

## PAPER

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# Ferroelectric modulation of $\text{CuCo}_2\text{O}_4$ nanorods for controllable alkaline water electrolysis†

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As a technology for emerging environmental applications, water electrolysis is a significant approach for producing clean hydrogen energy. In this work, we used an efficacious piezoelectric method to significantly improve the catalytic water splitting activity without affecting the morphology as well as the components by altering the bulk charge separation state inside the material. The obtained  $\text{CuCo}_2\text{O}_4$  nanorods were treated under a corona polarization apparatus, which significantly enhanced ferroelectricity relative to that before the polarization increasing the physical charge separation and piezoelectric potential energy, enhancing the green hydrogen production. The polarized  $\text{CuCo}_2\text{O}_4$  nanorods exhibit excellent water electrolysis performance under alkaline conditions, with hydrogen evolution overpotential of 78.7 mV and oxygen evolution overpotential of 299 mV at  $10 \text{ mA cm}^{-2}$ , which is much better than that of unpolarized  $\text{CuCo}_2\text{O}_4$  nanorods. Moreover, the Tafel slopes of polarized  $\text{CuCo}_2\text{O}_4$  nanorods are  $86.9 \text{ mV dec}^{-1}$  in the HER process and  $73.1 \text{ mV dec}^{-1}$  in the OER process, which are much lower than commercial catalysts of Pt/C ( $88.0 \text{ mV dec}^{-1}$  for HER) or  $\text{RuO}_2$  ( $78.5 \text{ mV dec}^{-1}$  for OER), proving faster kinetic on polarized  $\text{CuCo}_2\text{O}_4$  nanorods due to their higher electroconductibility and intrinsic activity. In particular, polarized  $\text{CuCo}_2\text{O}_4$  nanorods are identified as promising catalysts for water electrolysis with robust stability, offering outstanding catalytic performance and excellent energy efficiency.

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## 1. Introduction

Hydrogen ( $\text{H}_2$ ) with a high energy density ( $142 \text{ MJ kg}^{-1}$ ) is an ideal alternative fuel to replace fossil fuels, which cause energy crisis and environmental pollution.<sup>1–4</sup> It is well known that hydrogen production from water electrolysis, which is driven by waste heat or from renewable energy, is an efficient and promising technology for producing high-purity hydrogen.<sup>5,6</sup> Hitherto, many highly efficient electrocatalysts have been reported for replacing the benchmark platinum (Pt) and iridium/ruthenium dioxide ( $\text{IrO}_2/\text{RuO}_2$ ) catalysts to reduce the energy barrier during the cathodic hydrogen electrolysis reaction (HER) and the anodic oxygen electrolysis reaction (OER) processes over the water electrolyzer. However, the singular

binding interaction with key reaction intermediates of those electrocatalysts greatly limits the efficiency of  $\text{H}_2$  production.<sup>7–9</sup> One promising candidate for breaking this single-surface design is the design of polarized electrocatalysts, by which the polarization direction presents two distinct chemical surfaces.<sup>7</sup> This unique electrocatalyst design with switchable ferroelectric polarization provides an additional mechanism to regulate the vacant and occupied d-orbitals of ferroelectric materials, which causes great interest in the energy conversion field.<sup>10,11</sup>

To date, various ferroelectric catalysts have been exploited for heterogeneous catalysis, showing potential application in oxygen evolution reaction (OER),<sup>12–14</sup> hydrogen evolution reaction (HER),<sup>15–17</sup> oxygen reduction reaction (ORR),<sup>18,19</sup>  $\text{CO}_2$  electrocatalytic reduction,<sup>20,21</sup> and fuel oxidation,<sup>22,23</sup> which should be ascribed to the effective separation of charges and their subsequent effects. Feng and co-workers believed that the ferroelectricity of  $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_3$  strengthens the orbitals of Fe 3d and O 2p and facilitates electron transfer on the catalyst/electrolyte interface.<sup>15</sup> Fenning *et al.* reported that upward polarization on well-defined (001) surfaces reduces the work function relative to downward polarization and provides multiple adsorbate interactions, leading to a lower barrier for the HER process.<sup>7</sup> Kou's group also identified several ferroelectric catalysts for controllable  $\text{CO}_2$  reduction due to their switchable

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polarization regulating the paths of CO<sub>2</sub> reduction and reaction barrier, resulting in different final products.<sup>11</sup> Most of the reported ferroelectric catalysts possess a large particle size and small specific surface area, leading to lesser active site exposure and catalytic performance boundedness. Ferroelectric catalysts with polarization outside the plane and abundant pores inside the plane can be established by layer stacking, which is the necessary condition to obtain true ferroelectric metals with polarization switching and Fermi level non-zero density states.<sup>24,25</sup> Correspondingly, porous structures of ferroelectric catalysts further possess many structural merits for electrocatalysis to boost the charge and electron transfer, catalytic activities, and stability.<sup>26,27</sup>

Given that the catalytic activity relies on the surface active sites and the adsorption of reactants/intermediates and charge transfer, the ferroelectric catalysts with the introduction of pores are promising approaches for generating larger exposed surface area and providing multiple adsorbate interactions that can enhance their catalytic performance.<sup>28</sup> Herein, we synthesized a ferroelectric catalyst of CuCo<sub>2</sub>O<sub>4</sub> nanorods with a diameter of 4.37 nm, which were polarized by the corona polarization apparatus and denoted as polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods. Comparing CuCo<sub>2</sub>O<sub>4</sub> nanorods without polarization, polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods showed a larger electrochemical surface area (ECSA) and faster electron transfer kinetics that can boost the reaction process of water electrolysis. Meanwhile, by combining multiple adsorbate interactions, the free energy of the key step reaction ( $\Delta G_{\max}$ ) was much lower than that of CuCo<sub>2</sub>O<sub>4</sub> nanorods without polarization. As a result, the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods showed an overpotential of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods for HER at 10 mA cm<sup>-2</sup> was 78.7 mV with a Tafel slope of 86.9 mV dec<sup>-1</sup>, which was much lower than that of the unpolarized CuCo<sub>2</sub>O<sub>4</sub> nanorods (161.0 mV and 112.1 mV dec<sup>-1</sup>) under alkaline conditions. Simultaneously, the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods with an overpotential of 299 mV and a Tafel slope of 73.1 mV dec<sup>-1</sup> at 10 mA cm<sup>-2</sup> for the OER process were comparable to the commercial RuO<sub>2</sub> (339 mV and 78.5 mV dec<sup>-1</sup>), indicating superior water splitting activity. Impressively, the electrolyzer of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods||polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods can be driven by a cell voltage of 1.51 V to reach the current density of 10 mA cm<sup>-2</sup>, which can maintain well after 35 h of long-time stability tests. This work not only studies in-depth the binding strength of adsorbents and reaction surfaces but also promotes the practical applications of ferroelectric catalysts.

## 2. Experimental

### 2.1 Reagents and chemicals

Cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ≥99.00%), copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, ≥99.99%), Urea (≥99%), and oleic acid were purchased from Aladdin. Ethanol and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water of ≥18 MΩ cm<sup>-1</sup> was used in all the experiments.

### 2.2 Synthesis of CuCo<sub>2</sub>O<sub>4</sub> nanorods

15 mL of ethanol with 10 mL of deionized water and 515.4 mg of urea with 4 mL of oleic acid were combined and stirred for 30 min, referred to as solution A. 10 mL of 86 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was concentrated with 10 mL of 43 mmol of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, which was called solution B. Solution B was transferred to solution A, stirred for 30 min, and then transferred to a reaction vessel and heated at 180 °C for 9 h, followed by centrifugation for 3 times with acetone and ethanol, and the residue was dried at 60 °C, after which it was air-fired at 400 °C for 3 h.

### 2.3 Electrochemical measurements

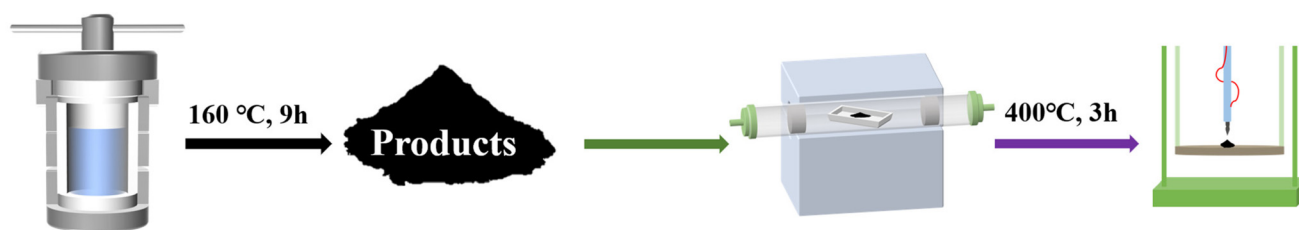
The CHI 660E electrochemical workstation was used for all electrochemical measurements. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV), chrono-potentiometry and chrono-amperometry were carried out in 1M KOH using a conventional three-electrode system. This three-electrode system consisted of a modified glassy carbon electrode (GCE) with a diameter of 3 mm (working electrode area of 0.071 cm<sup>2</sup>) as the working electrode, a saturated glycolic electrode (SCE) as the reference electrode and a graphite electrode as the counter electrode. Potentiometric measurements were calibrated to the reversible hydrogen electrode (RHE) according to the equation  $E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \text{ pH} + 0.242$ . Level values were calibrated by 95% *i*R compensation of the LSV measurements. Electrocatalytic inks were prepared by adding 10 mg of the prepared catalyst to 5 ml of a mixed solution containing deionized water, isopropanol, and 5% Nafion (V/V/V = 8/2/0.05). Following a 30-minute sonication process, a well-dispersed ink dispersion was obtained. Then, 20 μl of the suspended ink was dropped onto the surface of the working electrode (loading ~0.11 mg cm<sup>-2</sup>) and dried at room temperature.

### 2.4 Physical characterization

Transmission electron microscopy (TEM) images were characterised on JEM-2100UHR and EDX analysis was performed at an operating voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained on a Hitachi SU8020 cold emission field emission electron microscope, operating at an accelerating voltage of 5 kV. Atomic force microscopy (AFM) images were collected on a Dimension ICON, Bruker, instrument. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXIS ULTRA using the C 1s peak at 284.5 eV as a reference to correct binding energy. X-ray diffraction (XRD) patterns were collected on a RigakuD/max-2400 instrument to analyse the crystal structure of CuCo<sub>2</sub>O<sub>4</sub>.

## 3. Results and discussion

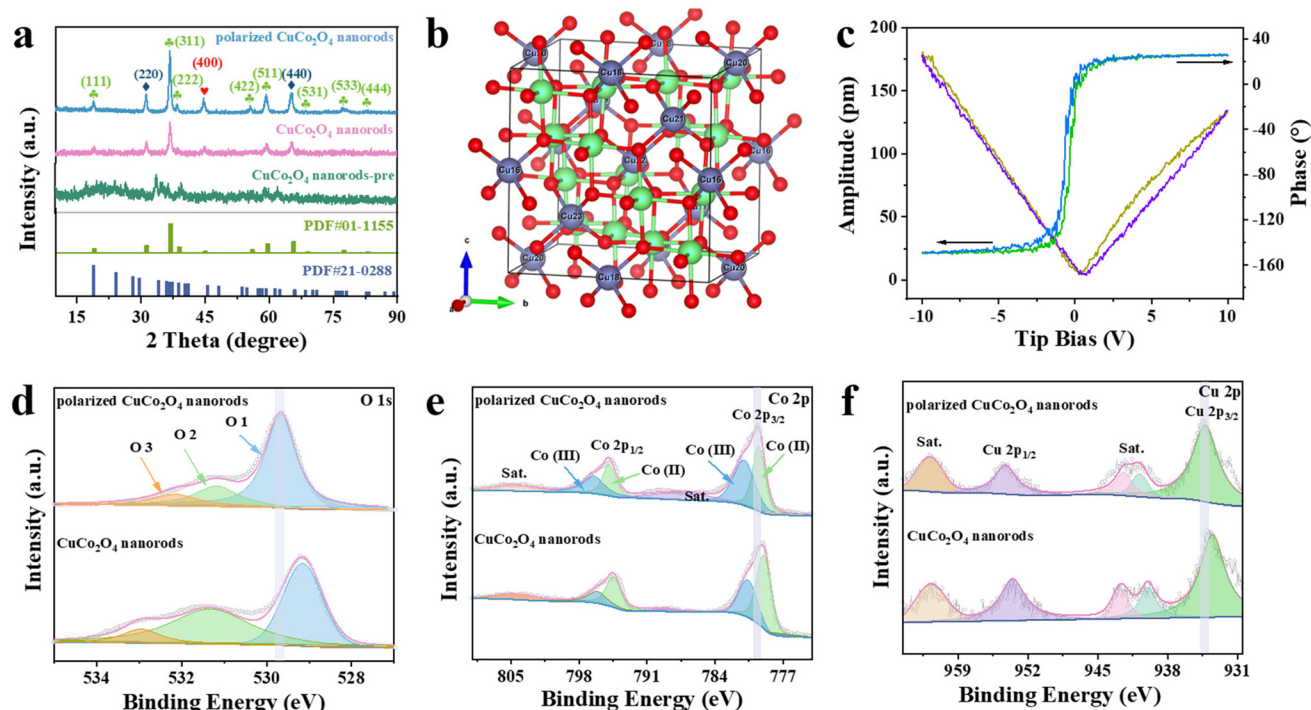
The polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods were prepared by following the steps shown in Scheme 1. Firstly, The Co<sup>2+</sup> and Cu<sup>2+</sup> ions precursors were added to the mixed solution combining ethanol, oleic acid, urea, and deionized water. After ultrasonic



**Scheme 1** The preparation process for polarized  $\text{CuCo}_2\text{O}_4$  nanorods.

dispersion for 30 min, the above solution was quickly transferred to a stainless steel autoclave (lined with Teflon) and maintained at 180 °C for 9 h. Then,  $\text{CuCo}_2\text{O}_4$  nanorods-pre was transferred to a tube furnace, annealing at 400 °C for 3 h. Finally, the obtained  $\text{CuCo}_2\text{O}_4$  nanorods were polarized at 22 kV by the corona poling method. The presence of oleic acid inhibits the overgrowth of nanorods and prevents their agglomeration, creating an energy barrier to counteract the adsorption, which can improve the generation of  $\text{CuCo}_2\text{O}_4$  nanorods.<sup>29</sup> The crystal structure of the prepared polarized  $\text{CuCo}_2\text{O}_4$  nanorods (Fig. 1a) was studied by XRD, which showed a perovskite phase (Fig. 1b). Furthermore, the crystal topology diagram of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods is shown in Fig. S1.† Due to the annealing process, repeated measurements in the  $2\theta$  range of  $5^\circ$ – $90^\circ$  were performed at high resolution, indicating a high degree of crystallinity. Meanwhile,

$\text{CuCo}_2\text{O}_4$  nanorods after the ferroelectric regulation by corona polarization, the (422) and (533) peaks are significantly higher compared to the corresponding peaks of the unpolarized  $\text{CuCo}_2\text{O}_4$  nanorods. The samples before and after polarization showed diffraction peaks at  $19.1^\circ$ ,  $31.4^\circ$ ,  $37.0^\circ$ ,  $39.0^\circ$ ,  $45.1^\circ$ ,  $56.0^\circ$ ,  $59.6^\circ$ ,  $65.7^\circ$ ,  $69.0^\circ$ ,  $77.5^\circ$ , and  $83.2^\circ$ , fitting well with the (111), (220), (311), (222), (400), (422), (511), (440), (531), (533) and (444) lattice planes of cubic  $\text{CuCo}_2\text{O}_4$  (JCPDS 01-1155) (Fig. 1a). Both before and after polarization show the same morphology, which confirms that the crystal structure of the sample is not changed after polarization. This crystalline phase change is attributed to the ferroelectric regulation between quasi-electric and ferroelectric in  $\text{CuCo}_2\text{O}_4$  nanorods.<sup>30</sup> In addition, the butterfly-shaped amplitude profile revealed by the high-resolution piezoelectric force microscopy (PFM) of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods verifies excellent



**Fig. 1** (a) XRD plots of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods and  $\text{CuCo}_2\text{O}_4$  nanorods-pre; (b) crystal structure diagram of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods (blue for Cu atoms, green for Co atoms, and red for O atoms); (c) amplitude butterfly loops, and piezoresponse phase hysteresis loops for polarized  $\text{CuCo}_2\text{O}_4$  nanorods; (d–f) XPS plots of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods and  $\text{CuCo}_2\text{O}_4$  nanorods: (d) O 1s; (e) Co 2p; (f) Cu 2p.

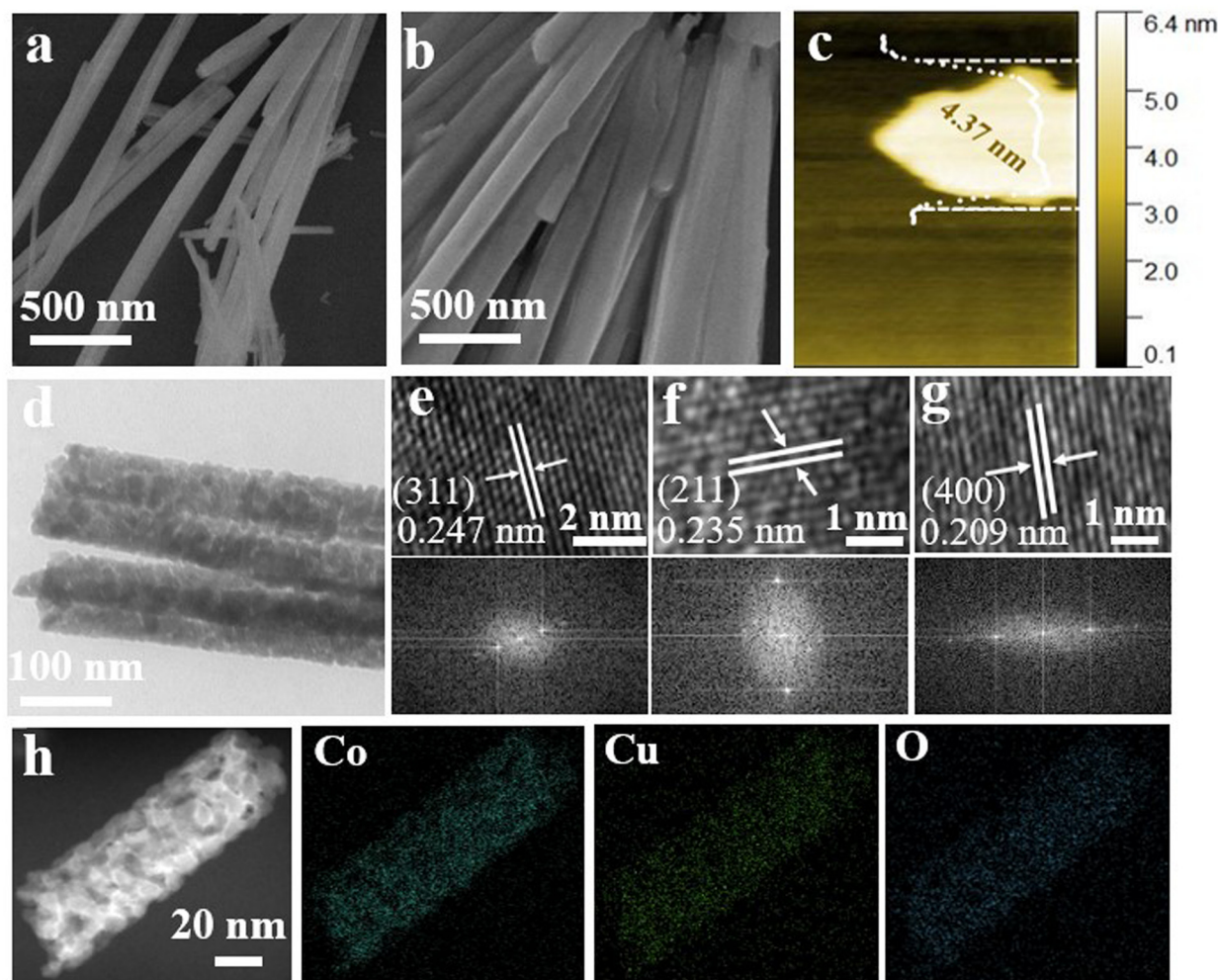


local piezoelectric response (Fig. 1c) compared to that in the unpolarized  $\text{CuCo}_2\text{O}_4$  nanorods (Fig. S2†), which further suggests that the polarized samples can maintain their stable ferroelectric switching properties.

The elemental composition and chemical state of polarized  $\text{CuCo}_2\text{O}_4$  nanorods were measured by the X-ray photoelectron spectroscopy (XPS) technique. The full XPS spectrum of the as-prepared polarized  $\text{CuCo}_2\text{O}_4$  nanorods showed distinguishable peaks for the elements of Co, Cu, and O with an atomic ratio of 2.76 : 1.25 : 9.57 (Fig. S3 and S4†), well in agreement with the EDS and ICP-OES measurements (Fig. S5 and Table S1†). As shown in Fig. 1d, the three peaks of O 1s at 532.17, 531.21, and 529.68 eV can be attributed to water molecules, the surface chemisorbed oxygen such as  $\text{O}_2^{2-}$  or  $\text{O}^-$  (belonging to defectoxide and the hydroxyl-like group), and metal-oxygen bonds, respectively.<sup>31–33</sup> The Co 3p spectrum can be deconvoluted into two peaks appearing at 779.62 eV and 774.99 eV, associating with the representative peaks of Co  $2\text{p}_{3/2}$  and Co  $2\text{p}_{1/2}$ , respectively (Fig. 1e).<sup>34</sup> Comparing the peaks of  $\text{CuCo}_2\text{O}_4$  nanorods without polarization, both Co  $2\text{p}_{3/2}$  and Co  $2\text{p}_{1/2}$  peaks of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods shift by  $\sim 0.50$  eV to

higher binding energies, and the increased Co binding energy results in electrons closer to the core, indicating that  $\text{Co}^{2+}$  has excellent electron trapping ability. The high-resolution Cu 2p spectra in Fig. 1f shows that the peaks at  $\sim 941.64$  and  $961.77$  eV are assigned to  $\text{Cu}^{2+}$  2p, which positively shifts from the standard binding energies of  $\text{Cu}^{2+}$  2p. These suggest that the electron transforms from  $\text{Cu}^{2+}$  2p to  $\text{Co}^{2+}$  2p.<sup>35,36</sup> This suggests that after polarization, the electrons from the Cu site may migrate to the Co site, the electron density of the Co site increases, and the electrons are first drawn from the Co site for the reaction when the HER and OER reactions are underway, and the Co site can accept the excited electrons and contribute them to the adsorbed intermediates under the effect of polarization, which facilitates the electrolysis of the water reaction.<sup>37</sup>

To elucidate the electron transfer mechanism, the microstructure and morphology of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods were further investigated by SEM and TEM techniques. The smooth surface of  $\text{CuCo}_2\text{O}_4$  nanorods-pre becomes relatively rough after annealing at  $400^\circ\text{C}$  (Fig. S6 and S7†). Simultaneously, the corona polarization process does not affect the morphological structure (Fig. 2a and b). The surface

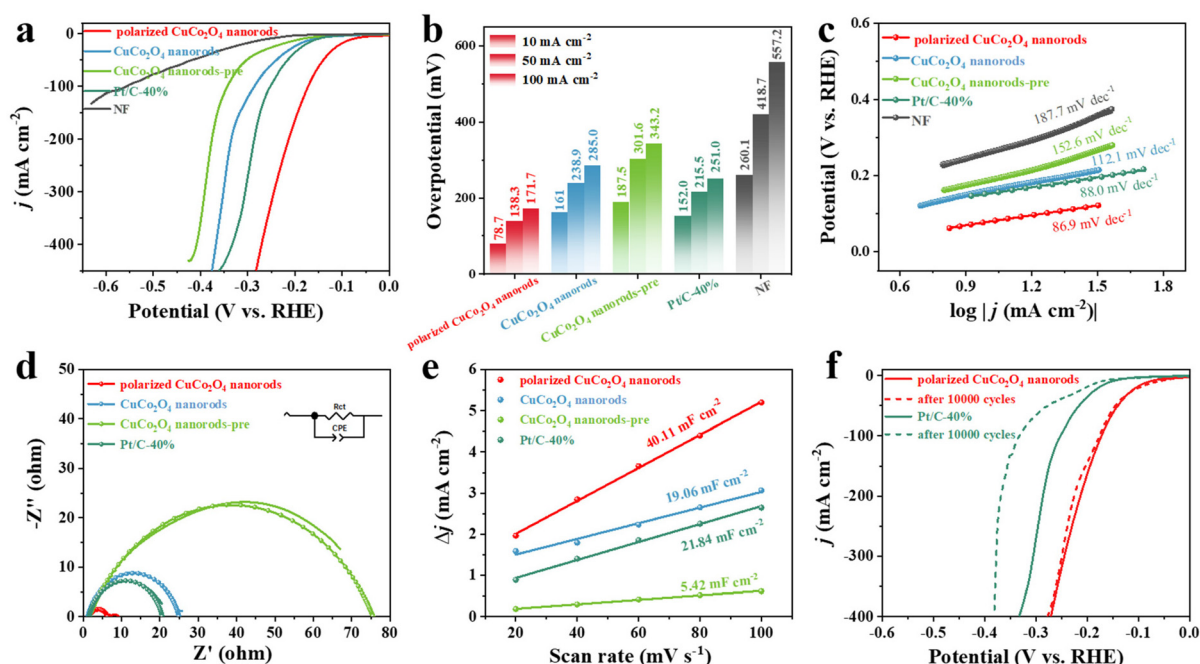


**Fig. 2** (a) SEM images of  $\text{CuCo}_2\text{O}_4$  nanorods; (b) SEM images, (c) AFM, (d) TEM, (e–g) partially magnified HRTEM and corresponding FFT images, (h) STEM-EDX elemental mapping maps of polarized  $\text{CuCo}_2\text{O}_4$  nanorods.

area and total pore volume are  $31.91 \text{ m}^2 \text{ g}^{-1}$  and  $0.17 \text{ cm}^3 \text{ g}^{-1}$  for the polarized  $\text{CuCo}_2\text{O}_4$  nanorods as determined by Brunauer–Emmett–Teller (BET) surface area measurements (Fig. S8a and b†), which are higher than those of  $\text{CuCo}_2\text{O}_4$  nanorods-pre, indicating a mesoporous structure. The thickness of  $4.37 \text{ nm}$  for the polarized  $\text{CuCo}_2\text{O}_4$  nanorods was further measured by AFM (Fig. 2c) and was well consistent with the above results. A magnified TEM image of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods demonstrates the significant porous nanosheet structures (Fig. 2d), providing a large surface area with more exposed active sites. High-resolution TEM (HRTEM) and fast Fourier transform (FFT) images confirm the perovskite crystal structure of polarized  $\text{CuCo}_2\text{O}_4$  nanorods. Briefly, the lattice edges of the individual nanorods expose  $d(400) = 0.209 \text{ nm}$ ,  $d(311) = 0.247 \text{ nm}$  and  $d(211) = 0.235 \text{ nm}$  crystal spacing, indicating a high degree of crystallinity (Fig. 2e–g). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and their corresponding elemental mapping images demonstrate the uniform distribution of Co, Cu, and O elements in polarized  $\text{CuCo}_2\text{O}_4$  nanorods (Fig. 2h), further indicating the composition of crystal  $\text{CuCo}_2\text{O}_4$ .<sup>38</sup>

The HER performance of the samples was studied on a CHI 660E electrochemical workstation with a standard three-electrode system in  $1 \text{ M KOH}$  solution. Fig. 3a shows the linear scanning voltammetry (LSV) curves for polarized  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods-pre, and  $40 \text{ wt\% Pt/C}$ , where  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods-pre, and  $40 \text{ wt\% Pt/C}$  serve as the reference samples. It is

obvious that polarized  $\text{CuCo}_2\text{O}_4$  nanorods exhibit a higher current density ( $j$ ) and lower current onset potential than  $\text{CuCo}_2\text{O}_4$  nanorods and  $\text{Pt/C}$ , suggesting that polarization can significantly increase the activity of basic HER. Additionally, the pure nickel foam sample has almost no HER activity under alkaline conditions, suggesting that the activity is mainly derived from surface-loaded metal oxides. The overpotentials at  $10 \text{ mA cm}^{-2}$ ,  $50 \text{ mA cm}^{-2}$ , and  $100 \text{ mA cm}^{-2}$  are denoted as  $\eta_{10}$ ,  $\eta_{50}$ , and  $\eta_{100}$ , respectively. The  $\eta_{10}$  of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods for HER is  $78.7 \text{ mV}$ , comparable to that of the commercial  $\text{Pt/C-40\%}$  while exhibiting lower  $\eta_{50}$ , and  $\eta_{100}$  values of  $138.3 \text{ mV}$  and  $171.7 \text{ mV}$  (Fig. 3b), respectively, which is further superior to most of the state-of-the-art non-noble catalysts reported recently (Table 1), indicating a potential application at a larger current density. Meanwhile, the Tafel slope of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods is  $86.9 \text{ mV dec}^{-1}$ , smaller than that of  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods-pre, and  $40 \text{ wt\% Pt/C}$  ( $112.1 \text{ mV dec}^{-1}$ ,  $152.6 \text{ mV dec}^{-1}$ , and  $88.0 \text{ mV dec}^{-1}$ ) (Fig. 3c), which revealed more favorable reaction kinetics on the polarized  $\text{CuCo}_2\text{O}_4$  nanorods. The lower Tafel slope of  $86.9 \text{ mV dec}^{-1}$  reveals that the reaction process follows the Volmer–Heyrovsky mechanism as the electron polarization reduces the extra  $\Delta G(\text{H}_2\text{O})$  that boosts the adsorption and activation of  $\text{H}_2\text{O}$ . The above results reveal that the polarization process enables a faster HER kinetic rate, implying a lower energy barrier for water dissociation and  $\text{OH}^-$  desorption. Moreover, the samples that polarized under different voltages were further provided, which show the same morphological structures while exhibiting different catalytic performance



**Fig. 3** HER electrocatalytic performance of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods-pre and commercial  $\text{Pt/C-40\%}$  in  $1.0 \text{ M KOH}$  solution: (a) LSV polarization curves of HER activity with a scan rate of  $5 \text{ mV s}^{-1}$ ; (b) overpotentials at  $10$ ,  $50$ , and  $100 \text{ mA cm}^{-2}$ ; (c) corresponding Tafel plots; (d) Nyquist plots of equivalent circuit models; (e) linear fit of capacitive current to the CV scan rate; (f) LSV polarization curves of the HER activity of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods and  $\text{Pt/C-40\%}$  after  $10\,000$  CV cycles.

**Table 1** The catalytic performance of non-noble catalysts for HER

| Catalyst  | Electrolyte | Overpotential<br>mV | Current density<br>mA cm <sup>-2</sup> | Tafel slope<br>mV dec <sup>-1</sup> | Ref.      |
|---|-------------|---------------------|--|-------------------------------------|-----------|
| Polarized CuCo <sub>2</sub> O <sub>4</sub> nanorods               | 1 M KOH     | 78.7                | 10                                     | 86.9                                | This work |
| CuCo <sub>2</sub> O <sub>4</sub> /CoOOH/NF                        | 1 M KOH     | 125                 | 10                                     | 75.1                                | 46        |
| P-doped CuCo <sub>2</sub> O <sub>4</sub>                          | 1 M KOH     | 152                 | 10                                     | 115.7                               | 47        |
| Ni <sub>3</sub> S <sub>2</sub> /FeS                               | 1 M KOH     | 190                 | 10                                     | 56.3                                | 48        |
| Co-MoC/Mo <sub>2</sub> C  | 1 M KOH     | 82                  | 10                                     | 53                                  | 49        |
| Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub>                  | 1 M KOH     | 143                 | 10                                     | 81.7                                | 50        |
| WP <sub>2</sub> NSs/W   | 1 M KOH     | 90                  | 10                                     | 80.88                               | 51        |
| NiFeP NP supported by carbon                                      | 1 M KOH     | 160                 | 10                                     | 75.8                                | 52        |
| Co <sub>0.05</sub> Cu <sub>0.05</sub> @CNWs                       | 1 M KOH     | 160                 | 10                                     | 172                                 | 53        |
| Cu-Co-Se  | 1 M KOH     | 152                 | 10                                     | 94                                  | 54        |
| Cu-Ni <sub>3</sub> S <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub> | 1 M KOH     | 79                  | 10                                     | 50.4                                | 55        |

(Fig. S9, S10†). The polarization voltage of 22 kV used in this work can form a very strong electric field on the surface of the electrode, accelerating the migration rate of electrons and ions, which promotes the electrochemical reaction and increases the rate of electrocatalytic reaction. When the polarization voltage is lower than 22 kV, the polarization effects of samples are not obvious, leading to lower electroconductibility and intrinsic activity of active sites (Fig. S11, S12, S13†).<sup>39–42</sup> When the polarization voltage is higher than 22 kV, samples show similar electroconductibility and intrinsic activity as that polarized under 22 kV (Fig. S11, S12, S13†). Therefore, the high electric field strength can promote the transport of substances in solution, including ions and molecules, which is conducive to increasing the concentration of reactive substances on the electrode surface, enhancing the electrocatalytic reaction. Meanwhile, the active sites after polarization can improve the adsorption of free radicals and reactive oxygen species due to the unique electron effect between Cu and Co atoms.<sup>26,43–45</sup> In addition, the polarization voltage of 22 kV was further widely used in research and industrial production in the field of electrochemistry.

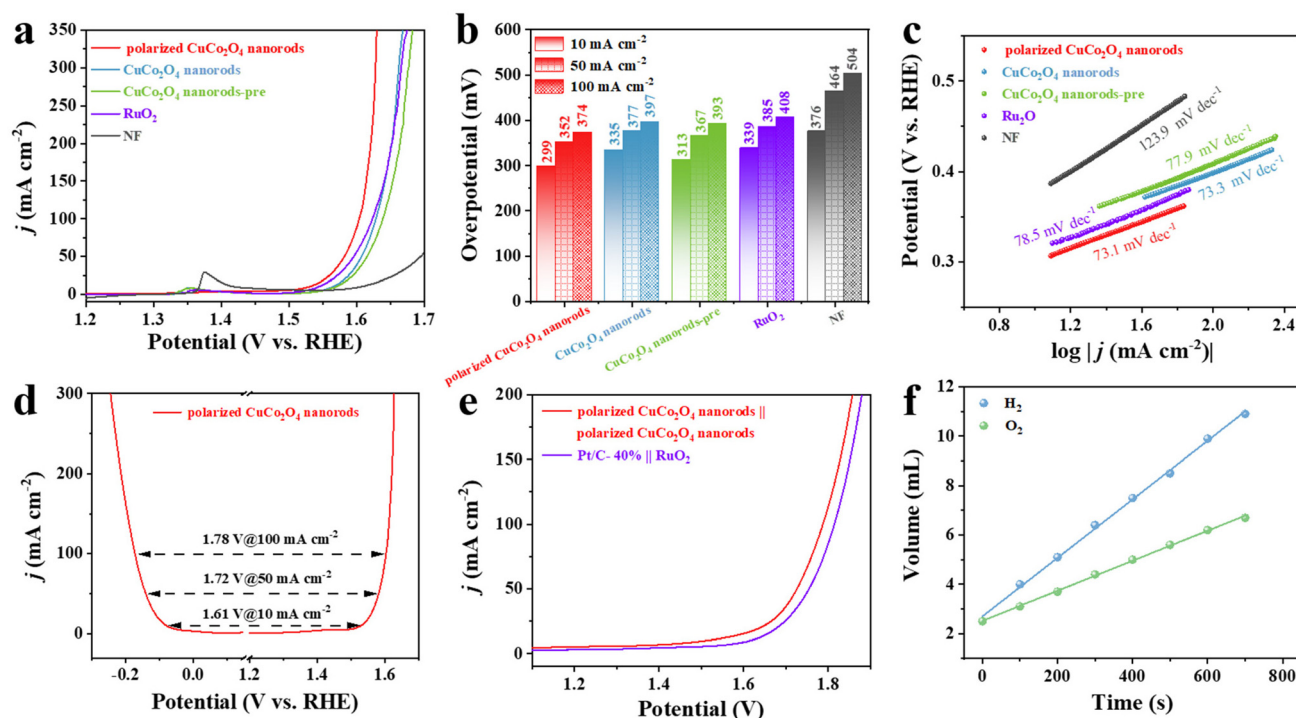
Furthermore, electrochemical impedance spectroscopy (EIS) was used to evaluate the electron transfer kinetics of different catalysts. Among them, polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods showed the lowest charge transfer resistance ( $R_{ct}$ ) with 4.8  $\Omega$  (Fig. 3d), demonstrating its favorable charge transfer ability during the OER process. As an important parameter, the electrochemical active surface area (ECSA) values can determine the intrinsic activity of the catalysts. Therefore, the double-layer capacitance ( $C_{dl}$ ) was measured by cyclic voltammetry (CV) curves at different scan rates as it was in line with the ECSA value. As shown in Fig. 3e, the  $C_{dl}$  of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods (40.11 mF cm<sup>-2</sup>) was significantly higher than those of CuCo<sub>2</sub>O<sub>4</sub> nanorods and CuCo<sub>2</sub>O<sub>4</sub> nanorods-pre (19.06 mF cm<sup>-2</sup> and 5.42 mF cm<sup>-2</sup>) grudge matched with commercial Pt/C (21.84 mF cm<sup>-2</sup>), still displaying the higher intrinsic catalytic activity. Stability is another key factor in the evaluation of electrocatalysts. As shown in Fig. 3f, the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods electrode showed negligible degradation after 10 000 CV cycles at a rather fast scan rate of 100 mV s<sup>-1</sup>, which is outstanding than commercial Pt/C-40%. Meanwhile, the prepared polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods also

showed excellent stability when tested at 10 mA cm<sup>-2</sup> for 50 h with almost no current density change (Fig. S14†). Moreover, the  $\eta_{50}$  of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods negatively shifts 4 mV, which is much smaller than that of CuCo<sub>2</sub>O<sub>4</sub> nanorods (38 mV) (Fig. S15†).

To further explore the OER performance of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods, OER polarization curves under alkaline conditions were first tested. As shown in Fig. 4a–c, when compared to CuCo<sub>2</sub>O<sub>4</sub> nanorods, CuCo<sub>2</sub>O<sub>4</sub> nanorods-pre, the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods exhibited the lowest OER overpotential and Tafel slope of 299 mV and 73.1 mV dec<sup>-1</sup>, respectively, indicating its superior activity and favorable kinetics process. Furthermore, the overpotential of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods at the current density of 100 mA cm<sup>-2</sup> is 374 mV, which is much lower than that of CuCo<sub>2</sub>O<sub>4</sub> nanorods (397 mV), CuCo<sub>2</sub>O<sub>4</sub> nanorods-pre (393 mV), even commercial RuO<sub>2</sub> (408 mV) and most recently reported catalysts (Table 2), demonstrating the superior OER performance of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods. Similar to the results for HER, the as-prepared polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods also show outstanding stability when tested at 10 mA cm<sup>-2</sup> for 35 h with no negligible decay (Fig. S16†). Whereas, the CuCo<sub>2</sub>O<sub>4</sub> nanorods exhibit significant attenuation in 1.0 M KOH solution, revealing the beneficial role of polarization (Fig. S16†). Moreover, the overpotential of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods shows a negligible shift at 10 mA cm<sup>-2</sup> after long-term OER stability tests (Fig. S17†), further indicating excellent OER stability. After the long-term stability test, SEM and TEM scanning and XPS plots of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods were further measured (Fig. S18, S19, S20†) which showed no significant changes compared to the initial polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods, further confirming their excellent stability.

Due to their good OER and HER performance, polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods can serve as a bifunctional electrode catalyst for an overall water electrolyzer. The difference corresponding to the overpotentials of HER and OER polarization curves ( $\Delta E = \eta_{OER} + \eta_{HER}$ ) at various current densities was used to evaluate the performance of the water electrolyzer. The  $\Delta E$  value of the polarized CuCo<sub>2</sub>O<sub>4</sub> nanorods at the current densities of 10 mA cm<sup>-2</sup> is 1.61 V, exhibiting a strong prospect in water splitting application (Fig. 4d). Based on the good catalytic activity for OER and HER in 1.0 M KOH solution, polar-





**Fig. 4** OER electrocatalytic performance of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods,  $\text{CuCo}_2\text{O}_4$  nanorods-pre and commercial  $\text{RuO}_2$  in 1.0 M KOH solution: (a) LSV polarization curves of OER activity with a scan rate of  $5 \text{ mV s}^{-1}$ ; (b) overpotentials at 10, 50, and  $100 \text{ mA cm}^{-2}$ ; (c) corresponding Tafel plots; (d)  $\Delta E$  values of polarized  $\text{CuCo}_2\text{O}_4$  nanorods at 10, 50, and  $100 \text{ mA cm}^{-2}$  current densities; (e) LSV polarization curves for polarized  $\text{CuCo}_2\text{O}_4$  nanorods/NF(±) and  $\text{RuO}_2$ /NF(±)||Pt/C-40%/NF(-); (f) curves of  $\text{H}_2$  and  $\text{O}_2$  produced by polarized  $\text{CuCo}_2\text{O}_4$  nanorods/NF(±) as a function of time.

**Table 2** The catalytic performance of non-noble catalysts for OER

| Catalyst  | Electrolyte | Overpotential<br>mV | Current density<br>$\text{mA cm}^{-2}$ | Tafel slope<br>$\text{mV dec}^{-1}$ | Ref.      |
|---|-------------|---------------------|--|-------------------------------------|-----------|
| Polarized $\text{CuCo}_2\text{O}_4$ nanorods                  | 1 M KOH     | 299                 | 10                                     | 73.1                                | This work |
| $\text{FeCoCNFs}$   | 1 M KOH     | 377                 | 10                                     | 59.9                                | 56        |
| $\text{CoNC/NCNTs@CNF}$                                       | 1 M KOH     | 330                 | 10                                     | 82                                  | 57        |
| $\text{Co-ZIF-350-air micro-fibers}$                          | 1 M KOH     | 370                 | 10                                     | 55                                  | 58        |
| $\text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4\text{@CNFs-2}$ | 1 M KOH     | 350                 | 10                                     | 51.4                                | 59        |
| $\text{h-Co}_3\text{O}_4/\text{CeO}_2\text{@N-CNF}$           | 1 M KOH     | 310                 | 10                                     | 85                                  | 60        |
| $\text{CuCoO/S-CP-Ar-30}$                                     | 0.1 M KOH   | 330                 | 10                                     | 114.9                               | 61        |
| $\text{Fe-CoO/C-800 nanofibers}$                              | 1 M KOH     | 362                 | 10                                     | 60                                  | 62        |
| $\text{Ti}_3\text{C}_2\text{Tx/CuCo}_2\text{O}_4/\text{NF}$   | 1 M KOH     | 360                 | 10                                     | 49                                  | 63        |
| $\text{Ti}_3\text{C}_2\text{Tx/CuCo}_2\text{O}_4/\text{GC}$   | 1 M KOH     | 380                 | 10                                     | 71                                  | 63        |
| $\text{NiCo-500-15}$  | 1 M KOH     | 320                 | 10                                     | 67                                  | 64        |

ized  $\text{CuCo}_2\text{O}_4$  nanorods were further tested for the overall decomposition performance of polarized  $\text{CuCo}_2\text{O}_4$  nanorods as a two-electrode system for both anode and cathode on an overall water decomposition device (Fig. 4e). As shown in Fig. 4e, the cell voltages of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods at the current densities of 10, 50, and  $100 \text{ mA cm}^{-2}$  are only 1.51 V, 1.72 V, and 1.78 V, respectively, which is second only to the latest electrolyzer consisting of  $\text{RuO}_2$ /NF(+) and Pt/C-40%/NF(-) (1.62 V, 1.75 V, and 1.81 V), confirming that polarized  $\text{CuCo}_2\text{O}_4$  nanorods possess excellent HER and OER activities. These results show that polarized  $\text{CuCo}_2\text{O}_4$  nanorods/NF can effectively serve as both anode and cathode material and are

very effective in reducing the total water cracking tank potential. Furthermore, the long-term stability of the optimum electrolyzer-polarized  $\text{CuCo}_2\text{O}_4$  nanorods/NF(±) was evaluated through a chrono-current (CA) stability test. The polarized  $\text{CuCo}_2\text{O}_4$  nanorods/NF(±) electrolyzer exhibited high stability, with no significant change in the initial current density compared to the current density after the 35 hour stability test (Fig. S21†). Simultaneously, the LSV curves show that there is almost no change after the long-term stability tests, suggesting excellent durability (Fig. S22†). Fig. S23† shows the precipitation of  $\text{H}_2$  at the cathode and  $\text{O}_2$  at the anode during the operation of the polarized  $\text{CuCo}_2\text{O}_4$  nanorods/NF(±) electroly-

zer, which indicates that bubbles can be effectively shunted off the electrode surface due to the high porosity of the electrodes without significant accumulation of bubbles on the electrode surface. The volume of  $H_2$  and  $O_2$  produced on the cathode and anode with polarized  $CuCo_2O_4$  nanorods-based water electrolyzer was evaluated by the drainage method. As shown in Fig. S24,<sup>†</sup> the volume of  $O_2$  and  $H_2$  increases with the reaction process and agrees well with the large number of bubbles generated on the electrodes (Fig. S23<sup>†</sup>). The output ratio of  $O_2$  and  $H_2$  is about 1:1.95, close to the theoretical value of 1:2 (Fig. 4f), which confirms that the faradaic efficiency (FE) is close to 100%. Overall, the electrochemical evaluation of HER, OER, and overall water splitting confirm the strong potential of polarized  $CuCo_2O_4$  nanorods for practical applications with low cost.

## 4. Conclusion

In conclusion, we have certified the electronic polarization of the polarized  $CuCo_2O_4$  nanorods with a thickness of 4.37 nm, which may be related to their state density. Owing to the optimized electron polarization, polarized  $CuCo_2O_4$  nanorods exhibit remarkable HER and OER performance, greatly superior to that of  $CuCo_2O_4$  nanorods and almost as good as the best commercial Pt/C-40% catalysts. In particular, polarized  $CuCo_2O_4$  nanorods showed the highest electrocatalytic HER activity under alkaline conditions for both overpotential and Tafel slope, which were 138.3 mV at 50 mA cm<sup>-2</sup> and 86.9 mV dec<sup>-1</sup> at 10 mA cm<sup>-2</sup>, respectively, far exceeding the sample of  $CuCo_2O_4$  nanorods without polarization. More importantly, when employed as the cathode and anode of the water electrolyzer, the polarized  $CuCo_2O_4$  nanorods/NF(±) just required a cell voltage of 1.51 V to achieve the current density of 10 mA cm<sup>-2</sup>. This work presents a novel idea for evaluating electron polarization in improving the mass and electron transfer on the interface of electrode/electrolyte, and it opens up a new strategy for obtaining a low-cost and high-performance water electrolyzer.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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