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## **Supplementary Information**

# An organic polymer CuPPc-derived Copper Oxide as a Highly

### **Efficient Electrocatalyst for Water Oxidation**

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#### General materials and instruments

Cu foam (CF) was purchased from Kunshan Jijinsheng Electronic technology Co. Ltd. 1,2,4,5-tetracyanobezene (TCNB) (>98%) were purchased from TCI. KOH (99.99%) was purchased from Alfa. Other chemical reagents were analytically pure and used without further purification. Ultra-pure water (18.2 M $\Omega$  cm) for all the reactions or measurements was obtained from a Milli-Q system (Millipore, Direct-Q 3 UV).

SEM images and EDX spectra were obtained by using Nova NanoSEM 450 equipment. Images were obtained with an acceleration voltage of 10 kV and EDX Electronic spectra were obtained with an acceleration voltage of 20 kV. TEM and HRTEM images were taken on (FEI TF30) TEM system operating at 300 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific ESCALAB 250 instrument using 200 W K $\alpha$  radiation. The binding energy (BE) was calibrated with respect to the C 1s level 284.6 eV of adventitious carbon. FT-IR spectra were obtained by ThermoFisher 6700. X-ray diffraction (XRD) analysis was conducted on Rigaku D/Max 2400 (Japan) using Cu K $\alpha$  radiation ( $\lambda = 0.1541$  nm) at a scanning rate of 5°/min in the 20 range of 5-80°.

#### Preparation of the CuPPc/CF electrodes

A piece of CF (3 cm x 2 cm) was cleaned ultrasonically first with 3 M HCl, DI water and ethanol for 30 min in each. The cleaned CF and 0.25 g TCNB powder were put into two quartz boat and laid two boats in a tube furnace (distance between two boats  $\approx$  1 cm). The tube furnace was heated to a certain temperature (300, 350, 400, 450, 500 °C) with a rapid speed of 10 °C/min in a vacuum environment and kept for 120 min. After the program finished, the furnace was cooled to room temperature.

#### Electrochemistry

All electrochemical experiments were carried out using a CHI 660E Electrochemical Analyzer at room temperature. In a typical test, an undivided three-electrode configuration with 20 mL electrolyte was used in the experiments. A piece of CF or as-prepared electrode was used as a working electrode (WE), and the geometric area of WE was maintained as 1 cm<sup>2</sup>. Hg/HgO (1 M KOH) was used as a reference electrode (RE) and Pt wire was used as a counter electrode (CE). The reference electrode was calibrated by using redox couple  $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$  (E<sub>1/2</sub> = 1.26 V vs. NHE) as a standard. All potentials reported here were converted to the RHE scale using equation E (RHE) = E (RE) + 0.059 pH + 0.112 V. At each LSV experiment, the resistance was obtained from EIS experiment and manually corrected to LSV curve.

The polarization curves were obtained by linear sweep voltammetry (LSV) tests conducted in 1.0 M KOH, at a scan rate of 1 mV s<sup>-1</sup> and with manual compensation of resistance. Tafel plots

were obtained by linear fitting the Faradic region of LSV curves mentioned above. Electrochemical impedance spectroscopy (EIS) of catalysts and other samples were recorded under a bias of 1.58 V vs. RHE over a frequency of 0.1 Hz to 1 MHz with an amplitude potential of 5 mV.

For testing the durability of catalyst, an undivided three-electrode configuration with 40 mL 1.0 M KOH solution was used. In the test, 1 cm<sup>2</sup> CuPPc-450, Hg/HgO (1 M KOH) and Pt wire were used as WE, RE and CE, respectively.

Before TOF calculation, the surface concentration of the catalytic active site was calculated by following equation<sup>S1</sup>:

$$4RTi_{n}/n^{2}F^{2}Av = \Gamma$$

When the  $i_p$  was plotted against the scan rate (Figure S7), the equation turned to:

 $slope = n^2 F^2 A \Gamma / 4RT$ 

Where, n is electron transfer during oxidation process of catalyst (n = 1 for Cu<sup>3+</sup>/Cu<sup>2+</sup>), F is the Faraday constant (96485 C mol<sup>-1</sup>), A is the surface area of the electrode (1 cm<sup>2</sup>),  $\Gamma$  is the surface concentration of catalytic active site (mol cm<sup>-2</sup>), R is the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and T is temperature (K). The  $\Gamma$  was calculated as 0.32 mmol cm<sup>-2</sup>.

For the TOF calculation, another equation was applied<sup>S2</sup>:

 $TOF = JAN_A/nF\Gamma$ 

*J* is the current density at given  $\eta$  (A cm<sup>-2</sup>), *A* is the surface area of the electrode (cm<sup>2</sup>), *N*<sub>A</sub> is Avogadro number (6.022 × 10<sup>23</sup>), n is electrons transfer number for evolving one mole of product (n =4 for OER), *F* is the Faraday constant (96485 C mol<sup>-1</sup>),  $\Gamma$  is the surface concentration of catalytic active site calculated above. The relationship between  $\eta$  and TOF was plotted in **Figure S8**.

For Faraday efficiency evaluation, we use a single compartment gas-tight cell equipped with the three-electrode system. In the system, 1 cm<sup>2</sup> CuPPc-450 used as the working electrode, Hg/HgO (1 M KOH) and Pt mesh used as the reference electrode and counter electrode, respectively. Prior to measurement, the solution was degassed by bubbling Ar for 2 h. The experiment was carried out at 1.48 V *vs*. RHE without *iR* compensation in 1.0 M pH 13.6 KOH solution for various of time (2 h, 4 h, 6 h, 10 h, 20 h, 30 h, 40 h and 50 h). After the bulk electrolysis, the amount of evolved oxygen in the headspace was taken and quantified by GC. For estimation of leaked O<sub>2</sub> from the air, the air was also sampled and analyzed by GC analysis under the same condition. The peak area of leaked O<sub>2</sub> was estimated according to the equation of A(leaked O<sub>2</sub>) = [A(O<sub>2</sub> in the air)/A(N<sub>2</sub> in the air)] × A(leaked N<sub>2</sub>). Then, the peak area of leak O<sub>2</sub> was deducted from the peak area of total peak area of O<sub>2</sub>, and then the quantity of O<sub>2</sub> generated during the bulk electrolysis experiment was determined. The Faradaic efficiency can be calculated as Faradaic efficiency =  $4F \times nO_2/Q$ , where Q is the total amount of charge passed through the cell under the constant potential, *F* is the Faraday constant (96485 C mol<sup>-1</sup>).

To measure  $C_{dl}$ , CVs were swept between 0.814 V ~ 0.914 V vs. RHE in 1.0 M KOH at scan rates 20, 40, 60, 80, 100, 120, and 140 mV s<sup>-1</sup>. The  $C_{dl}$  values were estimated by plotting  $\Delta J/2$  at 0.864 V vs. RHE against scan rates. The slopes were twice the  $C_{dl}$ . The curves were shown in Figure S13.



**Figure S1** FT-IR spectra of CuPPc-500 (wine), CuPPc-450 (red), CuPPc-400 (green), CuPPc-350 (bule), and CuPPc-300 (black).



Figure S2 SEM images of (a) CuPPc-300, (b) CuPPc-350, (c) CuPPc-400, (d) CuPPc-450, and (e) CuPPc-500 in a 50  $\mu$ m scale.



Figure S3 EDS analysis of CuPPc-450.



Figure S4 Elemental mapping of the selected area of CuPPc-450 electrode.



Figure S5 XPS survey of fresh CuPPc-450.



**Figure S6 (a)** Activation process of CuPPc-450 electrode, **(b)** Manually compensated polarization curves of freshly prepared CuPPc-450 electrode (blue), activated CuPPc-450 electrode (red), and bare CF (gray) in a 1.0 M KOH solution. RE: HgO/Hg; CE: Pt wire; scan rate:  $1 \text{ mV s}^{-1}$ ; electrode area:  $1 \text{ cm}^2$ .



Figure S7 (a) CVs of CuPPc-450 at different scan rates, (b) plot of  $i_p$  against scan rate.



Figure S8 Relationship between TOF and overpotential.



Figure S9 SEM images of CuPPc-450 after 50 h of electrolysis.



Figure S10. XRD patterns of post-catalyst (green), and the patterns of as-prepared catalyst (red) for comparison.



Figure S11 (a) XPS survey, sections of the XPS spectra around (b) C 1s, (c) N 1s, and (d) O 1s of the catalyst after OER.



**Figure S12** Faraday efficiency of freshly prepared CuPPc-450 electrode. Dark gray line: current curve at 1.48 V vs. RHE. Red ring and line: Faraday efficiencies at 2 h, 4 h, 6 h, 10 h, 20 h, 30 h, 40 h and 50 h. Note: each dot was measured separately, and the longest current curve was chosen for clarity.



 Figure S13. CV curves of (a) CF, (b) CuPPc-300, (c) CuPPc-350, (d) CuPPc-400, (e)

 CuPPc-450, and (f) CuPPc-500 swept between  $0.814 \text{ V} \sim 0.914 \text{ V}$  vs. RHE in 1.0 M

 KOH at seven different scan rates (20, 40, 60, 80, 100, 120, and 140 mV s<sup>-1</sup>) for

 estimation

 of

  $C_{dl}$ 

Electrodes	Test condition	η <sub>10</sub> (mV)	Tafel slope (mV∙dec <sup>-1</sup> )	Stability	References
Copper foam (CF) as the substrate					
CuPPc-450/CF	рН 13.6, 1.0 М КОН	287 355 (η <sub>100</sub> )	60.1	10 mA·cm <sup>-2</sup> @1.53 V vs. RHE, 50 h	This work
Dendritic Cu/Cu <sub>2</sub> O/CuO	рН 13.6, 1 М NaOH	290	64	10 mA cm <sup>-2</sup> @1.81 V vs. RHE, 20 h	83
Cu <sub>2</sub> O–Cu Hybrid Foams	рН 13.6, 1 М КОН	350	67.52	10 mA cm <sup>-2</sup> @ 1.58 V <i>vs.</i> RHE, 50 h	S4
Cu(OH) <sub>2</sub> -NWs/CF	рН 13.0, 0.1 М NaOH	530	86	10 mA cm <sup>-2</sup> @ 1.76 V vs. RHE, 7 h	85
CuO/C hollow-shell	рН 13.6, 1 М КОН	286	66.3	10 mA cm <sup>-2</sup> @ 1.52 V <i>vs.</i> RHE, 50 h	S6
Cu <sub>2</sub> O <sub>x</sub> S <sub>1-x</sub>	рН 13.6, 1 М КОН	361 ( <b>η</b> <sub>50</sub> )	-	~ 43 mA cm <sup>-2</sup> @ 1.61 V vs. RHE, 8 h	S7
Cu <sub>3</sub> P/CuO	рН 13.6, 1 М КОН	315	74.8	10 mA cm <sup>-2</sup> @ 1.58 V <i>vs.</i> RHE, 50 h	S8
Cu(TCNQ) /CuO	рН 13.6, 1 М КОН	317 ( <b>ŋ</b> <sub>25</sub> )	85	~ 30 mA cm <sup>-2</sup> @ 1.57 V <i>vs.</i> RHE, 24 h	S9
CuS <sub>0.55</sub>	рН 13.6, 1 М КОН	386 ( <b>η</b> 100)	33	10 mA cm <sup>-2</sup> @ 1.56 V <i>vs.</i> RHE, 5 h	S10
CuO <sub>x</sub> -NLs	pH 11.0, 0.2 M CBS	450	44	> 17 mA cm <sup>-2</sup> @1.81 V vs. RHE, 20 h	S11
Other electrodes					
Cu <sub>2</sub> Se-Cu <sub>2</sub> O/Ti foam	pH 11.0, 0.2 M CBS	465	140	10 mA cm <sup>-2</sup> @ 1.70 V vs. RHE, 20 h	S12
CuO/FTO	рН 13.6, 1 М КОН	430( <b>η</b> <sub>1</sub> )	61.4	3 mA cm <sup>-2</sup> @ 1.73 V <i>vs.</i> NHE, 24 h	S13
Cu7Te4 nanosheets/GC	рН 13.0, 0.1 М КОН	460	103	10 mA cm <sup>-2</sup> @ 1.69 V vs. RHE, 6 h	S14
Cu <sub>3</sub> N/nickel foam	рН 13.6, 1 М КОН	$286 \pm 4$	118.5 ± 0.5	10 mA cm <sup>-2</sup> @ 1.52 V vs. RHE, 14 h	S15

 Table S1 Catalytic performances for a variety of Cu-based material WOCs

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