Heterostructured catalysts based on Cu and oxides are promising for the efficient conversion of CO$_2$ to multi-carbon products. In this protocol, we describe the fabrication and characterization of Cu/oxide heterostructured catalysts and the evaluation approach of electrochemical CO$_2$ reduction reaction (CO$_2$RR) 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 CO$_2$RR performance of as-fabricated electrodes.

Publisher’s note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.
Protocol for fabrication and evaluation of oxide-modified Cu foils as heterostructured electrodes for electrochemical CO₂ reduction

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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 (CH3OH, 99.5%) | Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) | CAS: 67-56-1 |
| Potassium acetate (CH3COOK, 99.9% metals basis) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 127-08-2 |
| Ethanol (C2H5OH, 99.7%) | Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) | CAS: 64-17-5 |
| Acetone (CH3COCH3, 99.5%) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 75-07-0 |
| Propionaldehyde (C3H6CHO, 98%) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 123-38-6 |
| Ethylene glycol (OHCH2CH2OH, 99.5%) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 107-21-1 |
| n-Propanol (C3H7OH, 99.5%) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 71-23-8 |
| Dimethyl sulfoxide (C2H6SO, 99.7% with molecular sieves, water ≤50 ppm) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 67-68-5 |
| Deuterium oxide (D2O, 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 (ZrO2, 99.99% metal basis, 40–60 nm) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 1314-23-4 |
| Silicon dioxide (SiO2, 99.5%, 20–30 nm) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 14808-60-7 |
| Hafnium oxide (HfO2, 99.99% metal basis, 40–60 nm) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 12055-23-1 |
| Gallium oxide (Ga2O3, 99.8% metal basis, 500 nm) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 12024-21-4 |
| Aluminum oxide (Al2O3, 99.99% metal basis, 20–30 nm) | Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) | CAS: 1344-28-1 |
| Potassium bicarbonate (KHCO3, 99.5%) | Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China) | CAS: 298-14-6 |
| Potassium phosphate dibasic (K2HPO4, 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 |
| CO2 gas (99.995%) | N/A | N/A |
| Ar gas (99.99%) | N/A | N/A |
| Standard gas (containing H2, CO, CH4, C2H6, C2H4, N2) | 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@SiO2 (Au core 55 nm, SiO2 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 |
- 1H nuclear magnetic resonance (NMR, 600 MHz) | Agilent | DD2-600 |
- Scanning electron microscopy equipped with Energy dispersive spectrometer (SEM-EDS) | SEM: Hitachi | SU8010 |
- Transmission electron microscope equipped with Energy dispersive spectrometer (TEM-EDS) | TEM: JEOL | JEM-2100F |
- Ultra-high resolution Scanning electron microscopy-Focused ion beam equipped with Energy dispersive spectrometer (SEM-FIB-EDS) | TESCAN | X-MaxN 80T IE250 |
- X-ray diffraction (XRD) | PANalytical | PANalytical X’Pert PRO |

(Continued on next page)
### MATERIALS AND EQUIPMENT

#### ZrO₂ inks with different concentration

| Reagent   | Final concentration | Amount   |
|-----------|---------------------|----------|
| ZrO₂      | 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 |
|-----------|---------------------|--------|
| HfO₂      | 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 |
|-----------|---------------------|--------|
| Al₂O₃     | 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 |
|----------|---------------------|--------|
| SiO₂     | 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 |
|----------|---------------------|--------|
| Ga₂O₃    | 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 |
|----------|---------------------|--------|
| KHCO₃    | 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 |
|----------|---------------------|--------|
| K₂HPO₄  | 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 D_2O

| Reagent  | Final concentration | Amount   |
|----------|---------------------|----------|
| DMSO     | 2 mM                | 0.2 mmol |
| D_2O     | 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_3OH    | 15, 7.5, 1.5, 0.5 mM| 1.5, 0.75, 0.15, 0.05 mmol |
| CH_3COOK  | 15, 7.5, 1.5, 0.5 mM| 1.5, 0.75, 0.15, 0.05 mmol |
| C_2H_5OH  | 15, 7.5, 1.5, 0.5 mM| 1.5, 0.75, 0.15, 0.05 mmol |
| CH_3CHO   | 15, 7.5, 1.5, 0.5 mM| 1.5, 0.75, 0.15, 0.05 mmol |
| CH_3COCH_3 | 15, 7.5, 1.5, 0.5 mM | 1.5, 0.75, 0.15, 0.05 mmol |
| CH_3CHO   | 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 regents 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_2H_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_2H_6    | 1,014 ppm           | N/A    |
| N_2 as carrier gas | N/A     | N/A    |
| Total     | N/A                 | N/A    |

Note: Storage Duration: ~1 year.
**STEP-BY-STEP METHOD DETAILS**

**Fabrication of oxide-modified Cu electrode**

© Timing: 2 h

ZrO$_2$-modified Cu electrode is prepared by a drop-coating method according to the following steps.

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

2. Prepare the ZrO$_2$ ink.
   a. Weigh 10 mg of ZrO$_2$ on an analytical balance and carefully transfer to a 2 mL centrifuge tube.
   b. Add 480 µL of ethanol, 480 µL of DI water, and 40 µL of Nafion solution (5% in a mixture of lower aliphatic alcohol and water) using a pipettor sequentially.
   c. Sonicate the suspension using the ultrasonic cleaning machine at 25°C for 1–2 h to obtain a uniformly dispersed suspension (named ZrO$_2$ ink).
ZrO\textsubscript{2} ink solution should be sonicated for a few minutes before each use to avoid settling of ZrO\textsubscript{2} nanoparticles.

3. Drop-coat 32 \( \mu L \) of ZrO\textsubscript{2} ink solution on each side of Cu foil (64 \( \mu L \) in total) and dry in air on a hot plate at 110\(^\circ\)C for 10 min to obtain the ZrO\textsubscript{2}-modified Cu electrode (Figures 1D–1H).

**Note:** ZrO\textsubscript{2} ink solution should be sonicated for a few minutes before each use to avoid settling of ZrO\textsubscript{2} nanoparticles.

4. Prepare other oxide-modified Cu electrodes according to the following step, which is the same as the preparation of ZrO\textsubscript{2}-modified Cu electrode (steps 1–3).
   a. Mechanically polish Cu foil.
   b. Weigh 10 mg of HfO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, and Ga\textsubscript{2}O\textsubscript{3} nanoparticles and disperse in the mixture of DI water, ethanol, and Nafion solution to prepare HfO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, and Ga\textsubscript{2}O\textsubscript{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 Cu/ZrO$_2$-X, where X is the ZrO$_2$ loadings (mg); default Cu/ZrO$_2$ refers to Cu/ZrO$_2$-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 Cu/ZrO$_2$-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 Cu-Cu$_2$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 (Cu/ZrO$_2$-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 Cu/ZrO$_2$-X electrode according to step 5.
   b. Remove the Teflon tape on the electrode.
   c. Immers the Cu/ZrO$_2$-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: Cu-Cu$_2$O-X was harvested from Cu/ZrO$_2$-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$_2$RR measurement.

**Fabrication of ZrO$_2$-modified reconstructed Cu electrode (named Cu/ZrO$_2$-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 (Cu/ZrO$_2$-X). The second step is to remove the ZrO$_2$ coating on the Cu surface by sonication to expose the reconstructed Cu surface (Cu-Cu$_2$O-X). The third step is to re-load Y mg cm$^{-2}$ of ZrO$_2$ nanoparticles on the reconstructed Cu electrode (Cu/ZrO$_2$-X-Y).

7. Prepare Cu/ZrO$_2$-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.
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).

Confine the working area of 0.64 cm² by encapsulating the electrode with Teflon tape (Figure 3A).

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).

For Cu/ZrO2-2-0.05, the synthesis procedure is similar to that of Cu/ZrO2-1-1.

Prepare Cu/ZrO2-2 electrode according to step 5.

Remove the ZrO2 coating on the Cu surface to prepare Cu-Cu2O-2 according to step 6.

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.

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.

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.

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.

Subsequently, remove the ZrO2 coating again to obtain the Cu-Cu2O-8 electrode.

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

The Cu@ZrO2 nanoparticles are prepared by ultrasonically collecting the ZrO2 nanoparticles on Cu/ZrO2 electrode.
a. Firstly, prepare the Cu/ZrO$_2$ electrode according to steps 1–3.

b. 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.

c. 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°C for 6 h.

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$_2$O electrode, (B) re-loading and drying ZrO$_2$ ink on one side of Cu-Cu$_2$O electrode on a hot plate at 110°C.

(C) Cu/ZrO$_2$-1-1 electrode.
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).
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.

   \[
   E(\text{vs RHE}) = E(\text{vs Ag/AgCl}) + 0.197 + 0.059 \times \text{pH}
   \]  
   (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.
Quantify the gas and liquid products of electrochemical CO\textsubscript{2} reduction by online gas chromatography (GC) and \textsuperscript{1}H nuclear magnetic resonance (\textsuperscript{1}H NMR), respectively.

**Timing:** 1 week

18. Gas chromatography is equipped with the flame ionization detector (FID) and the thermal conductivity detector (TCD). The gas stream containing CO\textsubscript{2} and gas products flows out of the electrolytic cell, passes through an autosampler, and enters the gas chromatography.

a. First, separate CO\textsubscript{2} and gas products (H\textsubscript{2}, CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}) 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 H\textsubscript{2}.

c. Then, passes through a methanizer that converts CO\textsubscript{2} 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 CO\textsubscript{2}RR 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 CO\textsubscript{2}RR 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 H\textsubscript{2}, CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{4} (Table 1).

c. Figures 6A and 6B show the GC traces from FID and TCD channels of Cu/ZrO\textsubscript{2} tested at \(-1.05\) V vs RHE. The concentrations of H\textsubscript{2}, CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{4} 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.

\[
\frac{n}{R \times T} = \frac{p \times V}{R \times T} = \frac{1.013 \times 10^5 \text{ Pa} \times 1 \times 10^{-6} \text{ m}^3}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 299.15 \text{ K}} = 4.073 \times 10^{-5} \text{ mol}
\]  

(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\textsuperscript{mol}^{-1}\textsuperscript{K}^{-1}), and T is the temperature (K), which are constants under electrochemical CO\textsubscript{2} 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 H\textsubscript{2}, CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{4} molecules according to Equation (3).

\[
Q_{\text{gas products}} = c \times n \times Z \times N_A \times e
\]  

(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\textsubscript{A} is the Avogadro constant (6.02 \times 10\textsuperscript{23} \text{ mol}^{-1}), and e is the electric quantity for one electron (1.602 \times 10\textsuperscript{-19} \text{ C}).

d. Calculate the total charge consumed according to Equation (4).
\[ Q_{\text{total}} = I \times t \quad \text{(Equation 4)} \]

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

\[ t = \frac{V}{v} = \frac{1 \text{ mL}}{20 \text{ mL/min}} = 0.05 \text{ s} \]

\[ = 3 \text{ s} \quad \text{(Equation 5)} \]

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) | \( \text{H}_2 \) | \( \text{CO} \) | \( \text{CH}_4 \) | \( \text{C}_2\text{H}_4 \) | \( \text{C}_2\text{H}_6 \) |
|---------------------|----------------|----------------|----------------|----------------|----------------|
| Low concentration   | 103            | 104            | 104            | 104            | 104            |
| High concentration  | 1005           | 1007           | 1008           | 1014           | 1018           |
| Peak area           | \( \text{H}_2 \) | \( \text{CO} \) | \( \text{CH}_4 \) | \( \text{C}_2\text{H}_4 \) | \( \text{C}_2\text{H}_6 \) |
| Low concentration   | 965.5          | 79753.5        | 82726.5        | 158689.5       | 157761         |
| High concentration  | 9777           | 804667         | 825807.5       | 1604148        | 1579314        |
i. Take C$_2$H$_4$ in Figure 6A as an example, the peak area of C$_2$H$_4$ obtained from the GC trace is 742216, thus the concentration of C$_2$H$_4$ is 468.3 ppm calculated from the calibration curve. The charge consumed for producing 1 mL of 468.3 ppm C$_2$H$_4$ is calculated according to Equation (3).

$$Q_{C_2H_4} = 468.3 \times 10^{-6} \times 4.073 \times 10^{-5} \text{mol} \times 12 \times 6.02 \times 10^{23} \text{mol}^{-1} \times 1.602 \times 10^{-19} \text{C} = 0.0221 \text{C}$$

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.

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

iii. Hence, the Faradic efficiency for C$_2$H$_4$ is determined as

$$FE_{C_2H_4} = \frac{0.0221 \text{ C}}{0.048 \text{ C}} \times 100\% = 46.04\%$$

21. $^1$H nuclear magnetic resonance ($^1$H NMR) can be used to directly detect liquid products in the presence of electrolyte. Since the peak areas of liquid products in $^1$H 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
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 $^1$H NMR spectroscopy.

22. Obtaining calibration curves for liquid products.
   a. Firstly, prepare 2 mM DMSO in D$_2$O as an internal standard solution.
   b. 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).
   c. Finally, mix 500 µL of standard solution with 150 µL of internal standard solution and transfer to the NMR sample tube for $^1$H NMR measurement.
   d. 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.
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$_2$RR in our system. The characteristic peaks of various liquid products in the $^1$H 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$_3$OH, single peak at 1.79 ppm for CH$_3$COO$^-$, triplet peak at 1.06 ppm for C$_2$H$_5$OH, and triplet peak at 3.44 ppm for C$_3$H$_7$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$_2$RR.
   a. 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 $^1$H NMR measurement.
   b. Secondly, determine the peak area ratio of liquid product and internal standard, and calculate the concentration of liquid product according to the calibration curve.
   c. Then, calculate the concentration of liquid product ($C_{\text{liquid}}$) according to the calibration curve shown in Figure 7E.
   d. Calculate the charge consumed for producing $V$ mL of $C_{\text{liquid}}$ mM liquid products according to the Equation (7).

\[ Q_{\text{liquid product}} = C_{\text{liquid}} \times V \times N_A \times Z \times e \]  

(Equation 7)

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

e. 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).

\[ FE_{\text{liquid product}} = \frac{Q_{\text{liquid product}}}{Q_{\text{total}}} \times 100\% \]  

(Equation 8)

i. Take C$_2$H$_5$OH in Figure 8 as an example, the peak area ratio of C$_2$H$_5$OH/DMSO is 0.445, thus the concentration of C$_2$H$_5$OH is 0.624 mM according to the calibration curve of
The charge consumed for producing 30 mL of 0.465 mM C$_2$H$_5$OH is calculated according to Equation (7).

\[
Q_{\text{C}_2\text{H}_5\text{OH}} = 0.624 \times 10^{-3}M \times 30 \times 10^{-3}L \times 6.02 \times 10^{23}\text{mol}^{-1} \times 12 \times 1.602 \times 10^{-19}C = 21.66 \text{ C}
\]

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 C$_2$H$_5$OH is determined as

\[
\text{FE}_{\text{C}_2\text{H}_5\text{OH}} = \frac{21.66 \text{C}}{76.35 \text{C}} \times 100\% = 28.4\%
\]

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 CO$_2$RR 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).

\[
J_{\text{product}} = \frac{l \text{ mA} \times FE_{\text{product}}}{S} \quad \text{(Equation 9)}
\]

where \(l\) 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 (\(S = 1 \text{ cm}^2\)) 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).

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

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

Where \(C_{dlCu}\) is 38.2 \(\mu\text{F cm}^{-2}\), \(S\) is the geometric area of electrode (\(S = 1 \text{ cm}^2\) in CV test).

26. Calculate the ECSA corrected current density according to the Equation (12).
Where $S_{\text{ECSA}}$ is the electrochemical active surface area of the electrode.

**Note:** All CV tests are carried out in an H-type electrolysis cell with the CO$_2$-saturated 0.1 M KHCO$_3$ electrolyte.

### Evaluate the stability of Cu/ZrO$_2$ electrode

**Timing:** 70 h

Stability is an important index to evaluate the electrochemical CO$_2$ reduction performance of a catalyst. In this work, we evaluate the stability of Cu/ZrO$_2$ electrode by a chronopotentiometry test.

27. Firstly, prepare the Cu/ZrO$_2$ 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 KHCO$_3$ 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 CO$_2$ reduction

**Timing:** 10 h

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

(A and B) Cyclic voltammetry measurements on Cu and Cu/ZrO$_2$ electrodes.

(C and D) (C) Electrochemical double-layer capacitance ($C_{\text{dl}}$) and (D) electrochemical active surface area ($S_{\text{ECSA}}$) of Cu and Cu/ZrO$_2$ electrodes.

$$I_{\text{ECSA}} = \frac{1}{S_{\text{ECSA}}} \int_{E_{\text{ECSA}}} J_{\text{ECSA for product}} = \frac{1}{S_{\text{ECSA}}} \frac{1}{F} E_{\text{product}}$$

(Equation 12)
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 μg/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 ×) 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 CO$_2$RR intermediates and the reaction barriers of various reaction pathways for CO$_2$RR 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 CO$_2$RR 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 M$_4$O$_x$ (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 M$_4$O$_x$.
   c. Therefore, adopt the M$_4$O$_x$H$_y$ 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 M$_4$O$_x$H$_y$ 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 CO$_2$RR process using the Equation (13).
   
   
   \[
   E_{ads} = E_{adsorbate} + E_{slab} - E_{slab} - E_{adsorbate}
   \]

   (Equation 13)

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

   \[
   \Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field}
   \]

   (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). ΔG$_U$ = 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 ΔG$_{pH}$ = $k_b T \times \ln 10 \times pH$. 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 CO$_2$ reduction. The adsorption energies of CO$_2$RR 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 CO$_2$RR performance, the structure-property relationship of Cu/oxide catalysts can be elucidated.
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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