

Electronic Supplementary Information

Experimental Section

Materials: TCNQ, sodium dodecyl benzene sulfonate (SDS), CuCl₂, KOH, HCl and Cu foam were purchased from Beijing Chemical Corp. RuCl₃·3H₂O and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Water used throughout all experiments was purified through a Millipore system.

Preparation of Cu(TCNQ)/CF: Cu(TCNQ)/CF was prepared by a vapor-solid chemical reaction as follows. Cu foam was treated in HCl and then cleaned by sonication in water and ethanol for five times to remove surface impurities. A piece of as-pretreated Cu foam (4 cm × 2 cm) and 0.35 g pure TCNQ powders were put in two individual porcelain boat. The TCNQ porcelain boat was in the heating center and the Cu foam porcelain boat was about 0.5 cm from the heating center. The tube furnace was heated to 250 °C with a rapid speed of 18 °C/min in a vacuum environment and kept for 120 min. The furnace was then allowed to cool to room temperature.

Preparation of CuO-TCNQ/CF: To obtain CuO-TCNQ/CF, Cu(TCNQ)/CF was used as the working electrode with HgO electrode as the reference electrode and graphite as the counter electrode, and cyclic voltammetry of 1000 cycles was proceeded in the range of 0.4 ~ 0.8 V.

Preparation of CuO/CF: 0.2 g SDS was added into 10 mL CuCl₂ solution. After adding K₂CO₃, the mixture solution was transferred into the 25 mL Teflon-lined stainless-steel autoclave and maintained at 85 °C for 12 h. After cooled to room temperature, the product was washed with ultrapure water for several times to obtain CuO nanoparticles. CuO ink was prepared by dispersing 32 mg of CuO catalyst into 960 μL of water/ethanol (v/v = 1:1) solvent containing 40 μL of 5 wt% Nafion and sonicated for 1 h. Then 25 μL of the CuO ink was loaded onto a bare Cu foam of 0.25 cm² in geometric area.

Preparation of RuO₂ and RuO₂/CF: RuO₂ was prepared according to previous report.¹ Briefly, 0.01 mol RuCl₃·3H₂O and 1.0 mL NaOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. The precipitates were collected by

centrifugation and washed with water for three times, followed by dried at 80 °C. Finally, the product was annealed at 300 °C for 3 hours under air atmosphere. RuO₂ ink was prepared by dispersing 30 mg of RuO₂ catalyst into 480 μL of water/ethanol (v/v = 1:1) solvent containing 20 μL of 5 wt% Nafion and sonicated for 1 h. Then 13.3 μL of the RuO₂ ink was loaded onto a bare Cu foam of 0.25 cm² in geometric area. The RuO₂/CF was prepared well.

Characterizations: XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM images were collected on a tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. FT-IR spectra were acquired with a Perkin-Elmer 580B spectrophotometer (Perkin-Elmer, United States).

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a standard three-electrode system using CuO-TCNQ/CF as the working electrode, graphite as the counter electrode, and HgO electrode as the reference electrode. The potentials reported in this work were calibrated to RHE unless especially specified using the following equation: $E(\text{RHE}) = E(\text{Hg/HgO}) + (0.098 + 0.059 \text{ pH}) \text{ V}$. Polarization curves were obtained by linear sweep voltammetry with a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were recorded at the open-circuit potential in an appropriate frequency range. The solution resistances (R_s) are 2.16, 3.37 and 5.28 Ω for the three catalyst electrodes, respectively. All experiments were carried out at room temperature (25 °C).

Diameter calculation: The diameter of CuO nanoparticles are calculated by the Scherrer equation (1):

$$D = K\lambda/(\beta\cos\theta) \quad (1)$$

Where K is the Scherrer constant ($K = 0.89$); λ is the wave length of diffracted wave ($\lambda = 0.154$ nm); θ is the angle of diffraction; β is the width of half height (FWHM) which should be applied in radian measure.

In the diameter calculation, the β is obtained from the Jade software analysis with the value of 1.04 of the two main peaks of CuO in Figure S1. The calculated D is the average height of the nanocrystal which is grown perpendicular to the orientation of the lattice plane.

TOF calculation: The TOF for each active site was calculated by the equation (2):

$$\text{TOF} = JA/4Fm \quad (2)$$

Where J is current density (A cm^{-2}) at defined overpotential of the electrochemical measurement in 1.0 M KOH; A is the geometric area of the testing electrode; 4 indicates the mole of electrons consumed for evolving one mole O_2 ; F is the Faradic constant (96485 C mol^{-1}); m is the number of active sites (mol), which can be extracted from the linear relationship between the oxidation peak currents and scan rates by the equation (3):

$$\text{slope} = n^2F^2A\Gamma_0/4RT \quad (3)$$

where n is the numbers of electron transferred; $m = A\Gamma_0$; Γ_0 is the surface concentration of active sites (mol cm^{-2}); R and T are the ideal gas constant and the absolute temperature, respectively.

Determination of FE: The oxygen generated at anode was confirmed by gas chromatography (GC) analysis and measured quantitatively by using a calibrated pressure sensor to monitor the pressure change in the anode compartment of a H-type electrolytic cell. The FE was calculated by comparing the amount of experimentally measured oxygen generated by potentiostatic anodic electrolysis with theoretically calculated oxygen (assuming 100% FE). GC analysis was carried out on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of one point per second.

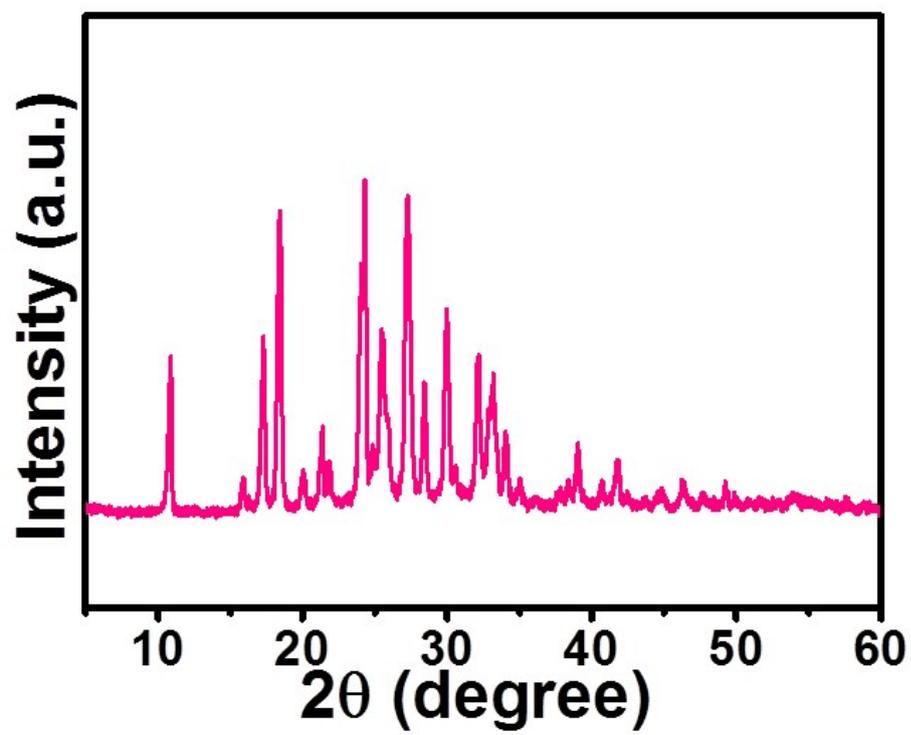


Fig. S1. XRD pattern of pure TCNQ.

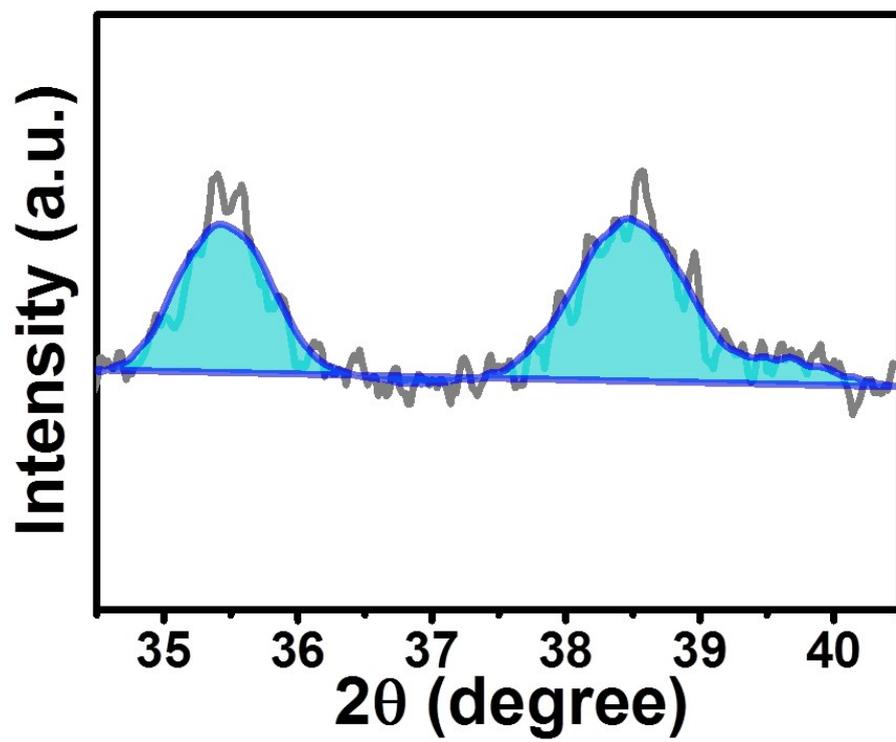


Fig. S2. XRD pattern of CuO in CuO-TCNQ.

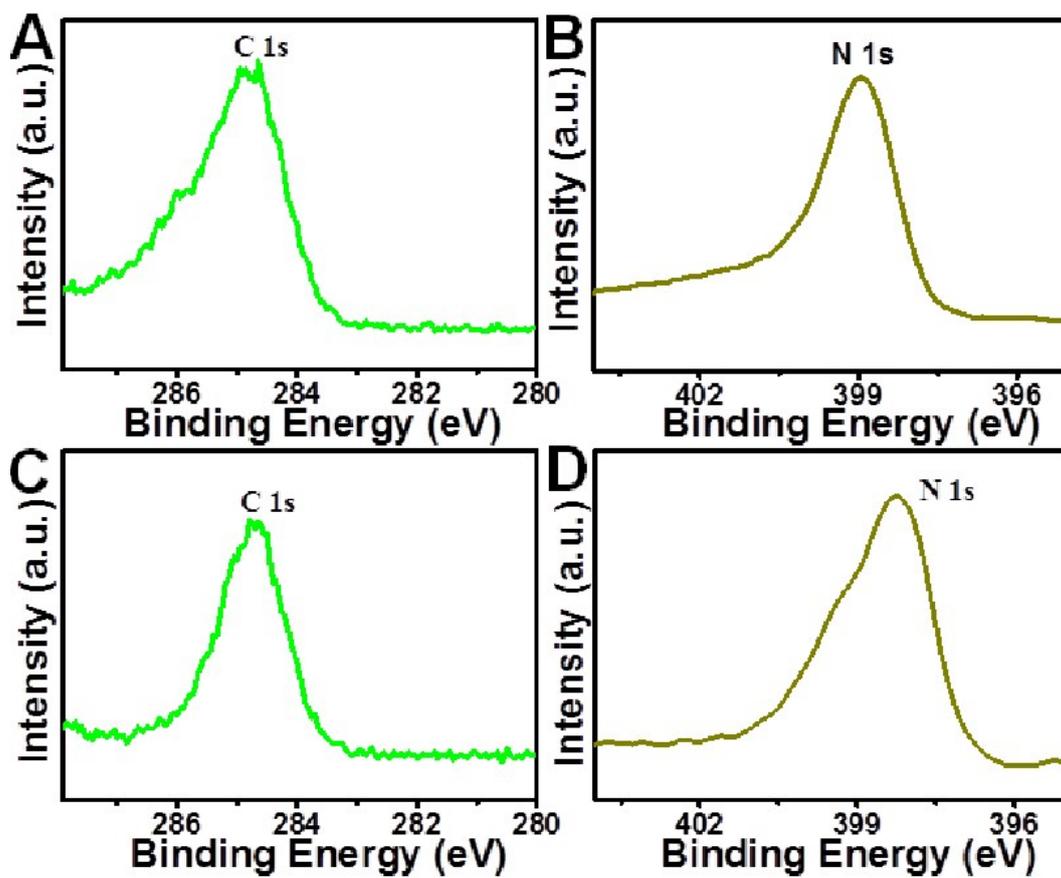


Fig. S3. XPS spectra in the (A, C) C 1s and (B, D) N 1s regions for (A, B) Cu(TCNQ) and (C, D) CuO-TCNQ.

Table S1. Comparison of OER performance for CuO-TCNQ/CF with other non-noble-metal OER catalysts under alkaline conditions.

Catalyst	j (mA cm ⁻²)	η (mV)	Electrolyte	Ref.
CuO-TCNQ/CF	25	317	1.0 M KOH	This work
	50	355		
dendritic copper oxide (Cu/Cu ₂ O/CuO)	25	~ 350	1.0 M NaOH	2
	50	~ 425		
nanostructured Cu oxide	5	550	1.0 M NaOH	2
Cu/Cu(OH) ₂ -CuO nanorods	10	417	0.1 M KOH	3
Cu oxide film	10	430	1 M KOH	4
CuO nanowires	10	530	0.1 M NaOH	5
Cu ₂ O nanowires	10	590	0.1 M NaOH	5
CuO _x nanowires	10	630	0.1 M NaOH	5
2D CuO nanosheet bundles	10	350	1.0 M KOH	6
CuO nanostructure	1	~ 440	0.1 M KOH	7
Cu ₂ O nanostructure	1	~ 485	0.1 M KOH	7
Cu ₂ O/Cu	1	~ 450	0.1 M KOH	8

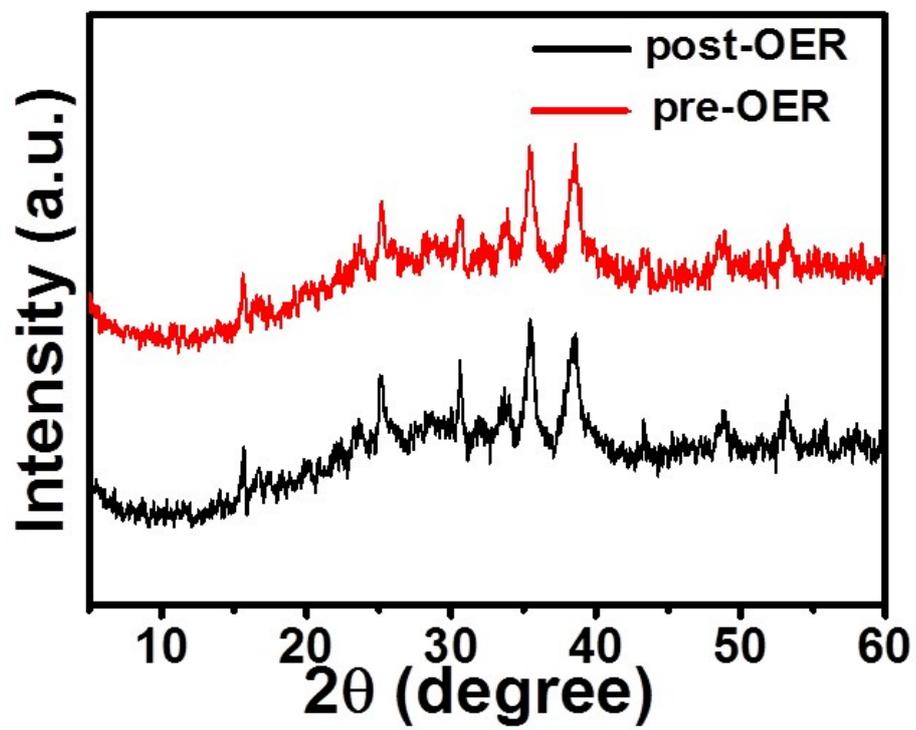


Fig. S4. XRD patterns of CuO-TCNQ before and after OER electrolysis.

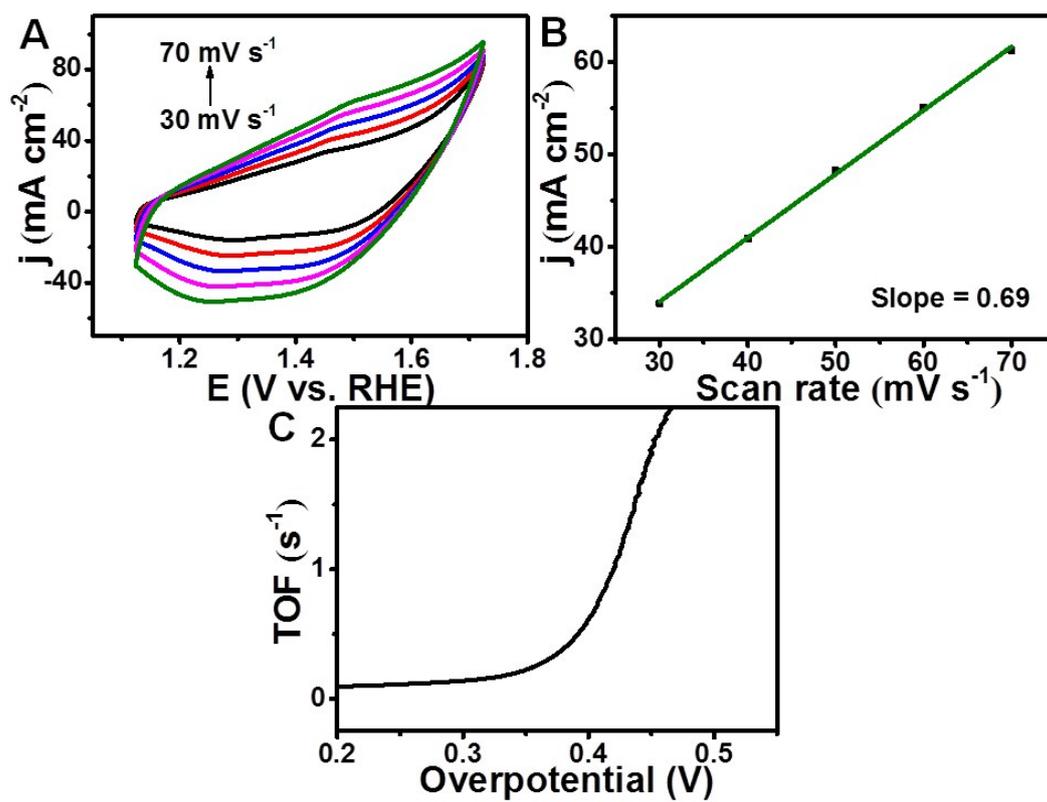


Fig. S5. (A) CVs of CuO-TCNQ/CF at different scan rates in 1.0 M KOH. (B) Oxidation peak current versus scan rate plot for CuO-TCNQ/CF. (C) The relationship between TOF and overpotential.

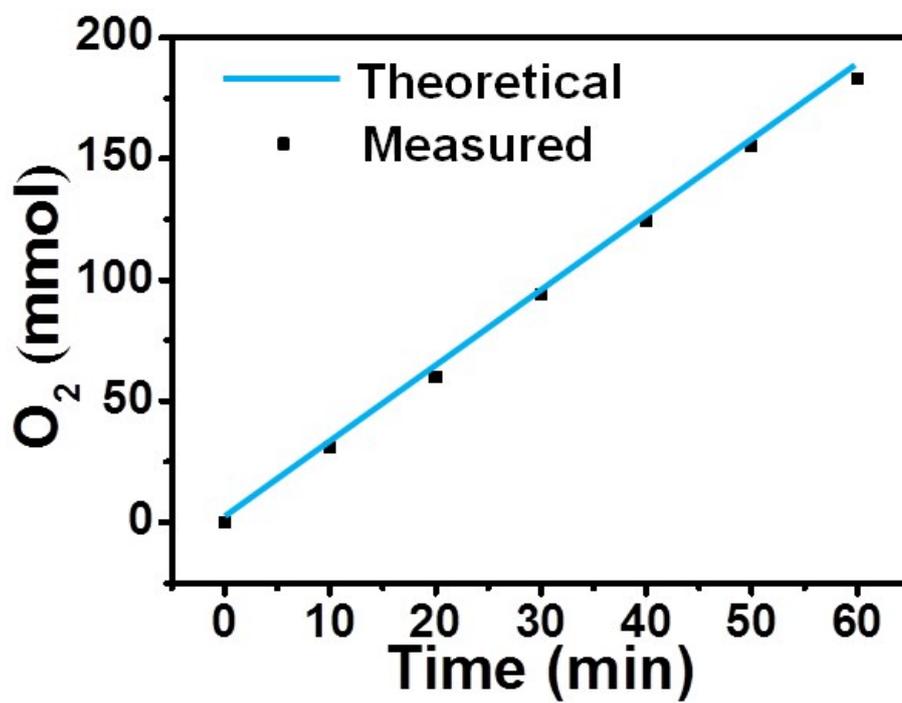


Fig. S6. The amount of gas theoretically calculated and experimentally measured vs. time for oxygen evolution versus time for CuO-TCNQ/CF.

References

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