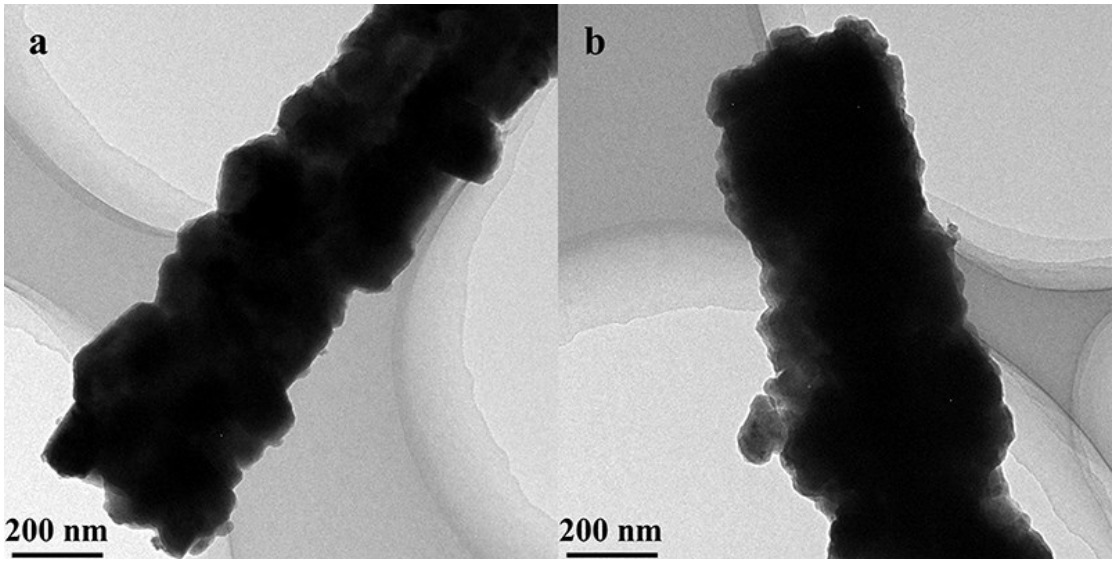


**Fig. S9** TEM images of $Cu_2S$ NAs-CF prepared with different sulfur sources: a) thiourea, b) thioacetamide, respectively.

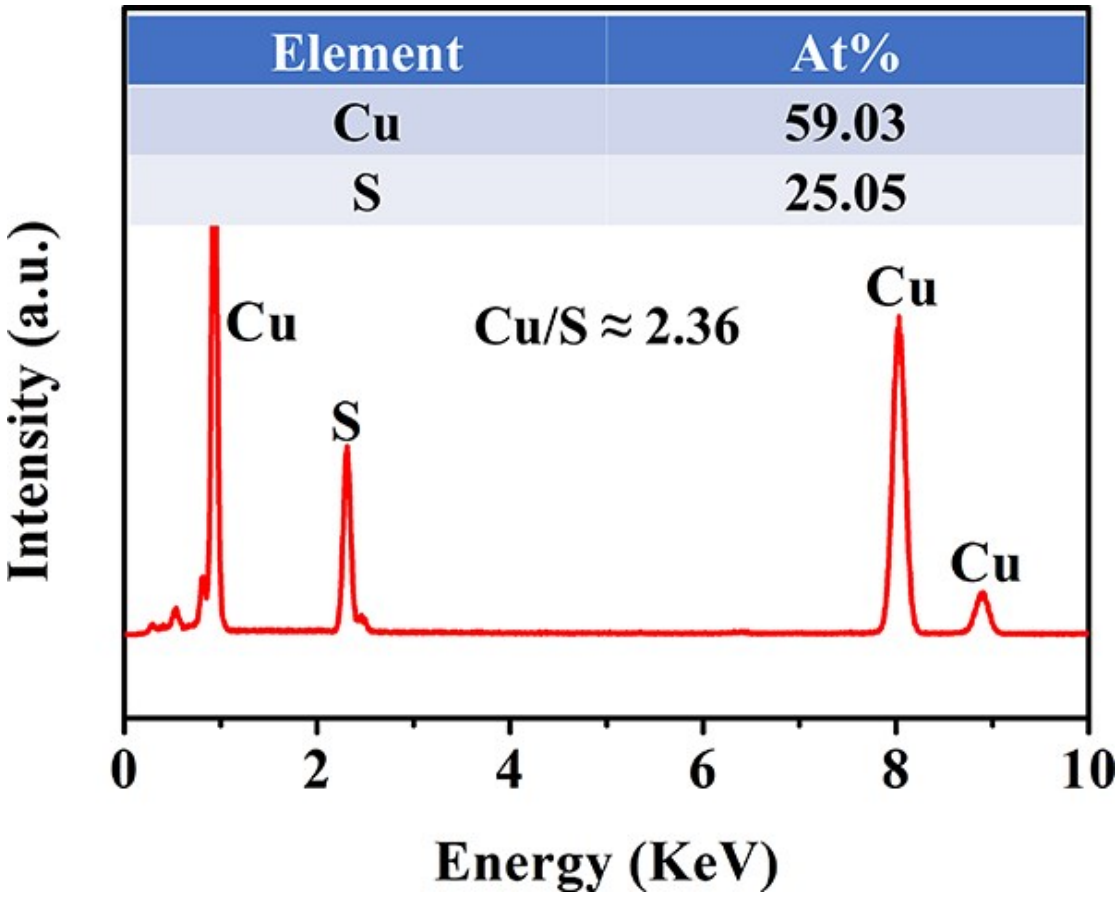


**Fig. S10** EDX spectrum of a hierarchical $Cu_2S$ hollow nanowire peeled from $Cu_2S$ HNAs-CF.

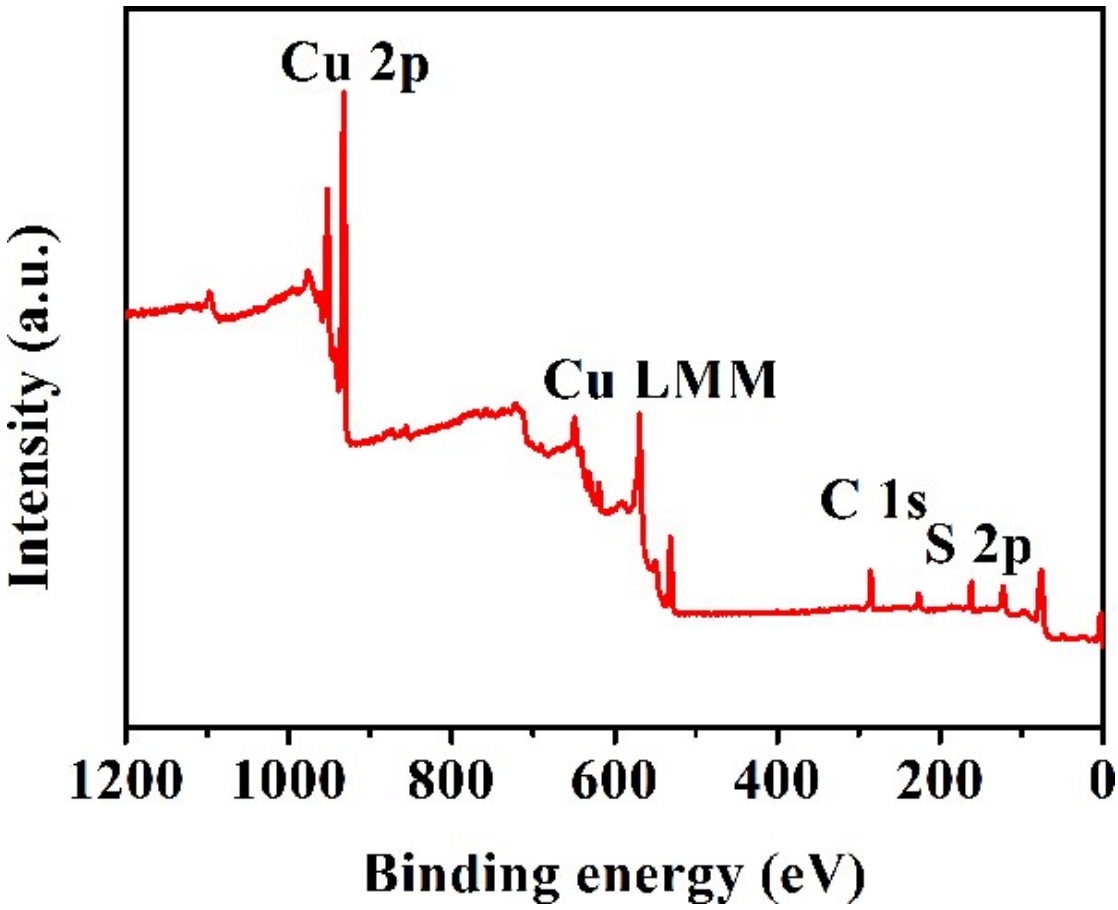


**Fig. S11** XPS survey spectrum of the hierarchical $Cu_2S$ HNAs-CF.

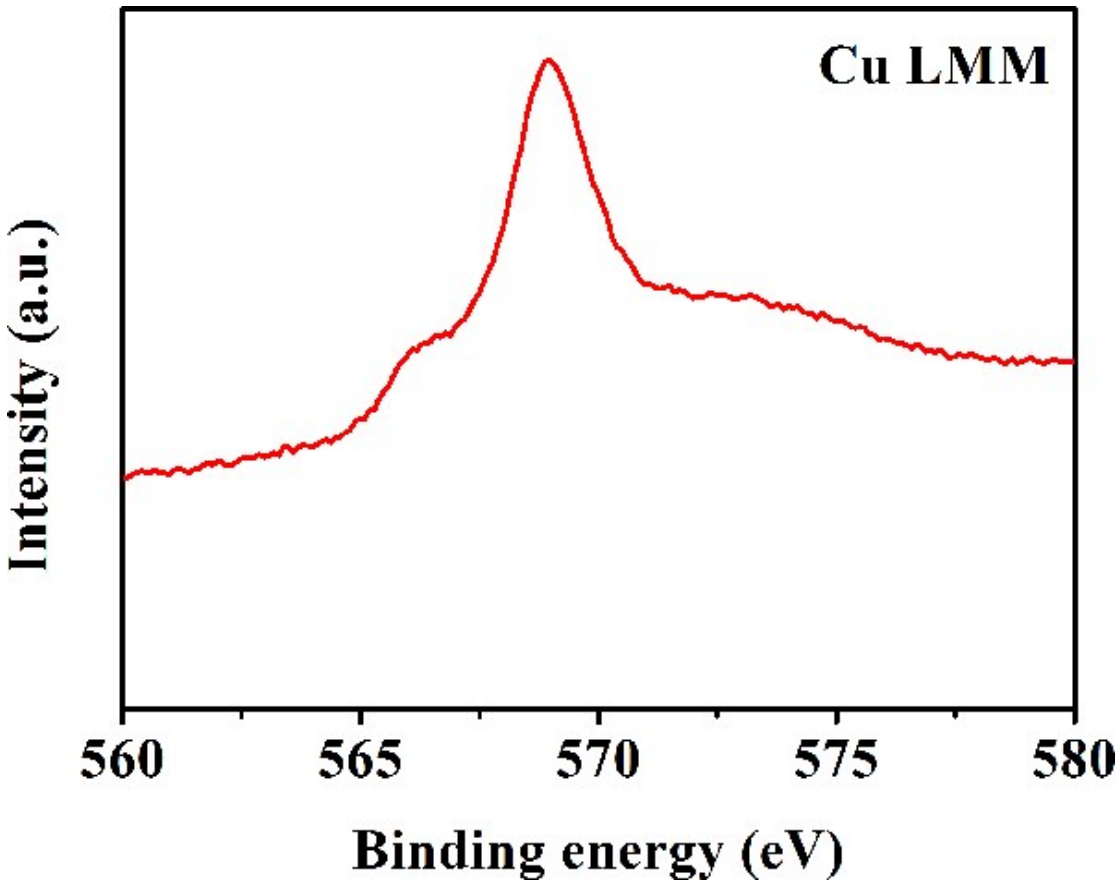


**Fig. S12** Auger Cu LMM spectrum of the hierarchical $Cu_2S$ HNAs-CF.

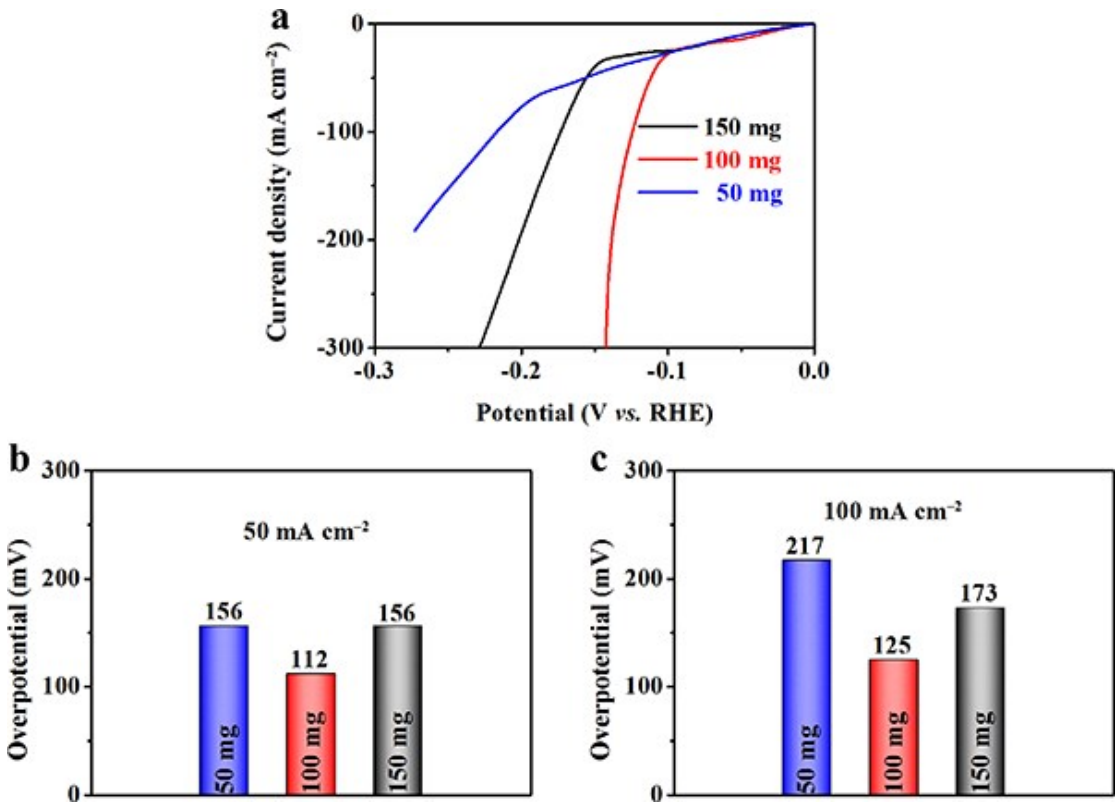


**Fig. S13** (a) LSV curves of hierarchical $Cu_2S$ HNAs-CF prepared with different quantities of reactants, (b, c) the corresponding overpotentials to reach the current densities of 50 and 100 mA $cm^{-2}$, respectively.

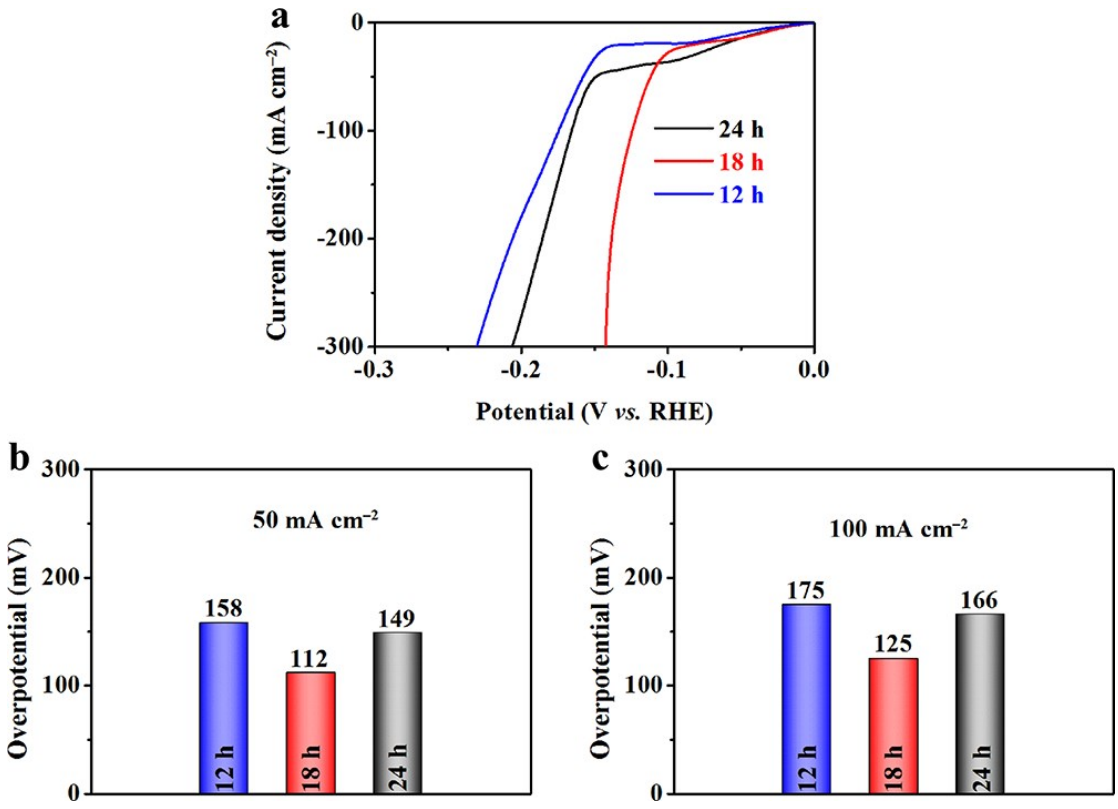


**Fig. S14** (a) LSV curves of hierarchical $Cu_2S$ HNAs-CF prepared with different reaction times, (b, c) the corresponding overpotentials to reach the current densities of 50 and 100 mA $cm^{-2}$, respectively.

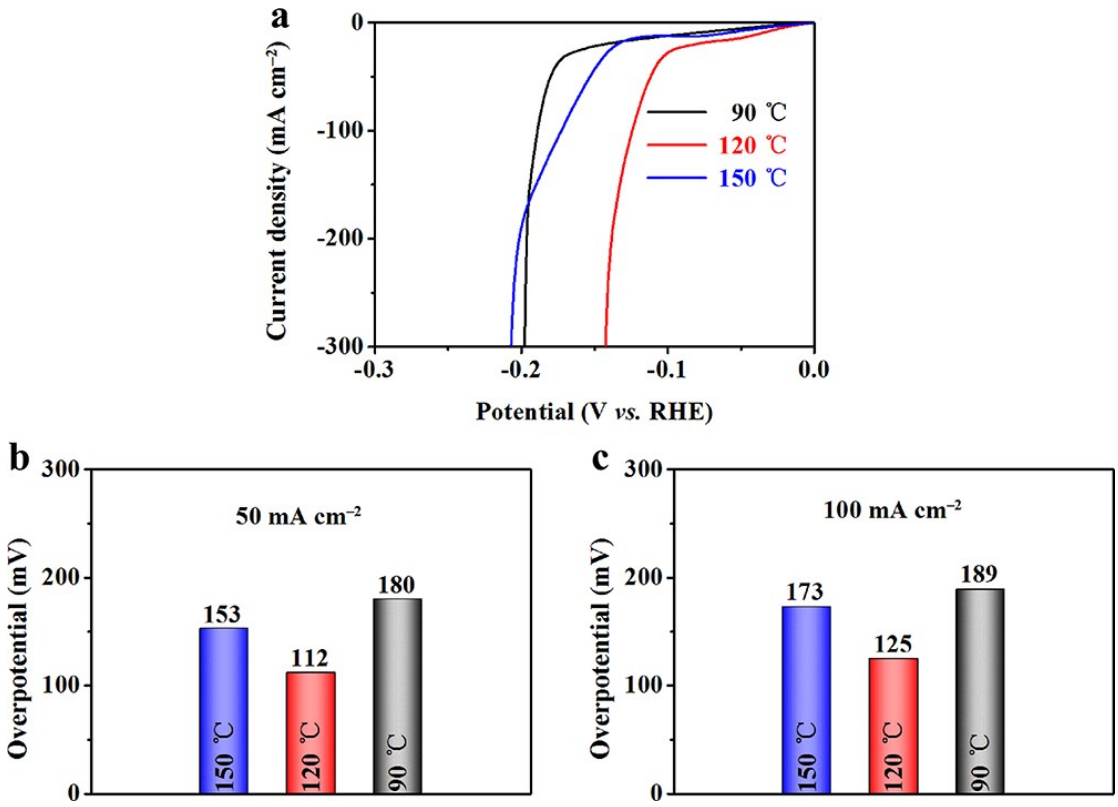


**Fig. S15** (a) LSV curves of hierarchical $Cu_2S$ HNAs-CF prepared at different temperatures, (b, c) the corresponding overpotentials to reach the current densities of 50 and 100 mA $cm^{-2}$, respectively.

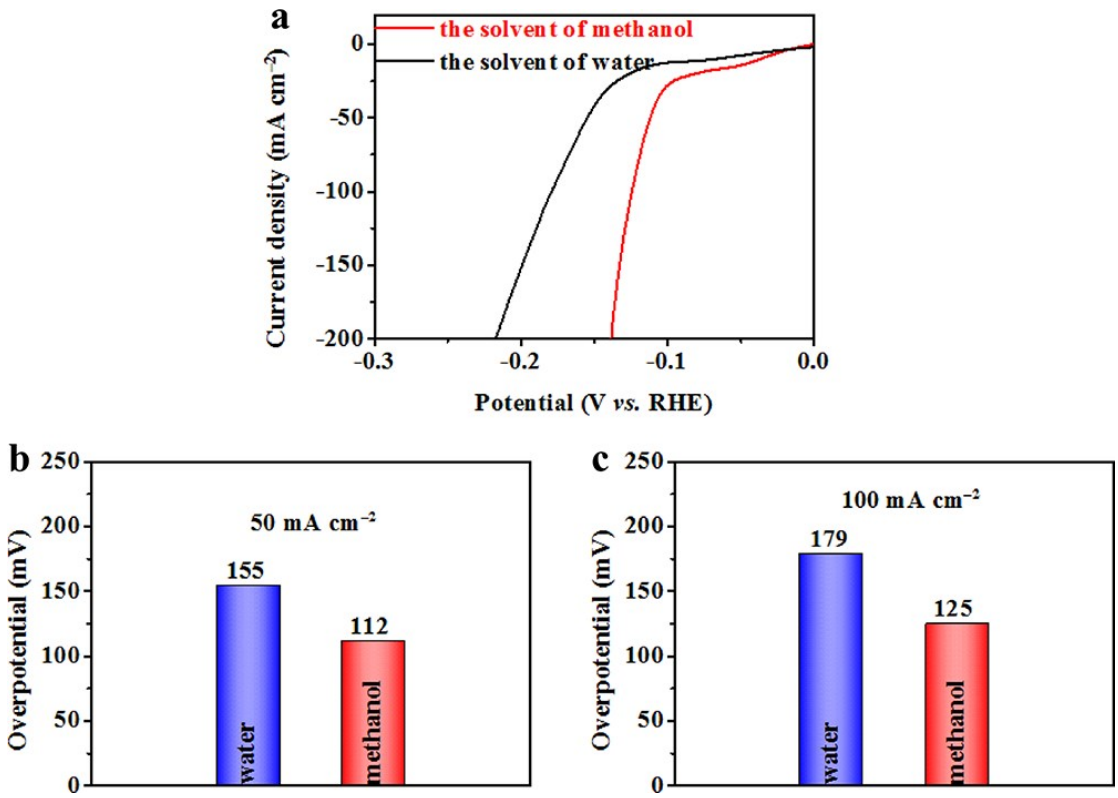


**Fig. S16** (a) LSV curves of hierarchical $Cu_2S$ HNAs-CF prepared in different solvents, (b, c) the corresponding overpotentials to reach the current densities of 50 and 100 mA $cm^{-2}$, respectively.

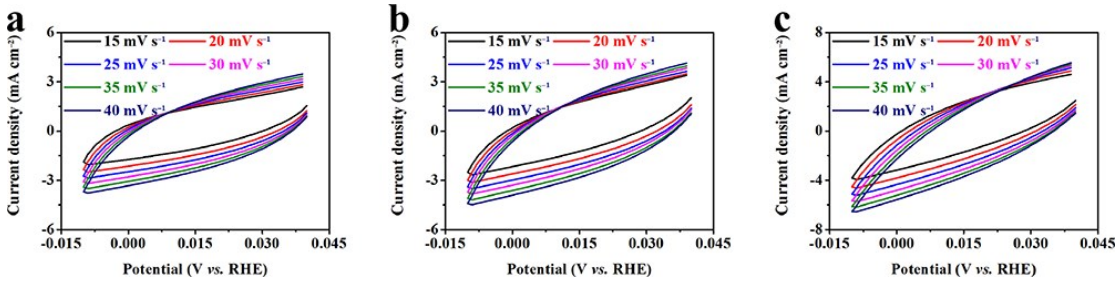


**Fig. S17** CV curves at different scan rates for $Cu_2S$ NAs-CF prepared with different sulfur sources: a) thiourea, b) thioacetamide, c) sodium diethyldithiocarbarnate trihydrate, respectively.

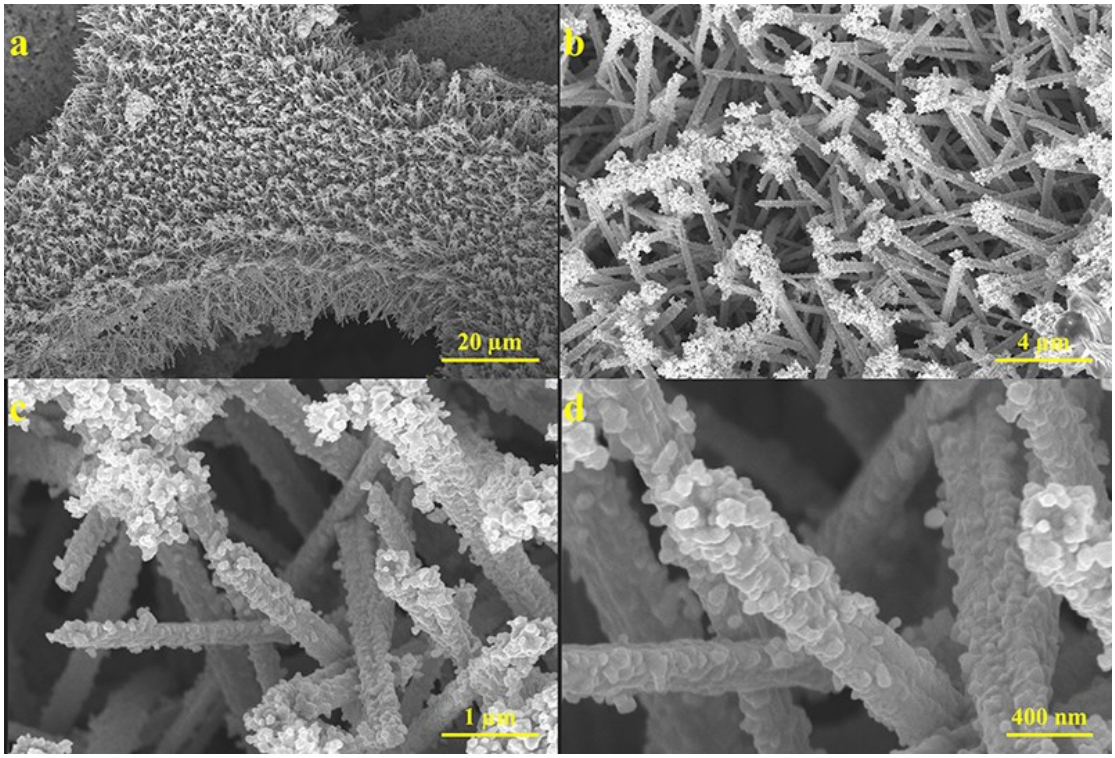


**Fig. S18** SEM images of hierarchical $Cu_2S$ HNAs-CF after HER test.

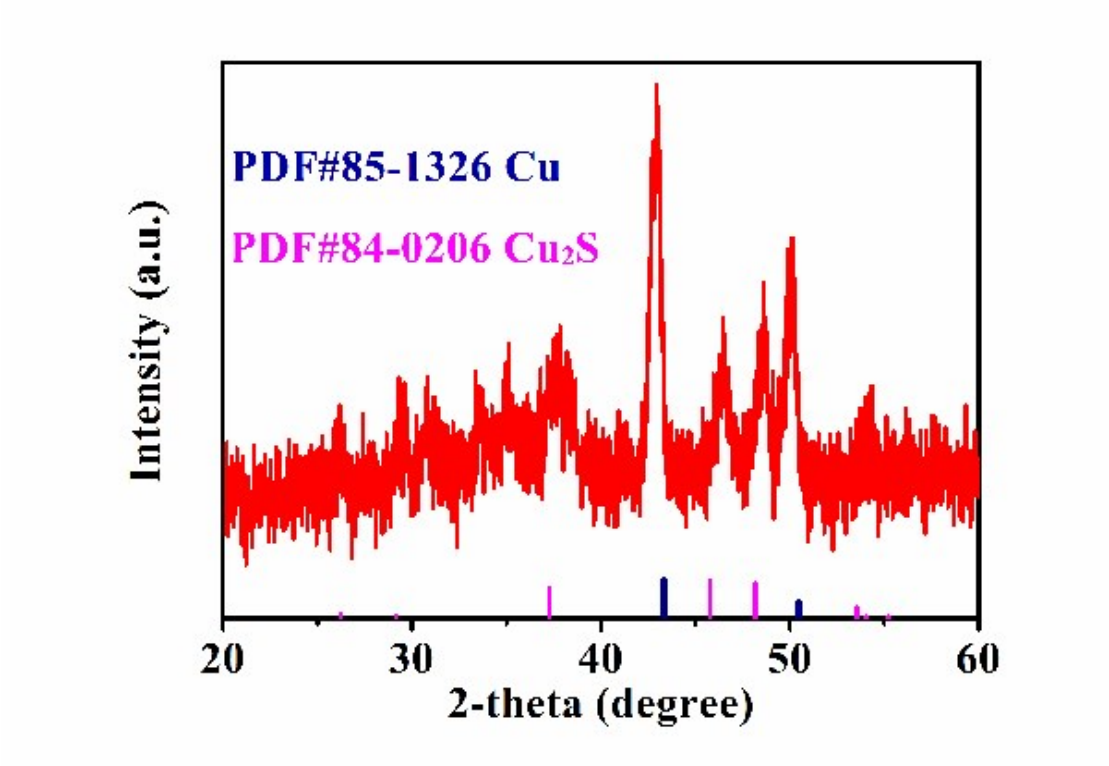


**Fig. S19** PXRD patterns of hierarchical $Cu_2S$ HNAs-CF after HER test.

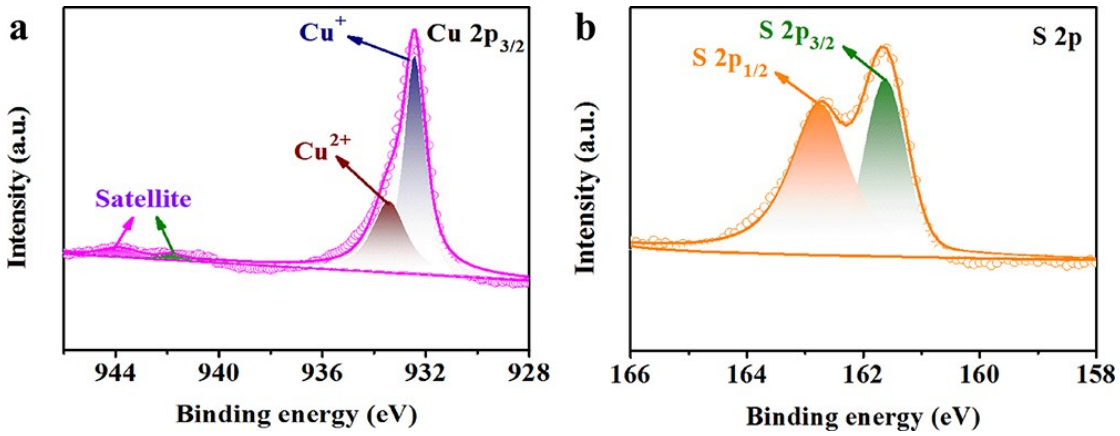


**Fig. S20** a) Cu $2p_{3/2}$, b) S 2p XPS spectra of hierarchical $Cu_2S$ HNAs-CF after HER test.

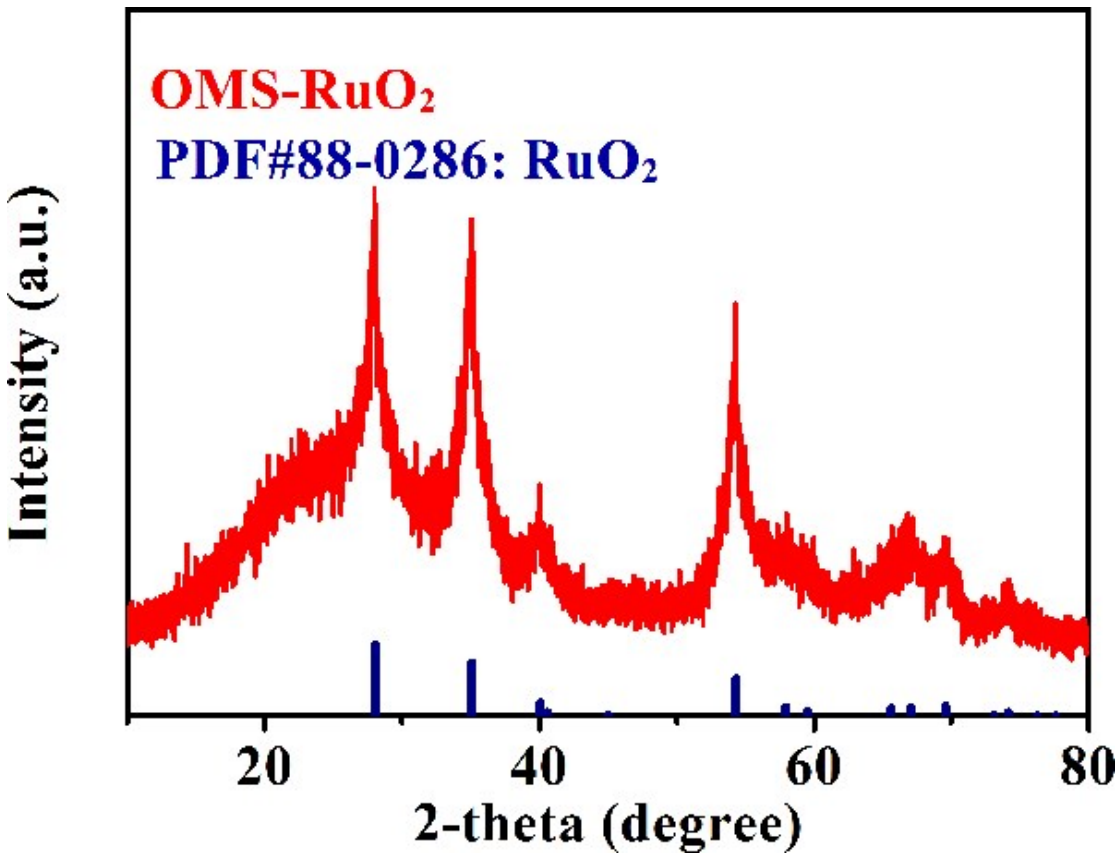


**Fig. S21** PXRD pattern of OMS-$RuO_2$.

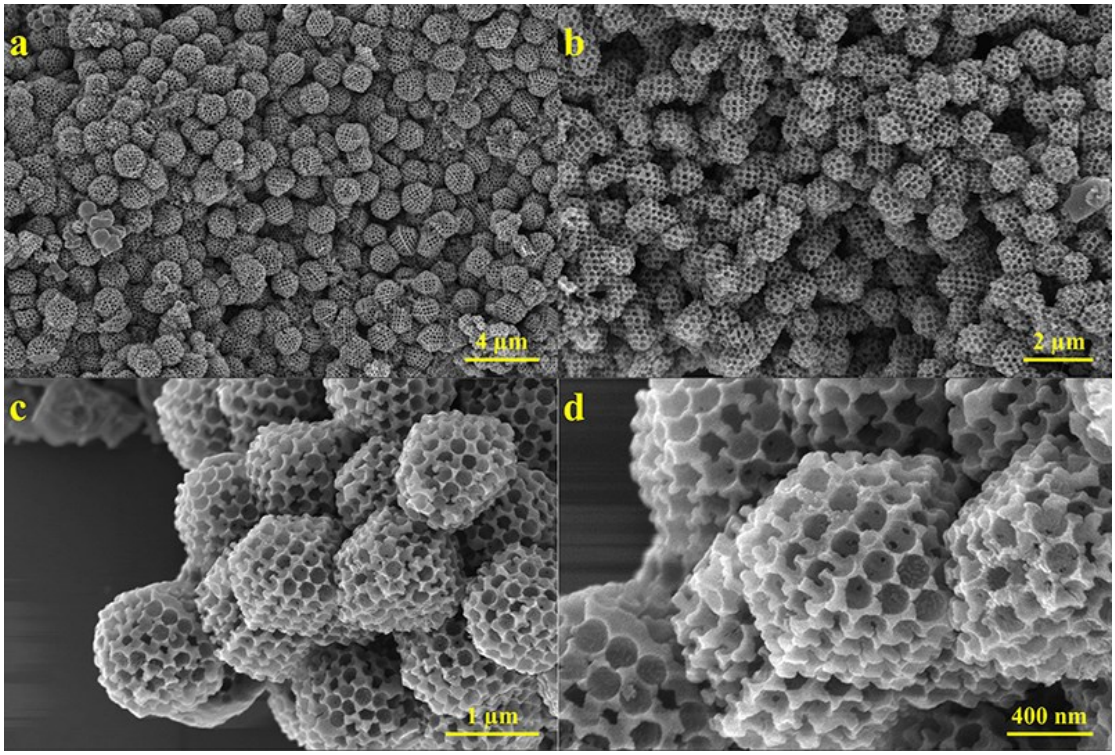


**Fig. S22** SEM images of OMS-$RuO_2$.

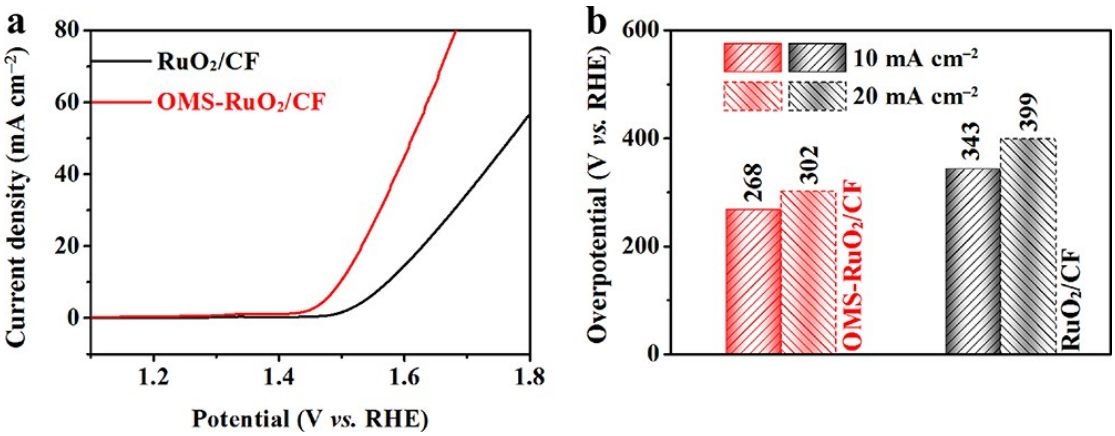


**Fig. S23** OER performances of $RuO_2$/CF and OMS-$RuO_2$/CF and corresponding overpotentials.

**Table S1** Comparison of hierarchical $Cu_2S$ HNAs-CF with some recently reported representative HER electrocatalysts.

| Catalyst | Overpotential (mV) | Electrolyte | Reference |
|---|---|---|---|
| **Hierarchical $Cu_2S$ HNAs-CF** | 112@50 mA $cm^{-2}$<br>125@100 mA $cm^{-2}$ | 1.0 M KOH | This work |
| **PtC/CF** | 108@50 mA $cm^{-2}$<br>160@100 mA $cm^{-2}$ | 1.0 M KOH | This work |
| R-$MoS_2$@NF | 105@40 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Mater.* **2018**, *30*, 1707105 |
| $CeO_2$/$Cu_3P$/NF | 148@20 mA $cm^{-2}$ | 1.0 M KOH | *Nanoscale,* **2018**, *10*,2213 |
| $Ni_2P$/$NiTe_2$ | 143@100 mA $cm^{-2}$ | 1.0 M KOH | *Energy Environ. Sci.* **2020**, 13, 1799−1807 |
| $MoS_2$/$NiO_3H$ | 200@217 mA $cm^{-2}$ | 1.0 M KOH | *Small* **2020**, *16*, 2002212 |
| Hier-NiFe@sCNTs | 126@500 mA $cm^{-2}$ | 1.0 M KOH | *Small* **2020**, 2002511 |
| $Co_3S_4$/EC-MOF/CC | 183@100 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Mater.* **2019**, *31*, 1806672 |
| $Ni_3N$-VN/NF | 218@100 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Mater.* **2019**, *31*, 1901174 |
| NFN($Fe_2Ni$)-MOF/NF | 256@250 mA $cm^{-2}$<br>293@500 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Energy Mater.* **2018**, *8*, 1801065 |
| Ni/$Mo_2C$(1:2)-NCNFs/GC | 195@100 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Energy Mater.* **2019**, *9*, 1803185 |
| $MoNi_4$/$MoO_{3-X}$ | 52@100 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Mater.* **2017**, *29*, 1703311 |
| CuCoP | 288@50 mA $cm^{-2}$ | 1.0 M KOH | *ACS sustain. Chem. Eng.* **2019**, *7,* 3092−3100 |
| Ni-Cu-P alloy | 230@100 mA $cm^{-2}$ | 1.0 M KOH | *ACS Appl. Mater. Interfaces* **2018**, *10,* 35224−35233 |
| Cu-CoNi-OH/NF | 171@100 mA $cm^{-2}$ | 1.0 M KOH | *J. Electrochem. Soc.* **2018**, *165,* H866−H871 |
| $CuO_x$@$Co_3O_4$ | 242@50 mA $cm^{-2}$<br>265@100 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2018**, *6*, 14431−14439 |
| NiCuP | 146@50 mA $cm^{-2}$<br>216@100 mA $cm^{-2}$ | 1.0 M KOH | *Nanoscale,* **2017**, *9,* 4401−4408 |

| | | | |
|---|---|---|---|
| Ni-P/CP | 250@100 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Funct. Mater.* **2016**, *20*, 4067−4077 |
| WP NAs/CC | 280@100 mA $cm^{-2}$ | 1.0 M KOH | *ACS Appl. Mater. Interfaces* **2014**, *6*, 21874−21879 |
| WN NAs/CC | 445@100 mA $cm^{-2}$ | 1.0 M KOH | *Electrochim. Acta* **2015**, *154*, 345−351 |
| Ni/C NFs | 480@100 mA $cm^{-2}$ | 2.0 M KOH | *Electrochim. Acta* **2015**, *159*, 1−7 |
| CoP film | 158@100 mA $cm^{-2}$ | 1.0 M KOH | *Appl. Catal. B.* **2015**, *154*, 345−351 |

| Sample | $Cu_2S$ HNAs-CF | $Cu_2S_{TU}$ NAs-CF | Pt/C | $Cu_2S_{TAA}$ NAs-CF |
|---|---|---|---|---|
| **Rs (Ω)** | **2.383** | **2.807** | **2.816** | **2.395** |
| **Rct (Ω)** | **6.387** | **13.78** | **3.165** | **14.21** |

**Table S2** The fitted $R_s$ and $R_{ct}$ of $Cu_2S$ NAs-CF and compared samples.

**Table S3** Comparison of the $Cu_2S$ HNAs-CF|| OMS-$RuO_2$/CF pair with some recently reported representative electrocatalysts toward overall water splitting.

| Catalyst | Cell voltage at 10/20 mA $cm^{-2}$ | Electrolyte | Reference |
|---|---|---|---|
| $Cu_2S$ HNAs-CF\|\| OMS-$RuO_2$/CF | 1.561 V@10 mA $cm^{-2}$<br>1.655 V@20 mA $cm^{-2}$ | 1.0 M KOH | This work |
| PtC/CF\|\|$RuO_2$/CF | 1.623 V@10 mA $cm^{-2}$<br>1.731 V@20 mA $cm^{-2}$ | 1.0 M KOH | This work |
| $Co_1Mn_1CH$ | 1.68 V@10 mA $cm^{-2}$ | 1.0 M KOH | *J. Am. Chem. Soc.* **2017**, *139*, 8320−8328 |
| $NiCo_2O_4$ | 1.74 V@20 mA $cm^{-2}$ | 1.0 M KOH | *Angew. Chem. Int. Ed.* **2016**, *55*, 6290−6294 |
| EG/$Ni_3Se_2$/$Co_9S_8$ | 1.62 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Nano letters* **2017**, *17*, 4202−4209 |
| Ni-Fe-P-B@CFP | 1.58 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Nano Research* **2018**, *13, 447−454* |
| Co-$MoS_2$ | 1.58 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Chem. Commun.* **2018**, *54*, 3859−3862 |
| $Ni_3N$/CMFs/$Ni_3N$ | 1.652 V@20 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2017**, *5*, 9377−9390 |
| NC-CNT/CoP | 1.63 V@10 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2018**, *6*, 9009−9018 |
| $Co_9S_8$/$WS_2$/Ti foil | 1.65 V@10 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2017**, *5*, 23361−23368 |
| NiSe | 1.75 V@20 mA $cm^{-2}$ | 1.0 M KOH | *Angew. Chem. Int. Ed.* **2015**, *32*, 9483 |
| $Co_5Mo_{1.0}P$ NSs@NF | 1.68 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Nano Energy* **2018**, *45, 448−455* |
| Ni/$Mo_2C$-NCNFs | 1.64 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Energy Mater.* **2019**, *9*, 1803185 |
| CuCoP | 1.8 V@10 mA $cm^{-2}$ | 1.0 M KOH | *ACS sustain. Chem. Eng.* **2019**, *7,* 3092−3100 |
| CoP | 1.66 V@20 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Funct. Mater.* **2015**, *25*, 7337−7347 |
| NF@NiMoCo | 1.56 V@10 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2019**, *7*, 2156 |
| Co@N-CS/N-HCP@CC | 1.545 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Energy Mater.* **2019**, *9*, 1803918 |
| NiCoP/NF | 1.64 V@20 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2017**, *5*, 14828−14837 |

| | | | |
|---|---|---|---|
| Ni-Co-P | 1.62 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Energy Environ. Sci.* **2018**, *11*, 872−880 |
| $Co_3S_4$@$MoS_2$ | 1.58 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Nano Energy* **2018**, *47, 494-502* |
| $Ni_3S_2$-NGQDS/NF | 1.58 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Small*. **2017**, *13*, 1700264 |
| $Ni_{0.33}Co_{0.67}S_2/NiCo_2O_4$ | 1.65 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Energy Mater.* **2015**, *5*, 1402031 |
| CoP NFs | 1.65 V@10 mA $cm^{-2}$ | 1.0 M KOH | *ACS Catal.* **2020**, *10*, 412−419 |
| NiCuP | 1.6 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Nanoscale,* **2017***, 9,* 4401−4408 |
| $Cu_3N$/CuO | 1.61 V@10 mA $cm^{-2}$ | 1.0 M KOH | *ACS Energy Lett.* **2019**, *4*, 747−754 |
| NiCoP@$Cu_3P$/CF | 1.593 V@10 mA $cm^{-2}$ | 1.0 M KOH | *J. Mater. Chem. A* **2018**, *6*, 2100−2106 |
| CuCoO-NWs | 1.61 V@10 mA $cm^{-2}$ | 1.0 M KOH | *Adv. Funct. Mater.* **2016**, *26*, 8555−8561 |