

Supporting Information

Stabilization of Cu⁺ by tuning CuO-CeO₂ interface for selective electrochemical CO₂ reduction to ethylene

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Experimental section

Materials

All chemicals used in this work were of analytical grade and used as supplied. Commercial Cu₂O (Product number: C108789), Cu(Ac)₂·H₂O (Product number: C108085), Ce(NO₃)₃·6H₂O (Product number: C105376), and KOH (Product number: P112285) were purchased from Aladdin. Carbon powder (CABOT XC72R) was received from CABOT. Nafion solution (5.0 wt%) was supplied by Sigma-Aldrich. Nafion membranes were provided by Alfa Aesar. Deionized water (18.2 megohm·cm) was obtained from a Millipore system. Carbon dioxide gas (99.999% purity) and argon gas (99.999% purity) were both provided by Beijing Haipu Gas Co., Ltd.

Synthesis of CuO-CeO₂/CB

Typically, a specific amount of $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ ethanol solution was first mixed with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and carbon black. The mixture was dispersed in 15 mL of ethanol, which was subjected to bath ultrasonication for 0.5 h to form a uniform dispersion (Table S1). Different amounts of 0.5 M KOH ethanol solution were then slowly added into the dispersion under vigorous magnetic stirring to ensure an appropriate pH value for the reaction system. The system was allowed to react for 5 h in an oil bath at 80 °C. After reaction, the solid products were repeatedly washed with ethanol and water, and then dried at 60 °C for use.

Characterization

X-ray powder diffraction (XRD) was performed with a D/MAX-RC diffractometer operated at 30 kV and 100 mA with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The instrument was equipped with an electron flood and a scanning ion gun. All spectra were calibrated according to the C 1s binding energy at 284.8 eV. Raman spectra were collected with a Renishaw in Via Raman microscope with an He/Ne Laser excitation at 532 nm (2.33 eV). HAADF-STEM was recorded using a JEOL ARM200 microscope with a 200 kV accelerating voltage. STEM samples were prepared by depositing a droplet of suspension onto a Cu grid coated with a Lacey Carbon film. Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were carried out in a quartz tube reactor equipped with a thermal conductivity detector (TCD) using a Micromeritics AutoChem HP 2950 instrument. Before each measurement, the sample was first pre-treated in pure Ar at 200 °C for 30 min. Subsequently, a certain amount of the pre-treated sample was heated in a gas flow (50 cm^3/min) of 10% H_2 in Ar from 50 to 750 °C at a ramp rate of 10 °C/min. CO_2 adsorption isotherms were measured on an Autosorb IQ Station 1 analyzer at 298 K. The sample was degassed at 120 °C for 5 h prior to CO_2 adsorption measurements.

Cathode preparation

Typically, 1.2 mg of catalyst was dispersed in 241.2 μL of solution containing

isopropanol, deionized water, and 5 wt% Nafion solution with a corresponding volume ratio of 120: 120: 1.2 by ultrasonication for 30 min to form a homogeneous ink. The catalyst ink was then loaded onto a carbon paper electrode with an area of 1.2 cm × 1 cm and dried under ambient conditions. For linear sweep voltammograms in Ar- or CO₂-saturated 0.1 M KHCO₃ solution, 1 mg of a catalyst was dispersed in the mixture of 100 μL of ethanol, 100 μL of deionized water, and 100 μL of Nafion solution (1 wt%). Then the mixture was ultrasonicated for 30 min to form a homogeneous ink. 7.95 μL of the dispersion ink was then loaded onto glassy carbon electrode and dried under ambient conditions.

Electrochemical measurements

Controlled potential electrolysis of CO₂ was tested in an H-type cell system, which was separated by a Nafion 117 membrane. Before ECR tests, the Nafion membrane was pre-treated by heating in 5% H₂O₂ aqueous solution and 0.5 M H₂SO₄ at 80 °C for 1 h, respectively. Then the Nafion membrane was immersed in deionized water under ambient conditions for 30 min and then washed with deionized water. Toray Carbon fiber paper with a size of 1.2 cm × 1 cm was used as working electrode. Pt wire and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. The potentials were controlled by an electrochemical working station (CHI 760E, Shanghai CH Instruments Co., China). All potentials in this study were measured against the Ag/AgCl reference electrode (in 3 M KCl solution) and converted to the RHE reference scale by

$$E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.21 \text{ V} + 0.0591 \times \text{pH} \quad (\text{Eq. S1})$$

Electrocatalytic CO₂ reduction was conducted in CO₂-saturated 0.1 M KHCO₃ solution at room temperature and atmospheric pressure. When saturated with CO₂, the pH of the electrolyte was 6.8. CO₂ was purged into the KHCO₃ solution for at least 30 min to remove residual air in the reservoir, then controlled potential electrolysis was performed at each potential for 60 min.

Linear sweep voltammograms in Ar- or CO₂ atmosphere were carried out in a three-electrode system using Ag/AgCl as reference electrode, Pt wire as counter electrode, and glassy carbon as working electrode on a CHI 760E potentiostat (CHI 760E., Shanghai CH Instruments Co., China). Rotating disk electrode (RDE) experiments were run on an AFMSRCE RDE control system (Pine Inc., USA). The electrolyte is 0.1 M KHCO₃ solution with Ar or CO₂ purged for at least 30 min.

Gaseous products from the cell were analyzed using an Agilent 7890B GC system. Two thermal conductivity detectors and a flame ionization detector were applied to analyze and differentiate the injected samples. To characterize the gas product, 20 mL of the gas products in the dead volume of a gas bag (~1 L) was injected into the GC under identical experimental conditions (e.g., pressure, temperature, and time) using a sample lock syringe. CO and H₂ peaks were detected at 11.4 and 3.7 min, respectively. The liquid products such as formic acid were quantified by ¹H NMR (400 MHz) using a solvent pre-saturation technique to suppress the water peak. FE was determined from the amount of charge passed to produce each product divided by the total amount of charge passed at a specific time or during the overall run.

Calculation details

All calculations were performed using spin-polarized density functional theory (DFT) methods implemented in the Vienna Ab initio Simulation Package (VASP) with projector-augmented wave pseudopotential (PAW).¹⁻³ We used revised PBE (RPBE) functional developed by Hammer *et al.*^{4, 5} Cutoff energy was set to 400 eV. The convergence criteria for the electronic energy difference and forces are 10⁻⁵ eV and 0.05 eV / Å, respectively.

The Cu(100), Cu₂O(100) and CuO(100) were modelled by (3 x 3) surface supercell with three layers. The bottom two layers were fixed at their optimized bulk structure, while other atoms were fully relaxed. All slab models include more than 18 Å of vacuum in the c-axis. A (2 x 2 x 1) Monkhorst-Pack mesh of k-points were sampled.⁶

Table S1. The recipes for synthesizing CuO-CeO₂/CB samples by tuning CeO₂ mass content at a constant CuO loading of 6.0 wt%.

Precursor account	CeO ₂ mass content (wt%)						CeO ₂ /CB
	0.0	10.0	20.0	30.0	40.0	50.0	
$C_{\text{Cu}(\text{Ac})_2}/\text{M}$	0.02	0.02	0.02	0.02	0.02	0.02	0.0
$V_{\text{Cu}(\text{Ac})_2}/\mu\text{L}$	700.0	700.0	700.0	700.0	700.0	700.0	0.0
$m_{\text{Ce}(\text{NO}_3)_3}/\text{mg}$	0.0	4.71	9.42	14.00	18.84	23.55	14.00
m_{CB}/mg	17.55	15.68	13.82	12.00	10.08	8.22	13.16
C_{KOH}/M	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$V_{\text{KOH}}/\mu\text{L}$	300.0	300.0	300.0	300.0	300.0	300.0	300.0

Table S2. The recipes for synthesizing CuO-CeO₂/CB samples by tailoring CuO mass content at a constant CeO₂ loading of 30.0 wt%.

Precursor account	CuO mass content (wt%)				
	0.75	1.5	3.0	6.0	12.0
$C_{\text{Cu}(\text{Ac})_2}/\text{M}$	0.02	0.02	0.02	0.02	0.02
$V_{\text{Cu}(\text{Ac})_2}/\mu\text{L}$	88.0	175.0	350.0	700.0	1400.0
$m_{\text{Ce}(\text{NO}_3)_3}/\text{mg}$	14.0	14.0	14.0	14.0	14.0
m_{CB}/mg	12.98	12.84	12.56	12.0	10.88
C_{KOH}/M	0.5	0.5	0.5	0.5	0.5
$V_{\text{KOH}}/\mu\text{L}$	240.0	260.0	280.0	300.0	350.0

Table S3. The ECR activity optimized by altering the concentration of the copper salt precursor.

Sample	$C_{\text{Cu}(\text{Ac})_2}/\text{M}$	$\text{FE}_{\text{C}_2\text{H}_4}/\%$
CuO-CeO ₂ /CB(0.01)	0.01	41.2
CuO-CeO ₂ /CB(0.02)	0.02	50.0
CuO@CeO ₂ /CB(0.04)	0.04	35.8

Table S4. The relative percentages of Cu⁰, Cu⁺, and Cu²⁺ in CuO-CeO₂/CB samples treated at different conditions based on XPS estimations.

Catalyst	Cu ⁰ (%)	Cu ⁺ (%)	Cu ²⁺ (%)
CuO-CeO ₂ /CB-fresh	0.0	23.4	76.6
CuO-CeO ₂ /CB-Ar_200	5.6	19.6	74.8
CuO-CeO ₂ /CB-H ₂ O(g)_200	5.3	19.1	75.6
CuO-CeO ₂ /CB-8.0% H ₂ /Ar_200	7.6	18.4	74.0
CuO-CeO ₂ /CB-Air_200	0	16.5	83.5

Table S5. The ECR activity optimized by modulating the feeding sequence of the metal salt precursors.

Sample	Feeding sequence _{metal salt precursors}	$\text{FE}_{\text{C}_2\text{H}_4}/\%$
CeO ₂ @CuO/CB	First: Cu(Ac) ₂ ·H ₂ O + CB Secondly: Ce(NO ₃) ₃ ·6H ₂ O	22.0
CuO-CeO ₂ /CB	Cu(Ac) ₂ ·H ₂ O + Ce(NO ₃) ₃ ·6H ₂ O + CB	50.0

First: $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} + \text{CB}$

$\text{CuO}@/\text{CeO}_2/\text{CB}$

37.8

Secondly: $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$

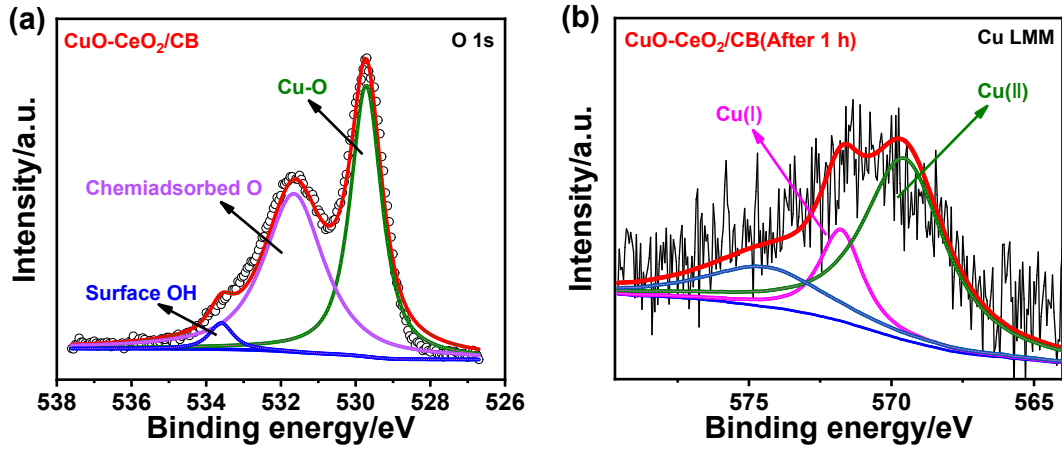


Fig. S1 (a) O 1s XPS spectrum of CuO-CeO₂/CB. (b) Cu LMM XPS spectrum of CuO-CeO₂/CB after 1 h of electrolysis.

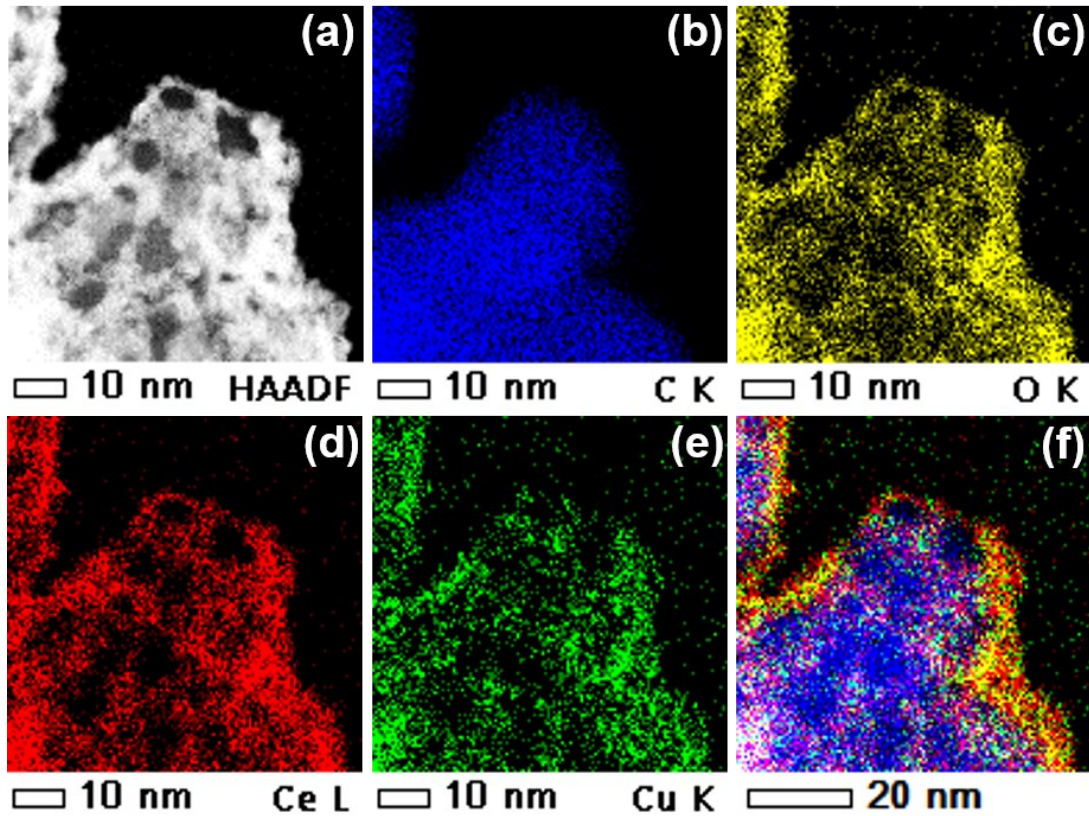


Fig. S2 (a) HAADF-STEM image of CuO-CeO₂/CB. EDS elemental maps of (b) C, (c) O, (d) Ce, (e) Cu, and (f) EDS elemental map of overlay over the region shown in image (a).

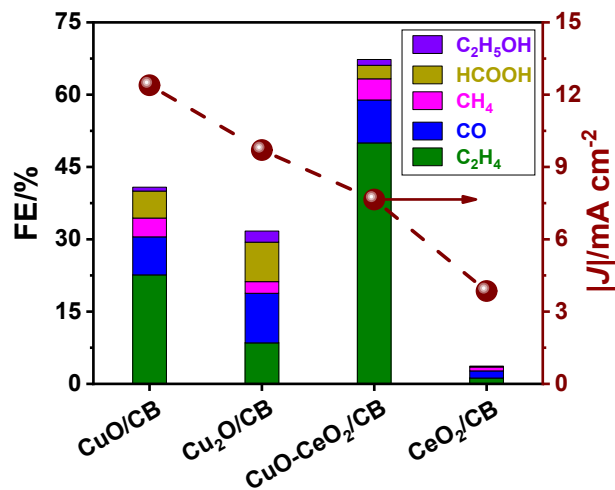


Fig. S3 FE and current density at -1.1 V (vs. RHE) of CuO/CB, CuO-CeO₂/CB, and CeO₂/CB along with commercial Cu₂O particles deposited on CB (Cu₂O/CB).

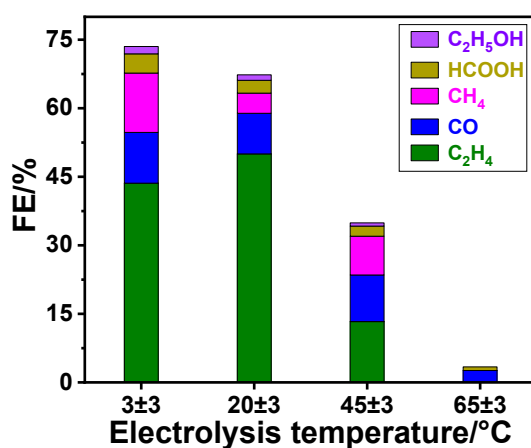


Fig. S4 FE of different ECR products as a function of electrolysis temperature over CuO-CeO₂/CB at -1.1 V (vs. RHE).

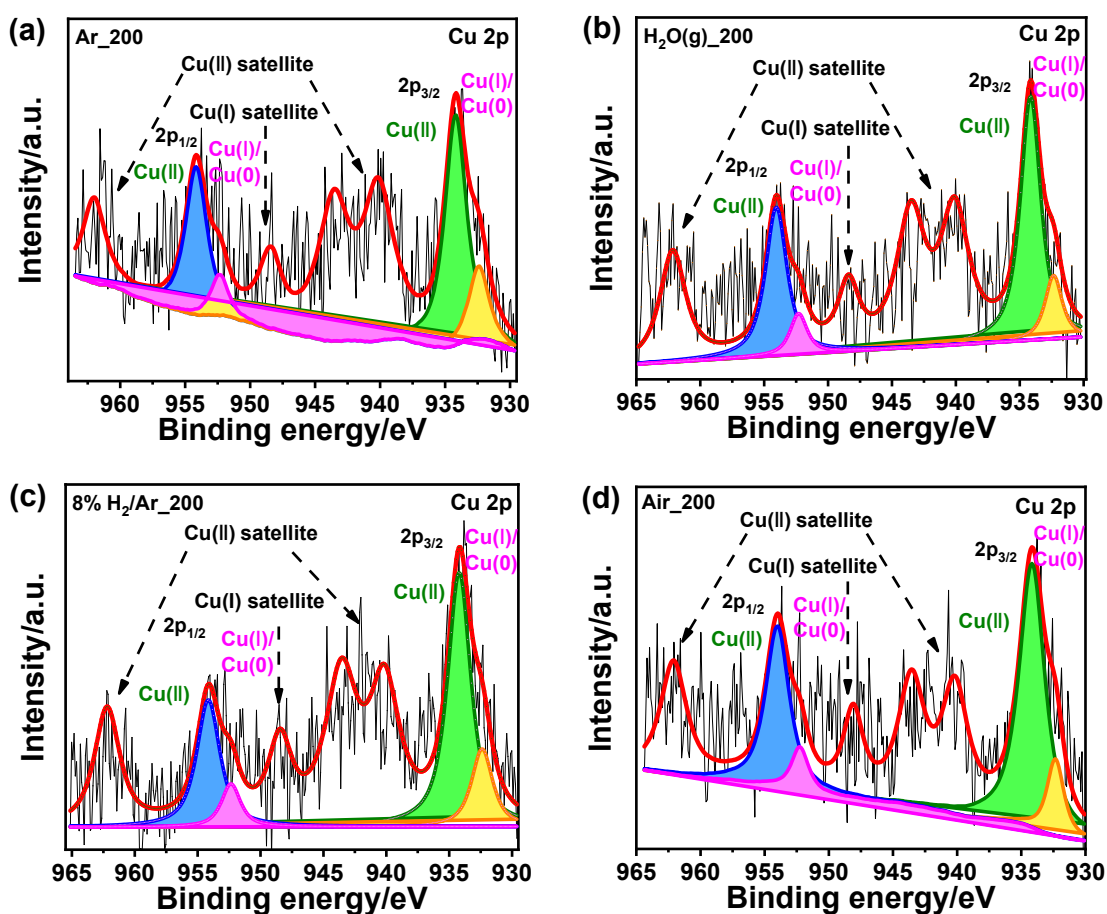


Fig. S5 Cu 2p XPS spectra of CuO-CeO₂/CB samples treated under (a) Ar, (b) water vapor, (c) 8.0% H₂/Ar, and (d) air at 200 °C for 1 h.

References

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