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## Effect of urea and ammonium fluoride ratio on CuCo<sub>2</sub>S<sub>4</sub>/NF as a highly efficient HER catalyst

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CuCo<sub>2</sub>S<sub>4</sub> as a spinel-structured transition metal sulfide is a highly effective HER catalyst due to its excellent endurance, low overpotential, and low Tafel slope. In this work, the CuCo<sub>2</sub>S<sub>4</sub>/Ni foam (NF) catalysts with various morphologies have been successfully synthesized by controlling the ratio of urea and ammonium fluoride (NH<sub>4</sub>F) based on the hydrothermal method. Urea and NH<sub>4</sub>F ratio exhibit a great influence on the microstructure and the HER catalytic performance of CuCo<sub>2</sub>S<sub>4</sub>/NF catalysts is discussed in detail.

### 1. Introduction

The environmental pollution caused by energy consumption has become an important problem faced by modern society. The excessive use of fossil fuels leading to serious environmental problems runs counter to the social responsibility of environmentally sustainable development.<sup>1–4</sup> Consequently, in order to reduce the dependence on fossil fuels, renewable energy has been paid more and more attention as a substitute for fossil fuels.<sup>5–9</sup> In this regard, hydrogen is considered a promising fuel. Electrochemical reactions that produce oxygen from oxygen evolution reactions (OER) and hydrogen from hydrogen evolution reactions (HER) have attracted a lot of research attention.<sup>10,11</sup> Problems of slow reaction and high energy consumption in energy supply technology such as hydrogen production, rechargeable metal–air batteries and renewable fuel cells can be solved by adding catalytic materials to the two semi-reactions.<sup>12–23</sup> Currently, Pt-based HER oxides and Ir/Ru OER catalysts are widely used as commercial catalysts in the above-mentioned fields.<sup>24</sup> However, the scarcity and high cost of these precious metals impede their extensive use.<sup>25–27</sup> Well-designed catalysts prepared using abundant Earth elements such as iron, cobalt, nickel and copper and their derivatives stand out as affordable alternatives.<sup>28–30</sup>

Recently, several non-noble metal catalysts for HER have been reported, such as transition metal chalcogenides.<sup>31–41</sup> Transition metal sulfides are promising candidate compounds due to their low cost and easily preparation. For instance, Ji<sup>42</sup> *et al.* used two continuous liquid–solid reactions to design CuS nanowires on copper foil at room temperature. Wang<sup>43</sup> *et al.* synthesized Co<sub>3</sub>S<sub>4</sub>/CoP in an Ar atmosphere through

simultaneous phosphating and sulfurization of cobalt hydroxide precursors. The material showed a very low HER onset potential, only 34 mV. Geng<sup>44</sup> *et al.* synthesized a metallic phase MoS<sub>2</sub> (M-MoS<sub>2</sub>) with two-dimensional structure for HER catalytic reaction by hydrothermal method. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the overpotential of the electrocatalyst was 175 mV at 10 mA cm<sup>−2</sup>, and the Tafel slope was 41 mV dec<sup>−1</sup>. After 1000 cycles by cyclic voltammetry (CV), the current density attenuation of MoS<sub>2</sub> nanosheets was less than 12%. Ji<sup>45</sup> *et al.* synthesized 3D flower-like CoS<sub>2</sub> microspheres by a typical hydrothermal method and mixed them with IL in isopropyl alcohol solution, and then prepared CoS<sub>2</sub>-IL catalyst for OER through multi-step solvent evaporation. In 0.1 M KOH solution, a voltage of 1.63 V is required to reach a current density of 10 mA cm<sup>−2</sup>. The Tafel slope of the electrocatalyst was 81.7 mV dec<sup>−1</sup>. After 1000 CV cycles, the voltage was only increased by 8 mV at 10 mA cm<sup>−2</sup>. However, the performance of these electrocatalysts are good at low H coverage, but with the increase of H coverage, the conductivity will decrease significantly.<sup>46</sup>

CuCo<sub>2</sub>S<sub>4</sub> is a paramagnetic sulfur spinel with ideal AB<sub>2</sub>S<sub>4</sub> molecular formula and metallic properties. Its structure and molecular formula indicate the presence of mixed valence metal cations, so it has high electrical conductivity and electrochemical activity.<sup>47,48</sup> Since its features are suitable for various reactions such as HER and OER, CuCo<sub>2</sub>S<sub>4</sub> has been reportedly studied in electrocatalysis applications.<sup>49</sup> For instance, Pawar<sup>50</sup> *et al.* directly fabricated highly porous CuCo<sub>2</sub>O<sub>4</sub> nanosheets on nickel foam by electrodeposition approach. In a 1 M KOH solution, the sample exhibited a low overpotential of 260 mV at 20 mA cm<sup>−2</sup> with a corresponding Tafel slope of 67 mV dec<sup>−1</sup> and an electrochemical surface area (ECSA) value of 4712.5 cm<sup>2</sup>. At different KOH solution (1 M and 3 M), the capacitance retention rates were 85% and 93%, respectively, after 5000 cycles. Sun<sup>51</sup> *et al.* prepared high-quality Ni doped CuCo<sub>2</sub>S<sub>4</sub> nanoparticles (NCCS NPs) using triethanolamine (TEOA) molecules by a simple hydrothermal

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method. In 0.5 M  $\text{H}_2\text{SO}_4$  solution, the overpotential reached 249 mV at  $10 \text{ mA cm}^{-2}$ , Tafel slope was  $105 \text{ mV dec}^{-1}$ , and the double layer capacitance value was  $3.4 \text{ mF cm}^{-2}$ . After 10 hours stability test of continuous current density of  $10 \text{ mA m}^{-2}$ , the capacitance retention of NCCS NPs catalyst did not decrease significantly. These studies show that  $\text{CuCo}_2\text{S}_4$  can reduce the overpotential, thereby speeding up OER. The increase in OER activity of Cu–Co sulfide is largely due to the synergistic effect of bimetallic structure between copper and other types of atoms to optimize the electronic structure, increase the number of active centers, improve the

conductivity, reduce the resistivity, and greatly promote the electrocatalytic activity. However, most OER catalysts perform well in alkaline solutions, the HER-role of  $\text{CuCo}_2\text{S}_4$  in alkaline media has not been developed on a large scale, so this material has a certain development potential.<sup>52–54</sup> Therefore, we selected  $\text{CuCo}_2\text{S}_4$  as HER catalyst to study.

In this work, because of urea and  $\text{NH}_4\text{F}$  affect the nucleation capacity of the compound and change the microscopic morphology of  $\text{CuCo}_2\text{S}_4$ , meaning that different microstructure can be synthesized in different ratio,<sup>55,56</sup> which can increase the number of active sites and improve HER performance,  $\text{CuCo}_2\text{S}_4/$

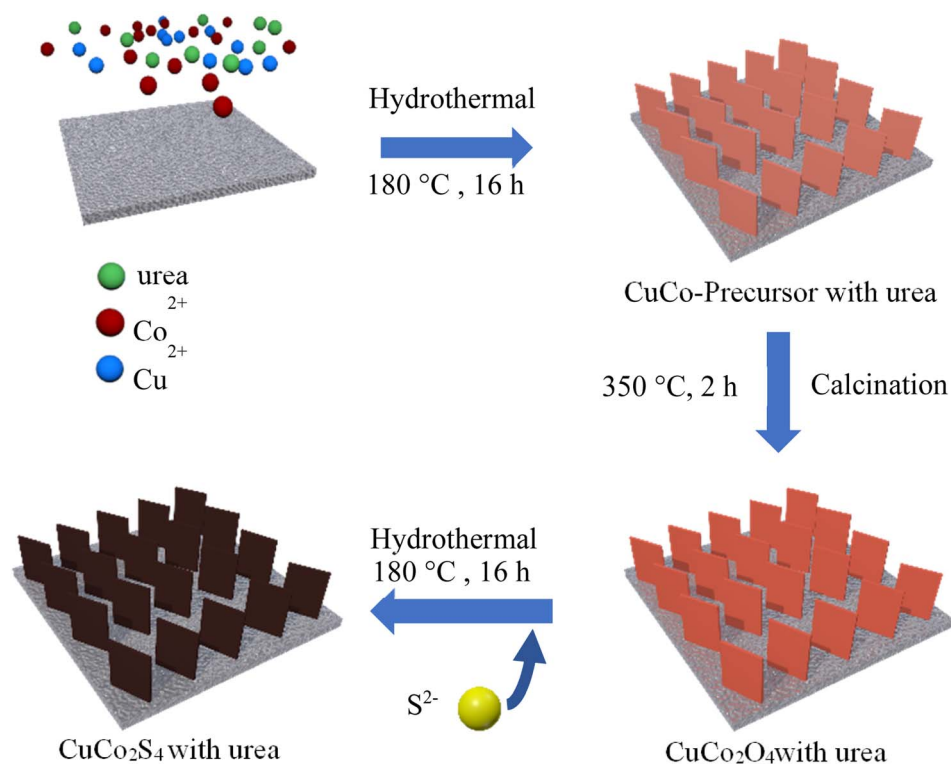


Fig. 1 Schematic illustration of the synthesis of  $\text{CuCo}_2\text{O}_4/\text{NF}$  nanowires with different urea ratios.

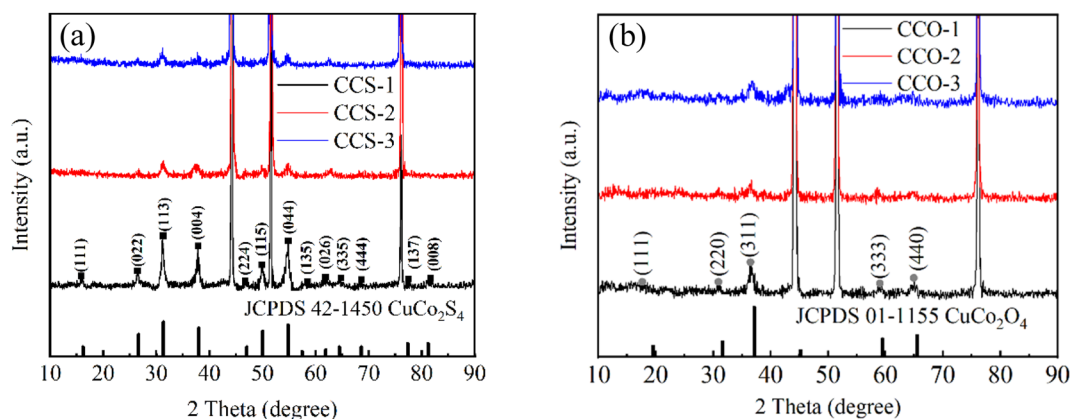


Fig. 2 (a) XRD patterns of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different urea ratios and (b) XRD patterns of  $\text{CuCo}_2\text{O}_4/\text{NF}$  catalyst with different urea ratios.

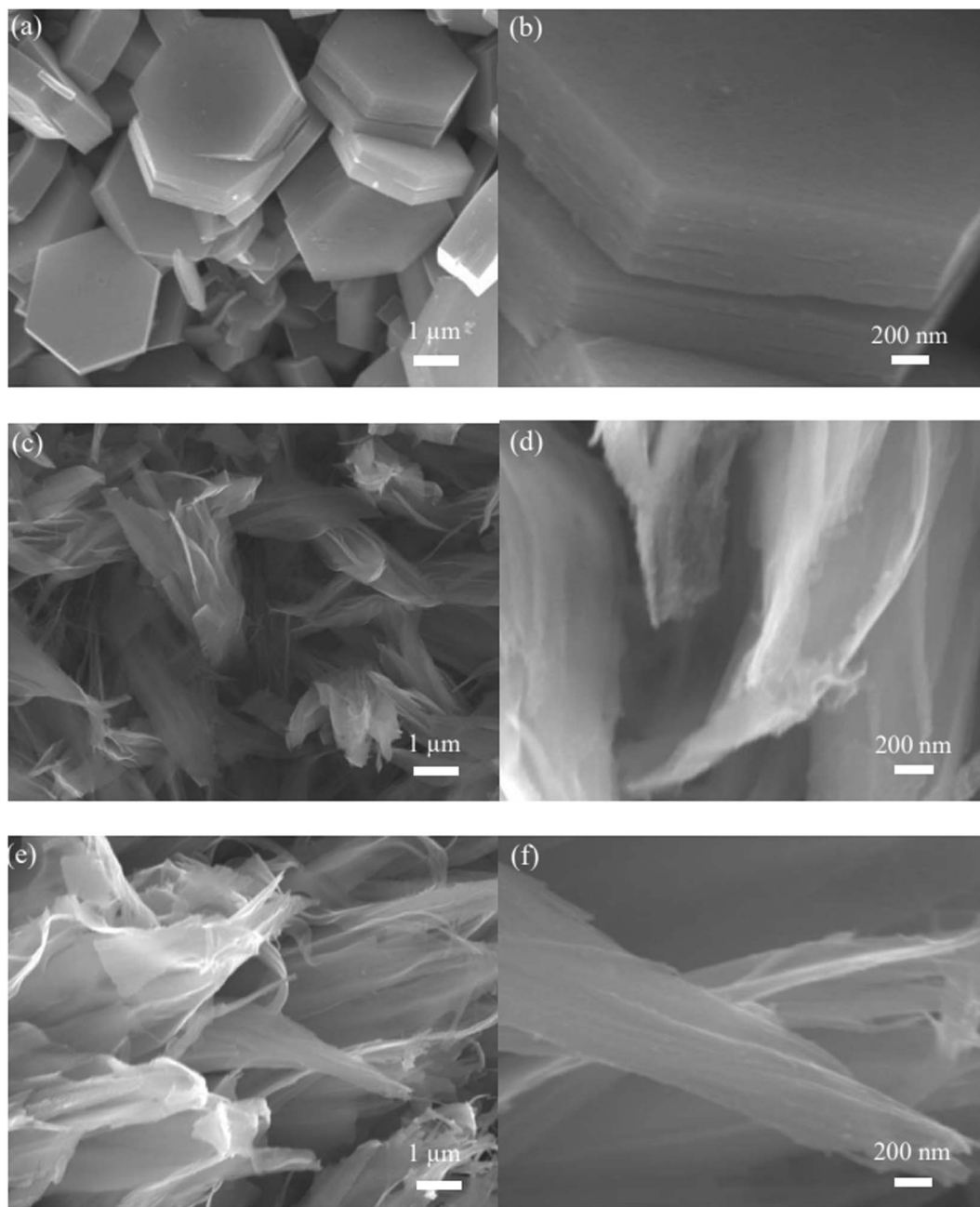


Fig. 3 SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different urea ratios: (a and b) SEM images of CCS-1 at low and high magnification, (c and d) SEM images of CCS-2 at low and high magnification, (e and f) SEM images of CCS-3 at low and high magnification.

NF catalysts with different morphology were synthesized by controlling urea and  $\text{NH}_4\text{F}$  ratio based on hydrothermal method, and then the influence of urea and  $\text{NH}_4\text{F}$  ratio on the microstructure and HER catalytic characteristics of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst was discussed in detail.

## 2. Experimental section

### 2.1 Effects of urea and $\text{NH}_4\text{F}$ ratio on the preparation of Cu-Co sulfide catalyst and electrocatalytic HER performance

**2.1.1 Preparation of  $\text{CuCo}_2\text{O}_4/\text{NF}$  catalyst materials.** The NF was prepared by cutting into pieces ( $2 \times 1 \text{ cm}^2$  in

a rectangle) and ultrasonically cleaned several times with absolute ethanol and deionized water (DI water), and dried at  $60 \text{ }^\circ\text{C}$  for 12 h and reserved for subsequent use. 1 mmol  $\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ , 2 mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 2 mmol urea were dissolved in 50 mL of DI water. The prepared rose-colored solution and NF were placed in the reaction kettle and kept at  $180 \text{ }^\circ\text{C}$  for 16 h. After cooling to room temperature, the NF with pink sample was removed, cleaned and dried at  $60 \text{ }^\circ\text{C}$  for 8 h. The  $\text{CuCo}_2\text{O}_4/\text{NF}$  catalyst was obtained by annealing at  $350 \text{ }^\circ\text{C}$  and  $2 \text{ }^\circ\text{C min}^{-1}$  in muffle furnace for 2 h. The optimal urea ratio can be determined by changing the urea ratio to 2, 4 and 8 mmol, with other parameters unchanged, and marked as

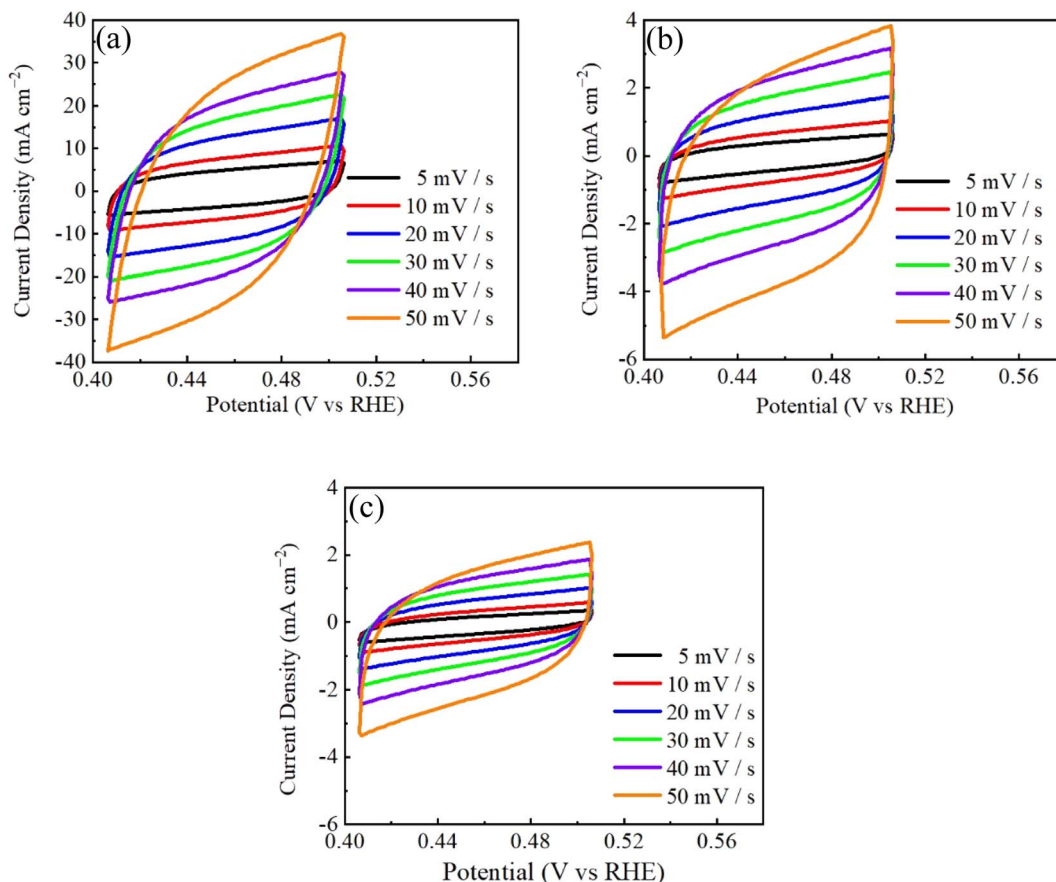


Fig. 4 CV curves of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different urea ratios: (a) CCS-1, (b) CCS-2, (c) CCS-3.

CCO-1, CCO-2, and CCO-3, respectively. 2 mmol  $\text{NH}_4\text{F}$  was added in the sample of the optimal urea ratio to study the influence of  $\text{NH}_4\text{F}$ , and other conditions were the same, finally, the optimized  $\text{CuCo}_2\text{O}_4/\text{NF}$  was obtained. Changing the  $\text{NH}_4\text{F}$  ratio to 2, 4, 8 mmol, with other parameters unchanged, and labeling as CCNO-1, CCNO-2 and CCNO-3, respectively, the optimal  $\text{NH}_4\text{F}$  ratio could be determined.

**2.1.2 Preparation of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst materials.** 3 mmol  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was dissolved in 50 mL of DI water. The obtained transparent solution and the  $\text{CuCo}_2\text{O}_4/\text{NF}$  catalyst material were put into a steel reactor, and then kept at 180 °C for 16 h. After cooling to room temperature, the obtained  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst precursor material was removed and cleaned, and then dried at 60 °C for 8 h to obtain  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst material.  $\text{CuCo}_2\text{O}_4/\text{NF}$  prepared by adding urea was labeled as CCS-1, CCS-2 and CCS-3 according to the urea ratio.  $\text{CuCo}_2\text{O}_4/\text{NF}$  prepared by adding  $\text{NH}_4\text{F}$  was labeled as CCNS-1, CCNS-2 and CCNS-3 according to the  $\text{NH}_4\text{F}$  ratio. The mass loading of the CCS-1, CCS-2, CCS-3, CCNS-1, CCNS-2 and CCNS-3 are  $0.0025 \text{ g cm}^{-2}$ ,  $0.0038 \text{ g cm}^{-2}$ ,  $0.0040 \text{ g cm}^{-2}$ ,  $0.0150 \text{ g cm}^{-2}$ ,  $0.0039 \text{ g cm}^{-2}$ , and  $0.0035 \text{ g cm}^{-2}$ , respectively.

## 2.2 Structural characterization of materials

X-ray diffractometer (XRD, D/max-2500/PC<sup>-1</sup>) with  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) at  $2\theta$  range of 10–90° was used to characterize crystal

structure of the materials. Field emission scanning electron microscope (FE-SEM, Sigma 500), High Resolution Transmission Electron Microscope (HRTEM) and energy dispersive spectrometer (EDS, Oxford AZtec X-Max 50) were used to analyze the morphology and surface element distribution of the samples. The instrument works at a high voltage of 30 kV, with a vacuum of 133 Pa and an acceleration voltage of 2 kV. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was used to study the elemental composition and chemical valence state of the sample.

## 2.3 Electrochemical characterization of the materials

The electrochemical performance was tested by Shanghai CHI660E electrochemical workstation. First of all, a three-electrode system was established as the electrochemical test platform, using the as-prepared materials as the working electrode, Hg/HgO as reference electrode, Pt plate as counter electrode, the electrolyte was 1 M KOH aqueous solution, and the current collector was pretreated NF.  $\text{CuCo}_2\text{O}_4$  was used as anode and  $\text{CuCo}_2\text{S}_4$  as cathode to assemble a two-electrode electrolytic cell. By analyzing CV curve, linear sweep voltammetry (LSV) curve, Tafel curve, electrochemical impedance spectroscopy (EIS) curve, double layer capacitance curve, long-term stability curve the electrochemical performance of electrode materials and practical application ability can be judged. All the

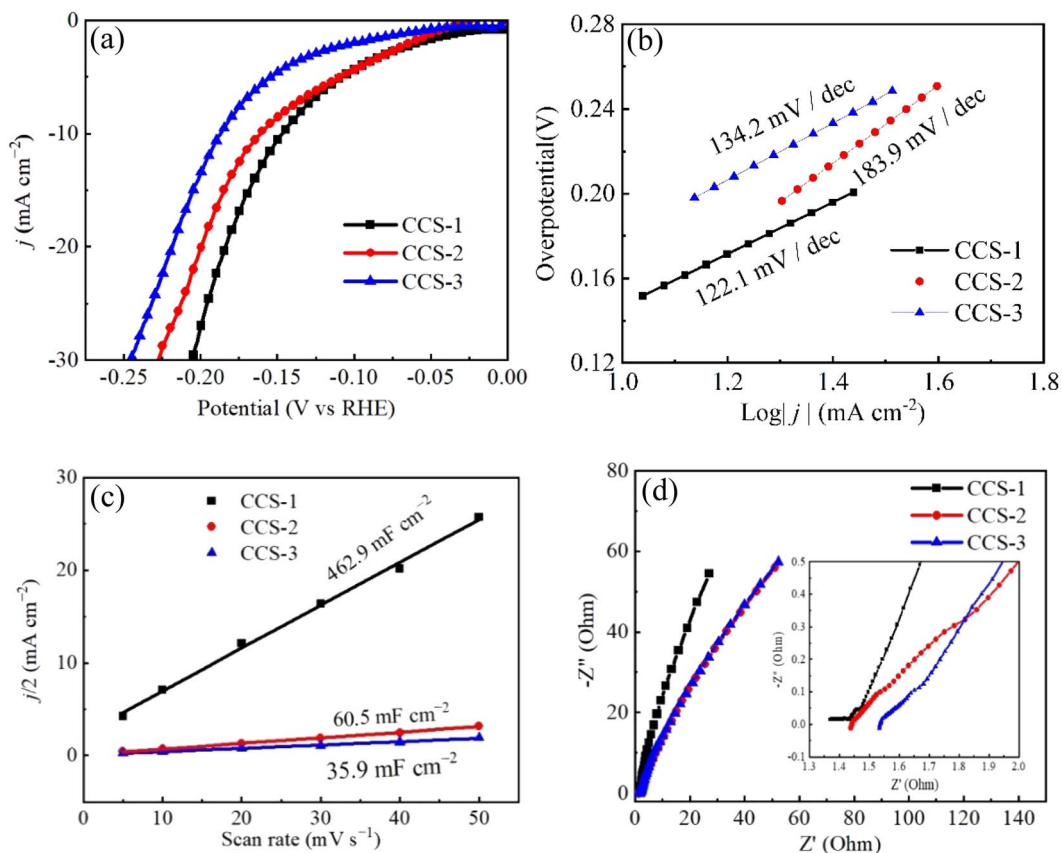


Fig. 5 HER performances of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different urea ratios: (a) LSV polarization curves, (b) Tafel curves, (c) double layer capacitance curves, (d) EIS curves.

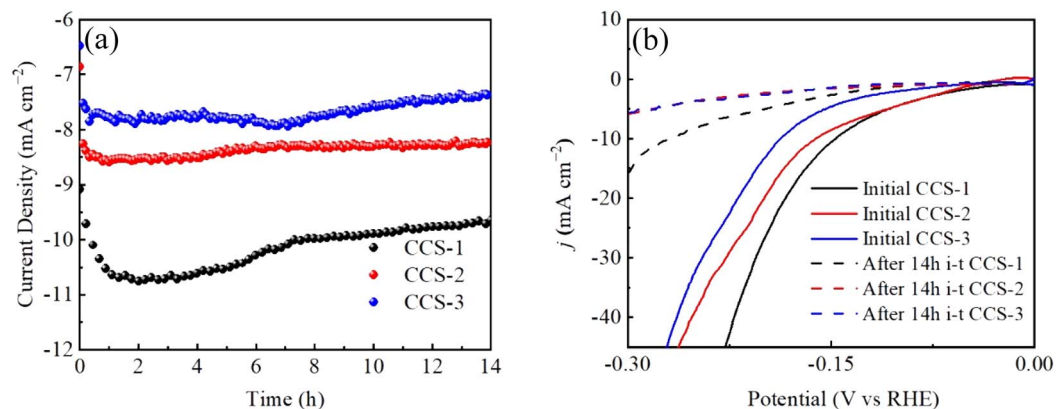


Fig. 6 Stability test curves of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different urea ratios: (a) long-term stability curves, (b) LSV polarization curves after long-term stability test.

potentials measured are converted into reversible hydrogen electrodes (RHE) at 25 °C by Nernst equation:<sup>57</sup>

$$E_{\text{RHE}} (\text{V}) = E_{\text{Hg}/\text{HgO}} (\text{V}) + 0.098 + 0.059 \text{ pH} \quad (1)$$

Over potential can be calculated by following equation:<sup>58</sup>

$$\eta = E_{(\text{RHE})} - 1.23 \text{ V} \quad (2)$$

The Tafel slope is given by the following equation:<sup>59</sup>

$$\eta = a + b \log|j| \quad (3)$$

where  $\eta$ ,  $a$ ,  $b$  and  $j$  are overpotential, fitting parameter, Tafel slope and current density, respectively.

The Electrochemical Active Surface Area (ECSA) can be determined by the following equation, where  $C_{\text{dl}}$  is the double-

layer capacitance of the electrode material and  $C_s$  is the specific capacitance.<sup>60</sup>

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

### 3. Results and discussion

#### 3.1 Effect of urea on the preparation of $\text{CuCo}_2\text{S}_4/\text{NF}$ catalyst and its electrocatalytic hydrogen evolution performance

$\text{CuCo}_2\text{S}_4$  with different urea ratios were synthesized by two-step hydrothermal method and calcination, as shown in Fig. 1. Firstly,  $\text{CuCo}_2\text{O}_4$  precursors were synthesized on nickel foam.

Secondly, the nanosheet-like precursors were calcined in air. Finally,  $\text{CuCo}_2\text{S}_4$  was obtained by sulfurization process.

Fig. 2(a) shows the XRD patterns of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts synthesized with different urea ratios. The diffraction peaks can be observed at  $2\theta$  values of  $16.131^\circ$ ,  $26.586^\circ$ ,  $31.271^\circ$ ,  $37.966^\circ$ ,  $46.993^\circ$ ,  $49.989^\circ$ ,  $54.793^\circ$ ,  $57.439^\circ$ ,  $61.889^\circ$ ,  $64.426^\circ$ ,  $68.594^\circ$ ,  $77.323^\circ$  and  $81.170^\circ$ . These diffraction peaks correspond to the (111), (022), (113), (004), (224), (115), (044), (135), (026), (335), (444), (137) and (008) crystal planes of the  $\text{CuCo}_2\text{S}_4$  phase (JCPDS no. 42-1450), respectively. Compared with Fig. 2(a) and (b), it can be seen that the  $\text{CuCo}_2\text{O}_4$  is completely transformed into  $\text{CuCo}_2\text{S}_4$  after the second hydrothermal process.

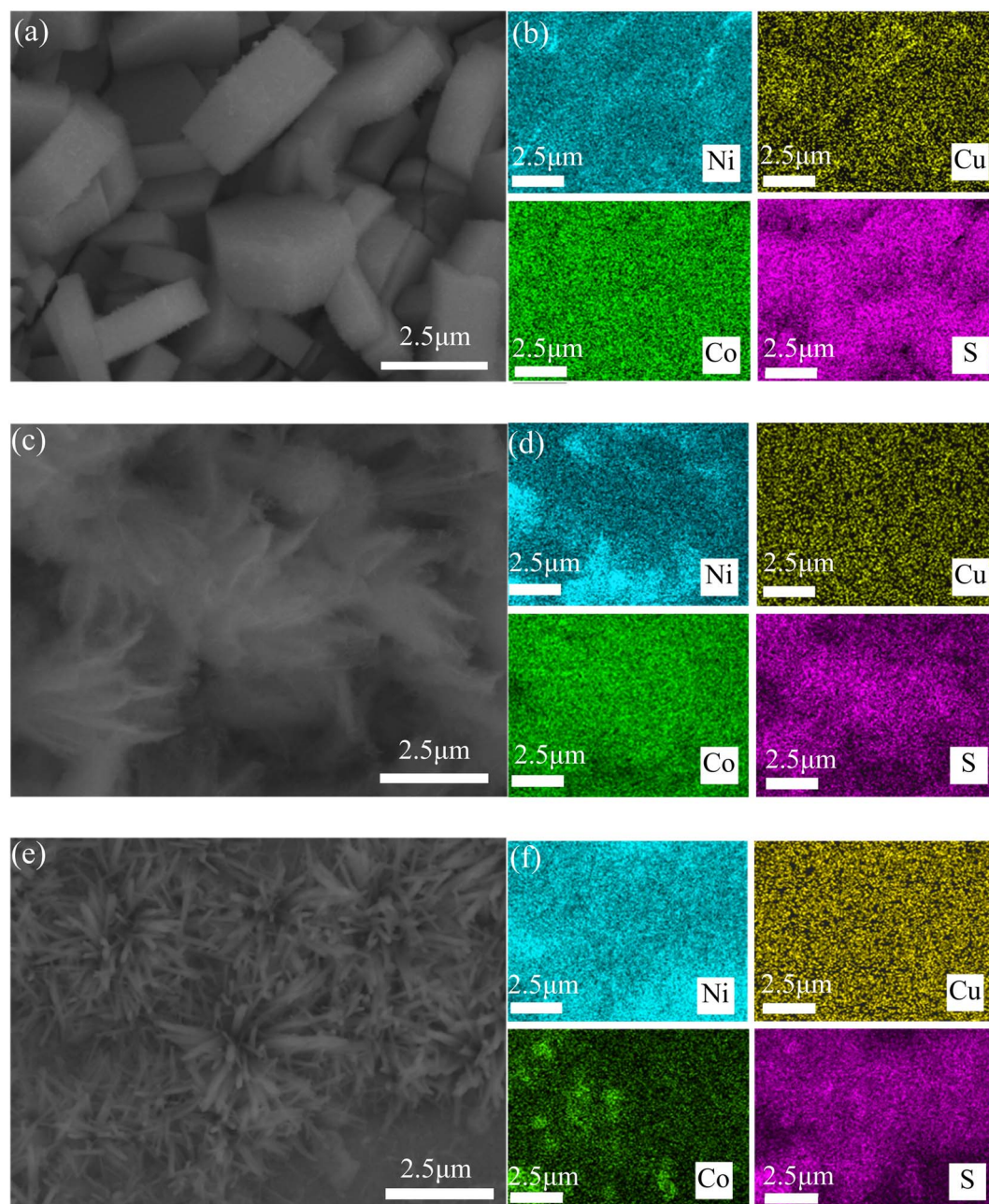


Fig. 7 SEM and EDS images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts with different urea ratios (a and b) CCS-1, (c and d) CCS-2, (e and f) CCS-3.

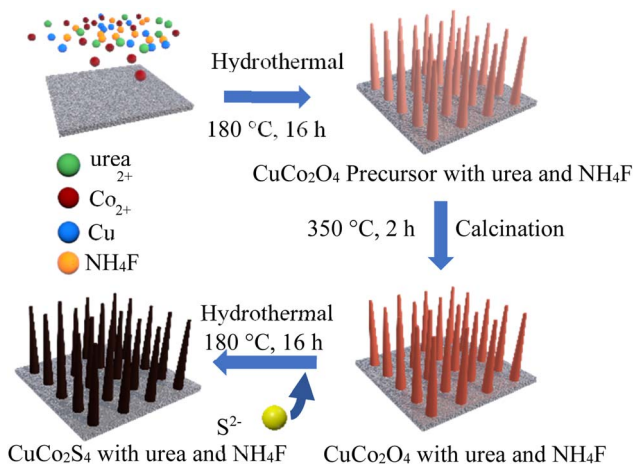


Fig. 8 Schematic illustration of the synthesis of  $\text{CuCo}_2\text{O}_4/\text{NF}$  nano-wires with different urea and  $\text{NH}_4\text{F}$  ratios.

Fig. 3 is the SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst. The microstructure of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst prepared with various urea ratio is obviously distinct. Fig. 3(a) and (b) are SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst prepared with 2 mmol urea. The microstructure of CCS-1 sample is obvious hexagonal nanosheet structure uniformly covered on NF, and the thickness of the single nanosheet is about 500 nm. Fig. 3(c) and (d) are SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst prepared with 4 mmol urea. The morphology of CCS-2 samples is banded nanosheet structure and uniformly grown on NF substrate. Fig. 3(e) and (f) are SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst prepared with 8 mmol urea. The morphology of CCS-3 sample is nanosheet structure like willow leaf, and the thickness of nanosheet is about 40 nm. The morphologies of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts are gradually refined and dispersed with the increment of urea ratio, which will affect the contact between the catalyst surface and the electrolyte. Moreover, the change of morphology will catalytic active sites of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts participate in the electrocatalytic reaction. Thus, HER catalytic performance of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst can be affected by the variable morphology.

Fig. 4 shows the CV curves of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts synthesized at various urea ratio in the non-Faraday area at scanning rates of  $5\text{--}50\text{ mV s}^{-1}$ . Comparison of the electrochemical properties of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts shows that the CV integral area of CCS-1 sample is the largest, and that of CCS-3 sample is the smallest.<sup>59</sup> The specific capacitance of the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts decreases with urea ratio increment. According to Fig. 3, the electrochemical performance of CCS-1 samples with hexagonal nanosheet structure is the best among the three. Therefore, the electrochemical properties of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst are significantly affected by different morphology.

In 1 M KOH solution, LSV is used to study HER catalytic performance of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts under a scanning rate of  $5\text{ mV s}^{-1}$ , as shown in Fig. 5. All polarization curves are iR compensation.  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst is used as the working electrode in the three-electrode system. Fig. 5(a) shows the polarization curves of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. When the current density is less than  $10\text{ mA cm}^{-2}$ , the overpotentials of CCS-1 and CCS-2 electrodes are almost the same. At  $10\text{ mA cm}^{-2}$ , the overpotentials of CCS-1 CCS-2 and CCS-3 electrodes are 147 mV, 161 mV and 187 mV, respectively. When the current density is higher than  $10\text{ mA cm}^{-2}$ , the overpotential of CCS-1 is significantly lower than that of CCS-2. At  $20\text{ mA cm}^{-2}$ , the overpotentials of CCS-1 CCS-2 and CCS-3 samples are 184 mV, 199 mV and 218 mV, respectively. The overpotential of CCS-1 sample is always the smallest. In addition, the electrochemical kinetics of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts were studied by Tafel slope, as shown in Fig. 5(b). The Tafel slope of CCS-2 sample is the highest, which is  $183.9\text{ mV dec}^{-1}$ . The Tafel slope of CCS-1 is much lower than that of CCS-2. The Tafel slope of CCS-1 sample is the lowest, and the corresponding value is  $122.1\text{ mV dec}^{-1}$ . Smaller Tafel slope is the result of more catalytic active sites leading to faster electrochemical reaction kinetics.<sup>61</sup> As shown in Fig. 3, the hexagonal nanosheet structure provides more catalytic active sites for CCS-1 samples, leading to faster electrochemical reaction of CCS-1 samples and thus better HER catalytic activity. Therefore, the hexagonal nanosheet structure is more favorable to the HER process.

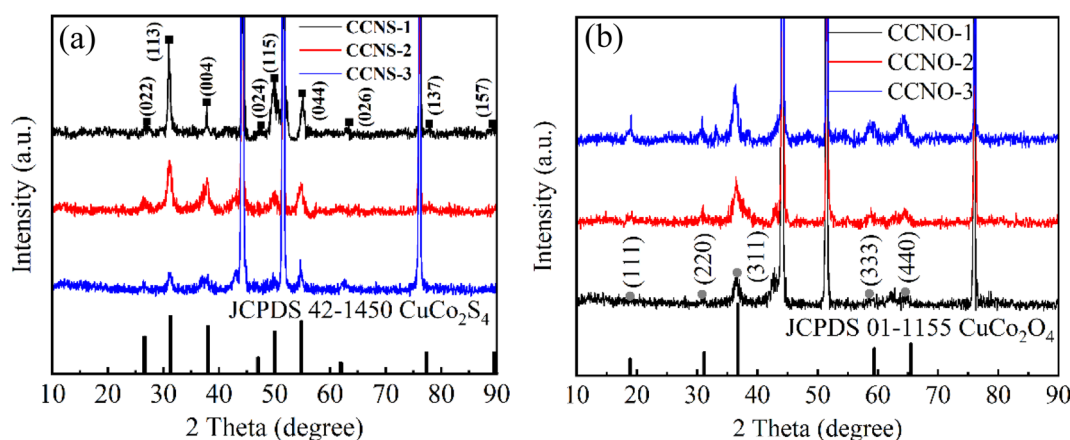


Fig. 9 (a) XRD patterns of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different  $\text{NH}_4\text{F}$  ratios. (b) XRD patterns of  $\text{CuCo}_2\text{O}_4/\text{NF}$  catalyst with different  $\text{NH}_4\text{F}$  ratios.

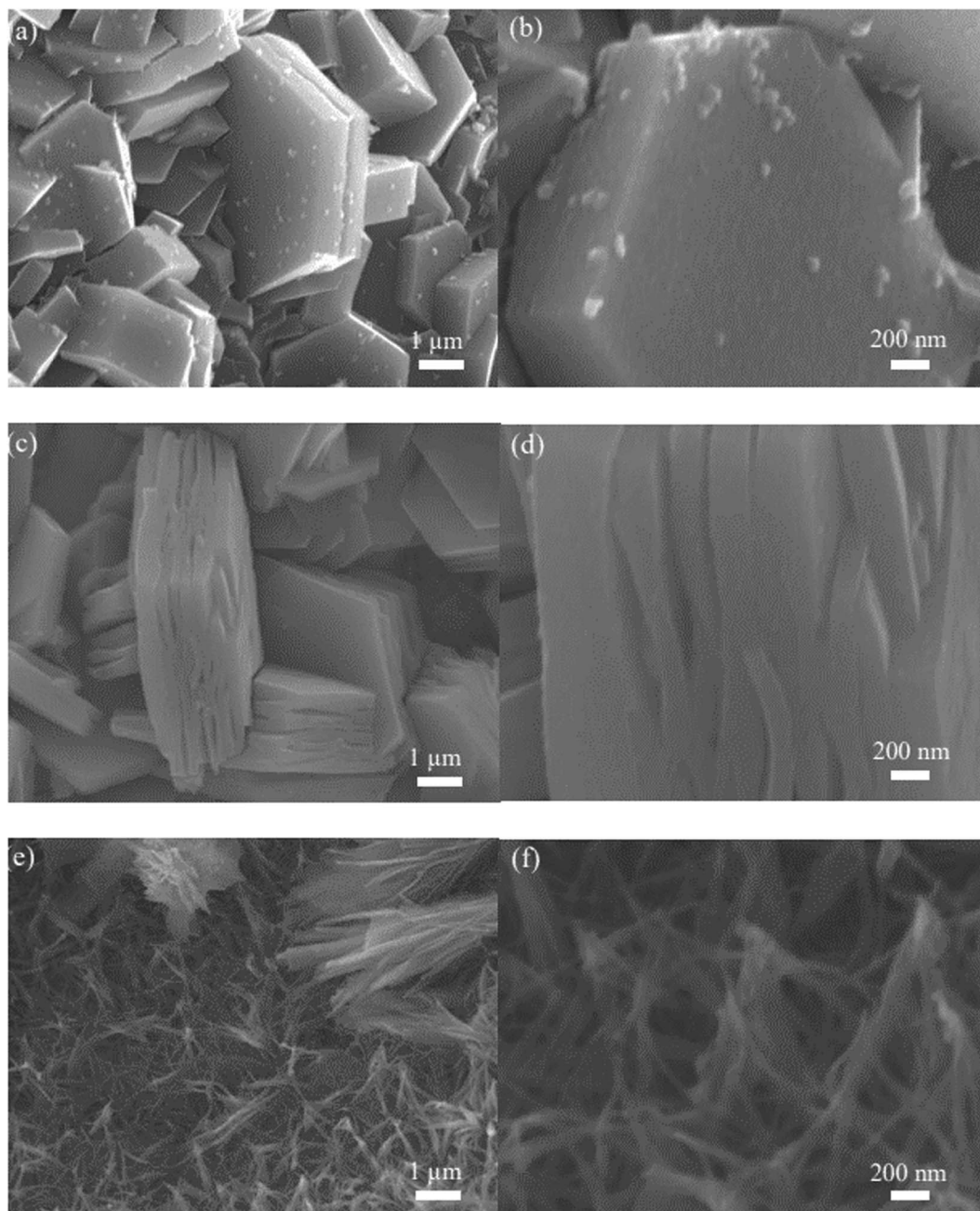


Fig. 10 SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different  $\text{NH}_4\text{F}$  ratios: (a and b) SEM images of CCNS-1 at low and high magnification, (c and d) SEM images of CCNS-2 at low and high magnification, (e and f) SEM images of CCNS-3 at low and high magnification.

Fig. 5(c) are the double-layer capacitance ( $C_{dl}$ ) curves according to the CV curves of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts calculated in Fig. 4.  $C_{dl}$  values reflect the ECSA values of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. It can be observed that the  $C_{dl}$  values of CCS-1, CCS-2 and CCS-3 samples are  $462.9 \text{ mF cm}^{-2}$ ,  $60.5 \text{ mF cm}^{-2}$  and  $35.9 \text{ mF cm}^{-2}$ , respectively. The  $C_{dl}$  value of CCS-1 sample was the highest, which reflected that CCS-1 sample had the most catalytic active sites. Fig. 5(d) illustrates the EIS curves of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. The catalytic activity of the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts is influenced by electrochemical charge

transfer kinetics and thus can be analyzed by EIS curves. The slope of CCS-1 sample in the low-frequency range is the largest among the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts, while the radius in the high-frequency one is the smallest among the three, indicating that CCS-1 sample has the fastest charge transfer rate, which contributes to the improvement of electrochemical reaction kinetics and HER catalytic activity, corresponding to the previous results.<sup>62</sup>

The long-term stability test is another important technique for evaluating the catalyst performance. The stability of three



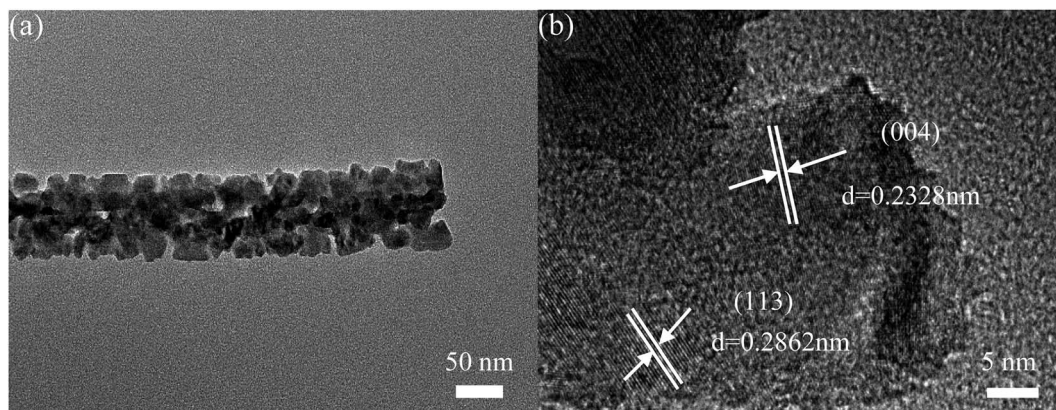


Fig. 11 TEM images of CCNS-3: (a) TEM image, (b) HRTEM image.

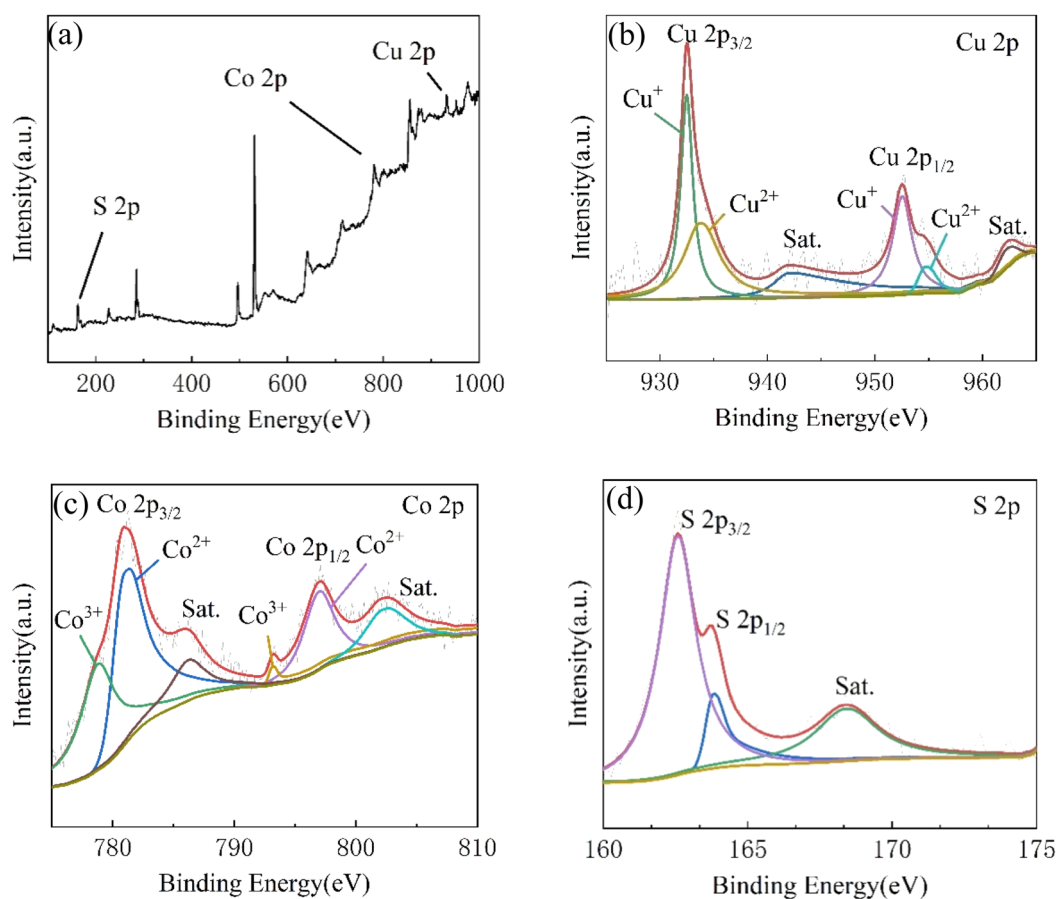


Fig. 12 XPS images of CCNS-3: (a) Survey XPS, (b) Cu 2p XPS, (c) Co 2p XPS, (d) S 2p XPS.

$\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts is tested by chronoamperometry at a scanning rate of  $10 \text{ mV s}^{-1}$  with the fixed voltage  $\eta = 0.6 \text{ V}$  for 14 h, as shown in Fig. 6. Because of hydrogen adhering to  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst within HER process, the curves fluctuate in different degrees. From Fig. 6(a) that the electric current density generated by CCS-1 sample is the maximum at the initial stage of the reaction, which also confirms the excellent catalytic

activity of HER of the previous CCS-1 sample. After the reaction time reached 2 h, the current density of CCS-1 samples began to decrease. After the reaction time reached 8 h, the decrease degree declines. The current density of CCS-2 is essentially the same for 14 h. The current density of CCS-3 samples also decreased from 8 h. Therefore, CCS-2 samples with banded nanosheet structure have good stability, which can be

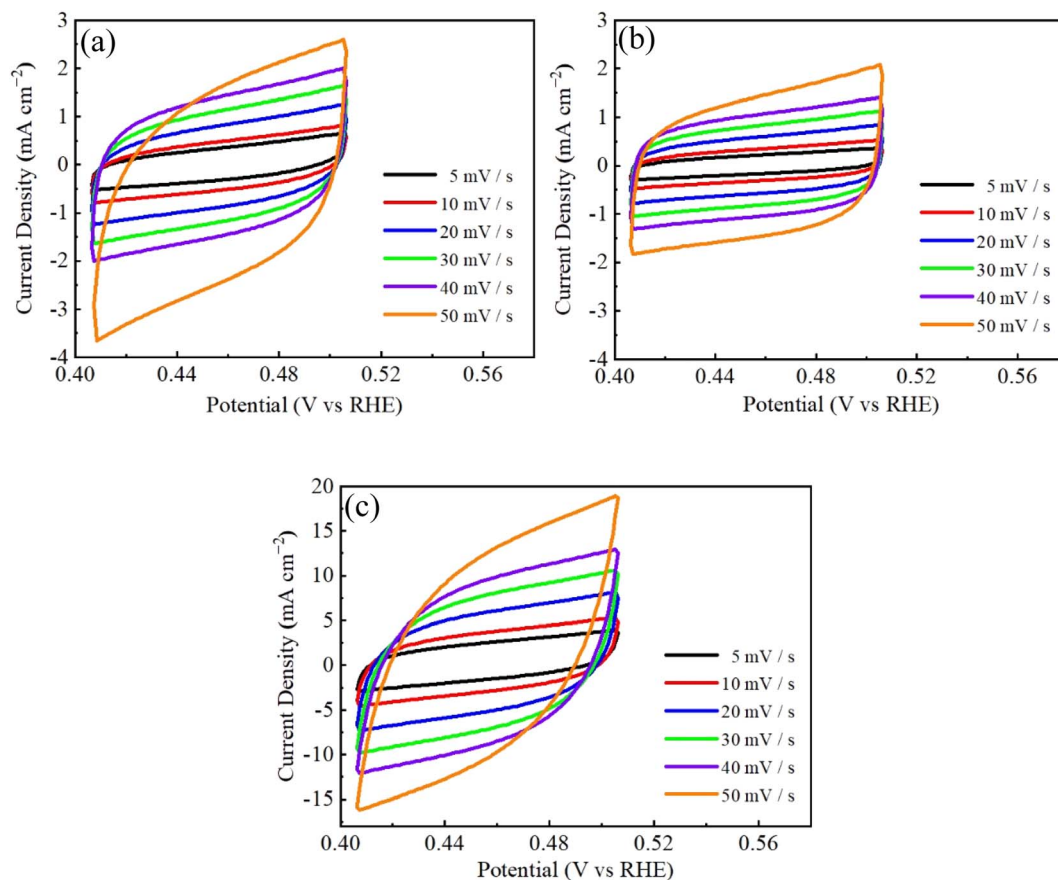


Fig. 13 CV curves of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different  $\text{NH}_4\text{F}$  ratios: (a) CCNS-1, (b) CCNS-2, (c) CCNS-3.

attributed to cross-banded nanosheets providing structural advantage with sufficient reactions. Fig. 6(b) demonstrates the HER performance of the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts degrades after 14 h.

Fig. 7 shows the elemental composition of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts after 14 h stability test. The distribution of Ni, Cu, Co and S elements can be clearly seen from the EDS spectra, indicating that after 14 h HER process, the composition of the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts did not change significantly, and they are still evenly distributed on the NF substrate.

### 3.2 Effect of $\text{NH}_4\text{F}$ on preparation of $\text{CuCo}_2\text{S}_4/\text{NF}$ catalyst and electrocatalytic hydrogen evolution performance

As shown in Fig. 8,  $\text{CuCo}_2\text{S}_4$  with different ratios of urea and  $\text{NH}_4\text{F}$  were prepared by hydrothermal method and calcination. Firstly,  $\text{CuCo}_2\text{O}_4$  nanowire was synthesized by hydrothermal method on nickel foam and calcined in air. And then  $\text{CuCo}_2\text{O}_4$  was sulfurized by hydrothermal method to obtain  $\text{CuCo}_2\text{S}_4$ .

Fig. 9(a) shows the XRD patterns of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts prepared with different  $\text{NH}_4\text{F}$  ratios. The diffraction peaks can be observed at  $2\theta$  values of  $16.131^\circ$ ,  $26.586^\circ$ ,  $31.271^\circ$ ,  $37.966^\circ$ ,  $46.993^\circ$ ,  $49.989^\circ$ ,  $54.793^\circ$ ,  $57.439^\circ$ ,  $61.889^\circ$ ,  $64.426^\circ$ ,  $68.594^\circ$ ,  $77.323^\circ$  and  $81.170^\circ$ . These diffraction peaks correspond to the (022), (113), (004), (224), (115), (044), (026), (137) and (157) crystal planes of  $\text{CuCo}_2\text{S}_4$  (JCPDS no. 42-1450), respectively.

There is no obvious diffraction peak except for three strong diffraction peaks at  $44.40^\circ$ ,  $51.76^\circ$  and  $76.26^\circ$ . From Fig. 9(a) and (b), we conclude that the material is completely converted from oxide to sulfide.

Fig. 10 shows the SEM images of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts with fixed urea ratio of 2 mmol and different  $\text{NH}_4\text{F}$  ratios. Fig. 10(a) and (b) are SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with  $\text{NH}_4\text{F}$  ratio of 2 mmol. The morphology of CCNS-1 sample is a complete hexagonal nanosheet structure. Fig. 10(c) and (d) are SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with ammonia fluoride ratio of 4 mmol. The morphology of CCNS-2 sample shows layered hexagonal nanosheet structure. Fig. 10(e) and (f) are SEM images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with  $\text{NH}_4\text{F}$  ratio of 8 mmol. The morphology of CCNS-3 sample exhibits interwoven nanowire structure.

The (Transmission Electron Microscope) TEM test of CCNS-3 was performed to further understand the microstructure of the catalyst. Fig. 11(a) displays that the CCNS-3 sample exhibits nanowires structure, which corresponds to the SEM images in Fig. 10(e) and (f). It can be seen from HRTEM in Fig. 11(b) that the lattice fringes are 0.2862 nm and 0.2328 nm which correspond to the (113) and (004) crystal planes, respectively.

In order to obtain the specific information about chemical composition and state of as-prepared materials, the CCNS-3 samples were characterized by XPS, and the results are

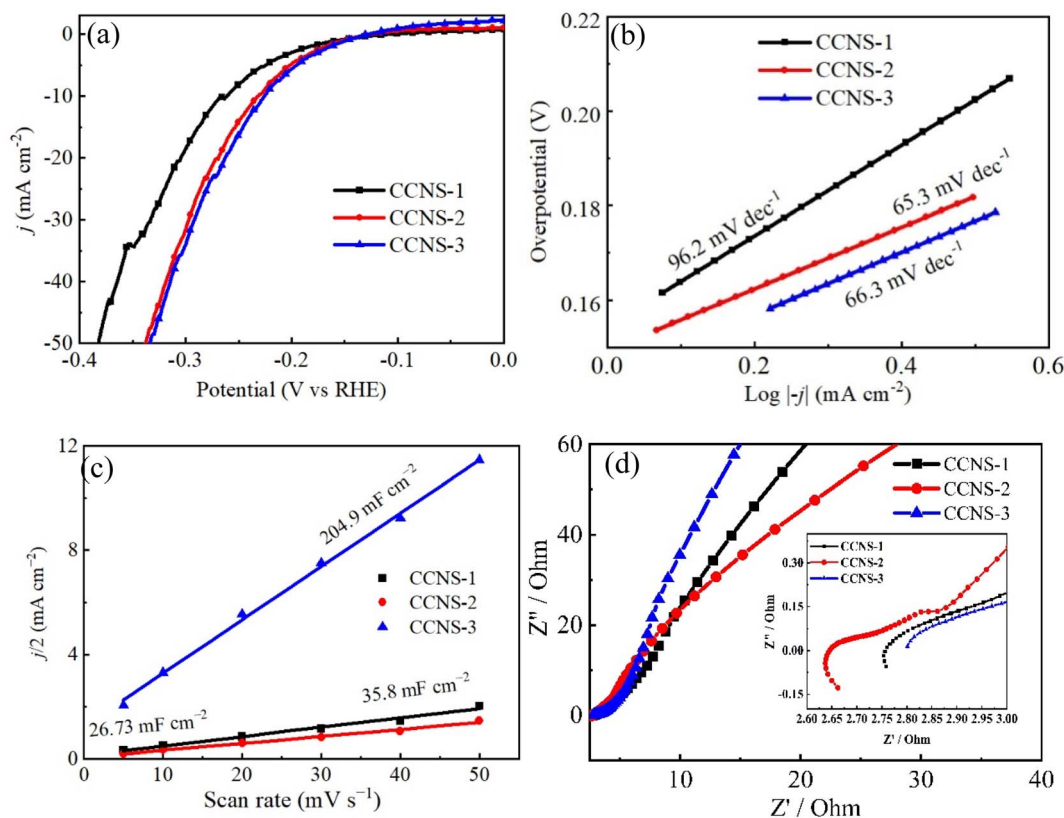


Fig. 14 HER performances of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different  $\text{NH}_4\text{F}$  ratios: (a) LSV polarization curves, (b) Tafel curves, (c) double layer capacitance curves, (d) EIS curves.

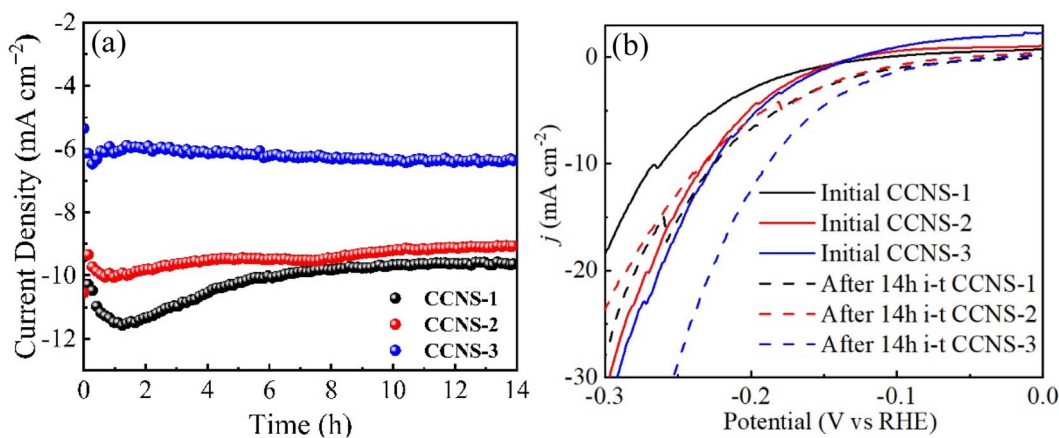


Fig. 15 Stability test curves of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with different  $\text{NH}_4\text{F}$  ratios: (a) long-term stability curves, (b) LSV polarization curves after long-term stability test.

shown in Fig. 12. Fig. 12(a) is the survey XPS spectrum of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst, showing the presence of Cu, Co and S. Fig. 12(b) shows the Cu 2p XPS, in which Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  are two spin orbits. The two peaks of the binding energy of 932.5 eV and 952.6 eV correspond to  $\text{Cu}^+$ . The two peaks at 933.8 eV and 954.8 eV correspond to  $\text{Cu}^{2+}$ . Two satellite peaks at 942.3 eV and 962.8 eV also indicate the presence of  $\text{Cu}^{2+}$ .<sup>63</sup> It can be seen from Fig. 12(c) that the Co 2p XPS contains two

spin orbits, Co  $2p_{3/2}$  and Co  $2p_{1/2}$ . The two significant peaks of binding energy at 781.4 eV and 797.1 eV are  $\text{Co}^{2+}$ , and the peaks at 778.9 eV and 793.2 eV are due to the presence of  $\text{Co}^{3+}$ . In addition to the main peak, two different satellite peaks can be found at 786.4 eV and 802.7 eV.<sup>64</sup> Fig. 12(d) demonstrates that in S 2p XPS, the two peaks at 162.6 eV and 163.9 eV point to S  $2p_{3/2}$  and S  $2p_{1/2}$ , respectively. And a satellite peak at 168.5 eV can be observed.<sup>65</sup>

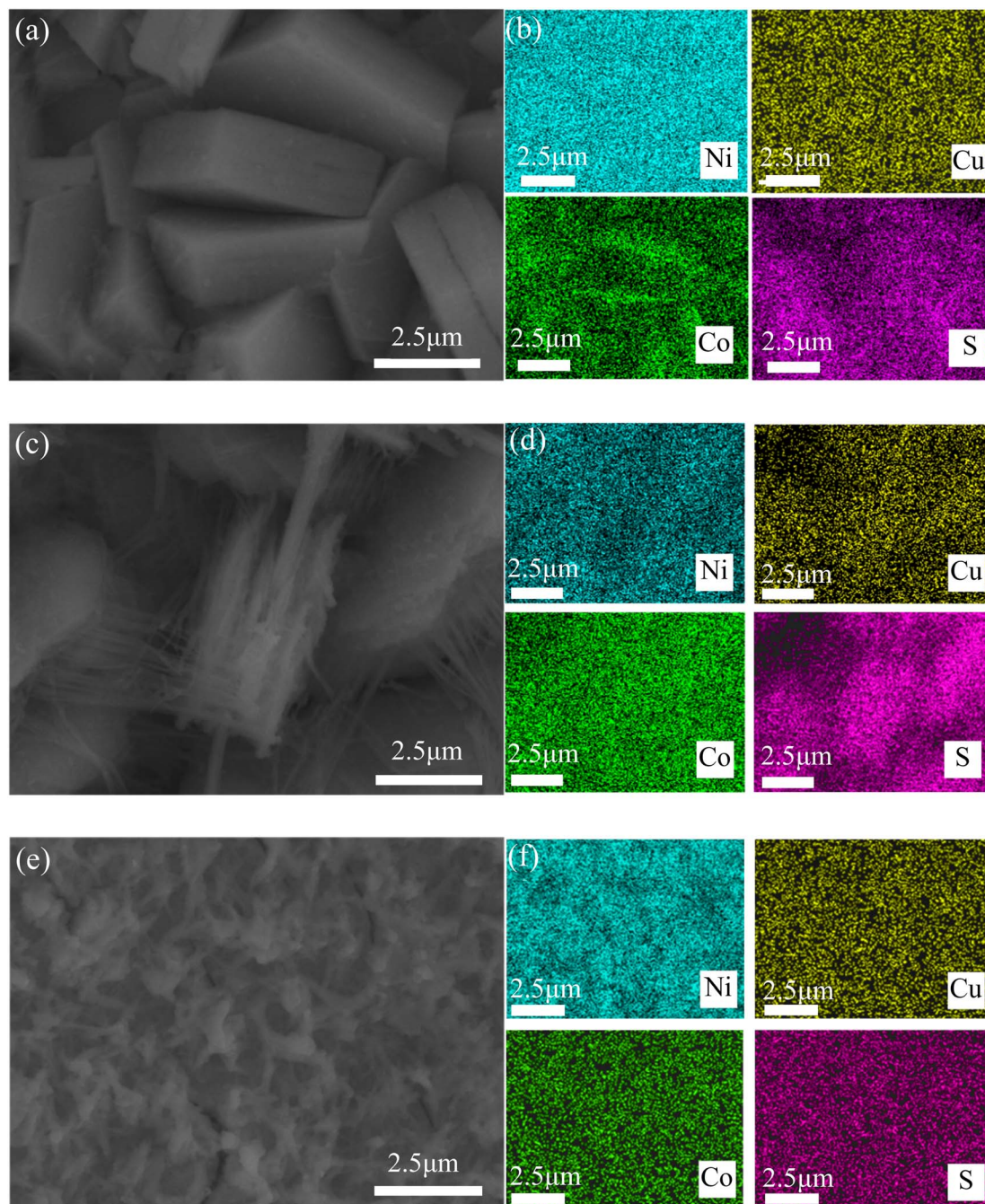


Fig. 16 SEM and EDS images of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts with different  $\text{NH}_4\text{F}$  ratios: (a and b) CCNS-1, (c and d) CCNS-2, (e and f) CCNS-3.

CV measurements were used to study three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts at varied scanning rates in the non-Faraday region, and the results are shown in Fig. 13. The CV integral area of CCNS-3 sample with nanowire structure is the largest, indicating that CCNS-3 sample has the most catalytic active sites in the whole HER catalytic reaction. Compared with Fig. 4, it was found that the electrochemical performance of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst decreased with an increment of urea ratio under the single effect of urea. However, the electrochemical performance of  $\text{CuCo}_2\text{S}_4/\text{NF}$  can be enhanced with the rise of  $\text{NH}_4\text{F}$  ratio under the synergistic action of  $\text{NH}_4\text{F}$  and urea.

Fig. 14(a) shows the polarization curves of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts tested by LSV at a scanning rate of  $5 \text{ mV s}^{-1}$  in 1 M KOH solution, and all the polarization curves are  $iR$  corrected. When the current density is  $10 \text{ mA cm}^{-2}$ , the overpotentials of CCNS-1, CCNS-2 and CCNS-3 samples are 261 mV, 231 mV and 226 mV, respectively. At  $20 \text{ mA cm}^{-2}$ , the overpotential of CCNS-1 is obviously larger than that of CCNS-2 and CCNS-3, while the overpotential of CCNS-2 and CCNS-3 is almost the same. Fig. 14(b) shows the Tafel curves of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts, reflecting the reaction kinetics of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. The Tafel slopes of CCNS-1, CCNS-2 and CCNS-3

samples are  $96.2 \text{ mV dec}^{-1}$ ,  $65.3 \text{ mV dec}^{-1}$  and  $66.3 \text{ mV dec}^{-1}$ , respectively. The Tafel slope of CCNS-1 is significantly higher than that of CCNS-2 and CCNS-3, while the Tafel slope of CCNS-2 and CCNS-3 shows little difference, which can correspond to the results in Fig. 14(a).<sup>65,66</sup> Fig. 14(c) shows the double layer capacitance values of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. The  $C_{dl}$  value of CCNS-3 is much higher than that of CCNS-1 and CCNS-2. This also corresponds to the CV curves of the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts in Fig. 13, indicating that there are many catalytic active sites in CCNS-3 sample.<sup>67</sup> Fig. 14(d) shows the EIS curves of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. CCNS-3 sample has a small radius in the high-frequency region and a large slope in the low-frequency region, indicating that CCNS-3 sample has good charge transfer and ion diffusing ability. According to the SEM images of the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts in Fig. 10, the CCNS-1 sample with complete hexagonal nanosheet structure may have a relatively compact morphology, and only the surface is involved in HER catalytic reaction process, resulting in poor HER catalytic performance of the CCNS-1 sample. The HER catalytic performance of CCNS-2 sample with layered hexagonal nanosheet structure is better because the gap between layers increases the contact area with the electrolyte. Because of the staggered nanowire structure, the CCNS-3 sample have a larger contact area with the electrolyte. Therefore, it has better HER catalytic performance.

Fig. 15(a) is a long-term stability test of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. The current density of CCNS-1 sample is higher at the beginning of the reaction. With the increase of reaction time, the current density of CCNS-1 sample firstly increased and then decreases. The current density reaches the highest at 1.2 h and stabilizes at 8 h. The decrease of current density may be caused by the destruction of the complete hexagonal nanosheet structure. The initial current density of CCNS-2 sample is lower than that of CCNS-1 sample, and the current density firstly increases and then decreases. The current density is the highest at 0.8 h and tends to be stable at 4 h. When the reaction time is extended to 8 h, the current density of CCNS-2 sample decreases again and stabilizes after 10 h, which may be caused by the gradual destruction of the layered hexagonal nanosheet structure in the reaction process. CCNS-3 sample has the lowest initial current density, but is relatively stable. With the increase of reaction time, the current density of CCNS-3 sample shows an increasing trend, which can be attributed to more and more interwoven nanowire structures of CCNS-3 sample. According to Fig. 15(b), after 14 h, the HER performance of CCNS-1 and CCNS-3 samples is improved, while the overpotential of CCNS-2 sample has no change when the current density is  $10 \text{ mA cm}^{-2}$ .

Fig. 16 shows EDS images of three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts. The three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts all contain Ni, Cu, Co and S elements with uniform distribution, indicating that the three  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalysts completely grow on the NF substrate.

## 4. Conclusion

In summary, several  $\text{CuCo}_2\text{S}_4/\text{NF}$  and  $\text{CuCo}_2\text{O}_4/\text{NF}$  catalysts are successfully prepared by hydrothermal method. The influence

of urea and  $\text{NH}_4\text{F}$  ratio on the microstructure and HER catalytic activity of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst has been discussed in detail. When urea is a single variable, the electrochemical performance of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst decreases with an increment of urea ratio. At the current density of  $10 \text{ mA cm}^{-2}$ , the overpotential and Tafel slope of the CCNS-1 sample are 147 mV and  $126.9 \text{ mV dec}^{-1}$  respectively, which is better than the other two samples. The electrochemical performance of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst is also improved with the increment of  $\text{NH}_4\text{F}$  ratio under the synergistic action of  $\text{NH}_4\text{F}$  and urea after urea ratio is fixed. At the current density of  $10 \text{ mA cm}^{-2}$ , the overpotential of CCNS-3 sample is better ( $\eta = 226 \text{ mV}$ ), and the Tafel slope is  $66.3 \text{ mV dec}^{-1}$ . It indicates that the Tafel slope of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with urea remains at a high level. However, the Tafel slope of  $\text{CuCo}_2\text{S}_4/\text{NF}$  catalyst with urea and  $\text{NH}_4\text{F}$  shows lower Tafel slope thus better catalytic activity. Therefore, this study exhibits the effect of urea and  $\text{NH}_4\text{F}$  ratio on  $\text{CuCo}_2\text{S}_4$  catalyst, indicating that the appropriate ratio of urea and  $\text{NH}_4\text{F}$  can enhance its catalytic performance, which provides references for the future research of HER electrocatalysts.

## Author contributions

Yifei Di and Xiangsen Meng carried out the experiment and wrote. Rongda Zhao and Jing Li revised the article. Fufa Wu and Jun Xiang provided financial support for this study. All authors reviewed the manuscript.

## Conflicts of interest

There are no conflicts of interest to declare.

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