

## Supporting Information

### **Self-sacrifice template construction of conductive $\text{Cu}_3(\text{HHTP})_2$ nanowhisker arrays@copper foam toward robust lithium storage**

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## 1. Experimental section

### 1.1. Preparation of $\text{Cu}_3(\text{HHTP})_2@\text{CF}$ electrodes

Cu foam (CF) was cut into 12 mm discs, and then successively washed with ethanol, 3 M hydrochloric acid, and water to remove impurities. After dried in air, the CF was immersed in a mixed solution of 2 mol L<sup>-1</sup> NaOH and 1 mol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (molar ratio 20 : 1) to react for 1 h. After thoroughly washed with ethanol and water, and dried, Cu(OH)<sub>2</sub> nanowires arrays grown on CF ( $\text{Cu}(\text{OH})_2@\text{CF}$ ) was obtained.

For synthesis of  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$  electrode,  $\text{Cu}(\text{OH})_2@\text{CF}$  discs were placed in 40 mL aqueous solution containing 77.76 mg (6 mmol L<sup>-1</sup>) of 2,3,6,7,10,11-hexahydroxytriphenyl (HHTP), and reacted for 0.5 h, 1 h, 4 h, and 12 h, respectively. After cleaning with ethanol, the discs were dried in air. The obtained  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$  electrodes were named as  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$ -1,  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$ -2,  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$ -3, and  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$ -4 corresponding to different reaction times.

Pure  $\text{Cu}_3(\text{HHTP})_2$  has been synthesized using  $\text{Cu}(\text{CH}_3\text{COO})_2$  and 2,3,6,7,10,11-hexahydroxytriphenyl (HHTP) through a solvothermal reaction according to our previous work.<sup>[1]</sup>

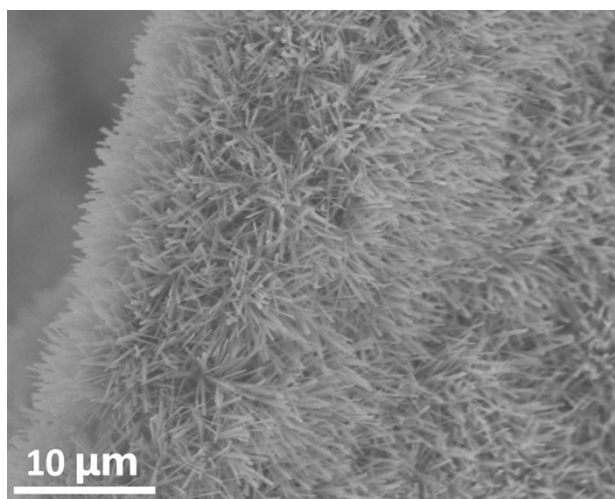
### 1.2. Material characterization

The micromorphology and microstructure of  $\text{Cu}_3(\text{HHTP})_2@\text{CF}$  electrodes were investigated by field emission scanning electron microscopy (FESEM, JEOL-6300F) and transmission electron microscopy (TEM, JEOL JEM-2100). Phase information of samples was detected by X-ray diffraction (XRD, Rigaku Ultima IV) and Raman microscope with a 532 nm laser excitation (InVia Reflex). Fourier transform infrared (FT-IR) spectroscopy (Nicolet iS50) and X-ray photoelectron spectroscopy (XPS, PHI VersaProbe III) were conducted to study the chemical compositions and functional

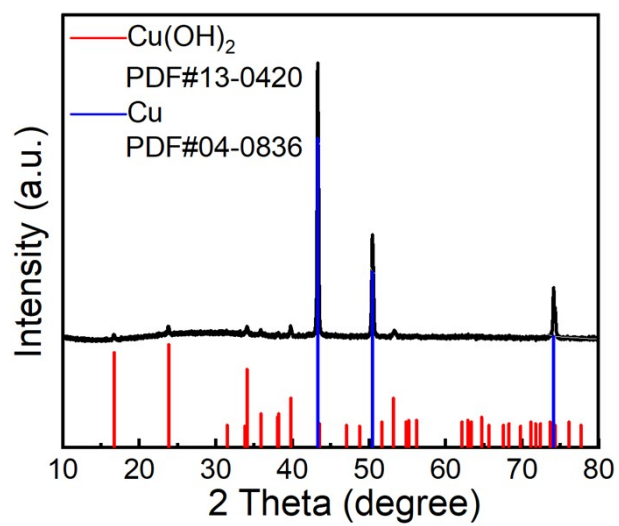
groups of the prepared samples. The specific surface area and pore size distribution were determined *via* the Brunauer-Emmett-Teller method, with N<sub>2</sub> adsorption-desorption tests conducted at 77 K (Quantachrome, USA).

### *1.3. Electrochemical measurements*

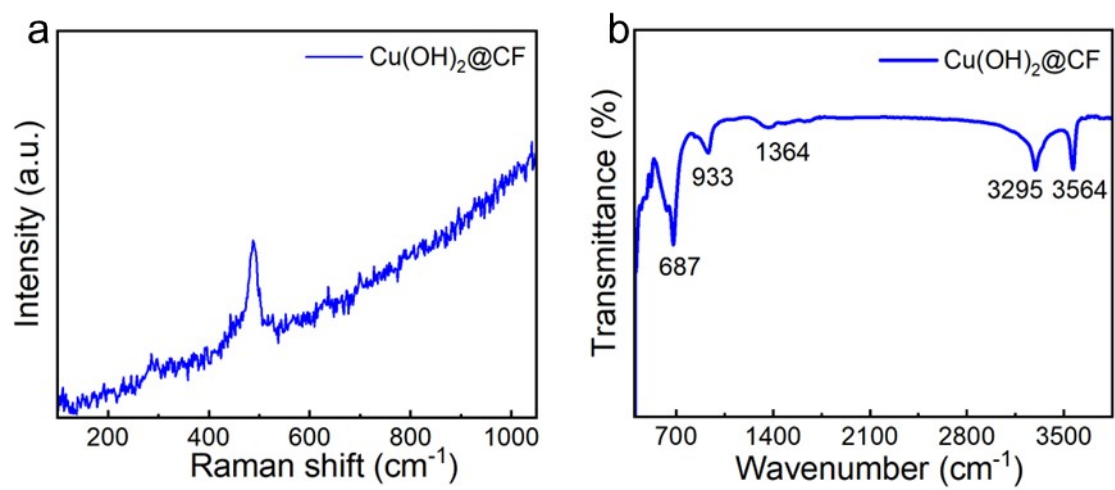
All the electrochemical measurements were tested in CR2032-type coin cells. Cu<sub>3</sub>(HHTP)<sub>2</sub>@CF electrodes were dried at 110 °C in a vacuum oven for 12 h and then used as anode directly. Celgard 2400 film was used as separator with a diameter of 19 mm and Li metal was used as counter electrode. The coin cells were assembled in an argon gas atmosphere glovebox. Cyclic voltammetry (CV) tests were carried out on the IVIUMSTAT workstation in the voltage window of 0.01 – 3.0 V. The galvanostatic charge/discharge plots were collected by the LAND battery-testing system (CT2001A). Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.01 to 100 KHz.



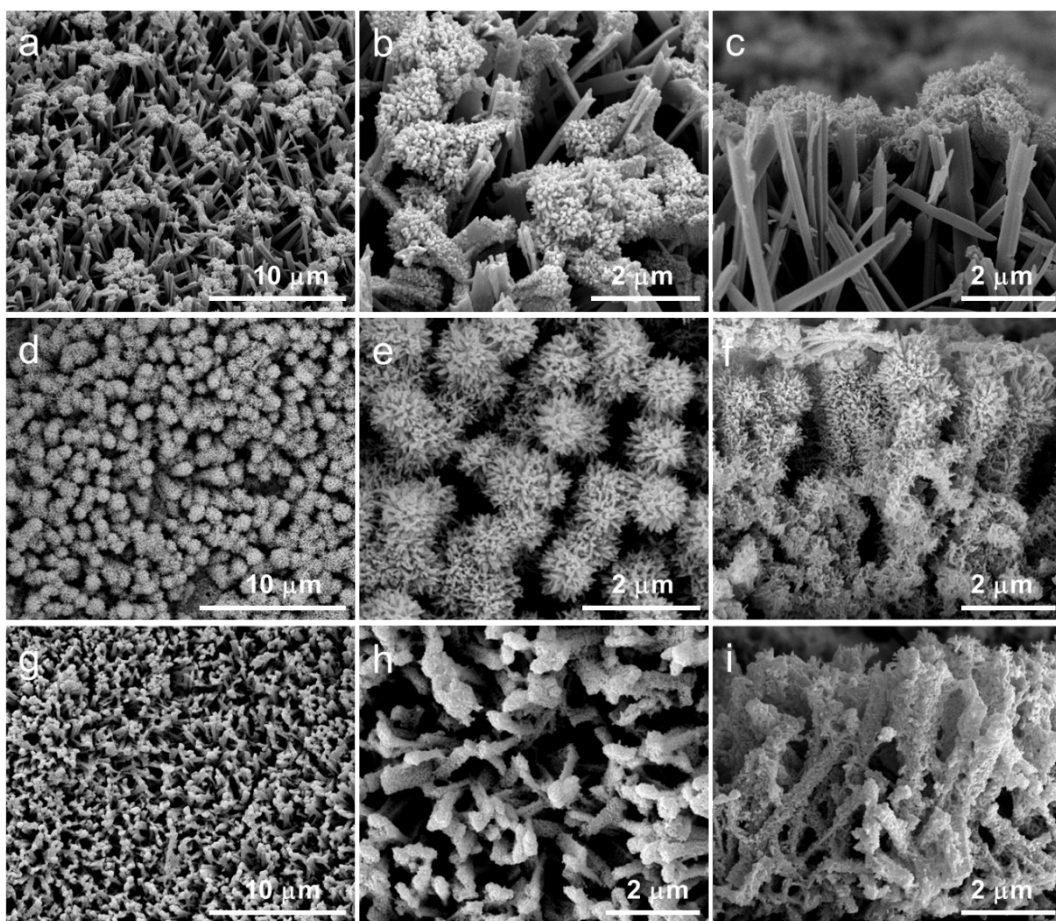
**Fig. S1** FESEM image of Cu(OH)<sub>2</sub>@CF.



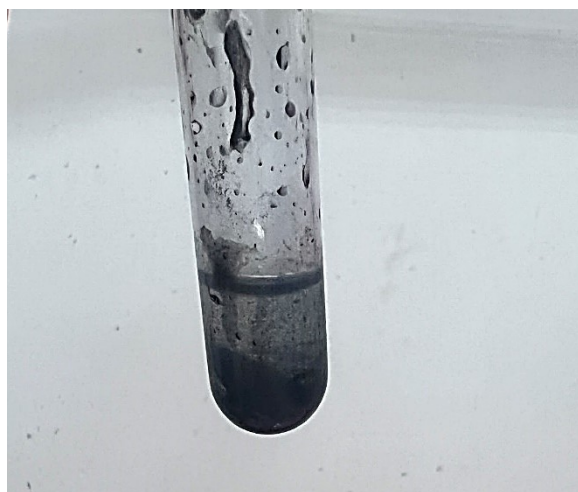
**Fig. S2** XRD pattern of Cu(OH)<sub>2</sub>@CF.



**Fig. S3** (a) Raman and (b) FT-IR spectra of Cu(OH)<sub>2</sub>@CF.

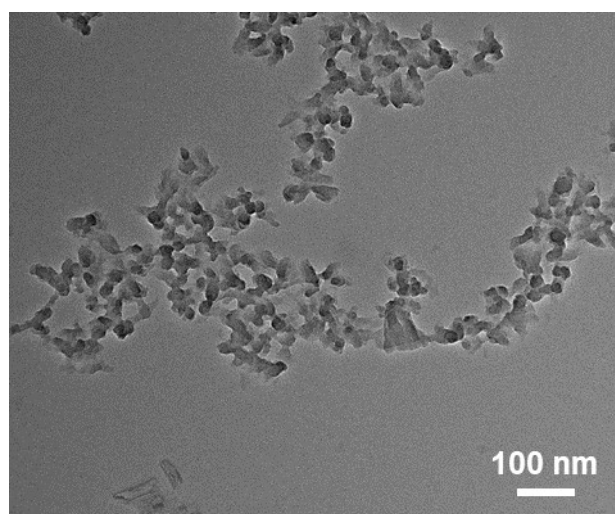


**Fig. S4** FESEM images of (a – c)  $\text{Cu}_3(\text{HHTP})_2@\text{CF-1}$ , (d – f)  $\text{Cu}_3(\text{HHTP})_2@\text{CF-2}$ , and (g – i)  $\text{Cu}_3(\text{HHTP})_2@\text{CF-4}$ .

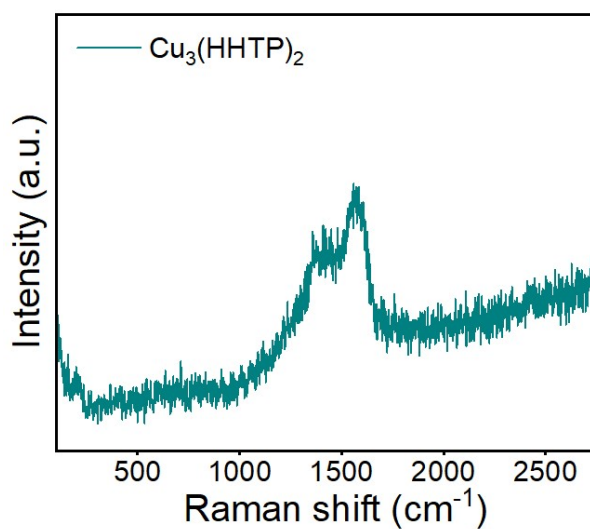


**Fig. S5** Digital graph for the residual solution after reaction for 12 h.



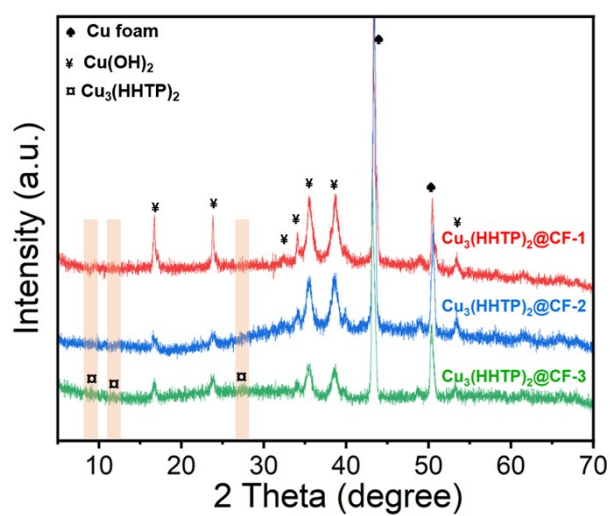


**Fig. S6** TEM image of  $\text{Cu}_3(\text{HHTP})_2@\text{CF-4}$ .

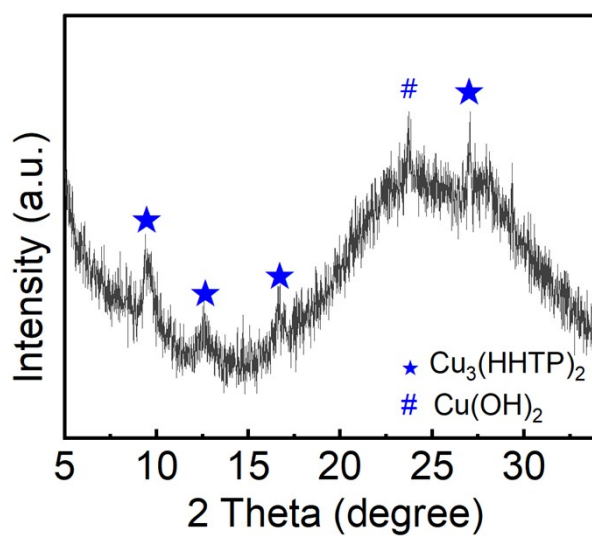


**Fig. S7** Raman spectra of pure  $\text{Cu}_3(\text{HHTP})_2$ .

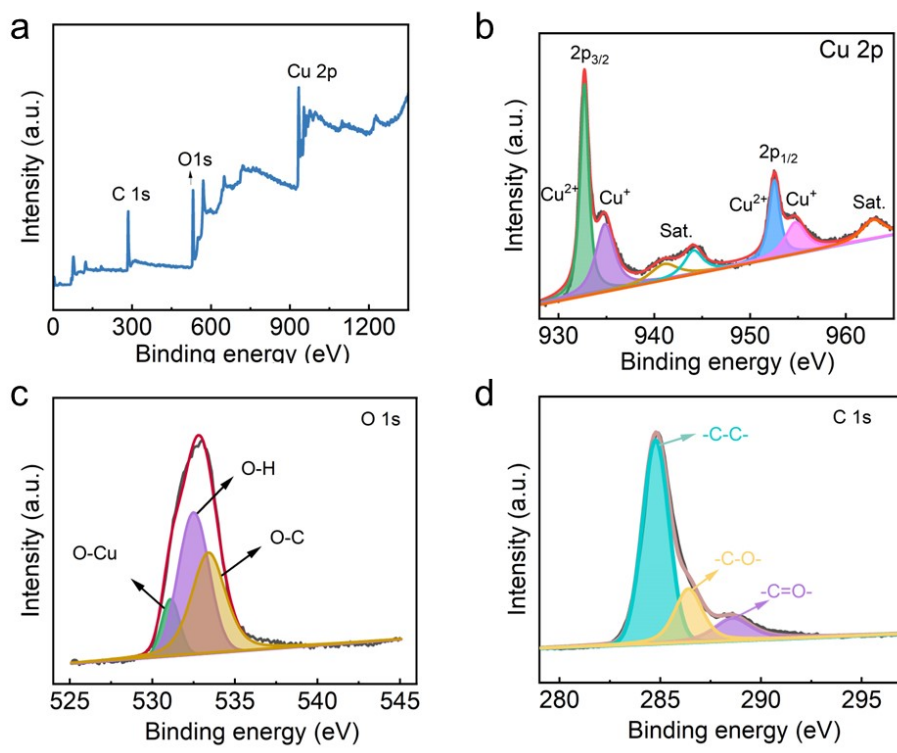
Raman test of pure  $\text{Cu}_3(\text{HHTP})_2$  was performed, as shown in **Fig. S7**. The Raman spectrum possessed major peak at  $\sim 1395$  and  $1570 \text{ cm}^{-1}$  belong to the stretching of aromatic C-C bonds. And, the Raman shift in  $\sim 190 \text{ cm}^{-1}$  is related to the metallic ions' vibration.<sup>[2]</sup>



**Fig. S8** XRD patterns of  $\text{Cu}_3(\text{HHTP})_2@\text{CF-1}$ ,  $\text{Cu}_3(\text{HHTP})_2@\text{CF-2}$ , and  $\text{Cu}_3(\text{HHTP})_2@\text{CF-3}$  electrodes.

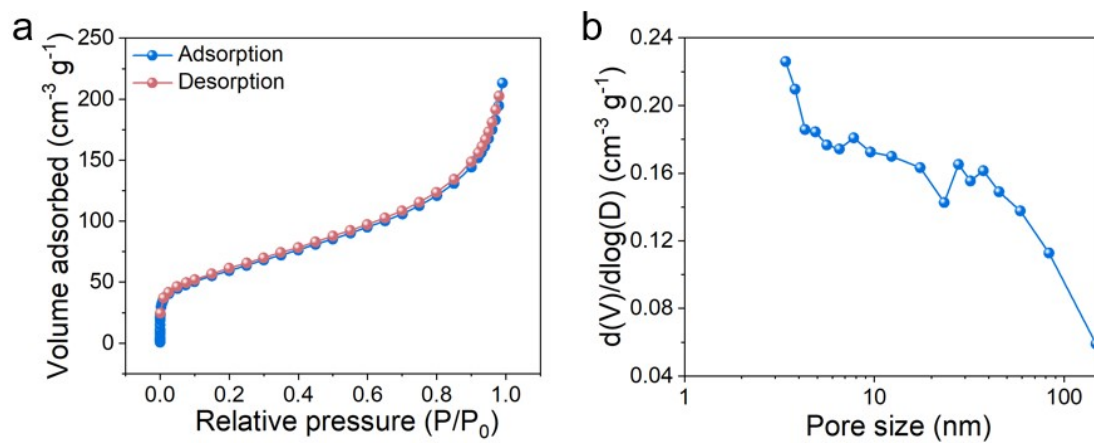


**Fig. S9** XRD pattern of  $\text{Cu}_3(\text{HHTP})_2@CF-4$  powder sample obtained by ultrasonic spalling from the electrode.

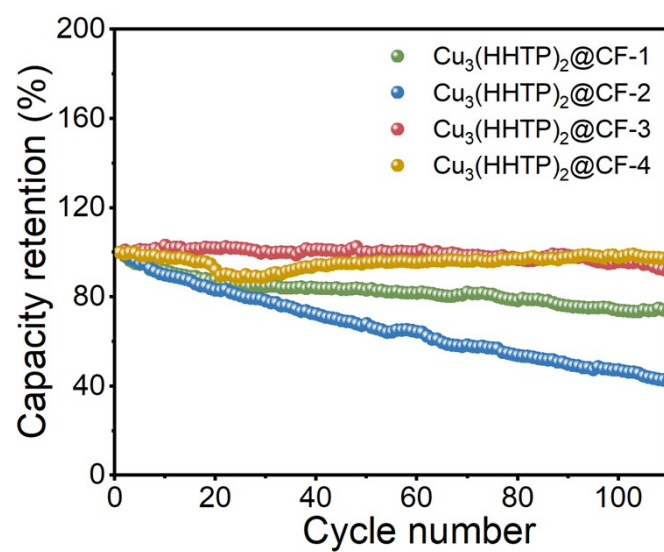


**Fig. S10** (a) XPS survey, (b) Cu 2p, (c) O 1s, and (d) C 1s spectra of  $\text{Cu}_3(\text{HHTP})_2@CF_4$ .

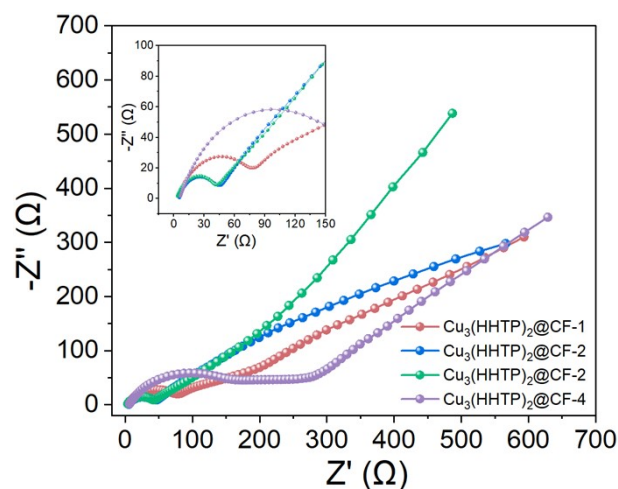
4.



**Fig. S11** (a)  $\text{N}_2$  adsorption-desorption isotherms and (b) pore size distribution plot of  $\text{Cu}_3(\text{HHTP})_2@CF-4$  powder.



**Fig. S12** Cycling performance of  $\text{Cu}_3(\text{HHTP})_2@CF$  electrodes at a current of 1 mA after 4-cycle activation.



**Fig. S13** Nyquist plots of Cu<sub>3</sub>(HHTP)<sub>2</sub>@CF electrodes as indicated.

Electrochemical impedance spectroscopy (EIS) tests were performed to address the good conductivity of the Cu<sub>3</sub>(HHTP)<sub>2</sub>@CF electrodes, as depicted in **Fig. S13**. The X-axis intercept in high frequency corresponds to the internal resistance ( $R_s$ ) from the cell itself and the contact resistance between the electrolyte and the electrode.<sup>[3]</sup> The diameter of half-circle in the middle frequency is related to the charge-transfer resistance ( $R_{ct}$ ). The straight line in the low-frequency region reflects the electrolyte ions diffusion impedance ( $Z_w$ ).<sup>[4,5]</sup> All samples show small  $R_s$  values, and among all Cu<sub>3</sub>(HHTP)<sub>2</sub>@CF electrodes, Cu<sub>3</sub>(HHTP)<sub>2</sub>@CF-3 shows the smallest charge-transfer resistance and  $Z_w$ . However, with reaction time up to 12 h, the excessive consumption of Cu(OH)<sub>2</sub> NWs results in the structure collapsed and partially fall off of Cu<sub>3</sub>(HHTP)<sub>2</sub> materials, leading to the increase of resistance.

## Reference

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