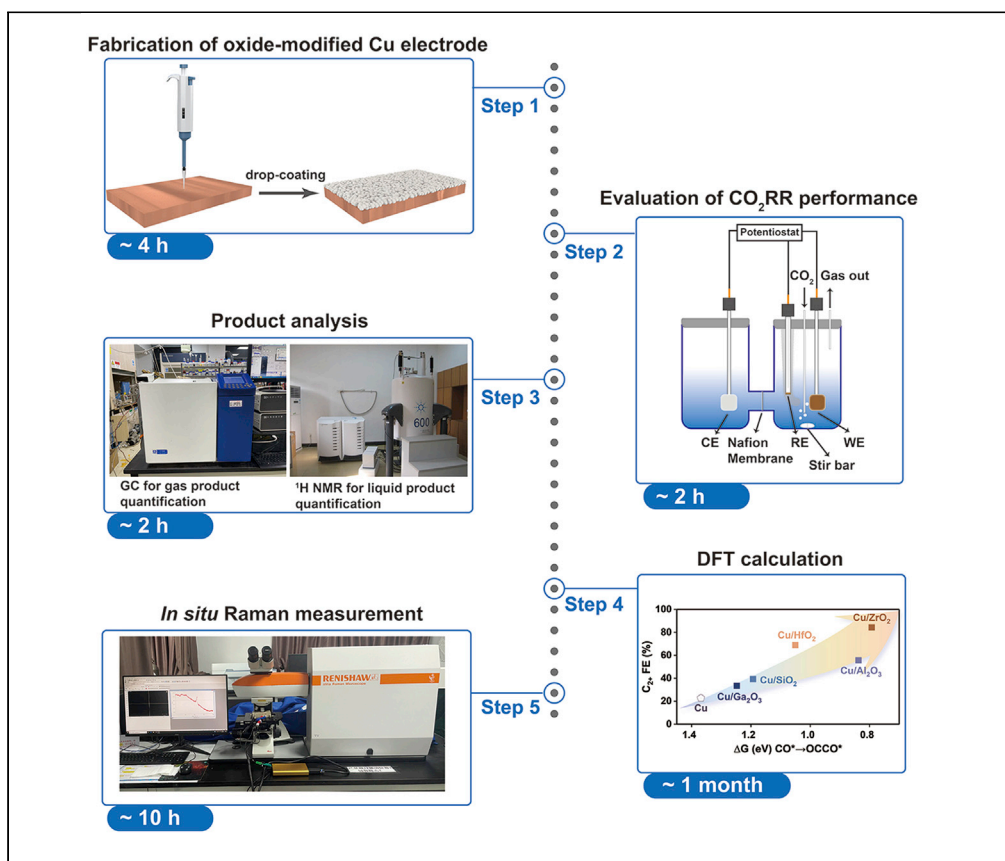


Protocol

Protocol for fabrication and evaluation of oxide-modified Cu foils as heterostructured electrodes for electrochemical CO₂ reduction



Heterostructured catalysts based on Cu and oxides are promising for the efficient conversion of CO₂ to multi-carbon products. In this protocol, we describe the fabrication and characterization of Cu/oxide heterostructured catalysts and the evaluation approach of electrochemical CO₂ reduction reaction (CO₂RR) performance in an H-type cell. We also provide the details of *in situ* surface-enhanced Raman measurement and theoretical calculations. The protocol can be useful for constructing self-supported electrodes and assessing the CO₂RR performance of as-fabricated electrodes.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

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Highlights
Detailed protocol for preparation and characterization of oxide-modified Cu electrode

Evaluate the CO₂RR performance of heterostructured catalysts in an H-type cell

Detailed calculation approach for the Faradaic efficiency of CO₂RR products

Detailed *in situ* surface-enhanced Raman characterization approach for CO₂RR

Li et al., STAR Protocols 3, 101637
September 16, 2022 © 2022
The Author(s).
<https://doi.org/10.1016/j.xpro.2022.101637>



Protocol

Protocol for fabrication and evaluation of oxide-modified Cu foils as heterostructured electrodes for electrochemical CO₂ reductionXiaotong Li,^{1,2,*} Qian Liu,¹ Jianghao Wang,¹ and Hao Bin Wu^{1,3,*}¹Institute for Composites Science Innovation (InCSI) and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China²Technical contact³Lead contact*Correspondence: ixt0408@zju.edu.cn (X.L.), hbwu@zju.edu.cn (H.B.W.)
<https://doi.org/10.1016/j.xpro.2022.101637>

SUMMARY

Heterostructured catalysts based on Cu and oxides are promising for the efficient conversion of CO₂ to multi-carbon products. In this protocol, we describe the fabrication and characterization of Cu/oxide heterostructured catalysts and the evaluation approach of electrochemical CO₂ reduction reaction (CO₂RR) performance in an H-type cell. We also provide the details of *in situ* surface-enhanced Raman measurement and theoretical calculations. The protocol can be useful for constructing self-supported electrodes and assessing the CO₂RR performance of as-fabricated electrodes.

For complete details on the use and execution of this protocol, please refer to Li et al. (2022).

BEFORE YOU BEGIN

Electrochemical measurement in a three-electrode H-type cell is a conventional approach to evaluate the performance and properties of electrocatalysts. Herein, the fabrication and performance evaluation of oxide-modified Cu electrodes are described in this protocol following a three-step procedure. At first, an oxide-modified Cu electrode is prepared by a drop-coating method; then the self-supported electrode is used as working electrode directly in an H-type cell to electrolysis CO₂; afterward, the products of CO₂RR are quantified by online gas chromatography (GC) and ¹H nuclear magnetic resonance (¹H NMR). Before one begins, the following preparations need to be performed.

Pretreatment of Nafion membrane (for electrochemical CO₂ reduction device)

⌚ Timing: 5 h

1. Immerse Nafion 115 membrane in a 5 wt.% H₂O₂ aqueous solution at 80°C for 1 h to remove organic impurities.
2. Wash the membrane with deionized water (DI water) several times and further immerse in DI water at 80°C for 1 h to remove residual H₂O₂.
3. Immerse the membrane in 1 M H₂SO₄ aqueous solution at 80°C for 1 h to convert the membrane to H⁺-type.
4. Wash the membrane with DI water several times and immerse in DI water at 80°C for 1 h, and repeat this operation twice to remove residual H₂SO₄.



KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Potassium formate (HCOOK, 99%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 590-29-4
Methanol (CH ₃ OH, 99.5%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 67-56-1
Potassium acetate (CH ₃ COOK, 99.9% metals basis)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 127-08-2
Ethanol (C ₂ H ₅ OH, 99.7%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 64-17-5
Acetone (CH ₃ COCH ₃ , 99.5%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 67-64-1
Acetaldehyde (CH ₃ CHO, 99.5%)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 75-07-0
Propionaldehyde (C ₂ H ₅ CHO, 98%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 123-38-6
Ethylene glycol (OHCH ₂ CH ₂ OH, 99.5%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 107-21-1
n-Propanol (C ₃ H ₇ OH, 99.5%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 71-23-8
Dimethyl sulfoxide (C ₂ H ₆ SO, 99.7% with molecular sieves, water ≤ 50 ppm)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 67-68-5
Deuterium oxide (D ₂ O, 99.9% D, for NMR)	Energy Chemical (Shanghai, China)	CAS: 7789-20-0
Copper foil (Cu, 99.5%, 0.1 mm thickness)	Tianjin Shentai Chemical Industry Co., Ltd. (Tianjin, China)	CAS: 7440-50-8
Zirconium dioxide (ZrO ₂ , 99.99% metal basis, 40–60 nm)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 1314-23-4
Silicon dioxide (SiO ₂ , 99.5%, 20–30 nm)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 14808-60-7
Hafnium oxide (HfO ₂ , 99.99% metal basis, 40–60 nm)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 12055-23-1
Gallium oxide (Ga ₂ O ₃ , 99.8% metal basis, 500 nm)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 12024-21-4
Aluminum oxide (Al ₂ O ₃ , 99.99% metal basis, 20–30 nm)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 1344-28-1
Potassium bicarbonate (KHCO ₃ , 99.5%)	Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China)	CAS: 298-14-6
Potassium phosphate dibasic (K ₂ HPO ₄ , 98%)	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)	CAS: 7758-11-4
Potassium chloride (KCl, 99.5%)	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	CAS: 7447-40-7
DuPont™ Nafion® PFSA polymer dispersions (D-520, 5% in a mixture of lower aliphatic alcohol and water)	DuPont company (America)	N/A
Proton exchange membrane (Nafion 115)	DuPont company (America), pretreatment conditions are shown in before you begin .	N/A
CO ₂ gas (99.995%)	N/A	N/A
Ar gas (99.99%)	N/A	N/A
Standard gas (containing H ₂ , CO, CH ₄ , C ₂ H ₄ , C ₂ H ₆ , N ₂)	N/A	N/A
3,000 mesh silicon carbide paper	KAFUWELL (Hangzhou, China)	N/A
Deionized water (18.25 MΩ cm)	Made by the pure water machine	N/A
Au@SiO ₂ (Au core 55 nm, SiO ₂ shell thickness 2 nm)	Shiyanjia Lad (Hangzhou, China)	FMA2109073
Tape for XAFS sample preparation	3M Scotch	N/A
Teflon tape	N/A	N/A
Software and algorithms		
Vienna ab initio simulation package (VASP)	N/A	https://www.vasp.at/
Other		
Gas chromatography (GC)	FULI	9790II
¹ H nuclear magnetic resonance (NMR, 600 MHz)	Agilent	DD2-600
Scanning electron microscopy equipped with Energy dispersive spectrometer (SEM-EDS)	SEM: Hitachi EDS: Oxford	SU8010 X-max80
Transmission electron microscope equipped with Energy dispersive spectrometer (TEM-EDS)	TEM: JEOL EDS: Oxford	JEM-2100F X-MaxN 80T IE250
Ultra-high resolution Scanning electron microscopy-Focused ion beam equipped with Energy dispersive spectrometer (SEM-FIB-EDS)	TESCAN	GAIA3
X-ray diffraction (XRD)	PANalytical	PANalytical X'Pert PRO

(Continued on next page)

Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)	Thermo Fisher Scientific	Escalab 250Xi
X-ray absorption fine structure (XAFS)	Beijing Synchrotron Radiation Facility (BSRF)	1W1B station
Raman	Renishaw	inVia Reflex Raman
Electrochemical station	BioLogic	MPG2
Electrochemical station	CH Instruments	CHI 760E
Ultrasonic cleaning machine	Prima	PM2-600TD
Pure water machine	ULUPURE	UPH-II-10T
Analytical balance	OHAUS	PX124ZH
High-speed centrifuge	Hettich	Universal 320
Gas mass flow controller (MFC)	HORIBA	STEC S500
H-type cell	Gaoss Union	N/A
<i>In situ</i> Raman electrolytic cell	Gaoss Union	C031-3

MATERIALS AND EQUIPMENT

ZrO₂ inks with different concentration

Reagent	Final concentration	Amount
ZrO ₂	0.5, 1, 2.5, 5, 10, 20 mg/mL	0.5, 1, 2.5, 5, 10, 20 mg
DI water	N/A	480 μL
Ethanol	N/A	480 μL
Nafion	N/A	40 μL
Total	N/A	1 mL

Note: Temperature: 20°C–30°C, Storage Duration: ~5 h.

HfO₂ ink

Reagent	Final concentration	Amount
HfO ₂	10 mg/mL	10 mg
DI water	N/A	480 μL
Ethanol	N/A	480 μL
Nafion	N/A	40 μL
Total	N/A	1 mL

Note: Temperature: 20°C–30°C, Storage Duration: ~5 h.

Al₂O₃ ink

Reagent	Final concentration	Amount
Al ₂ O ₃	10 mg/mL	10 mg
DI water	N/A	480 μL
Ethanol	N/A	480 μL
Nafion	N/A	40 μL
Total	N/A	1 mL

Note: Temperature: 20°C–30°C, Storage Duration: ~5 h.

SiO₂ ink		
Reagent	Final concentration	Amount
SiO ₂	10 mg/mL	10 mg
DI water	N/A	480 μL
Ethanol	N/A	480 μL
Nafion	N/A	40 μL
Total	N/A	1 mL

Note: Temperature: 20°C–30°C, Storage Duration: ~5 h.

Ga₂O₃ ink		
Reagent	Final concentration	Amount
Ga ₂ O ₃	10 mg/mL	10 mg
DI water	N/A	480 μL
Ethanol	N/A	480 μL
Nafion	N/A	40 μL
Total	N/A	1 mL

Note: Temperature: 20°C–30°C, Storage Duration: ~5 h.

KHCO₃ solution		
Reagent	Final concentration	Amount
KHCO ₃	0.1 M	0.1 mol
DI water	N/A	1 L
Total	N/A	1 L

Note: Temperature: 25°C, Storage Duration: ~1 week.

KCl solution		
Reagent	Final concentration	Amount
KCl	0.1 M	0.1 mol
DI water	N/A	1 L
Total	N/A	1 L

Note: Temperature: 25°C, Storage Duration: ~1 week.

K₂HPO₄ solution		
Reagent	Final concentration	Amount
K ₂ HPO ₄	0.1 M	0.1 mol
DI water	N/A	1 L
Total	N/A	1 L

Note: Temperature: 25°C, Storage Duration: ~1 week.

DMSO dissolved in D₂O

Reagent	Final concentration	Amount
DMSO	2 mM	0.2 mmol
D ₂ O	N/A	100 mL
Total	N/A	100 mL

Note: Temperature: 0°C–8°C, Storage Duration: ~1 month.

Four standard solutions for liquid products

Reagent	Final concentration	Amount
HCOOK	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
CH ₃ OH	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
CH ₃ COOK	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
C ₂ H ₅ OH	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
CH ₃ CHO	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
CH ₃ COCH ₃	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
C ₂ H ₅ CHO	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
OHCH ₂ CH ₂ OH	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
C ₃ H ₇ OH	15, 7.5, 1.5, 0.5 mM	1.5, 0.75, 0.15, 0.05 mmol
DI water	N/A	100 mL
Total	N/A	100 mL

Note: The concentrations of nine reagents are the same. Temperature: 25°C. It should be freshly prepared.

Low concentration standard gas

Reagent	Final concentration	Amount
H ₂	103 ppm	N/A
CO	104 ppm	N/A
CH ₄	104 ppm	N/A
C ₂ H ₄	104 ppm	N/A
C ₂ H ₆	104 ppm	N/A
N ₂ as carrier gas	n/a	N/A
Total	n/a	N/A

Note: Storage Duration: ~1 year.

High concentration standard gas

Reagent	Final concentration	Amount
H ₂	1,005 ppm	N/A
CO	1,007 ppm	N/A
CH ₄	1,008 ppm	N/A
C ₂ H ₄	1,014 ppm	N/A
C ₂ H ₆	1,018 ppm	N/A
N ₂ as carrier gas	N/A	N/A
Total	N/A	N/A

Note: Storage Duration: ~1 year.

Stock reagent

Reagent	Storage conditions
Mechanically polished Cu foil	It should be freshly prepared.

Instruments (for material Characterization):

Technique	Condition
X-ray diffraction (XRD)	Using an X'Pert PRO, PANalytical diffractometer with a Cu K α radiation source at a scan speed of 5° min ⁻¹ .
Scanning electron microscopy (SEM)	Acceleration voltage: 30 kV
Transmission electron microscope (TEM)	Acceleration voltage: 200 kV
Focused ion beam (FIB)	Gallium ion source
Raman	Using an inVia Reflex Raman microscope (Renishaw) equipped with a diode laser (633 nm) and a water immersion objective (50 ×) in a modified cell. Each spectrum was recorded using 50% laser power, 10s of exposure time, and by averaging 2 scans in extended mode.

Instruments (for CO₂RR):

Technique	Condition
Gas chromatography (GC)	Warming procedure: warm-up from 65°C (holding for 3.6 min) to 125°C with 15°C/min, then hold for 7.6 min at 125°C, and finally cool down to 65°C. Each spectrum is recorded with one warming procedure.
¹ H nuclear magnetic resonance (NMR)	Resonance frequency: 600 MHz
Electrochemical measurement	Condition
Cyclic voltammetry test (CV)	Perform at the potential ranging from +0.2 V to -0.6 V vs RHE at a scan rate of 50 mV s ⁻¹ for forty cycles
Linear sweep voltammetry test (LSV)	Perform at the potential ranging from -0.61 V to -1.81 V vs Ag/AgCl at a scan rate of 5 mV s ⁻¹
Chronoamperometry test (CA)	Perform at a selected cathodic potential ranging from -0.8 V to -1.1 V vs RHE for 1 h
Chronopotentiometry test (CP)	Perform at -17.2 mA cm ⁻²
iR-compensated	The solution resistances at all potential are automatically compensated by an electrochemical workstation (85% iR-compensated)

STEP-BY-STEP METHOD DETAILS

Fabrication of oxide-modified Cu electrode

⌚ Timing: 2 h

ZrO₂-modified Cu electrode is prepared by a drop-coating method according to the following steps.

- Mechanically polish Cu foil with a geometric area of 1.44 cm² (0.4 cm × 1.8 cm × 2 sides) by 3,000 mesh silicon carbide paper to remove pristine oxide layer and surface impurities.
 - Ultrasonically wash in DI water at 25°C for 6 min.
 - Wipe with dust-free paper to remove excess water (Figures 1A and 1B).
 - Define the working area of 0.64 cm² (0.4 cm × 0.8 cm × 2 sides) by encapsulating the Cu foil with Teflon tape (Figure 1C).

Note: Mechanically polished Cu foil should be prepared freshly for the following procedure to avoid re-oxidation of the Cu surface.

- Prepare the ZrO₂ ink.
 - Weigh 10 mg of ZrO₂ on an analytical balance and carefully transfer to a 2 mL centrifuge tube.
 - Add 480 μ L of ethanol, 480 μ L of DI water, and 40 μ L of Nafion solution (5% in a mixture of lower aliphatic alcohol and water) using a pipettor sequentially.
 - Sonicate the suspension using the ultrasonic cleaning machine at 25°C for 1–2 h to obtain a uniformly dispersed suspension (named ZrO₂ ink).

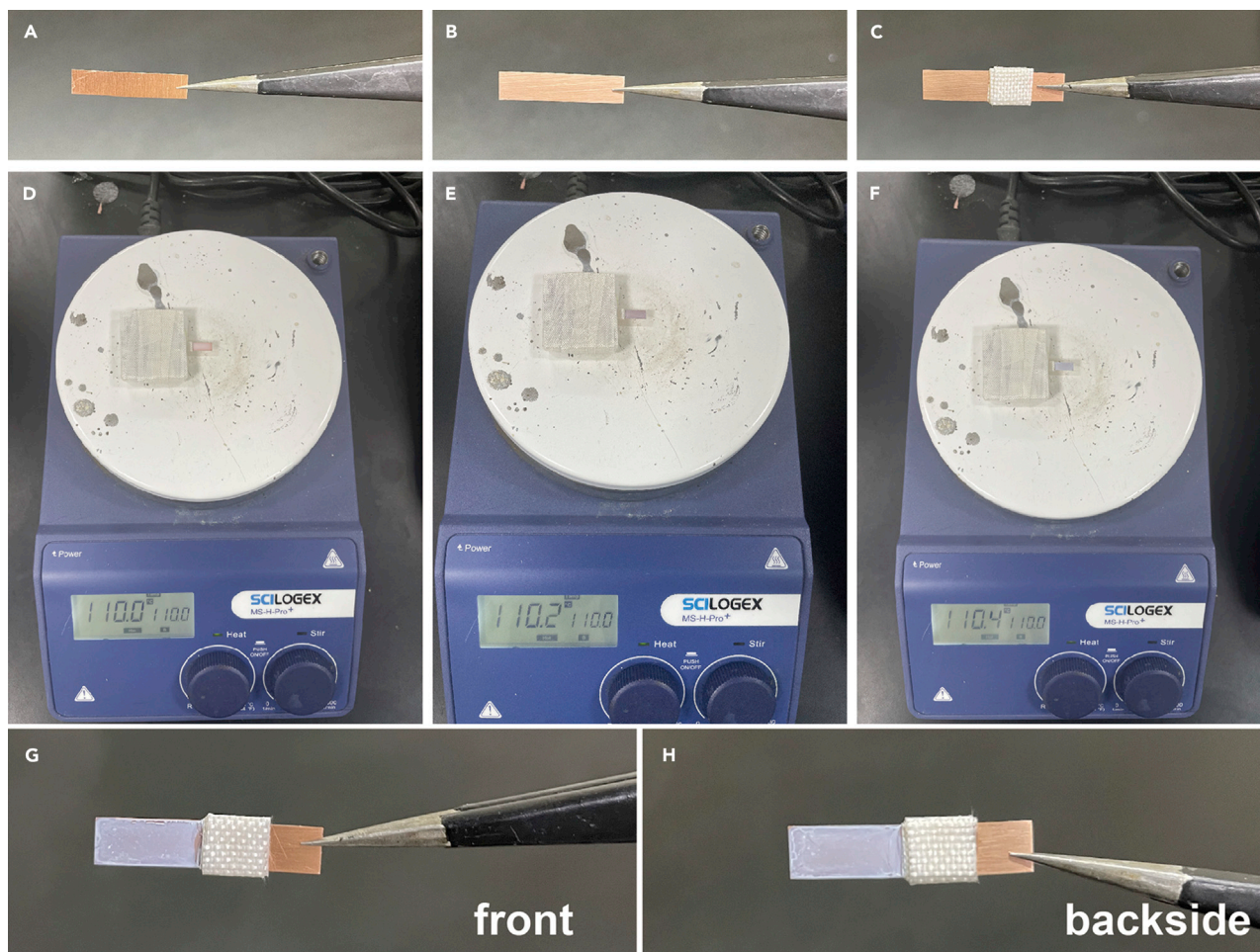


Figure 1. Photographs of the ZrO_2 -modified Cu electrode preparation

(A–H) Photo images of (A) pristine Cu foil, (B) mechanically polished Cu foil, (C) Cu foil with a defined working area by encapsulating the Cu foil with Teflon tape, (D) drop-coating and drying 16 μ L of ZrO_2 ink on one side of Cu on a hot plate at 110°C, (E) ZrO_2 -modified Cu electrode after first drying on a hot plate at 110°C (16 μ L of ZrO_2 ink), (F) ZrO_2 -modified Cu electrode after second drying on a hot plate at 110°C (32 μ L in total), (G, H) the front and back sides of the Cu/ ZrO_2 electrode.

Note: ZrO_2 ink solution should be sonicated for a few minutes before each use to avoid settling of ZrO_2 nanoparticles.

- Drop-coat 32 μ L of ZrO_2 ink on each side of Cu foil (64 μ L in total) and dry in air on a hot plate at 110°C for 10 min to obtain the ZrO_2 -modified Cu electrode (Figures 1D–1H).

Note: Cu foil is put on a hot plate before heating to 110°C, and the hot plate heats from 25°C to 110°C in 40 s. And the total 32 μ L of ZrO_2 ink is dropped onto the Cu foil in two portions, and the second portion is dropped onto the electrode after complete drying. Finally, the ZrO_2 -modified Cu (named Cu/ ZrO_2) electrode is dried on a hot plate for an additional 10 min.

- Prepare other oxide-modified Cu electrodes according to the following step, which is the same as the preparation of ZrO_2 -modified Cu electrode (steps 1–3).
 - Mechanically polish Cu foil.
 - Weigh 10 mg of HfO_2 , Al_2O_3 , SiO_2 , and Ga_2O_3 nanoparticles and disperse in the mixture of DI water, ethanol, and Nafion solution to prepare HfO_2 , Al_2O_3 , SiO_2 , and Ga_2O_3 inks, respectively.

- c. Drop-coat 32 μL of oxide inks on each side of mechanically polished Cu foil and dry in air on a hot plate at 110°C to prepare the corresponding oxide-modified Cu electrodes.
5. Prepare ZrO_2 -modified Cu electrodes with different ZrO_2 loadings (named $\text{Cu/ZrO}_2\text{-X}$, where X is the ZrO_2 loadings (mg); default Cu/ZrO_2 refers to $\text{Cu/ZrO}_2\text{-1}$) according to the following step which is the same as the preparation of ZrO_2 -modified Cu electrode (steps 1–3).
 - a. Mechanically polish the Cu foil.
 - b. Weigh 0.5, 1, 2.5, 5, and 20 mg of ZrO_2 nanoparticles and disperse in the mixture of DI water, ethanol, and Nafion solution to prepare ZrO_2 inks with different concentrations of ZrO_2 , respectively.
 - c. Drop-coat 32 μL of ZrO_2 inks on each side of mechanically polished Cu foil and dry in air on a hot plate at 110°C to prepare the ZrO_2 -modified Cu electrodes with different loadings.

Note: Since 40 mg of ZrO_2 nanoparticles are difficult to be dispersed uniformly in 1 mL Nafion-ethanol-aqueous solution, the $\text{Cu/ZrO}_2\text{-4}$ electrode is prepared by drop-coating 64 μL of ZrO_2 inks (20 mg/mL) on each side of mechanically polished Cu foil (128 μL in total). Moreover, the above-mentioned ZrO_2 ink solution should be sonicated for a few minutes before each use to avoid the settling of ZrO_2 nanoparticles.

Fabrication of surface-reconstructed Cu electrode (named $\text{Cu-Cu}_2\text{O-X}$)

⌚ Timing: 2 h

Surface-reconstructed Cu electrode is prepared in two steps. The first step is the preparation of ZrO_2 -modified Cu electrode ($\text{Cu/ZrO}_2\text{-X}$). The second step is to remove the ZrO_2 coating on the Cu surface by sonication to expose the reconstructed Cu surface.

6. Prepare surface-reconstructed Cu electrode.
 - a. Prepare the $\text{Cu/ZrO}_2\text{-X}$ electrode according to step 5.
 - b. Remove the Teflon tape on the electrode.
 - c. Immerse the $\text{Cu/ZrO}_2\text{-X}$ electrode in a mixture of DI water and ethanol (1:1 by volume) and sonicate until the ZrO_2 coating is completely removed (approximately 10 min).
 - d. Wipe with dust-free paper to remove excess water and ethanol.
 - e. Confine the working area of 0.64 cm^2 by encapsulating the electrode with Teflon tape (Figure 2).
 - f. Dry in air on a hot plate at 110°C for 10 min to completely remove residual ethanol and water.

Note: $\text{Cu-Cu}_2\text{O-X}$ was harvested from $\text{Cu/ZrO}_2\text{-X}$, where X is the loading of ZrO_2 .

⚠ **CRITICAL:** The final drying operation at 110°C is essential to avoid introducing ethanol impurities into the CO_2RR measurement.

Fabrication of ZrO_2 -modified reconstructed Cu electrode (named $\text{Cu/ZrO}_2\text{-X-Y}$)

⌚ Timing: 2 h

ZrO_2 -modified reconstructed Cu electrode is prepared in three steps. The first step is the preparation of ZrO_2 -modified Cu electrode ($\text{Cu/ZrO}_2\text{-X}$). The second step is to remove the ZrO_2 coating on the Cu surface by sonication to expose the reconstructed Cu surface ($\text{Cu-Cu}_2\text{O-X}$). The third step is to re-load Y mg cm^{-2} of ZrO_2 nanoparticles on the reconstructed Cu electrode ($\text{Cu/ZrO}_2\text{-X-Y}$).

7. Prepare $\text{Cu/ZrO}_2\text{-1-1}$ (named CC/Z) electrode.
 - a. Prepare Cu/ZrO_2 electrode according to steps 1–3.
 - b. Remove the Teflon tape on the electrode.

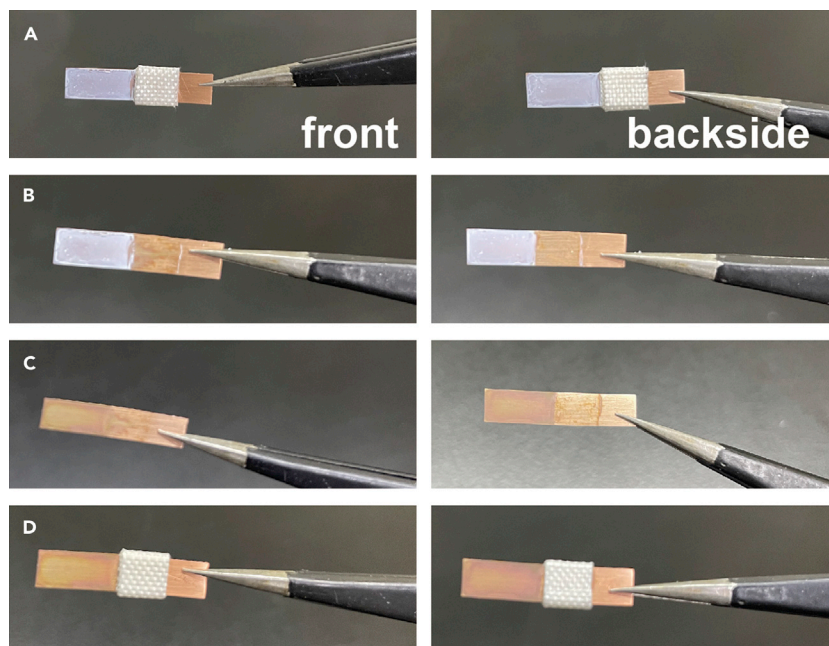


Figure 2. Photographs of the surface-reconstructed Cu electrode preparation (take Cu-Cu₂O as an example)
(A–D) Photo images of the front and back sides of (A) Cu/ZrO₂ electrode, (B) Cu/ZrO₂ electrode with removed Teflon tape, (C) Cu/ZrO₂ electrode after sonication, (D) Cu-Cu₂O electrode with a defined working area by encapsulating the electrode with Teflon tape.

- c. Immerse the Cu/ZrO₂ electrode in the mixture of DI water and ethanol (the volume ratio is 1:1) and sonicate until the ZrO₂ coating is completely removed (approximately 10 min).
- d. Confine the working area of 0.64 cm² by encapsulating the electrode with Teflon tape (Figure 3A).
- e. Re-coat 32 μL of ZrO₂ inks (10 mg/mL) on each side of Cu-Cu₂O (64 μL in total) and dry in air on a hot plate at 110°C for 10 min (Figures 3B and 3C).
8. For Cu/ZrO₂-2-0.05, the synthesis procedure is similar to that of Cu/ZrO₂-1-1.
 - a. Prepare Cu/ZrO₂-2 electrode according to step 5.
 - b. Remove the ZrO₂ coating on the Cu surface to prepare Cu-Cu₂O-2 according to step 6.
 - c. Re-coat 32 μL of ZrO₂ inks (0.5 mg/mL) on each side of Cu-Cu₂O-2 (64 μL in total) and dry in air on a hot plate at 110°C for 10 min.
9. For Cu/ZrO₂-8-0.5, the synthesis procedure is slightly different from that of Cu/ZrO₂-1-1 and Cu/ZrO₂-2-0.05.
 - a. Drop-coat 64 μL of ZrO₂ inks (20 mg/mL) on each side of Cu foil (128 μL in total) and dry in air on a hot plate at 110°C for 10 min.
 - b. Remove the ZrO₂ coat by sonication and then re-coat 64 μL of ZrO₂ inks (20 mg/mL) on each side of Cu foil (128 μL in total) and dry in air at 110°C.
 - c. Subsequently, remove the ZrO₂ coating again to obtain the Cu-Cu₂O-8 electrode.
 - d. Re-coat 32 μL of ZrO₂ inks (5 mg/mL) on each side of Cu-Cu₂O-8 (64 μL in total) and dry in air on a hot plate at 110°C for 10 min.

Synthesis of Cu@ZrO₂ nanoparticles

⌚ Timing: 8 h

10. The Cu@ZrO₂ nanoparticles are prepared by ultrasonically collecting the ZrO₂ nanoparticles on Cu/ZrO₂ electrode.

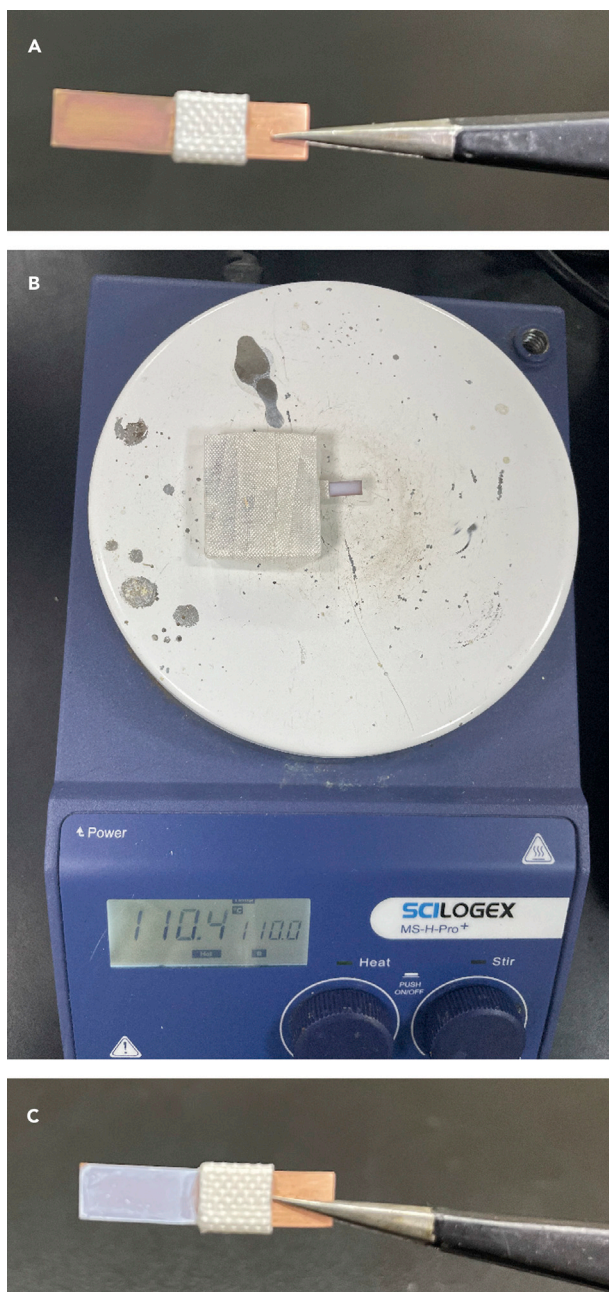


Figure 3. Photographs of the ZrO_2 -modified reconstructed Cu electrode preparation (take Cu/ ZrO_2 -1-1 as an example)

(A and B) Photo images of (A) Cu- Cu_2O electrode, (B) re-loading and drying ZrO_2 ink on one side of Cu- Cu_2O electrode on a hot plate at $110^\circ C$.

(C) Cu/ ZrO_2 -1-1 electrode.

- Firstly, prepare the Cu/ ZrO_2 electrode according to steps 1–3.
- Then, immerse the Cu/ ZrO_2 electrode in the mixture of DI water and ethanol (the volume ratio is 1:1) and sonicate until the ZrO_2 coating is completely removed.
- Finally, collect the powder by centrifuging the solution containing the ZrO_2 nanoparticles at 9,000 rpm for 3 min, wash once with DI water and ethanol, respectively, and dry in vacuum at $60^\circ C$ for 6 h.

Material characterizations of oxide-modified Cu electrodes

⌚ Timing: 6 h

Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscope (TEM), X-ray absorption spectroscopy (XAS), etc. are carried out to characterize the structure of the oxide-modified Cu electrodes.

11. For SEM, XRD, and XPS sample preparation, the flat electrode before and after CO₂RR are directly cropped into small pieces to characterize.
12. Prepare the TEM sample according to the following procedures.
 - a. Collect powder sample by scraping from flat electrode surface with a blade at first.
 - b. Disperse the powder in ethanol aqueous solution and sonicate for 10 min to obtain a uniform suspension.
 - c. Drop the suspension onto the molybdenum mesh, dry at room temperature, and examine the sample by TEM.
13. Prepare the XAS sample according to the following procedures.
 - a. Collect powder sample by scraping from flat electrode surface with a blade at first.
 - b. Adhere the powder onto a 3 M tape and use for XAS characterization.
 - c. Moreover, Cu₂O and CuO are used as references for XAS characterization. Cu₂O is synthesized according to a reported method (Gao et al., 2020). CuO is prepared by calcining Cu(NO₃)₂·3H₂O in a muffle furnace at 400°C for 2 h in air. And the heating rate is set to 15°C min⁻¹.
14. For focused ion beam (FIB), a gallium ion source is performed to directly cut the Cu/ZrO₂-2-0.05 surface with an area of 28 × 4 mm².

Note: To minimize the re-oxidation, the electrode after CO₂RR needs to be vacuum sealed before being transferred for all characterizations.

Electrochemical CO₂ reduction measurement of oxide-modified Cu electrodes

⌚ Timing: 1 week

Electrochemical CO₂ reduction measurement is carried out in an H-type cell with a three-electrode system in 0.1 M KHCO₃ electrolyte (Figure 4). All prepared self-supported electrodes (containing Cu/ZrO₂-X, Cu/oxide, Cu-Cu₂O-X, and Cu/ZrO₂-X-Y electrodes) in this work are used as working electrodes directly without further treatment.

15. Perform electrochemical CO₂ reduction measurement in an H-type cell, which is composed of two 60 mL-compartments and separated by a Nafion 115 proton exchange membrane with an area of 1.77 cm² (1.5 cm in diameter).
 - a. Fill the cathode and anode compartments with 30 mL of 0.1 M KHCO₃ as electrolyte, and the headspace volume of each compartment after filling electrolyte is 30 mL.
 - b. Assemble a three-electrode system in the H-type cell, in which a platinum sheet is used as a counter electrode in the anode compartment, and an Ag/AgCl electrode and the above self-supported electrode are used as reference electrode and working electrode, respectively, in the cathode compartment.
 - c. Before electrolysis, saturate the catholyte with CO₂ by continuously feeding CO₂ gas at a constant rate of 20 mL min⁻¹ to the catholyte for 30 min. Control the flow rate of CO₂ by a mass flow controller. Stir the catholyte with a magnetic stirrer throughout the electrolysis of CO₂ (default stirring speed was 500 rpm).

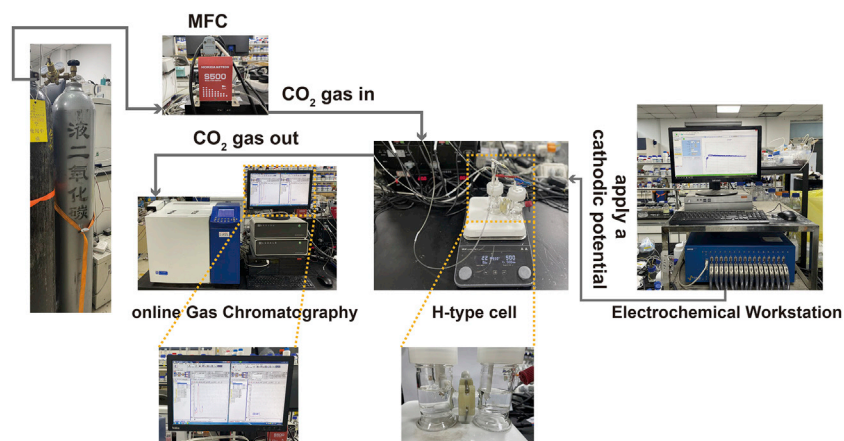


Figure 4. Photographs of the electrochemical CO₂ reduction measurement

Bio-Logic electrochemical workstation is used to apply a cathodic potential, the CO₂RR is performed in an H-type cell, the CO₂ gas flow rate is controlled by a mass flow controller (MFC), and the gas products are detected by online gas chromatography.

Note: Salt bridge filled with saturated KCl aqueous solution is assembled with reference electrode to decrease the solution resistance between the reference electrode and working electrode.

16. After completing the preparation in step 15, the electrolysis of CO₂ is ready to start.
 - a. Firstly, pre-activate the working electrode by performing a cyclic voltammetry test with the potential ranging from +0.2 to -0.6 V vs RHE at a scan rate of 50 mV s⁻¹ for 40 cycles.
 - b. Then, perform chronoamperometry measurements at a selected cathodic potential for 1–2 h. The applied potential ranges from -0.8 to -1.1 V vs RHE.

Note: To accumulate sufficient liquid products for quantification, the electrolysis time can be extended to 2 h at low negative potential.

17. To determine the activity of Cu and Cu/ZrO₂ electrodes, perform linear sweep voltammetry (LSV) tests in an H-type cell with Ar- or CO₂- saturated 0.1 M KHCO₃ electrolyte.
 - a. Firstly, saturate the catholyte with CO₂ or remove oxygen from the catholyte by continuously feeding CO₂ or Ar gas at a constant rate of 20 mL min⁻¹ to the catholyte for 30 min.
 - b. Then, pre-activate all working electrodes by performing cyclic voltammetry tests with the potential ranging from +0.2 to -0.6 V vs RHE at a scan rate of 50 mV s⁻¹ for 40 cycles.
 - c. Finally, perform linear sweep voltammetry measurements at the potential ranging from -0.61 to -1.81 V vs Ag/AgCl at a scan rate of 5 mV s⁻¹. The flow rates of CO₂ and Ar during LSV tests are controlled at 20 mL min⁻¹.

Note: The solution resistances at all potentials are automatically compensated by the electrochemical workstation (85% iR-compensated) and potentials are converted to the reversible hydrogen electrode (RHE) scale according to [Equation 1](#).

$$E(\text{vs RHE}) = E(\text{vs Ag / AgCl}) + 0.197 + 0.059 \times \text{pH} \quad (\text{Equation 1})$$

The pH of Ar-saturated 0.1 M KHCO₃ was 7.38 and that of CO₂-saturated 0.1 M KHCO₃ was 6.8.

Products analysis for electrochemical CO₂ reduction measurement

© Timing: 1 week

Quantify the gas and liquid products of electrochemical CO₂ reduction by online gas chromatography (GC) and ¹H nuclear magnetic resonance (¹H NMR), respectively.

18. Gas chromatography is equipped with the flame ionization detector (FID) and the thermal conductivity detector (TCD). The gas stream containing CO₂ and gas products flows out of the electrolytic cell, passes through an autosampler, and enters the gas chromatography.
 - a. First, separate CO₂ and gas products (H₂, CO, CH₄, C₂H₄) in the gas stream by the molecular sieve 5A capillary column and TDX-01 column.
 - b. The gas stream leaves the column and is first analyzed by the TCD to quantify H₂.
 - c. Then, passes through a methanizer that converts CO₂ and CO to methane.
 - d. Finally, into the FID that detects the carbon-containing gas products (Kuhl et al., 2012).

Note: The online gas chromatography is equipped with an autosampler for automated injection. The gas stream out of the electrolytic cell passes through the GC 6-way valve, and the valve is switched to inject single-point gas every 20 min (the sample loop volume in our GC is 1 mL). Except for the sampling time, the gas stream is vented during the electrolysis.

19. Precise quantification of gas products generated during CO₂RR requires a calibration curve for different gas products.
 - a. The calibration curve determines the linear relationship between gas concentration and peak area from GC. Thus, the concentration of gas products generated during CO₂RR can be determined according to the peak area from GC.
 - b. As shown in Figures 5A–5E, the standard gas concentrations versus corresponding peak areas obtained from the GC traces are plotted to obtain the calibration curves for H₂, CO, CH₄, and C₂H₄ (Table 1).
 - c. Figures 6A and 6B show the GC traces from FID and TCD channels of Cu/ZrO₂ tested at -1.05 V vs RHE. The concentrations of H₂, CO, CH₄, and C₂H₄ are obtained using the calibration curves.
20. Calculate the Faradic efficiencies of gas products according to the following equations.
 - a. Calculate the molar amount of gas sampling volume in each injection (*n*) at 26°C according to the ideal gas law.

$$n = \frac{P \times V}{R \times T} = \frac{1.013 \times 10^5 \text{ Pa} \times 1 \times 10^{-6} \text{ m}^3}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 299.15 \text{ K}} = 4.073 \times 10^{-5} \text{ mol} \quad (\text{Equation 2})$$

Where *V* is the sample loop volume in our GC (*V* = 1 mL), *P* is the pressure (Pa), *R* is the molar gas constant (8.314 J•mol⁻¹•K⁻¹), and *T* is the temperature (K), which are constants under electrochemical CO₂ reduction test conditions.

- b. According to the calibration curves in Figure 5E, determine the concentration of gas products (*c* in ppm).
- c. Calculate the charge consumed to get 1 mL of *c* ppm H₂, CO, CH₄, and C₂H₄ molecules according to Equation (3).

$$Q_{\text{gas products}} = c \times n \times Z \times N_A \times e \quad (\text{Equation 3})$$

Where *c* is the concentration of the gas product, *n* is the molar amount of 1 mL gas, *Z* is the number of electrons required to form 1 mol of gas product, *N_A* is the Avogadro constant (6.02 × 10²³ mol⁻¹), and *e* is the electric quantity for one electron (1.602 × 10⁻¹⁹ C).

- d. Calculate the total charge consumed according to Equation (4).

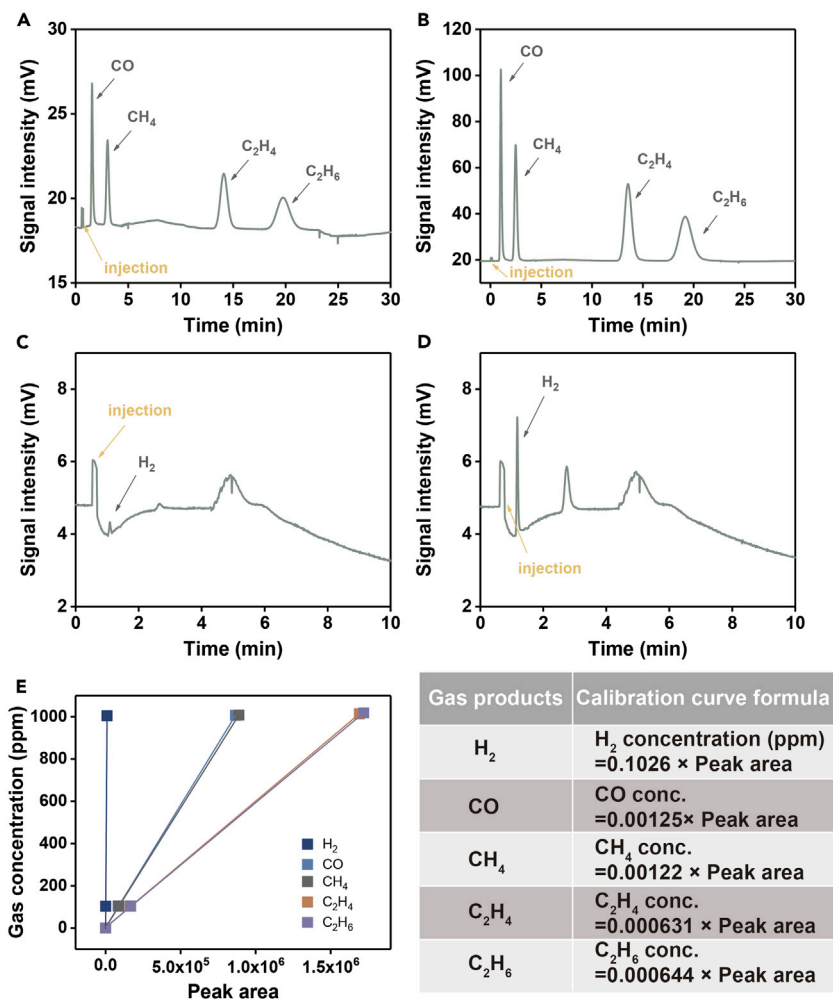


Figure 5. GC traces from FID and TCD channels of standard gas

(A–D) GC traces from (A and B) FID channel and (C and D) TCD channel of (A and C) standard gas with low concentration and (B and D) standard gas with high concentration. (E) Calibration curves for gas products.

$$Q_{total} = I \times t \quad (\text{Equation 4})$$

Where I is the current recorded at the time of sampling, t is the time required to fill the sample loop. The sample loop volume (V) in our GC is 1 mL, and the flow rate of gas stream (v) in this work is 20 mL/min. Thus, the time required to fill the sample loop is

$$t = \frac{V}{v} = \frac{1 \text{ mL}}{20 \text{ mL} \cdot \text{min}^{-1}} = 3 \text{ s} \quad (\text{Equation 5})$$

e. Finally, calculate the Faradaic efficiency for gas products according to [Equation \(6\)](#).

Table 1. The concentration of standard gases and the corresponding peak areas obtained from the GC traces

Concentration (ppm)	H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₆
Low concentration	103	104	104	104	104
High concentration	1005	1007	1008	1014	1018
Peak area	H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₆
Low concentration	965.5	79753.5	82726.5	158689.5	157761
High concentration	9777	804667	825807.5	1604148	1579314

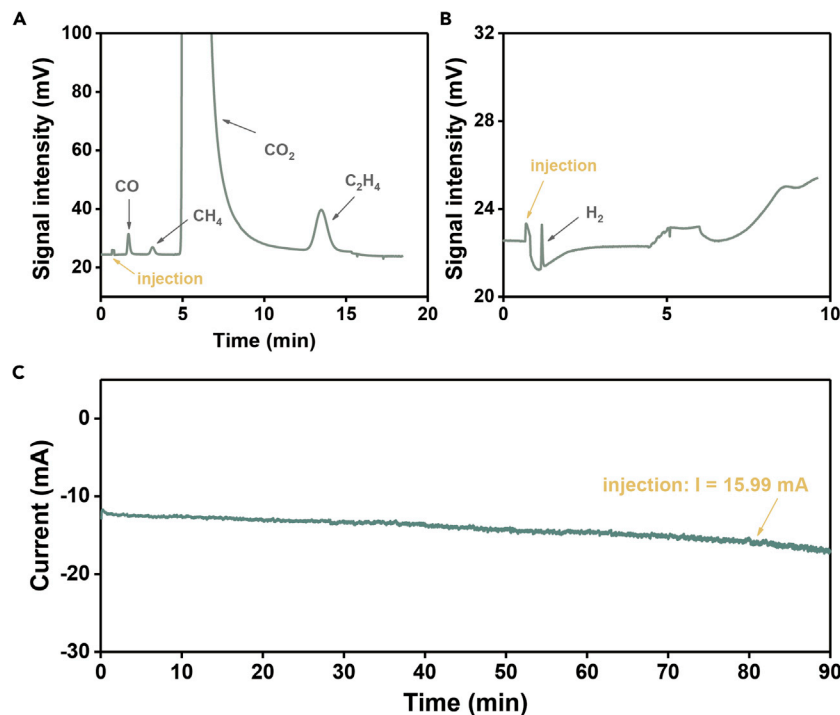


Figure 6. GC traces from FID and TCD channels of Cu/ZrO₂ tested at -1.05 V vs RHE

(A and B) GC traces from (A) FID channel, and (B) TCD channel.

(C) The chronoamperogram curve (i-t curve) of Cu/ZrO₂ tested at -1.05 V vs RHE.

$$FE_{\text{gas product}} = \frac{Q_{\text{gas products}}}{Q_{\text{total}}} \times 100\% \quad (\text{Equation 6})$$

- i. Take C₂H₄ in Figure 6A as an example, the peak area of C₂H₄ obtained from the GC trace is 742216, thus the concentration of C₂H₄ is 468.3 ppm calculated from the calibration curve. The charge consumed for producing 1 mL of 468.3 ppm C₂H₄ is calculated according to Equation (3).

$$Q_{\text{C}_2\text{H}_4} = 468.3 \times 10^{-6} \times 4.073 \times 10^{-5} \text{ mol} \times 12 \times 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.602 \times 10^{-19} \text{ C} = 0.0221 \text{ C}$$

- ii. Then, calculate the total charge consumed within 3 s of injection according to Equation (4). The recorded current is 15.99 mA at injection, as shown in Figure 6C.

$$Q_{\text{total}} = 15.99 \times 10^{-3} \text{ A} \times 3 \text{ s} = 0.048 \text{ C}$$

- iii. Hence, the Faradic efficiency for C₂H₄ is determined as

$$FE_{\text{C}_2\text{H}_4} = \frac{0.0221 \text{ C}}{0.048 \text{ C}} \times 100\% = 46.04 \%$$

21. ¹H nuclear magnetic resonance (¹H NMR) can be used to directly detect liquid products in the presence of electrolyte. Since the peak areas of liquid products in ¹H NMR spectra are often affected by shimming, phasing, and number of scans, the peak area does not use to quantify products. According to previous reports (Kuhl et al., 2012; Ren et al., 2015), the peak area ratio

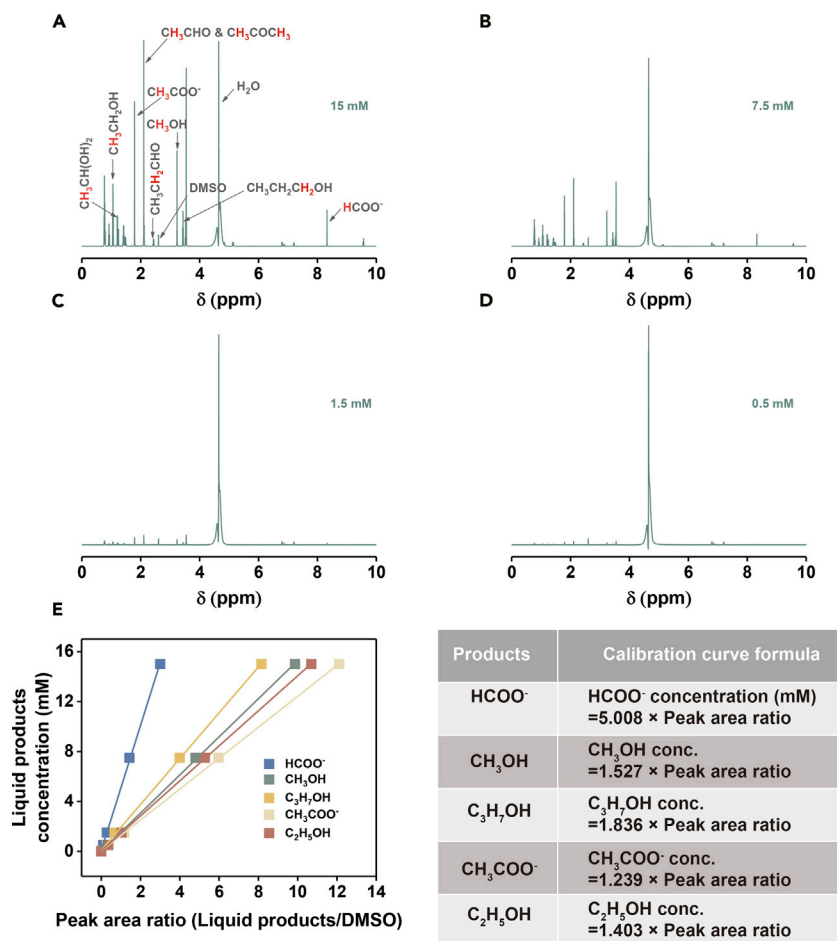


Figure 7. ¹H NMR spectra of standard solution containing a mixture of liquid products

(A–D) (A) 15 mM of liquid products, (B) 7.5 mM of liquid products, (C) 1.5 mM of liquid products, and (D) 0.5 mM of liquid products.

(E) Calibration curves for liquid products.

of internal standard and liquid product is often used to quantify the concentration of the liquid product. Therefore, peak area ratios of liquid products and internal standard versus the known concentrations of liquid products are plotted to obtain the calibration curves for liquid products quantification. Dimethyl sulfoxide (DMSO) is selected as the internal standard. Water suppression mode is used to decrease water peak intensity and make liquid products more visible in ¹H NMR spectroscopy.

22. Obtaining calibration curves for liquid products.

- Firstly, prepare 2 mM DMSO in D₂O as an internal standard solution.
- Secondly, prepare the standard solutions of liquid products containing potassium formate, methanol, potassium acetate, ethanol, ethylene glycol, n-propanol, acetaldehyde, acetone, and propionaldehyde with a given concentration (15 mM, 7.5 mM, 1.5 mM, and 0.5 mM, see [materials and equipment](#)).
- Finally, mix 500 μL of standard solution with 150 μL of internal standard solution and transfer to the NMR sample tube for ¹H NMR measurement.
- [Figures 7A–7D](#) show the NMR spectra for four standard solutions. [Figure 7E](#) shows the calibration curves for various liquid products, which exhibit good linear relationships.

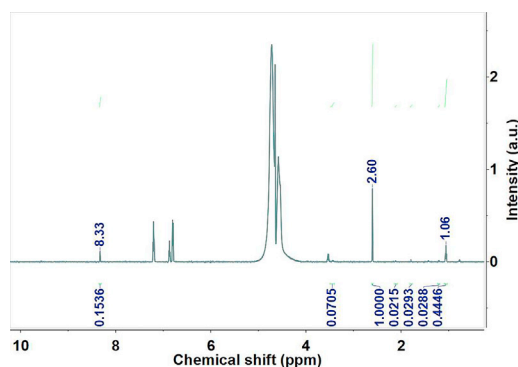


Figure 8. ^1H NMR spectra of the catholyte after 90 min of CO_2RR on Cu/ZrO_2 at -1.05 V vs RHE

e. Although there are nine target products in the standard solution, only five calibration curves for formate, methanol, acetate, ethanol, and n-propanol are plotted due to the following reasons. (1) The overlapping peaks of acetone and acetaldehyde at 2.1 ppm, (2) the overlapping peaks of ethylene glycol and ethanol at 3.54 ppm, (3) the strong volatility of acetaldehyde and propionaldehyde, (4) the existence of acetaldehyde and propionaldehyde in form of diol and keto in water, (5) the negligible yield of acetone, acetaldehyde, ethylene glycol, and propionaldehyde from CO_2RR in our system. The characteristic peaks of various liquid products in the ^1H NMR spectrum can be found in the literature (Kuhl et al., 2012).

Note: Single peak at 8.33 ppm for HCOO^- , single peak at 3.23 ppm for CH_3OH , single peak at 1.79 ppm for CH_3COO^- , triplet peak at 1.06 ppm for $\text{C}_2\text{H}_5\text{OH}$, and triplet peak at 3.44 ppm for $\text{C}_3\text{H}_7\text{OH}$ are used to divide the single peak at 2.6 ppm for DMSO to obtain the peak area ratio for quantification.

23. Quantification of liquid products of CO_2RR .

- Firstly, syringe out 500 μL of catholyte from electrolytic cell after 1–2 h electrolysis to mix with 150 μL of internal standard solution and transfer to the NMR sample tube for ^1H NMR measurement.
- Secondly, determine the peak area ratio of liquid product and internal standard, and calculate the concentration of liquid product according to the calibration curve.
- Then, calculate the concentration of liquid product (C_{liquid}) according to the calibration curve shown in Figure 7E.
- Calculate the charge consumed for producing $V\text{ mL}$ of $C_{\text{liquid}}\text{ mM}$ liquid products according to the Equation (7).

$$Q_{\text{liquid product}} = C_{\text{liquid}} \times V \times N_A \times Z \times e \quad (\text{Equation 7})$$

Where Z is the number of electrons required to form 1 mol of liquid product, N_A is the Avogadro constant ($6.02 \times 10^{23}\text{ mol}^{-1}$), and e is the electric quantity for one electron ($1.602 \times 10^{-19}\text{ C}$).

- Obtain the total charge consumed for the whole electrolysis by integrating the chronoamperogram curve (i - t curve). Hence, calculate the Faradic efficiency of liquid product according to the Equation (8).

$$FE_{\text{liquid product}} = \frac{Q_{\text{liquid product}}}{Q_{\text{total}}} \times 100\% \quad (\text{Equation 8})$$

- Take $\text{C}_2\text{H}_5\text{OH}$ in Figure 8 as an example, the peak area ratio of $\text{C}_2\text{H}_5\text{OH}/\text{DMSO}$ is 0.445, thus the concentration of $\text{C}_2\text{H}_5\text{OH}$ is 0.624 mM according to the calibration curve of

C₂H₅OH. The charge consumed for producing 30 mL of 0.465 mM C₂H₅OH is calculated according to Equation (7).

$$Q_{C_2H_5OH} = 0.624 \times 10^{-3} M \times 30 \times 10^{-3} L \times 6.02 \times 10^{23} mol^{-1} \times 12 \times 1.602 \times 10^{-19} C = 21.66 C$$

- ii. The total charge consumed by electrolysis in 90 min is 76.35 C by integrating the chronoamperogram curve in Figure 6C.
- iii. Hence, the Faradic efficiency for C₂H₅OH is determined as

$$FE_{C_2H_5OH} = \frac{21.66C}{76.35C} \times 100\% = 28.4 \%$$

Note: Avoid unit errors when calculating Faradaic efficiency.

Calculate the partial current density

⌚ Timing: 1 h

Partial current density is a key indicator to evaluate the catalytic activity of the CO₂RR product. The electrochemical active surface area (ECSA)-corrected current density can be used to evaluate the intrinsic activity of the catalyst by excluding the effect of surface roughness.

24. Calculate the partial current densities of products according to the Equation (9).

$$j_{product} = \frac{I \text{ mA} \times FE_{product}}{S} \quad (\text{Equation 9})$$

where *I* is the current recorded at the time of sampling gas products, and *S* is the geometric area of the working electrode.

25. The ECSA-corrected current density is calculated to compare the intrinsic activity of catalysts. The ECSAs of all working electrodes (*S* = 1 cm²) are determined by electrochemical double-layer capacitance measurement.
 - a. Firstly, determine the double-layer capacitance (*C_{dl}*) via cyclic voltammetry measurements, which are recorded in a non-faradaic region with a potential ranging from -0.14 to -0.04 V versus open circuit potential at scan rates of 20, 40, 60, 80, 100, 150 and 200 mV s⁻¹ (Figures 9A and 9B).
 - b. Then, plot the current density versus scan rates and perform linear fitting. The slope is considered as the *C_{dl}* of the working electrode (Figure 9C).
 - c. Calculate the *C_{dl}* ratio between the modified Cu electrode and the Cu foil to obtain the value of relative roughness (*R_f*) for modified Cu electrode according to Equation 10.
 - d. Finally, calculate the electrochemical active surface area for modified Cu electrode by the Equation (11) (Figure 9D).

$$R_f = \frac{C_{dl}}{C_{dlCu}} \quad (\text{Equation 10})$$

$$S_{ECSA} = R_f \times S \quad (\text{Equation 11})$$

Where *C_{dlCu}* is 38.2 μF cm⁻², *S* is the geometric area of electrode (*S* = 1 cm² in CV test).

26. Calculate the ECSA corrected current density according to the Equation (12).

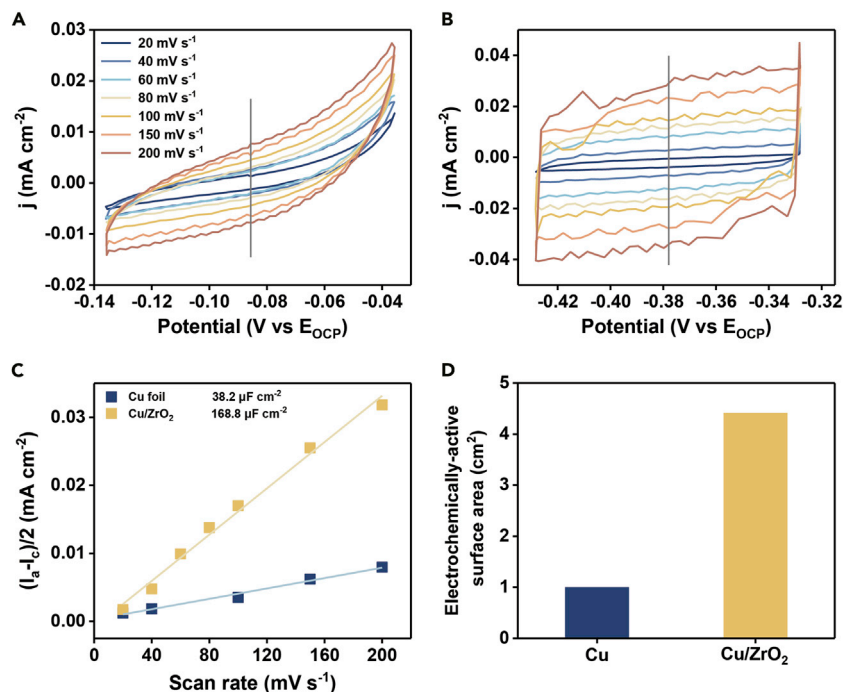


Figure 9. Evaluation of electrochemical active surface area (ECSA)

(A and B) Cyclic voltammograms measurements on Cu and Cu/ZrO₂ electrodes.

(C and D) (C) Electrochemical double-layer capacitance (C_{dl}) and (D) electrochemical active surface area (S_{ECSA}) of Cu and Cu/ZrO₂ electrodes.

$$j_{ECSA} = \frac{I \text{ mA}}{S_{ECSA}}; j_{ECSA \text{ for product}} = \frac{I \text{ mA} \times FE_{product}}{S_{ECSA}} \quad (\text{Equation 12})$$

Where S_{ECSA} is the electrochemical active surface area of the electrode.

Note: All CV tests are carried out in an H-type electrolysis cell with the CO₂-saturated 0.1 M KHCO₃ electrolyte.

Evaluate the stability of Cu/ZrO₂ electrode

⌚ Timing: 70 h

Stability is an important index to evaluate the electrochemical CO₂ reduction performance of a catalyst. In this work, we evaluate the stability of Cu/ZrO₂ electrode by a chronopotentiometry test.

27. Firstly, prepare the Cu/ZrO₂ electrode according to steps 1–3. Then, perform a chronopotentiometry test at -17.2 mA cm⁻² in an H-type cell. The catholyte and anolyte are 30 mL of 0.1 M KHCO₃ aqueous solution and are refreshed every 6 h to detect the liquid products.

Note: The current density (-17.2 mA cm⁻²) in response at -1.00 V vs RHE is chosen for the stability test.

In situ surface-enhanced Raman measurement for electrochemical CO₂ reduction

⌚ Timing: 10 h

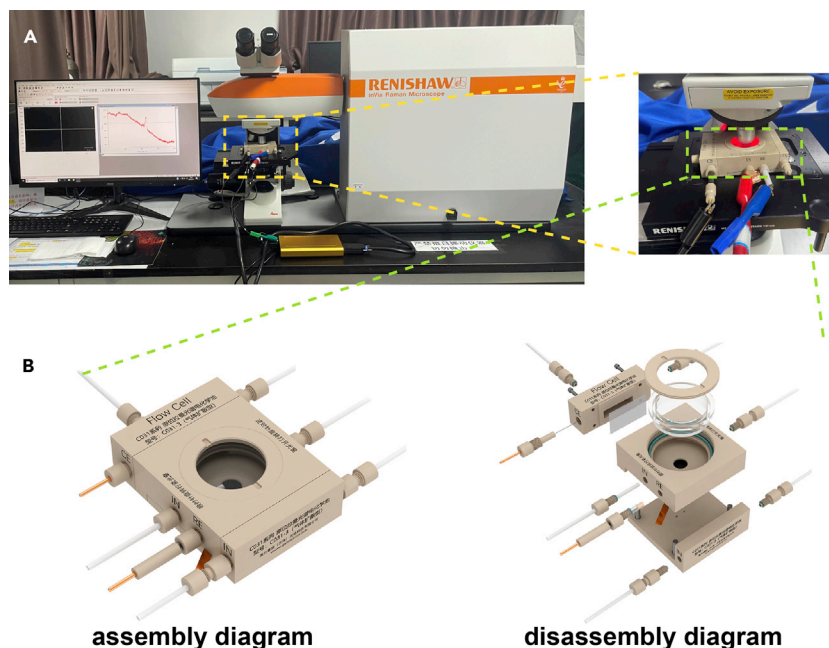


Figure 10. *In situ* surface-enhanced Raman spectroscopy

(A and B) (A) Photograph of the *in situ* electrochemical Raman spectroscopy system and (B) schematic diagram of the Raman cell (Adapted with permission from Gaoss Union).

To probe the composition evolution of the Cu/ZrO₂ electrode and the adsorption status of intermediates at the Cu-ZrO₂ interface during CO₂RR, conduct *in situ* surface-enhanced Raman spectroscopy measurements with the help of Au@SiO₂ nanoparticles to enhance the Raman signal.

28. Prepare the electrode for Raman measurement.
 - a. Prepare Cu/ZrO₂-8-0.5 electrode according to step 9.
 - b. To amplify the surface signal, Au@SiO₂ nanoparticles are used in Raman measurements.
 - i. Specifically, mix 500 μL of Au@SiO₂ solution (50 $\mu\text{g}/\text{mL}$) with 2 μL of Nafion solution, and then drop 15 μL of the mixed Au@SiO₂ ink onto the surface of electrodes (Cu and Cu-Cu₂O-8) and dry on a hot plate (110°C).
 - ii. For Au@SiO₂ modified Cu/ZrO₂ electrode, mix 15 μL of Au@SiO₂ ink with ZrO₂ inks (5 mg/mL) and re-coat on the Cu-Cu₂O-8 surface (denoted as Cu/ZrO₂-8-0.5).
29. Perform *in situ* surface-enhanced Raman measurement using an inVia Reflex Raman microscope (Renishaw) equipped with a diode laser (633 nm) and a water immersion objective (50 \times) in a modified electrochemical cell (Figure 10).
 - a. Firstly, calibrate the spectrometer by calibrating the Raman band of a silicon wafer.
 - b. Then, pre-activate working electrodes by performing cyclic voltammetry tests with the potential ranging from +0.2 to -0.6 V vs RHE at a scan rate of 50 mV s^{-1} for 10 cycles.
 - c. Afterward, perform the CO₂RR test coupled with Raman measurement in a three-electrode system on the electrochemical station (CHI 760E) in CO₂-saturated 0.1 M KHCO₃ electrolyte at selected potential ranging from -0.2 to -1.2 V vs RHE for 10 min with a potential interval of -0.2 V.
 - d. Start recording Raman spectra after CV test or after 5 min of CO₂ electrolysis. Each spectrum is recorded using 50% laser power, 10 s of exposure time, and by averaging 2 scans in extended mode.

DFT calculation

⌚ Timing: 1 month

Density function theory (DFT) calculations are performed to investigate the adsorption behavior of CO₂RR intermediates and the reaction barriers of various reaction pathways for CO₂RR at various Cu-oxide interfaces. The structure-property relationship of Cu/oxide catalyst can be elucidated by combining the results of DFT calculations with the CO₂RR performance.

30. Perform DFT calculations by using the Vienna ab initio simulation package (VASP), using the plane-wave basis with an energy cutoff of 500 eV, and the projector augmented wave (PAW) potentials.
 - a. Apply the generalized gradient approximation with the function of Perdew–Burke–Ernzerhof (GGA-PBE) to describe the exchange–correlation function.
 - b. Adopt Grimme’s semiempirical DFT-D3 scheme of dispersion correction to describe the van der Waals (vdW) interactions.
 - c. Set the convergence criteria of the residual Hellmann–Feynman force and energy during structure optimization to 0.02 eV Å⁻¹ and 10⁻⁵ eV, respectively.
31. At first, construct the computational models for Cu-oxide interfaces.
 - a. Use the model where an M₄O_x (M is Zr, Hf, Al, Si, Ga) cluster is deposited on a three-layer Cu (111) slab to stimulate the Cu-oxide interface.
 - b. To reflect the true oxide state under the electrochemical environment, hydrogenate the unsaturated oxygen atoms of M₄O_x.
 - c. Therefore, adopt the M₄O_xH_y clusters as the model in the DFT calculation.
 - d. Model the Cu (111) surface using a three-layer 5 × 5 surface slab with a vacuum layer of 20 Å. Use the Monkhorst-Pack25 k-point sampling of 3 × 3 × 1 mesh in this calculation.
32. Secondly, optimize the geometry configuration.
 - a. During geometry optimization, the M₄O_xH_y cluster and Cu atoms in the top one layer are allowed to relax while atoms in the bottom two layers are fixed.
 - b. Apply the COSMO-solvation effect during all calculations to modify the water-solid interface.
33. Finally, calculate the adsorption energy and Gibbs free energies.
 - a. Calculate the adsorption energy (E_{ads}) for the species in the CO₂RR process using the [Equation \(13\)](#).

$$E_{ads} = E_{adsorbate + slab} - E_{slab} - E_{adsorbate} \quad (\text{Equation 13})$$

- b. Calculate the Gibbs free energy by the approach developed by Nørskov et al., and evaluate ΔG by [Equation \(14\)](#).

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field} \quad (\text{Equation 14})$$

where ΔE , ΔZPE , and ΔS are the energy of reaction, the zero-point energy contribution, and entropy change, respectively. The ZPE of adsorbate is calculated based on the case of Cu (111). T is the temperature (set to 298.15 K). $\Delta G_U = eU$ is the free energy contribution related to electrode potential U . ΔG_{pH} is the correction of the H⁺ free energy, which can be calculated through $\Delta G_{pH} = k_B T \times \ln 10 \times \text{pH}$. The k_B is the Boltzmann constant and pH is set to 0 (acidic medium). ΔG_{field} is the free-energy correction resulting from the electrochemical double layer, which is negligible in this study. The proton-electron pair was assumed and the corresponding free energy was expressed using the reversible hydrogen electrode (RHE).

EXPECTED OUTCOMES

This protocol allows for the fabrication of oxide-modified Cu electrodes using a drop-coating method and their application in electrochemical CO₂ reduction. The adsorption energies of CO₂RR intermediates and the Gibbs free energies for various reaction pathways at Cu-oxide hetero-interfaces can also be calculated according to this protocol. By correlating the structure of Cu/oxide catalysts with CO₂RR performance, the structure-property relationship of Cu/oxide

catalysts can be elucidated. Among the screened Cu/oxide systems, Cu/ZrO₂ catalyst exhibits the optimal catalytic activity and selectivity for C₂₊ products attributing to the enhanced adsorption of CO₂/CO and decreased reaction barrier of the C-C coupling process.

LIMITATIONS

The protocol does have some limitations. First, although a flat Cu/oxide electrode is a simple model to study the structure-property relationship, the material characterizations, such as TEM, and XAS, are difficult to conduct for such a bulk material. Second, metallic Cu is easily re-oxidized after removing the cathodic potential, thus it is difficult to characterize the Cu valence state of the Cu electrode and Cu/ZrO₂ electrode after CO₂RR by *ex situ* characterizations. Third, the flat Cu/oxide electrode cannot be used in the flow cell and MEA, which hinders its practical application for CO₂RR.

TROUBLESHOOTING

Problem 1

Oxygen in air affects the accuracy of the *ex situ* characterization for the electrode after CO₂RR.

Potential solution

Transfer the electrode to characterize after vacuum sealing. See examples here.

Problem 2

The larger distance between the reference electrode and working electrode causes a larger solution resistance, which leads to a voltage drop compared to the applied voltage.

Potential solution

Install a salt bridge with a porous ceramic core on the reference electrode to shorten the distance between the reference electrode and the working electrode. Then, automatically compensate the solution resistance by an electrochemical workstation.

Problem 3

Adverse effects of metal ions (Ni⁴⁺, Fe³⁺, etc.), Cl⁻ ions in the used H-type cell for CO₂RR performance.

Potential solution

Before the electrolysis of CO₂, the H-type cell can be washed in an HNO₃ aqueous solution (pH ≈ 2) at 100°C for 1 h to remove impurities and washed in DI water at 100°C for 1 h to remove residual acid.

Problem 4

The total Faradaic efficiency for CO₂RR and HER is less than 100%.

Potential solution

Check that the concentration range of calibration curves includes the product concentration. Precise calibration curves ensure accurate results for gas and liquid products.

Problem 5

The weak Raman signals for flat Cu electrode under CO₂RR condition.

Potential solution

Modify flat electrodes with Au@SiO₂ nanoparticles to enhance the Raman signals. Please refer to step 28 for the preparation of the Au@SiO₂-modified electrode. See examples here and here.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Hao Bin Wu (hbwu@zju.edu.cn).

Materials availability

This study did not generate new unique materials.

Data and code availability

The published article includes all datasets/code generated or analyzed during this study.

ACKNOWLEDGMENTS

H.B.W. acknowledges the funding support from Natural Science Foundation of Zhejiang Province (LR21E020003), National Natural Science Foundation of China (22005266), and “the Fundamental Research Funds for the Central Universities” (2021FZZX001-09).

AUTHOR CONTRIBUTIONS

X.L. and H.B.W. conceived the idea. X.L. performed the experiments and analyzed the results. Q.L. carried out the theoretical calculations. X.L., Q.L., J.W., and H.B.W. co-wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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