

Supporting information

Heat-treated copper phthalocyanine on carbon toward electrochemical CO₂ conversion into ethylene boosted by oxygen reduction

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Chemicals

Copper phthalocyanine (CuPc, >99%) was purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, 99.5%) and KHCO₃ (analytical grade) were purchased from Aladdin Chemistry Co., Ltd. Carbon black (Ketjenblack EC600 JD) was obtained from Akzo Nobel Akzo Nobel, Holland. It was pretreated in nitric acid (3 M) at 80 °C for 1 h before use. Ultrapure water (18.2 MΩ cm⁻¹ at 25 °C) was obtained from Millipore water system (Synergy UV, France).

Experimental

Typically, 15 mg of CuPc powder and 15 mg of treated EC600 JD carbon powder were dispersed in 18 mL of DMF under sonication in a water-bath cleaner for 15 min. Next, the mixture was vigorously stirred at 25 °C for 4 h. CuPc/C was obtained after filtration and drying at 65 °C. Afterwards, CuPc/C was heat-treated at 400 °C for 2 h in Ar atmosphere with a ramping rate of 5 °C min⁻¹ from room temperature, labeled as CuPc/C-400. For comparison, CuPc/C was also heat-treated at 200, 300 and 500 °C.

Firstly, Cu foil was mechanically polished with sandpaper. Then, it was cleaned in isopropanol and ultrapure water under sonication each for 5 min, followed by drying in vacuum oven at 50 °C for further use. Additionally, an ink (1 mg mL⁻¹) was prepared by blending certain amount of CuPc/C-400 with water, ethanol and 5 wt% Nafion perfluorinated resin solution at a $V_{\text{water}}: V_{\text{ethanol}}: V_{\text{Nafion}}$ ratio of 1:9:0.06 by sonication for 5 min. Then, the homogeneous slurry was sprayed onto the two sides of the pretreated Cu foil with a loading of 1.0 mg cm⁻² on a hot plate at 60 °C, followed by heat treatment at 750 °C for 2 h in Ar atmosphere with a ramping rate of 5 °C min⁻¹ from room temperature, labeled as CuPc/C-Cu-750. In addition, Cu foil and carbon black on Cu foil were also heat-treated under the same conditions, named as Cu-750 and C-Cu-750, respectively. For comparison, 0.5, 2.0, and 3.0 mg cm⁻² of CuPc/C-400 on Cu foil were heat-treated while holding the other synthetic parameters constant. And 600, 700, 800, and 900 °C were also employed to heat-treat 1.0 mg cm⁻² of CuPc/C-400 on Cu foil as reference.

Characterizations

Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and elemental mappings of the samples were carried out on a Field Emission Scanning Electron Microscope (NOVA NanoSEM 450). Transmission electron microscopy (TEM) images were performed on electron microscope (JEM-2100). High-resolution TEM (HRTEM) images and elemental mappings of the samples were recorded on a FEI Tecnai G2 F30S-Twin microscope operated at 300 keV. X-ray diffraction (XRD) were collected on a Rigaku SmartLab 9 kW operating at 45 kV and 200 mA with Cu K α radiation ($\lambda = 0.15432$ nm) with a Cu K α radiation source (Rigaku). X-ray photo-electron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi spectrometer using monochromatic Al K α line (1486.6 eV) as the X-ray source (Thermo).

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was carried out on a PerkinElmer ICP-OES 7300DV (PerkinElmer). Thermogravimetric analysis (TGA) was carried out with dried Ar as the processing atmosphere at a ramping rate of 10 °C min⁻¹ (TA-Q600 SDT). Raman spectra were taken with DXR Microscope (Thermo Fisher). Ultraviolet-visible spectroscopy (UV-vis) was conducted by using a Specord S600 spectrophotometer (Analytic Jena). Surface hydrophilicity was analyzed using contact angle measuring instrument (KRUSS DSA100). Electrochemical impedance spectra (EIS) measurement was carried out on an electrochemical workstation in 0.5 M KHCO₃ aq. at -0.4 V vs. RHE with an amplitude of 5 mV. Surface roughness was analyzed by Atomic force microscope (AFM) with a tapping-mode (Cypher ES).

Electrochemical CO₂ reduction

Electrochemical measurements were carried out in a H-type cell with a proton exchange membrane (Nafion 115) to separate the two compartments at 25 °C. The electrolyte in each compartment was 100 mL of 0.5 M KHCO₃ aq, and the cathodic compartment was continuously purged with CO₂/O₂ (volume ratio: 80:20) at a flow rate of 20 mL min⁻¹ in comparison with N₂/O₂ (volume ratio: 80:20), N₂ (99.999%), CO₂ (99.999%), CO₂/O₂ (volume ratio: 95:5) and CO₂/O₂ (volume ratio: 90:10). A graphite rod was used as the counter electrode, and a Hg/Hg₂SO₄ as the reference electrode. All potentials discussed in this work were converted to RHE scale according to the equation of E (vs. RHE) = E (vs. Hg/Hg₂SO₄) + 0.65 + 0.0591 × pH. Gas products were detected using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) for H₂ quantification and two flame ionization detectors (FID) for the analysis of hydrocarbons and CO. GC was equipped with a packed Molecular Sieve 5A capillary column, a packed Porapak Q column, and a packed GDX-102 column. N₂ (99.999%) was used as the carrier gas. Liquid products were quantified using ¹H nuclear magnetic resonance (¹H NMR) on Bruker AVANCE III 500, Switzerland. The FE of gas products was calculated according to the equation below:

$$FE_i = \frac{Q_i}{Q_{total}} = \frac{v \cdot x}{22400 \cdot 60} \cdot n \cdot F$$

Where i represents each gas-phase product, x is the concentration of the gas-phase products, v is the flow rate of CO₂, n is the quantity of transferred electrons for gas products, F is the Faraday constant (96485 C mol⁻¹), I is the average current in certain period of electrolysis.

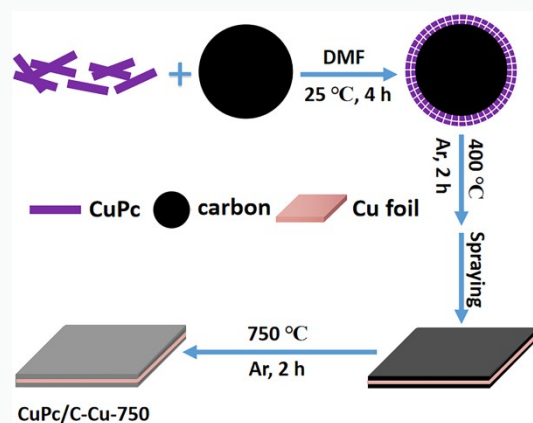


Fig. S1 Illustration of synthetic route of CuPc/C-Cu-750.

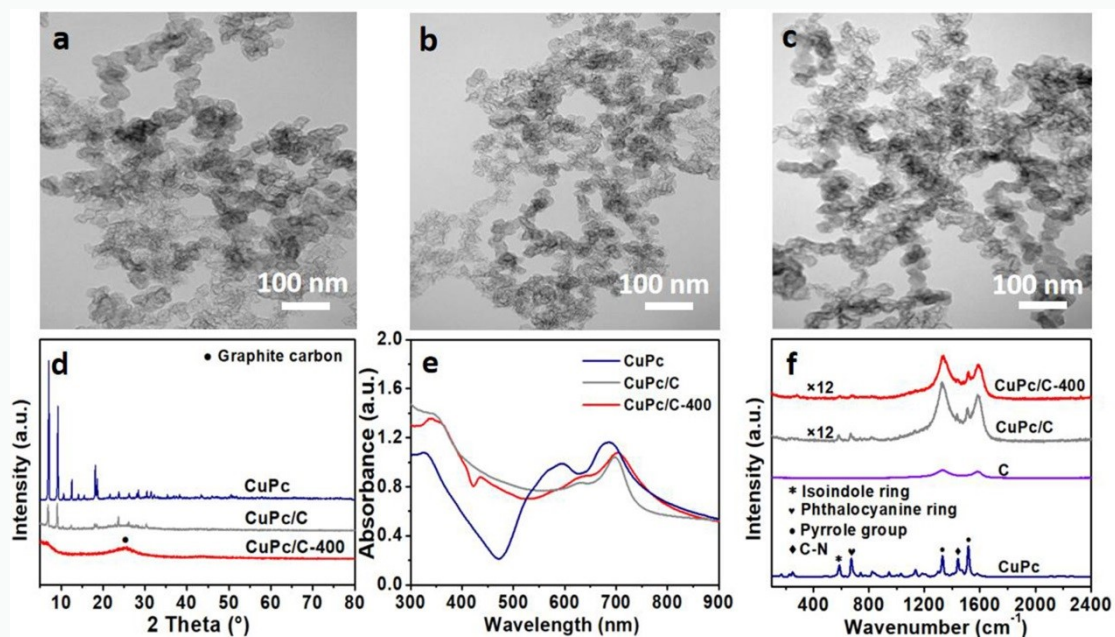


Fig. S2 (a-c) TEM images of carbon black, CuPc/C, and CuPc/C-400; (d) XRD of CuPc, CuPc/C, and CuPc/C-400; (e) UV-vis spectra of CuPc, CuPc/C, and CuPc/C-400; (f) Raman spectra of CuPc, carbon black, CuPc/C, and CuPc/C-400.



Fig. S3 Photograph of the supernatant of the slurries of CuPc/C-200, CuPc/C-300 and CuPc/C-400.

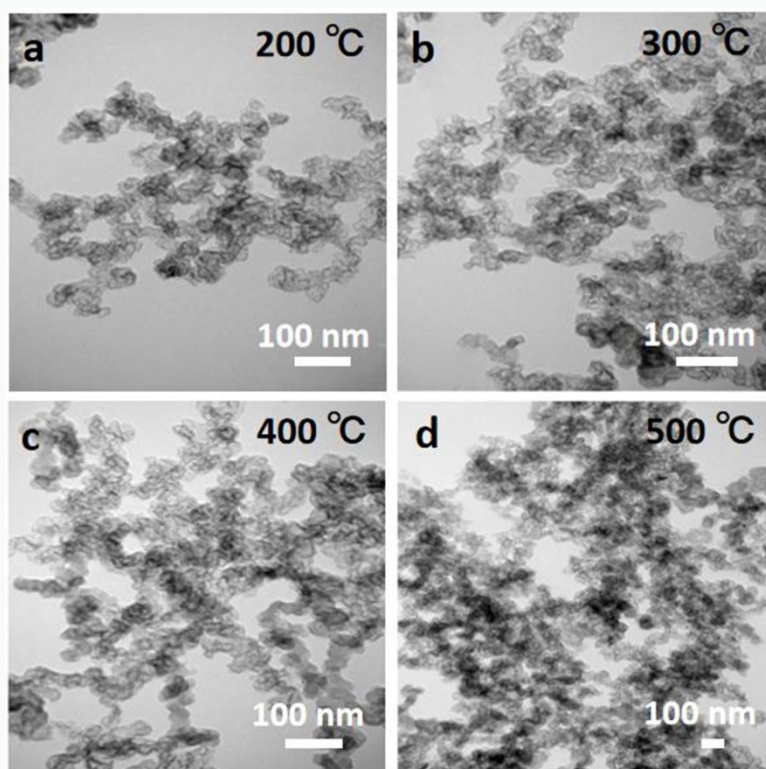


Fig. S4 TEM images of CuPc/C heat-treated at at 200 (a), 300 (b), 400 (c), and 500 °C (d).

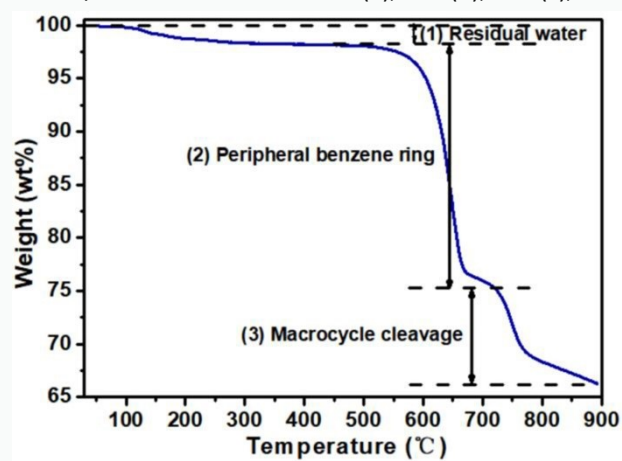


Fig. S5 TGA curve of CuPc with weight-loss assignment collected in Ar atmosphere with a ramping rate of 10 °C min⁻¹.

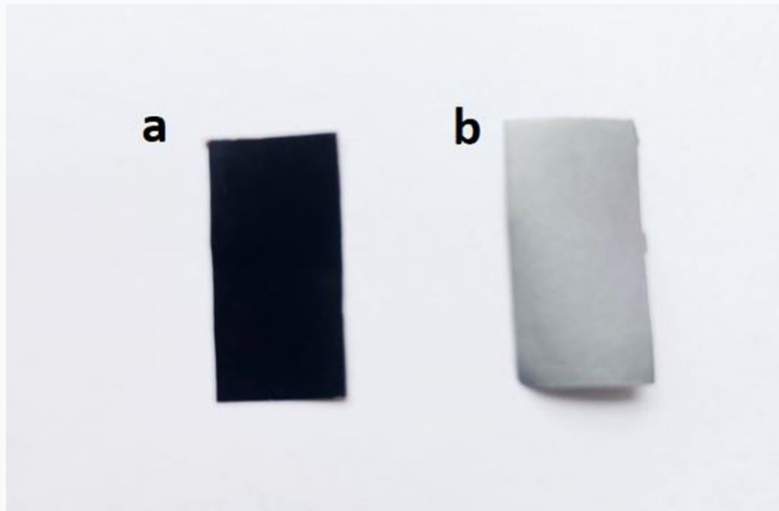


Fig. S6 Photograph of CuPc/C-400 coated Cu foil before pyrolysis (a) and after pyrolysis at 750 °C, labeled as CuPc/C-Cu-750 (b).

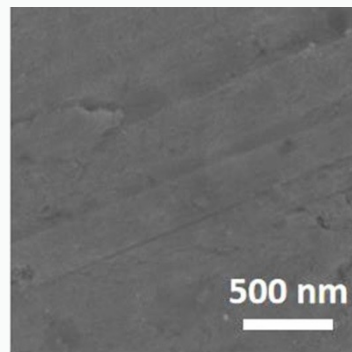


Fig. S7 Top view SEM image of Cu foil.

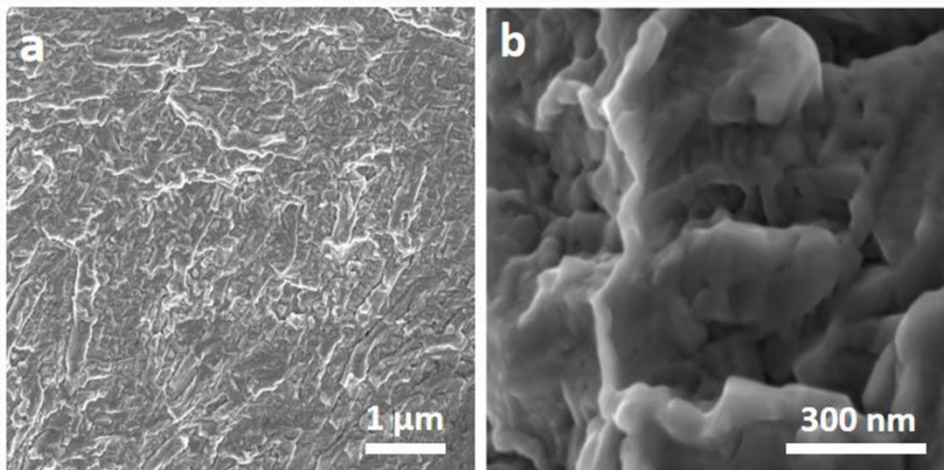


Fig. S8 Top view SEM images of CuPc/C-Cu-750 at different magnifications.

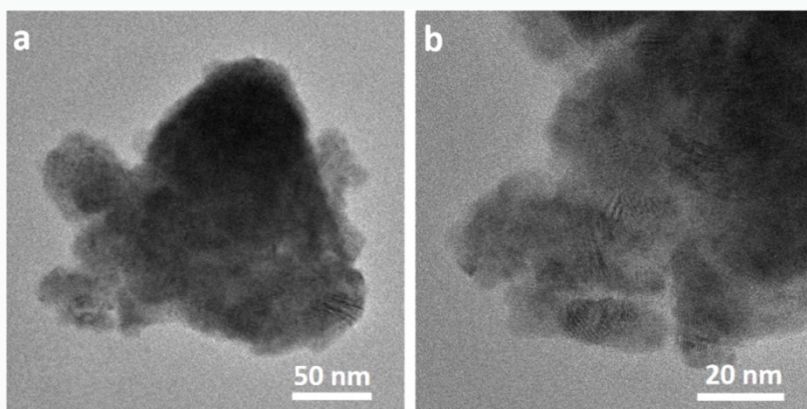


Fig. S9 TEM images of the peeled-off electrocatalyst layer from CuPc/C-Cu-750 at different magnifications.

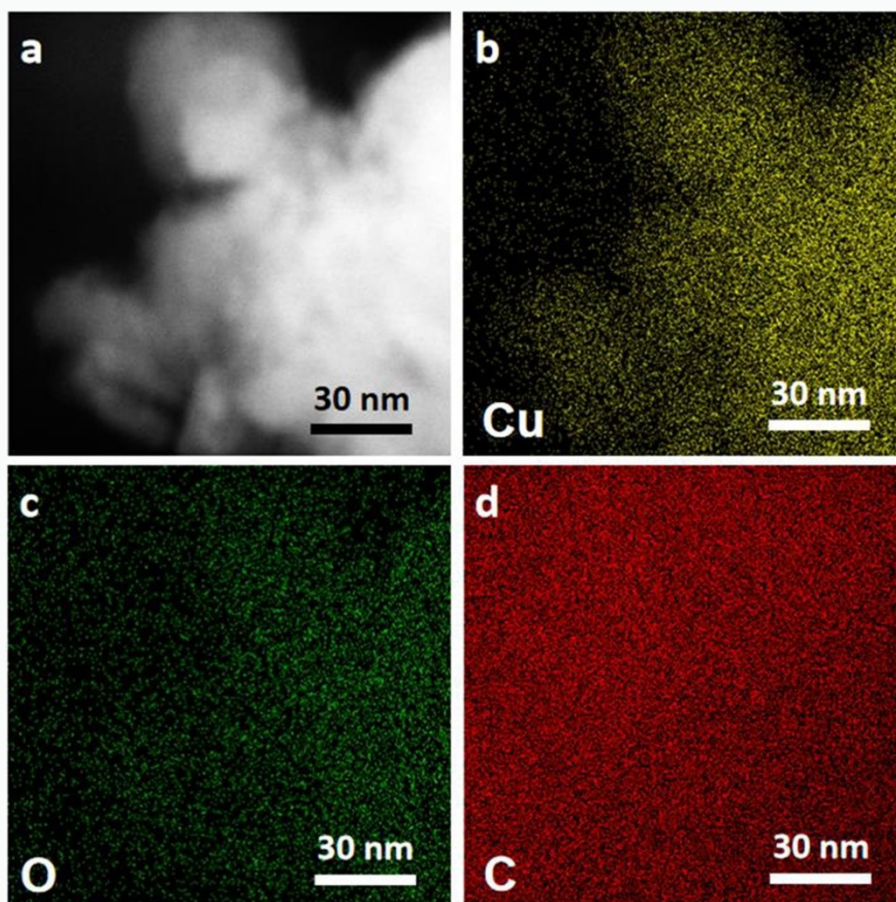


Fig. S10 TEM-EDS mapping of the peeled-off electrocatalyst layer from CuPc/C-Cu-750.

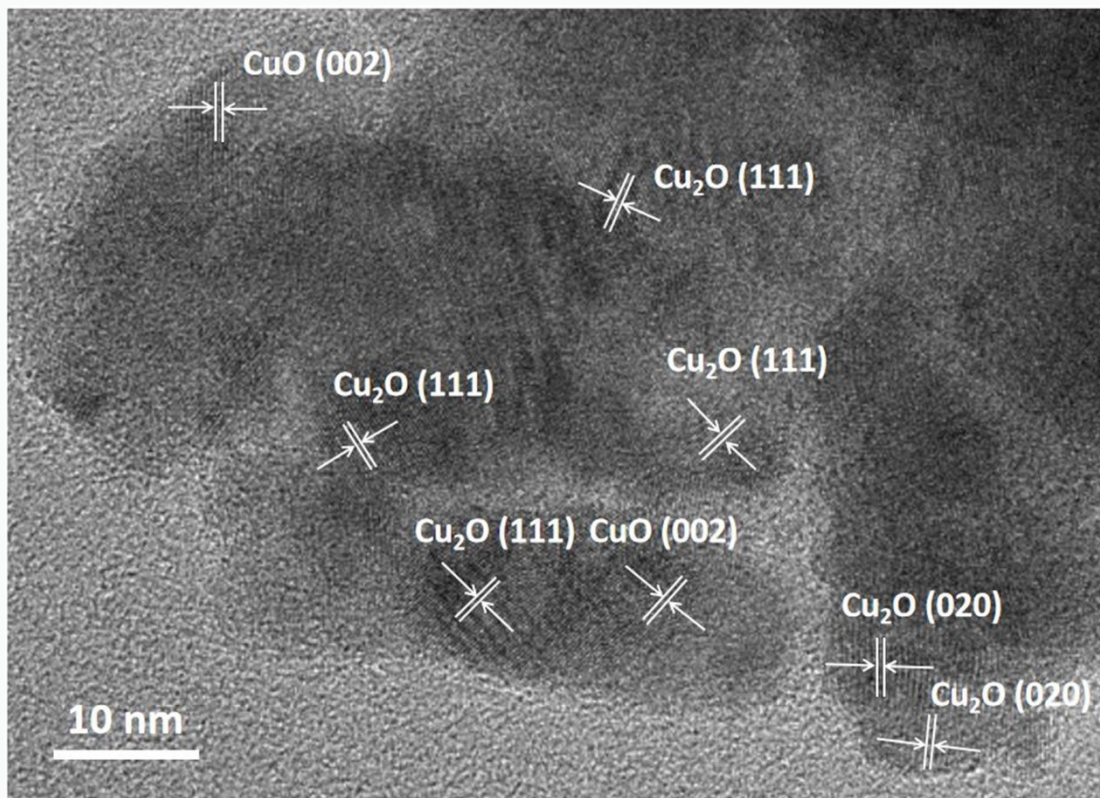


Fig. S11 HRTEM image of the peeled-off electrocatalyst layer from CuPc/C-Cu-750.

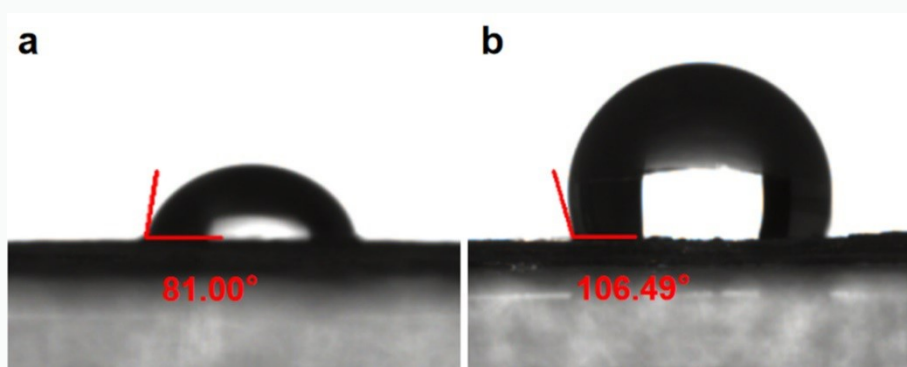


Fig. S12 Contact angle analysis of Cu foil (a) and CuPc/C-Cu-750 (b).

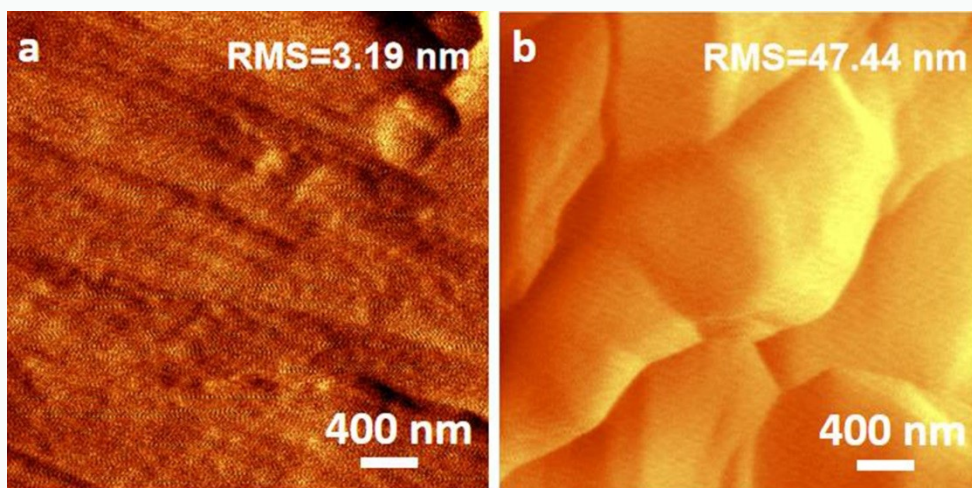


Fig. S13 AFM images of Cu foil (a) and CuPc/C-Cu-750 (b).

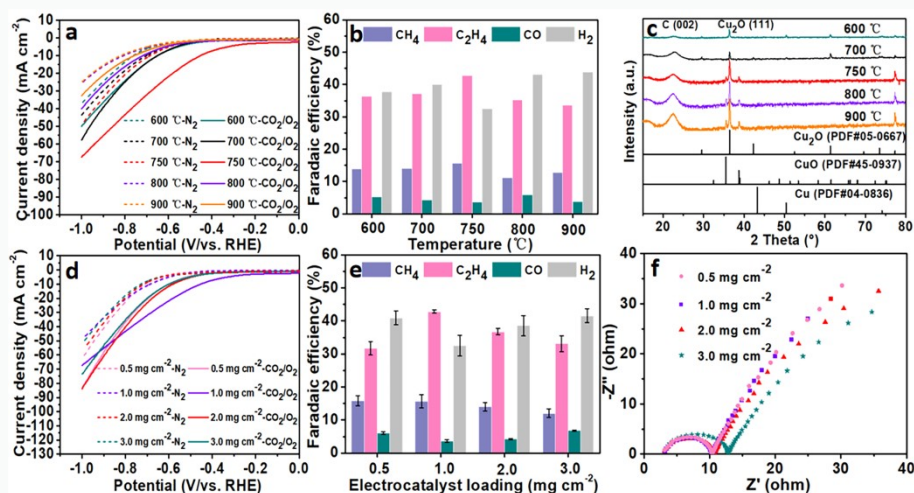


Fig. S14 CO₂RR performance and characterizations. (a) LSV curves recorded in N₂- and CO₂/O₂-saturated 0.5 M KHCO₃ aqueous solution for electrocatalysts synthesized at different temperatures; (b) FE of CO₂RR products at -0.4 V vs. RHE in CO₂/O₂ for electrocatalysts synthesized at different temperatures; (c) XRD patterns of electrocatalysts synthesized at different temperatures; (d) LSV curves recorded in N₂- and CO₂/O₂-saturated 0.5 M KHCO₃ aqueous solution for electrocatalysts synthesized with different loadings of CuPc/C-400; (e) FE of CO₂RR products at -0.4 V vs. RHE in CO₂/O₂ for electrocatalysts synthesized with different loadings of CuPc/C-400; (f) Nyquist plots of electrocatalysts synthesized with different loadings of CuPc/C-400.

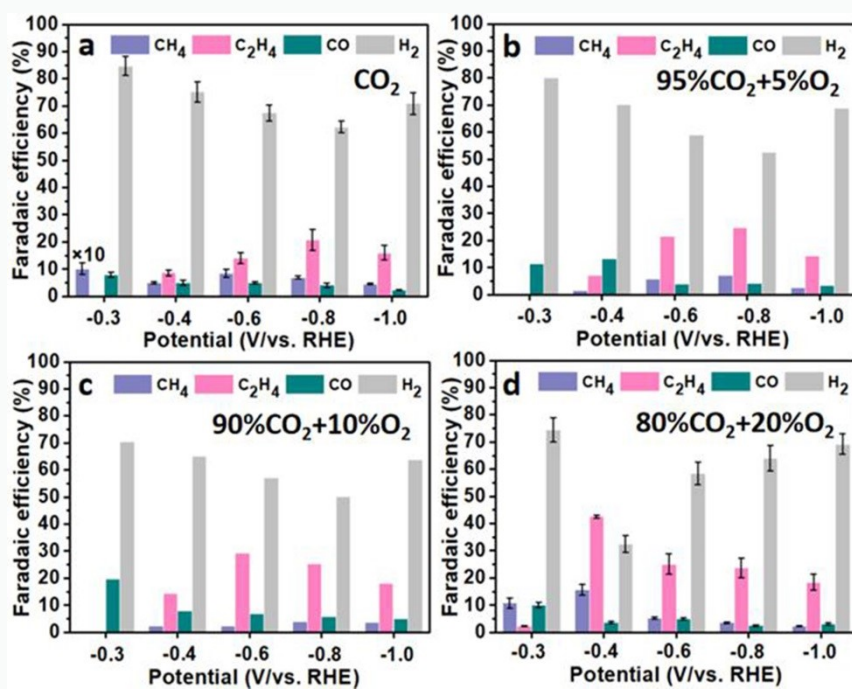


Fig. S15 FE of CO₂RR products of CuPc/C-Cu-750 in pure CO₂ (a), 95%CO₂+5%O₂ (b), 90%CO₂+10%O₂ (c), and 80%CO₂+20%O₂ (d) at different applied potentials.

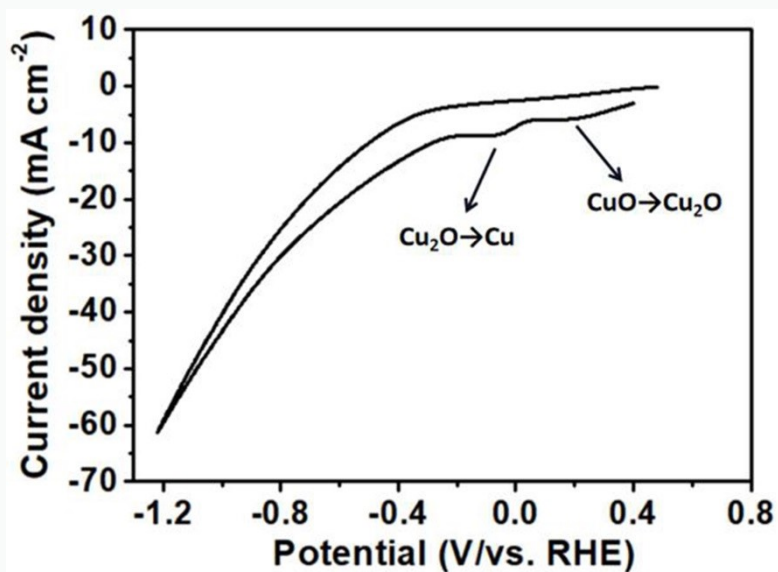


Fig. S16 CV curve of CuPc/C-Cu-750 recorded at 10 mV s⁻¹ in N₂-saturated 0.5 M KHCO₃ aqueous solution.

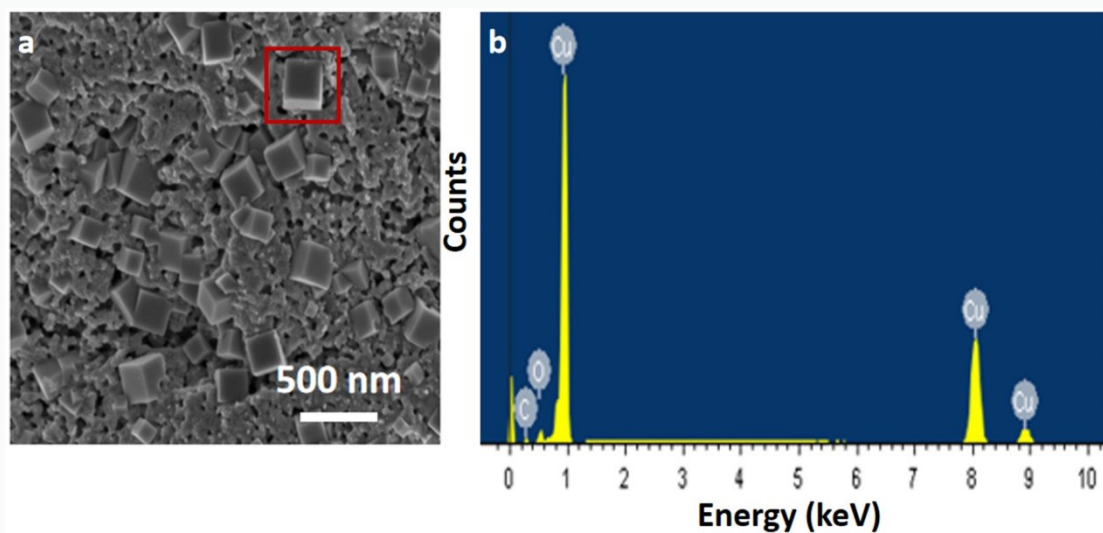


Fig. S17 (a) SEM image of CuPc/C-Cu-750 after 1 h of electrolysis at -0.4 V vs. RHE in CO₂/O₂(80:20)-saturated 0.5 M KHCO₃ aq.; (b) EDS spectrum of the selected nanocube in (a).