

Supplementary Information

Twin-boundary engineering boosted undercoordinated active sites for scalable conversion of CO₂ to ethylene

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1 **Methods and procedures**

2 **Gas diffusion electrode hydrophilic pre-treatment.**

3 Before starting the electrochemical depositing catalysts, the gas diffusion electrode (GDE, Freudenberg
4 22BB) was pre-treated with sulfuric acid (H_2SO_4 , ACS reagent, Sigma-Aldrich) by sonicating 20 minutes
5 to make the surface hydrophilic for further deposition. After the hydrophilic treatment, the redundant acid
6 on the GDE was rinsed with deionized water for 2 min, and the GDE was dried under the Ar stream at
7 room temperature for further usage.

8 **Preparation of single crystal Cu electrode by electrochemical deposition.**

9 The single crystal Cu working electrode was obtained through a chronoamperometry electrodeposition
10 approach. Two electrodes were applied for the electrochemical deposition with GDE as the working
11 electrode and Pt foil as the counter electrode, respectively. 0.2 M copper (II) sulfate pentahydrate
12 ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ACS reagent, Sigma-Aldrich) aqueous solution was applied as the electrolyte. The Cu
13 catalyst was electrodeposited on GDE at a constant current density of 50 mA cm^{-2} for 5 mins until the
14 total loading amount of 5.0 mg cm^{-2} was reached. After the deposition, the redundant electrolyte was
15 rinsed with deionized water three times and the as-prepared electrode was then dried under Ar flow at
16 room temperature for further measurement.

17 **Preparation of Cu electrode with variable twin-boundary densities.**

18 The Cu working electrode with variable densities of twin-boundary was obtained through a novel one-
19 step pulse-chronoamperometry electrodeposition method instead of the high-temperature annealing or
20 laser-assisted process.^{1,21,2} Two electrodes were applied for the electrochemical deposition with GDE as
21 working electrode and Pt foil as a counter electrode, respectively. 0.2 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was applied as the
22 electrolyte. The Cu catalyst was electrodeposited on GDE at a pulse current density of 50 mA cm^{-2} and
23 was ended until the total loading amount of 5.0 mg cm^{-2} was reached. After the deposition, the redundant
24 electrolyte was rinsed with deionized water three times and the as-prepared electrode was then dried under
25 Ar flow at room temperature for further measurement.

26 **Structural characterization and compositional analysis.**

Transmission electron microscopy images (TEM) were obtained using a JEOL 1400 microscope with an emission gun operating at 120 kV. High-resolution transmission electron microscope (HRTEM) and energy-dispersive X-ray (EDX) spectroscopy were performed on the JEOL 2200FS microscope with the emission gun operating at 200 kV. The samples were prepared by dropping ethanol dispersions of samples onto 300 mesh lacey carbon-coated gold grids. Fast Fourier transform (FFT) masked contrast refined HRTEM images were obtained using Gatan digital micrograph software. High-angle annular dark-field (HAADF) images were acquired using a JEOL-ARM200F TEM operated at 200 kV. The attainable spatial resolution of the microscope was 78 pm with a probe spherical-aberration corrector. The images were acquired with an illumination semi-angle of 25 mrad and a probe current of 100 pA. The dwell time for image acquisition was set at 10 μ s per pixel to ensure a desirable signal-to-noise ratio. The collection angles for the HAADF images were fixed at 90-250 mrad. To obtain high-quality scanning transmission electron microscopy (STEM) images with atomic resolution, the material was pre-treated at 60 °C in a vacuum oven for 4 h to remove any organic ligands on its surface. X-ray photoelectron spectroscopy (XPS) measurement was performed using an ESCALAB-250 instrument (Thermo Fisher Scientific, USA), performed with a monochromatic Al-K α (1486.6 eV) radiation source and a hemisphere detector with an energy resolution of 0.1 eV. Peak positions were all corrected by the C 1s spectrum at 284.8 eV. X-ray diffraction (XRD) measurement was performed on an Xpert Pro apparatus (Philips Pana Analytical, Cu K α ; λ = 1.5418 Å) operating at 40 kV and 20 mA. The scanning speed was set to 8° *per* min.

X-ray absorption spectroscopy measurements.

X-ray absorption spectra were collected at Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14W1. The storage ring is operated at an electron energy of 2.5 GeV with a beam current of 250 mA. A Si (111) double-crystal monochromatic was applied. The beam size used at the sample position was $\sim 900 \times 300 \mu\text{m}^2$. All the data were collected at ambient temperature applied in the transmission mode. The energy resolution ($\Delta E/E$) for the incident X-ray photons was estimated to be 2×10^{-4} . Conventional fluorescence mode was adopted for the Cu K-edge EXAFS measurements. To ascertain the reproducibility of the experimental data, at least three scan sets were collected and compared for each sample.

Extended X-ray absorption fine structure curve fitting and data analysis.

Extended X-ray absorption fine structures (EXAFS) curve fitting and data analysis were performed with Artemis and IFEFFIT software.^{3,4} Each sample of XAS data was aligned and processed using the Athena program. Spectra were baseline corrected using a linear pre-edge function between -200 and -50 eV and normalized using a linear or quadratic function between 150 and 700 eV, including a flattening function in the post-edge region. The XAFS signal was isolated from the adsorption edge background using a fit to a cubic spline with nodes defined by the AUTOBKG function in IFEFFIT, with a k -weight of 3 and with the Rbkg parameter set to 1. Fourier transformations of k^3 -weighted spectra were using a Kaiser-Bessel window with a $1 \text{ \AA}^{-1}$ sill width. The magnitude parts of the Fourier transformed spectra are shown throughout this manuscript with a radial distance scale that is not corrected for phase shift. For EXAFS fitting, theoretical scattering paths were calculated with FEFF6 using Artemis.⁵ All EXAFS spectra were fit for distances (ΔR), coordination number (CN), and mean-square displacement of interatomic distance (σ^2) using the Artemis interface with a fixed amplitude reduction factor (S_0^2) of $0.707 \sim 1.000$. The parameters such as interatomic distance ΔR , CN, the difference in threshold energy (ΔE_0) and Debye-Waller factor (σ^2) were first established with reasonable guesses and then were fitted in R-space. The error in the overall fits was determined using the R-factor, the goodness-of-fit parameter, in which R-factor = $\Sigma(\chi_{\text{data}} - \chi_{\text{fit}})^2 / \Sigma(\chi_{\text{data}})^2$ and good fits occur for R-factor < 0.05.

Electrochemical measurements in H-cell configuration.

The electrochemical measurements were performed using a mechanically polished glassy carbon electrode connected with a VSP potentiostat (Bio-Logic Science Instruments). The electrochemical activation process was performed by cyclic voltammetry scanning in 0.5 M potassium bicarbonate (KHCO_3 , 99.9%, Sigma-Aldrich) between 0 V and -1.5 V for 10 cycles with a scan rate of 0.05 V s^{-1} to remove the surface metal oxides. CO_2 reduction experiments were performed in a gastight two-compartment H-type electrochemical cell (H-cell) separated by a piece of proton exchange membrane (Nafion-117). The electrolyte consisted of a CO_2 saturated 0.5 M KHCO_3 solution with a final pH value of 6.82. The working electrode (WE) was prepared by electrochemical deposition on the GDE. A potassium chloride (KCl, ACS reagent, Sigma-Aldrich) saturated Ag/AgCl electrode and a Pt foil (1 cm x 3cm) were used as the reference

and counter electrodes, respectively. All potentials were calibrated to the reversible hydrogen electrode (RHE) by the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197 \quad (1)$$

Linear sweep voltammetry (LSV) was conducted in Ar-saturated and CO₂-saturated 0.5 M KHCO₃ solution between 0 V and -2.0 V *vs.* RHE to investigate the CO₂RR activity, respectively. A long-term stability measurement was recorded by taking a chronoamperometric curve at the constant potential of -1.1 V *vs.* RHE for as long as 24 hours. All data are presented without IR compensation. All the electrochemical tests were performed at room temperature.

Estimation of the ECSA *via* Pb underpotential deposition.

The electrochemically active surface area (ECSA) of the electrodes was determined using Pb underpotential deposition (UPD). The experiments were performed in argon (Linde, 99%) saturated electrolyte containing 1.0 mM Pb(ClO₄)₂ and 0.1 M HClO₄ with the electrochemical window between -0.80 V to -0.20 V *vs.* Ag/AgCl at a scan rate of 0.01 V s⁻¹. The presence of the UPD signals for the deposition and the stripping of Pb on the Cu-Ag alloy crystals was detected at -25.0 mV *vs.* Ag/AgCl and -27.7 mV *vs.* Ag/AgCl, respectively. The calculation of the active surface area was carried out assuming a theoretical adsorption charge of a Pb monolayer on copper of 310 μC cm⁻².⁶ The normalized current densities per geometric area of the electrode were divided by the ECSA to obtain the partial current densities.

Gas-phase product analysis.

Gas-phase product quantification was performed continuously using an online gas chromatograph (Agilent, Micro GC-490) equipped with a TCD detector and Molsieve 5A column. Hydrogen and Argon (Linde, 99.999%) were used as the carrier gases. Gas-phase products were collected every 15 mins for the H-cell and every 5 mins for the MEA electrolyzer using an automatic sampler to access catalyst selectivity and total partial current density. Gas product quantification was based on prior calibration of the system injecting mixtures with a known percentage of gases (Linde, order No. 103000567256/1).

Liquid-phase product analysis.

For the H-cell configuration, the liquid product was collected after 2 hours of chronoamperometry measurement at the specific potential. For the MEA configuration, the liquid products at the cathode were collected by using a cold trap connected to the cathode gas outlet. The liquid products in the anolyte were also analyzed to detect liquid products that may have crossed over the membrane to the catholyte.⁷ The liquid products were quantified using ¹H NMR spectroscopy. NMR spectra of freshly acquired samples were collected on a Bruker Avance III 600 MHz spectrometer with a cryoprobe Prodigy TCI in 10% D₂O using deionized water with 0.1% (w/w) of DSS (Sodium trimethylsilylpropanesulfonate) like the internal standard for the quantification of the formate (HCOO⁻), methanol (CH₃OH), ethanol (C₂H₅OH) and n-propanol (C₃H₇OH). A 1D sequence water suppression with excitation sculpting with gradients (zgpg30) was used for the acquisition (Number of scans = 32, Delay D1=30s) and a relaxation time between the pulses of 16 s was used to allow for complete proton relaxation. Liquid product quantification was based on prior calibration of the system injecting mixtures with a known percentage of liquid products.

Calculation of the turnover frequency.

TOF for CO₂ reduction reaction over the catalysts was calculated on the basis of amounts of products, electrolysis time, and the moles of Cu species on the electrode determined gravimetrically. The moles of Cu species were assumed to be the same as that in the precursors. To get a reliable amount, at least 10 of Cu electrodes were prepared, and the mass was calculated from the mass difference before and after electrodeposition.

SECCM measurement details.

SECCM measurements were made using a Park NX10 instrument (Park Systems, South Korea). The SECCM probe (nanopipette filled with 0.1 M KHCO₃ was approached to the catalyst, which served as WE mounted on the x, y, z-piezo positioner. A chloridized Ag wire was used as an Ag/AgCl quasi-reference counter electrode and was inserted into the top end of the nanopipette. A surface current (*i*_{surf}) threshold of ~2 pA was used to detect when the meniscus contacted the surface of the WE and to stop further translation. SECCM measurements were made at an array of equally spaced points (2 μm apart) in

a hopping mode. All potentials are reported vs. the Ag/AgCl quasi-reference counter electrode and finally calibrated to the reversible hydrogen electrode (RHE).

Electrochemical measurements in membrane electrode assembly configuration.

The membrane electrode assembly (MEA) electrolyzer (Dioxide Materials) was comprised of the Ag-Cu cathode, a Ti-IrO_x mesh anode and an anion exchange membrane (AEM, Sustainion® X37-50 grade RT membrane, Dioxide Materials). The anode and cathode flow field parts are constructed with titanium and stainless steel with geometric active areas of 4 cm² / 25 cm² respectively depending on the measurement.

The anode was prepared by depositing Iridium oxide (IrO_x) on a titanium mesh support (0.002-inch thickness, Fuel Cell Store) with a dip coating and thermal annealing method. First, the titanium mesh was degreased with acetone and DI water to remove the surface grease. Then it was etched in a 6 M hydrochloric acid (HCl, ACS reagent, Sigma-Aldrich) solution heated to 90 °C for 45 min to increase the surface roughness and create the nucleation site for further IrO_x decoration. After thoroughly washed with water, further dip coating was processed and the solution consisted of 30 mg of Iridium(III) chloride hydrate (IrCl₃.xH₂O, 99.8%, Alfa Aesar) dissolved in 10 mL of the 2-propanol solution together with a 10% concentrated HCl. The etched titanium mesh was then dipped into the IrCl₃ solution, and dried in an oven at 100 °C before calcination in air at 500 °C for 10 min. The dipping and calcination process was repeated 5 to 10 times until a total 2 mg cm⁻² loading amount for the IrO_x on the titanium mesh was achieved.⁷

Before usage, The AEM was activated in a 1.0 M aqueous KOH solution for at least 48 hours. Then washed with deionized water and stored in the water to keep 100% humidity for further usage.⁸ For the setup of MEA, the AEM was firstly placed between the anode and cathode flow fields and then been assembled. The flow fields were mainly responsible for the effective supply of aqueous anolyte solution and humidified CO₂ over the respective surfaces of the anode and cathode electrodes. The anode and cathode gaskets were placed between the flow fields and the respective electrodes to ensure proper sealing. A CO₂ saturated 1.0 M CsHCO₃ anolyte solution was circulated through the anode side of the electrolyzer with the constant flow rate of 30 ml min⁻¹ by a peristaltic pump with preciously calibrated (Hei-flow precision 01, Heidolph instruments), while the appropriate humidified CO₂ was supplied to the cathode side with the constant gas flow rate of 10 sccm. After three times of initial activation by the LSV scans

between 2.0 V to 5.0 V with 0.05 V s⁻¹ to remove the surface oxide, a full-cell potential of -2.8 V was applied to the electrolyzer and the potential was then gradually increased from -2.8 V with the increments of -0.10 V or -0.05 V. The voltage increments were made upon complete stabilization of the corresponding current, typically 15 to 20 min. The electrochemical data were recorded while simultaneously collecting the CO₂RR gas products by using an automatic sampler connected to the cathode outlet and further analyzed by an online GC. For each applied potential, the gas products were collected for at least 3 times with proper time intervals. A cold trap has also used to collect the liquid products before the sampler and the products were further quantified by ¹H NMR spectroscopy.

Calculation of Faradaic efficiency.

The Faradaic efficiency (FE) of each gas product was calculated as follows:

$$FE_{gas} = g_i \times v \times \frac{z_i}{RT} F P_0 \times \frac{1}{I_{total}} \times 100\% \quad (2)$$

The Faradaic efficiency of each liquid product was calculated as follows:

$$FE_{liquid} = l_i \times \frac{z_i}{Q_{total}} F \times 100\% \quad (3)$$

Calculation of full-cell energy efficiency.

The full-cell energy efficiencies (EE) was calculated as follows:

$$EE_{full-cell} = \frac{(1.23 - E_i) \times FE_i}{E_{cell}} \quad (4)$$

where g_i represents the volume fraction of gas product i; v represents the gas flow rate at the outlet in sccm; z_i represents the number of electrons required to produce one molecule of product i; I_{total} represents the total current; l_i represents the number of moles of liquid product i; and Q_{total} represents the charge passed while the liquid products are being collected. $P_0 = 1.01 \times 10^5$ Pa, $T = 273.15$ K, $F = 96,485$ C mol⁻¹ and $R = 8.314$ J mol⁻¹ K⁻¹; t represents the electrolysis time (h); S represents the geometric area of the electrode (cm²); E_i represents the thermodynamic potential (vs. RHE) for CO₂RR to species i and E_{cell} represents the cell voltage in two-electrode setup.

In-situ Raman measurements.

In-situ Raman measurements were carried out via Renishaw inVia Raman microscope equipped with an objective (Leica, ×50) under the 633 nm laser. For sample preparation, the catalyst was electrochemically

deposited on the GDE, and the back and edge of the GDE without deposition were covered with epoxy to prevent these sites from the hydrogen evolution reaction. The GDE with catalysts was then used as a working electrode and installed in a custom-designed *in-situ* Raman cell (Gaossunion, *in-situ* spectrum cell). The Ag/AgCl (KCl saturated) and Pt foil were applied as reference electrode and counter electrode, respectively. The cell was then filled with CO₂ saturated 0.5 M KHCO₃. Raman signals were processed with certain considerations and the laser power was kept below 1.5 mW to protect the sample from laser damage. Further, to ensure the quality of the Raman spectroscopic signal, we averaged 10 scans per spectrum and smoothed and baseline-corrected all spectra using the Renishaw WiRE (version 5.2) software for all the measurements. The assignment of Raman shift is based on cross-referenced literature.^{9,10}

Solar cell measurements.

The current-voltage characteristics of the solar panel were recorded using a dual-source meter unit (Keithley Model 2401B). For the photovoltaic-electrolysis experiments, a GaInAs/Ga(In)As/Ge triple-junction solar cell (HGSC-A100B-2S, Hasunopto, China) was coupled to a 2-electrode H-type cell. A Xenon lamp solar simulator (Oriel LS0106) equipped with a Schott K113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) was used to reproduce an AM1.5G illumination (100 mW cm⁻²). The current of the system was recorded using a PARSTAT MC potentiostat in chronoamperometry mode with an applied potential of 0.001V. The optical power was measured by an optical power meter (HP 81630, Agilent, USA).

PV-electrolysis measurements.

The current-voltage characteristics of the solar panel were recorded using a dual-source meter. A GaInAs/Ga(In)As/Ge triple-junction solar cell was used as a power source and coupled to a membrane electrode assembly to perform the electrolysis of CO₂. The areas of the cathode, anode and solar cell were adjusted to 2 cm² (Pt foil, 1×1 cm, two sides), 2 cm² (TB-Cu29.6 on GDE, 1×1 cm) and 2 cm² (GaInAs/Ga(In)As/Ge, 1×2 cm), respectively. The light source was a 450 W xenon lamp (Oriel) equipped with a Schott K113 Tempax sunlight filter to match the emission spectrum of the lamp to the AM1.5G standard. The current of the system was recorded by chronoamperometry by applying an 0.001V of external bias for different periods under chopped AM 1.5G illumination. The optical power of the sun was measured by an optical power meter.

Estimation of the solar-to-fuel (STF) conversion efficiency.

The solar-to-fuel conversion efficiency for the PV-driven electrolysis of nitrate was calculated by equation 5:¹¹

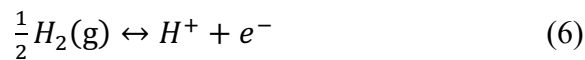
$$STF = (1.23 - E_{CO_2/C_2H_4}^0) \times I_{op} \times FE_{C_2H_4} / P_{sun} \quad (5)$$

where P_{sun} is the power of the sun (100 mW cm^{-2}), I_{op} is the current, $E_{CO_2/C_2H_4}^0$ is the standard potential ($-0.34 \text{ V vs. RHE, pH} = 7$).¹² The operating current (I_{op}) of the PV-electrolyzer system was determined from the intersection between the j-V characteristic and LSV curves of the PV cell and the 2-electrode cell. We found $I_{op} = \sim 7.56 \text{ mA cm}^{-2}$ at $V = \sim 4.0 \text{ V}$. The Faradaic efficiency ($\sim 70.1 \%$) of the 2-electrode system using TB-Cu_{29,6} as cathode was estimated at a full-cell potential of 4.0 V .

Calculation details.

All structures were optimized by density functional theory (DFT), the projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) scheme.¹³ All calculations were performed with Vienna Ab Initio Simulation Package (VASP).¹⁴⁻¹⁶ The energy cutoff of the plane-wave basis set was consistently set to 500 eV . The convergence criteria of $0.05 \text{ eV/\AA}$ and 10^{-4} eV were used for the forces and energy during the geometry optimizations. The DFT-D3 correction was used to describe the dispersion contribution. The structures of twin-boundary (TB) and planar Cu(111) were taken from the literature.¹⁷⁻¹⁹ A four-layer slab was used for both TB and Cu(111), in which the bottom two layers were fixed during all calculations. The slabs of TB and Cu(111) contains 96 and 64 copper atoms, respectively. To avoid the artificial inter-layer interaction, the c vector was set to $20 \text{ \AA}$ to ensure a vacuum larger than $12 \text{ \AA}$. The Brillouin zone was sampled with a $3 \times 3 \times 1$ Monkhorst-Pack grid.²⁰

DFT calculations were combined with the computational hydrogen electrode (CHE) approach to investigate the CO₂ reduction process. The use of CHE avoids explicit treatment of solvated protons and electrons using the following equation:



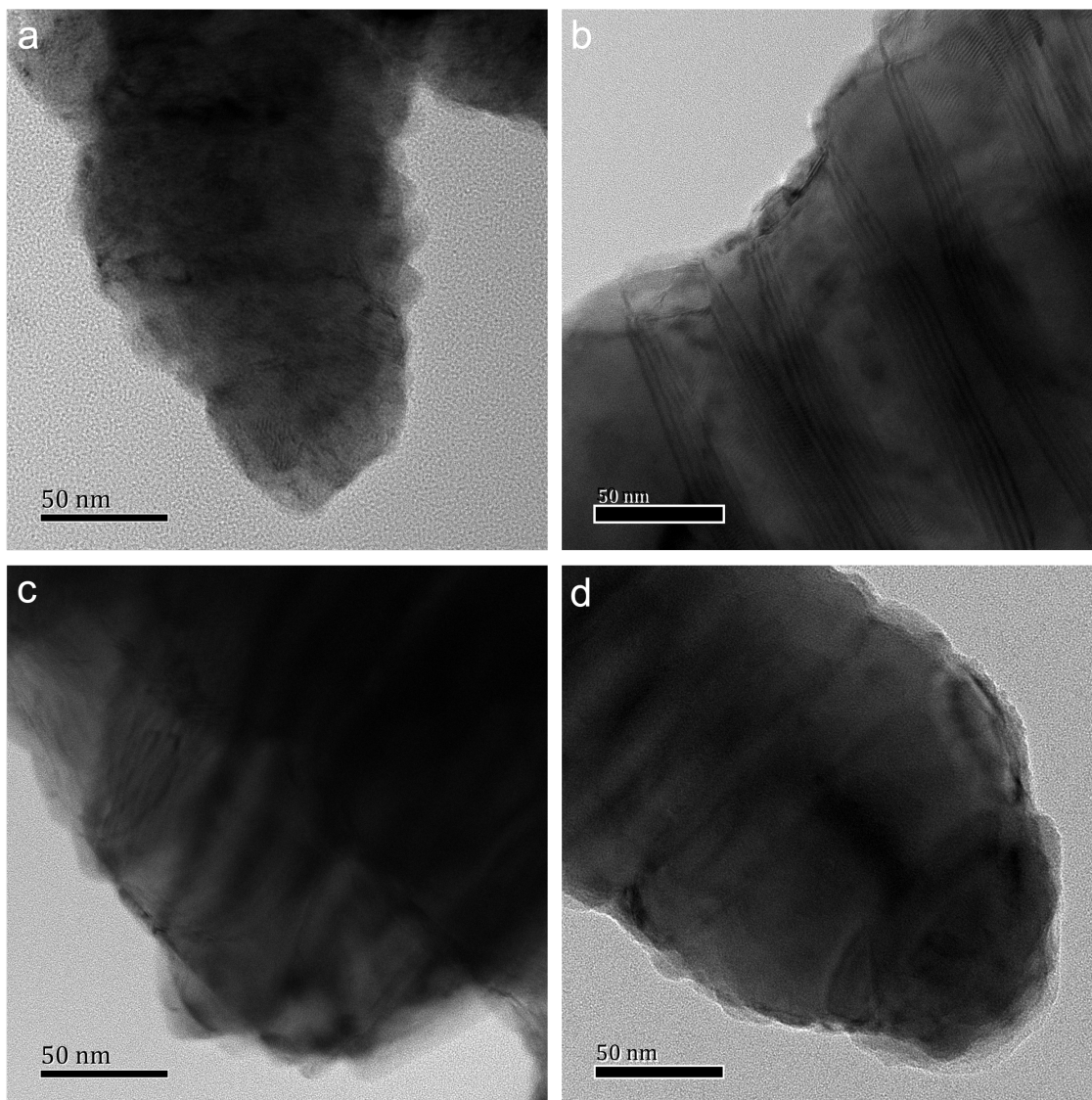
which further indicates the equilibrium of chemical potential:

$$\frac{1}{2}\mu(H_2) = \mu(H^+ + e^-) \quad (7)$$

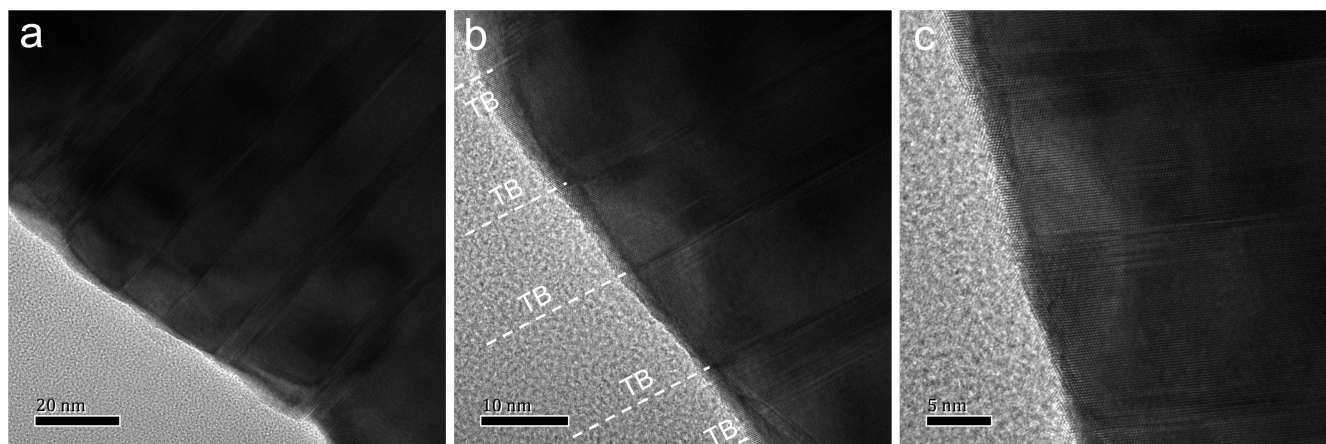
Using such equilibrium, it is possible to consistently evaluate the Gibbs free energy (G) for each intermediate in the reaction network. The Gibbs free energy was further calculated using the following equation:

$$G = E + ZPE + \int C_p dT - TS + k_b T \ln a(H^+) - neU \quad (8)$$

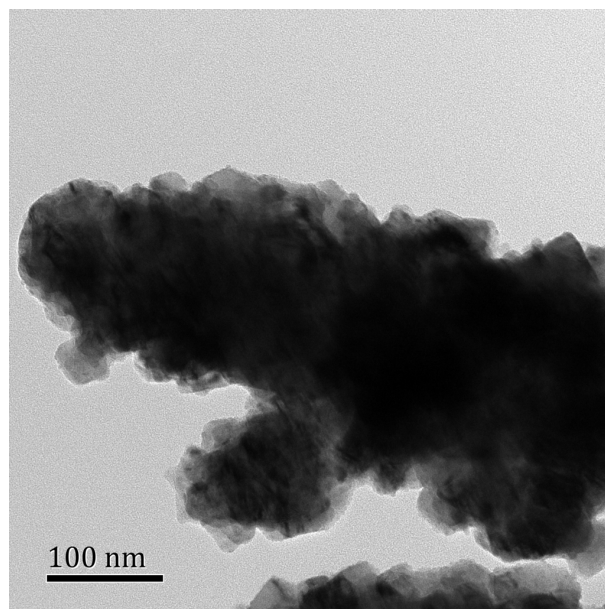
where E is the electronic energy, ZPE is the zero-point energy, C_p is the heat capacity, T is the temperature, S is the entropy, n is the number of electrons obtained by intermediate species upon its formation, e is the elementary charge. $k_b T \ln a(H^+)$ is the free energy correction of pH. All of the data were calculated at the standard condition (pH = 0, $T = 298.15$ K), therefore $k_b T \ln a(H^+) = 0$. For the adsorbates, only the vibrational contributions Gibbs free energy were considered (the atoms of the slabs were fixed during the vibration calculations). For gas or liquid phase molecules (H_2 , CO_2 and H_2O), the vibration, translation, and rotation contributions were taken into account.



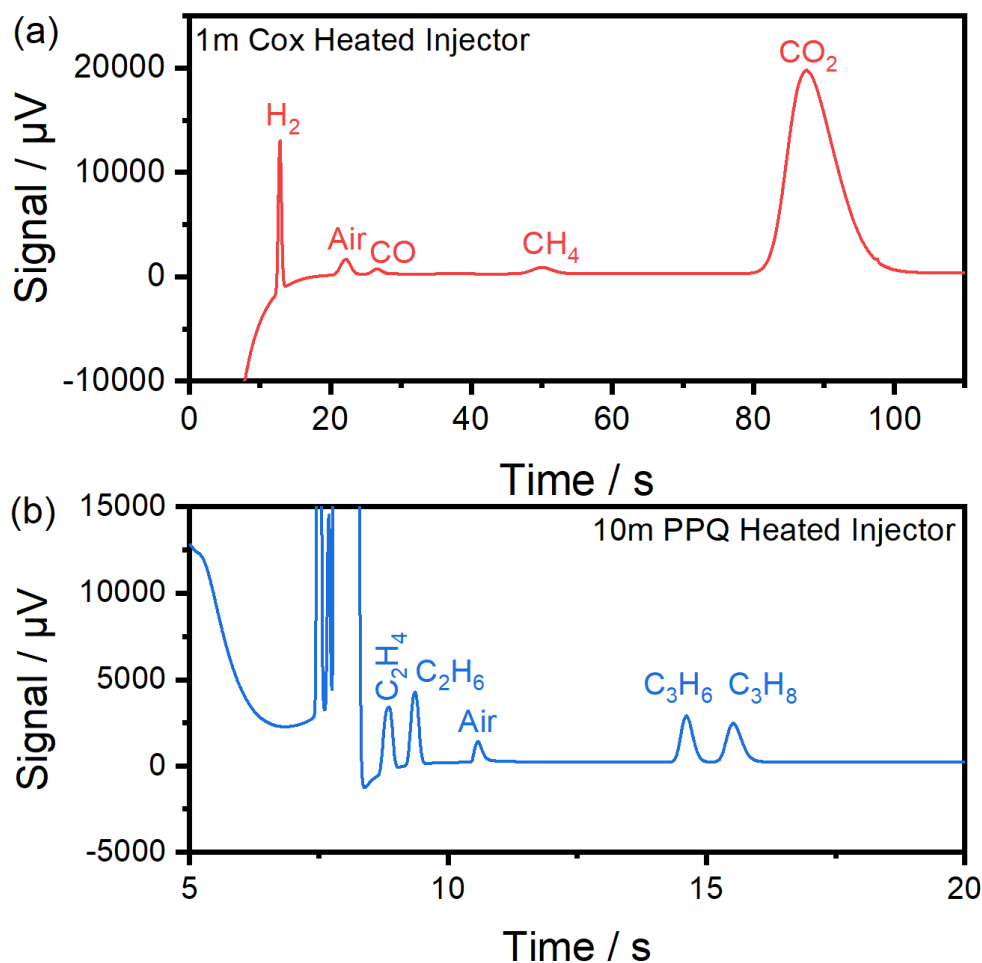
Supplementary Fig. 1 | HRTEM image of the Cu nanostructures with different TB densities. **a**, TB-Cu_{2.2}; **b**, TB-Cu_{7.9}; **c**, TB-Cu_{15.4} and **d**, TB-Cu_{29.6}.



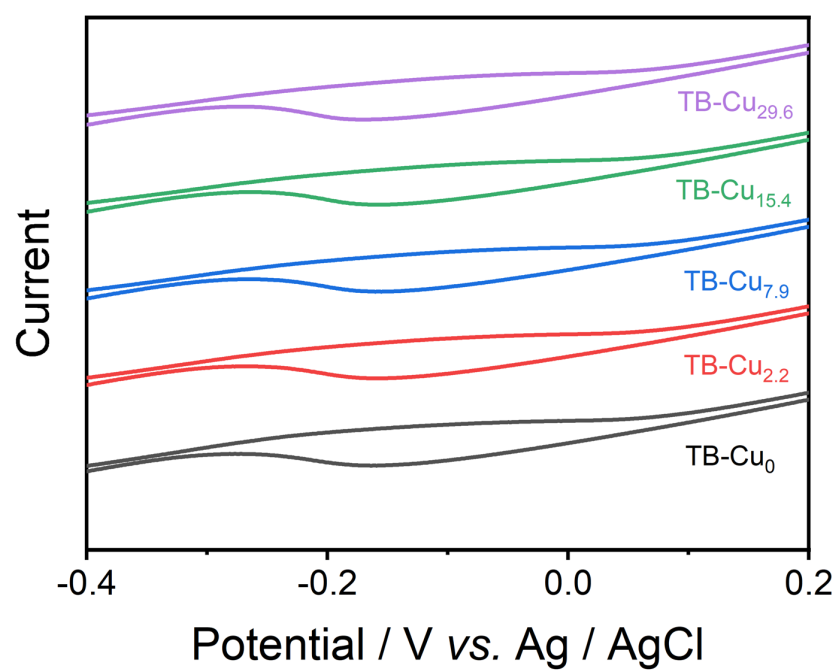
Supplementary Fig. 2 | HRTEM images for the TB-Cu_{29.6}. The twin boundaries can be easily observed as indicated .



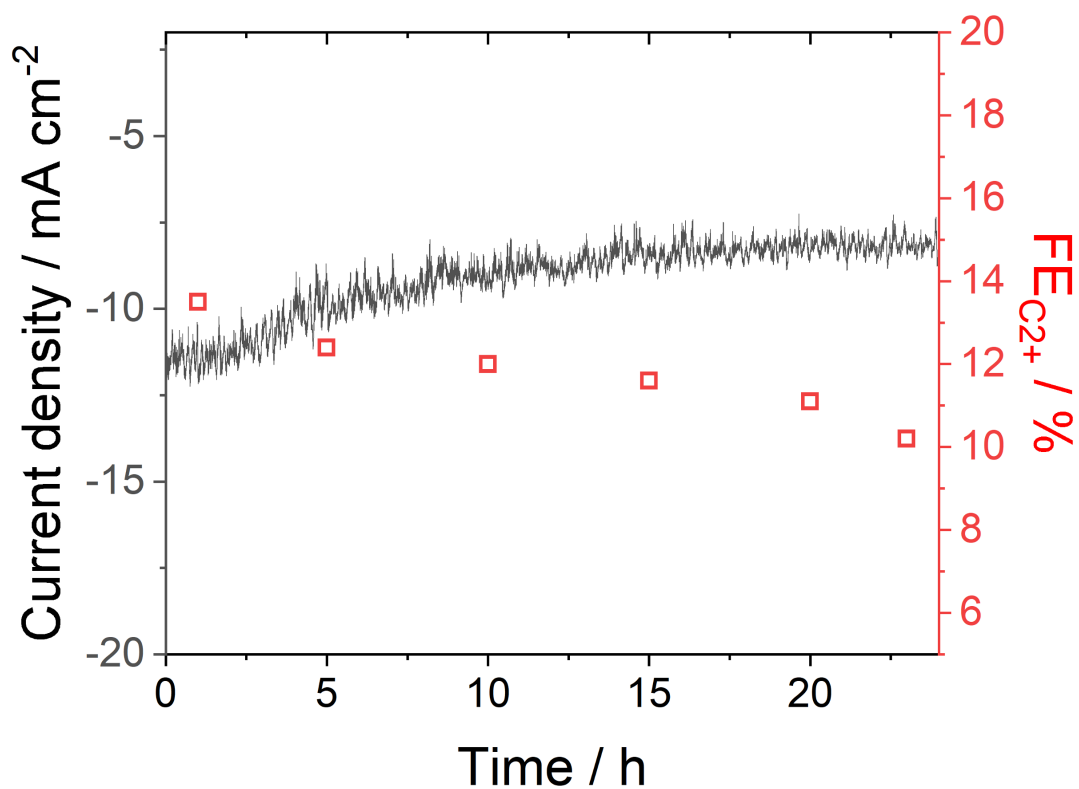
Supplementary Fig. 3 | TEM image for the pristine TB-Cu₀ deposited by the steady state electrodeposition method, no twin boundary could be overserved from the pristine Cu catalyst.



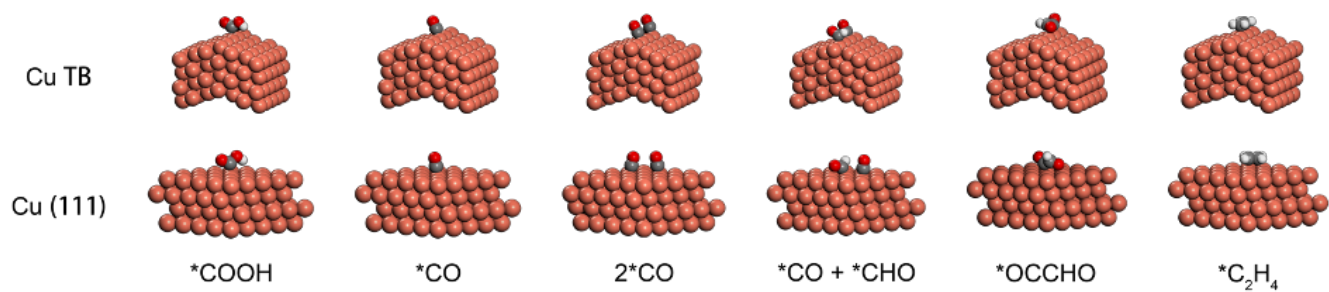
Supplementary Fig. 4 | Component calibration for the gas chromatography calibration curve. Gas chromatography calibration curves of the standard gas mixture with 1m Cox and 10m PPQ heated injector that show CO_2 (0.25%), H_2 (0.25%), CO (0.25%), CH_4 (0.25%), C_2H_4 (0.25%), C_2H_6 (0.25%), C_3H_6 (0.25%) and C_3H_8 (0.25%), respectively. The trace amount of air comes from the large space volume of the calibration gas line which does not appear and will not influence the quantification of the gas component.



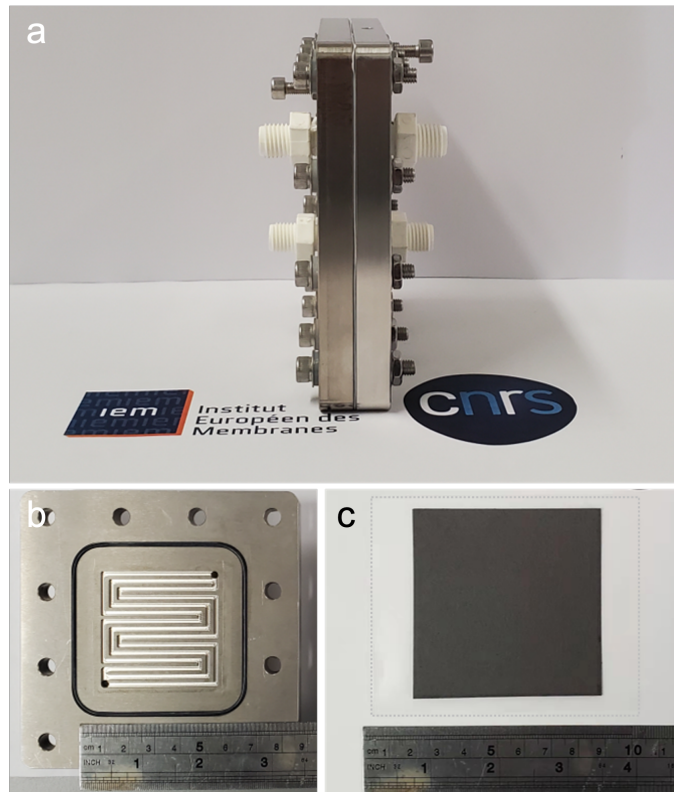
Supplementary Fig. 5 | Cyclic voltammetry curves of Pb-UPD the Cu-based catalysts with different TB densities.



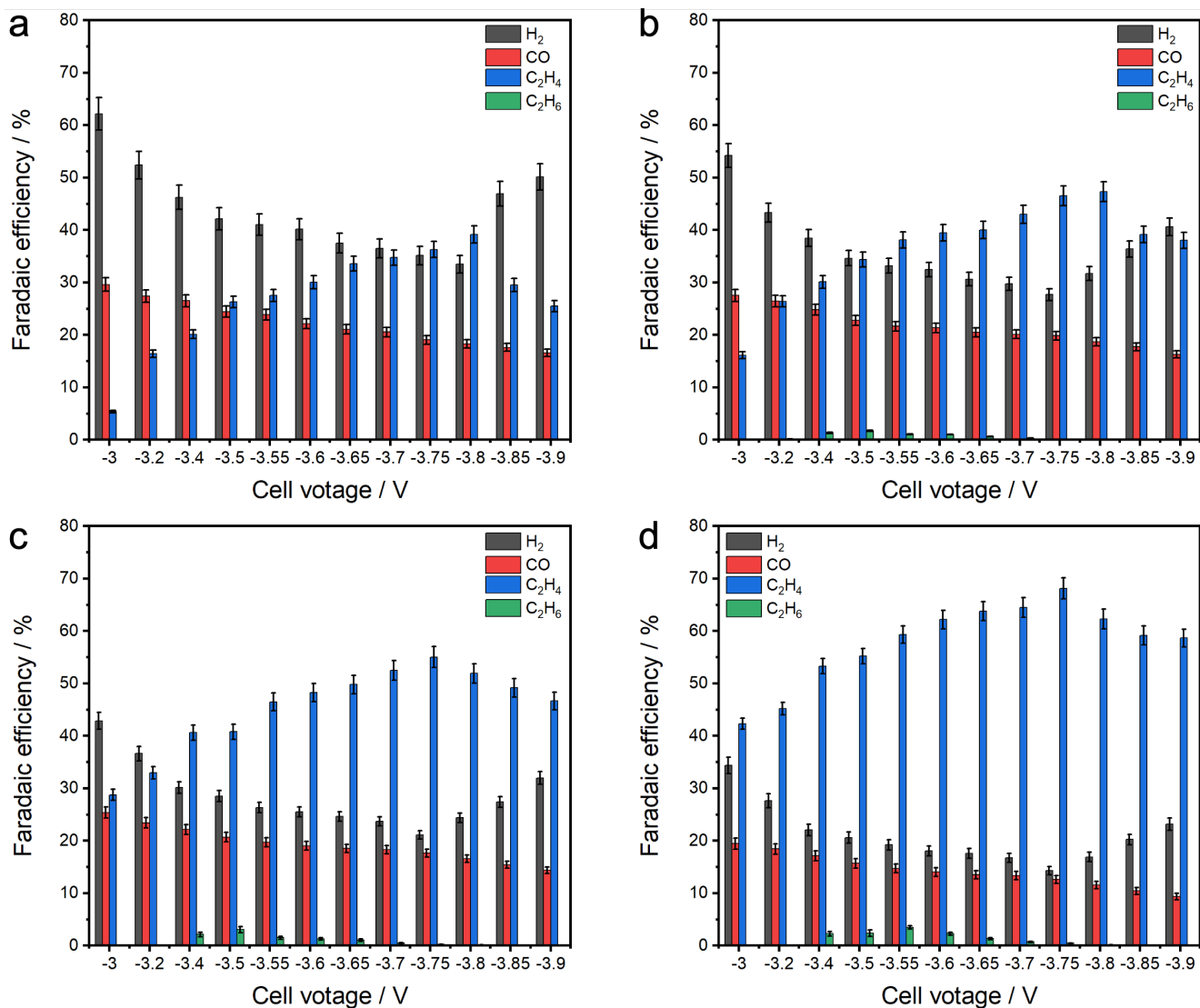
Supplementary Fig. 6 | Long-term stability measurement of TB-Cu₀ in CO₂-saturated 0.5 M KHCO₃ electrolyte under continuous feed-in of CO₂ (10 sccm) at -1.10 V vs. RHE for 24 hours.



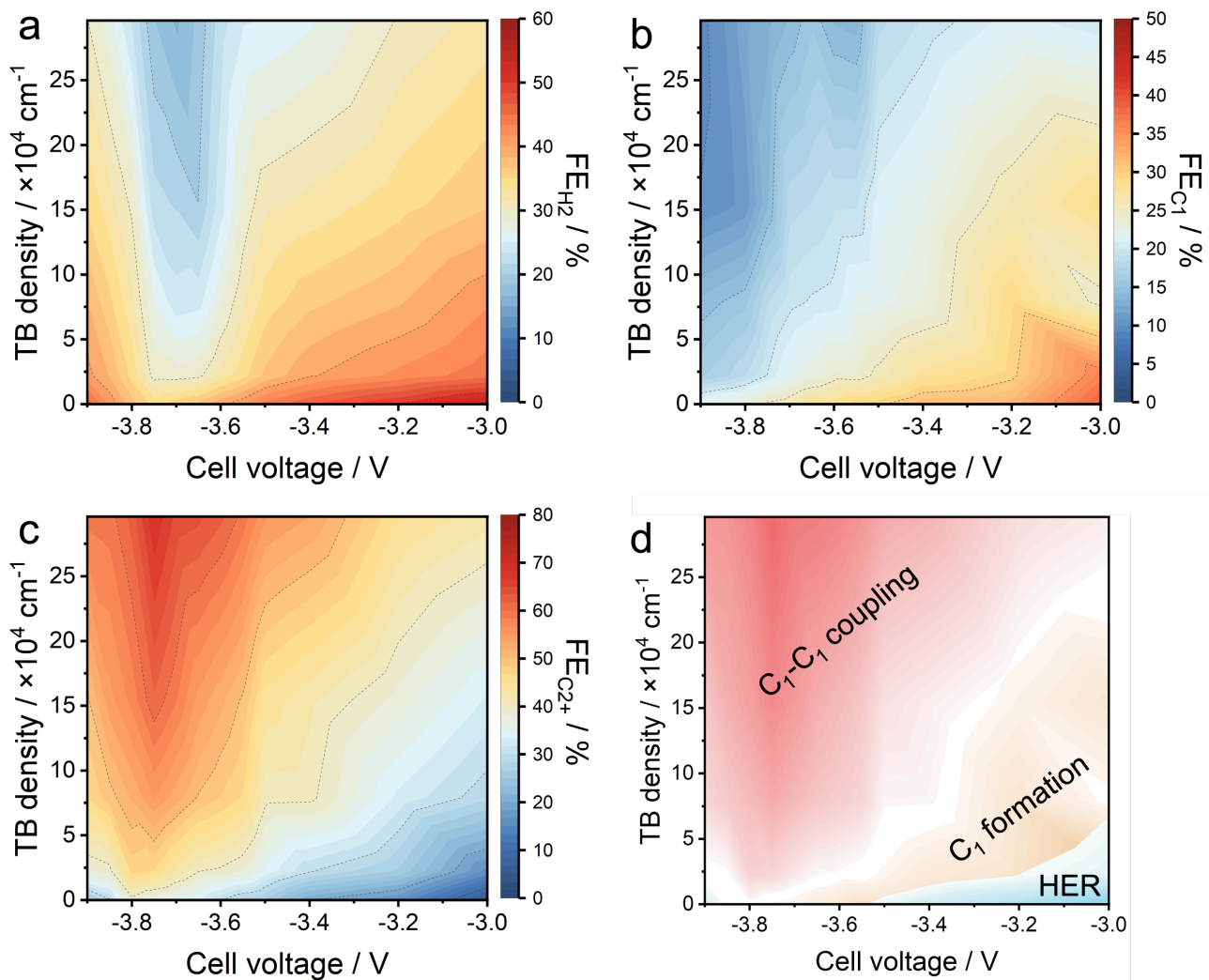
Supplementary Fig. 7 | Geometries of the optimized molecular structures for all the intermediates on both the Cu TB sites and Cu (111) facets.



Supplementary Fig. 8 | Photograph of the 25 cm² membrane electrode assembly (MEA) electrolyzer. **a**, Full view of the experimental setup. Views of the **b**, gas channel design **c**, Photograph of the 25 cm² gas diffusion layer modified with TB-Cu_{29,6}, hot pressed on an anion exchange membrane.



Supplementary Fig. 9 | Faradaic efficiency of different CO₂RR products under the configuration of 5 cm² MEA with different TB density Cu samples. a, TB-Cu_{2.2}. b, TB-Cu_{7.9}. c, TB-Cu_{15.4}. d, TB-Cu_{29.6}.

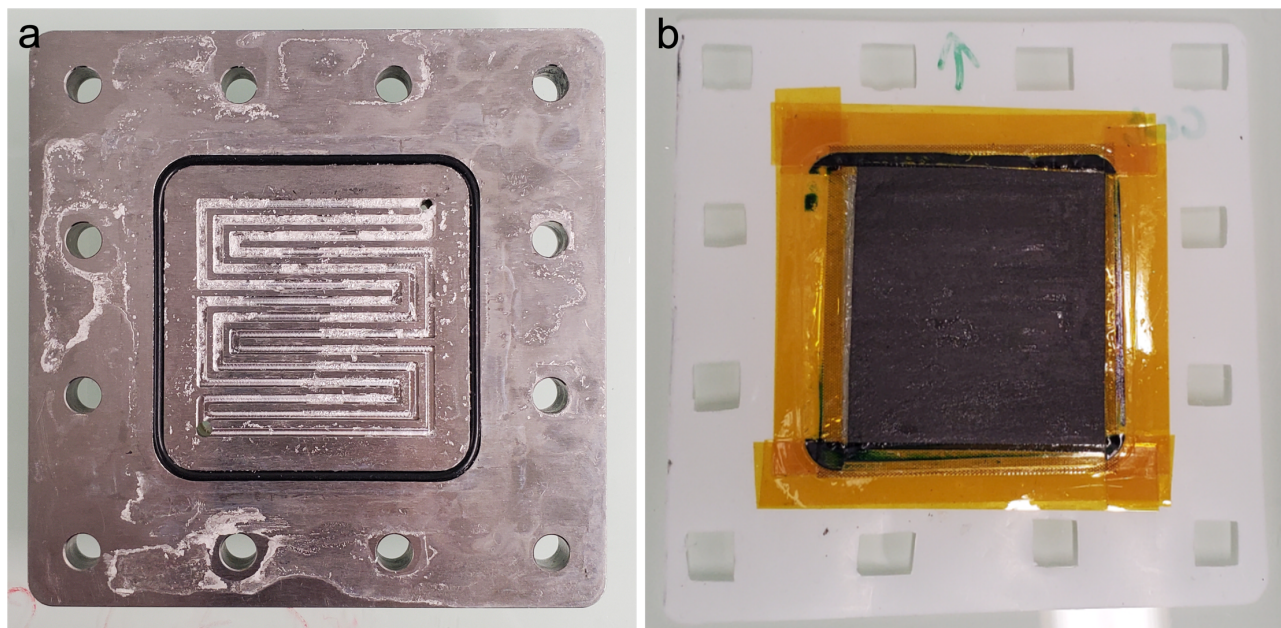


Supplementary Fig. 10 | **a-c**, 2D heatmaps of FE_{H_2} (**a**), FE_{C_1} (**b**) and FE_{C_2} on Cu-based samples under the variation of both TB density and potentials. **d**, Superposition of the different maps showing the preferential zones for the hydrogen evolution, the C_1 formation and the C_1 - C_1 coupling (C_2 formation).

1 **Supplementary Table 1** | Electrochemical CORR and CO₂RR studies of producing C₂ products on twin
2 boundary (TB)-rich and step/defect-rich Cu catalysts.

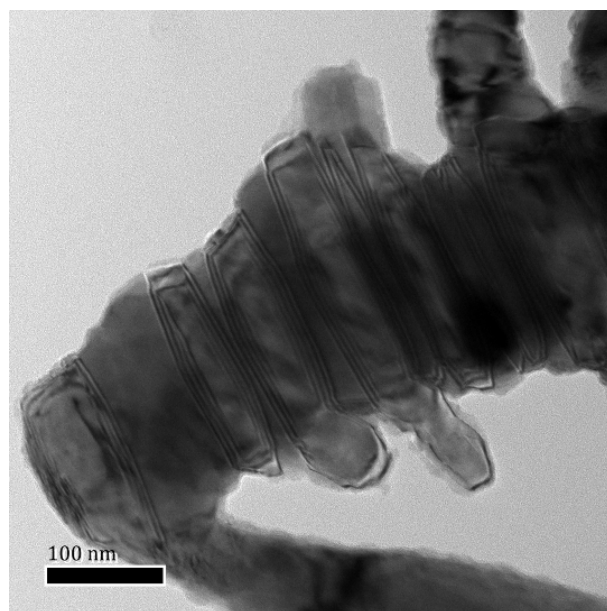
Catalyst	Reaction	Catalysis condition	Main products	Reference
TB-Cu _{29.6}	CO ₂ RR	0.5M KHCO ₃ , MEA	73.2% FE _{C2+} at -3.8 V	This work
TB-Cu ₀	CO ₂ RR	0.5M KHCO ₃ , MEA	36.4 % FE _{C2+} at -3.8 V	This work
GB-rich Cu NPs	CORR	0.1 M KOH, H-cell	36% FE _{C2H5OH} , 34% FE _{OAc-} , 28% FE _{H2} at -0.3 V vs. RHE	21
Oxide-derived GB-rich Cu	CORR	0.1 M KOH, H-cell	43% FE _{C2H5OH} , 43% FE _{H2} at -0.3 V vs. RHE	22
Cu NPs			> 94% FE _{H2} at -0.3 to -0.5 V vs. RHE	
Oxide-derived GB-rich Cu	CORR	0.1 M KOH, H-cell	55% FE _{H2} , 26% FE _{C2H5OH} , 14% FE _{OAc-} , at -0.3 V vs. RHE	23
GB-rich Cu NPs	CO ₂ RR	0.1 M KOH, flow cell	38% FE _{C2H4} , 30% FE _{C2H5OH} , 12% FE _{H2} , 8% FE _{CO} at -1.2 V vs. RHE	11
Oxide derived GB-rich Cu	CO ₂ RR	0.1 M KHCO ₃ , H-cell	50% FE _{H2} , 30% FE _{C2H4} , 10% FE _{CO} , 7% FE _{C2H5OH} at -1.2 V vs. RHE	24
Step/defect-rich Cu	CO ₂ RR	0.1 M KHCO ₃ , H-cell	53% FE _{C2H5OH} , 18% FE _{PrOH} , 13% FE _{H2} , 7% FE _{C2H4} at -1.1 V vs. RHE	25
		0.1 M KOH, flow cell	52% FE _{C2H5OH} , 14% FE _{PrOH} , 11% FE _{HCOO-} , 8% FE _{H2} , 7% FE _{C2H4} at -1 V vs. RHE	
Nanotwinned Cu	CO ₂ RR	0.1 M KHCO ₃ , H-cell	86% FE _{CH4} at -1.22 V vs. RHE	26

3
4



Supplementary Fig. 11 | Optical image of the a, MEA cathode counterpart and b, back side of the cathode GDE (no catalyst) after the high current long-term stability measurement. We observed both the appearance of salting out and the flooding effect which cause the decrease of both Faradaic efficiency and the specific current density for the C_{2+} product.

1

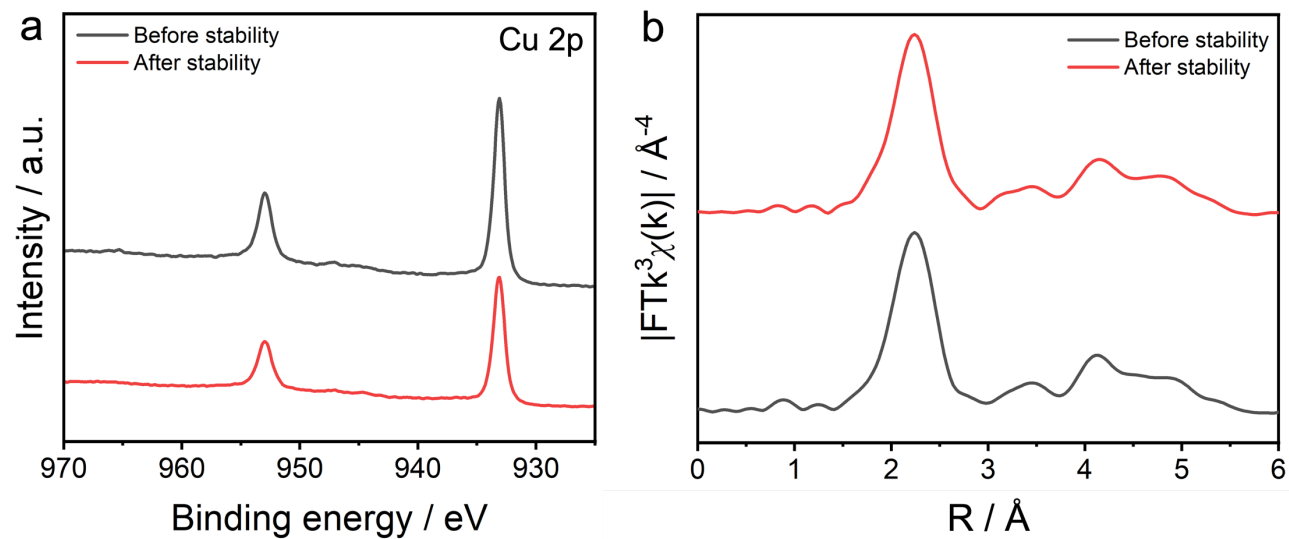


2

3

4 **Supplementary Fig. 12** | TEM image of the TB-Cu_{29.6} sample after the stability measurement.

5



Supplementary Fig. 13 | Surface valence state (XPS) and coordination environment characterization (EXAFS) of the TB-Cu_{29.6} before and after the stability measurement.

Supplementary Table 2 | Cu K-edge EXAFS curve fitting parameters extracted from Supplementary Fig. 13, obtained from the TB-Cu_{29.6} sample before and after the stability measurement.^a The estimated parameter errors are indicated in parentheses.

Sample	Path	CN	R(Å)	$\sigma^2(\times 10^{-3} \text{Å}^2)$	ΔE_0 (eV)	R factor (%)
Before reaction ^b	Cu-Cu	10.9±0.2	2.45±0.02	4.3±0.2	1.8±0.4	0.15
After reaction ^c	Cu-Cu	10.5±0.1	2.45±0.05	3.1±0.1	1.4±0.2	0.21

Supplementary Note 10 | ^aN, coordination number; R, distance between absorber and backscatter atoms; σ^2 , Debye-Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; R factor (%) indicates the goodness of the fit. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $N \pm 20\%$; $R \pm 1\%$; $\sigma^2 \pm 20\%$; $\Delta E_0 \pm 20\%$. S_0^2 was fixed to 0.707 as determined by Cu foil fitting. ^bFitting range: $3.0 \leq k (\text{Å}^{-1}) \leq 10.0$ and $1.0 \leq R (\text{Å}) \leq 3.0$. ^cFitting range: $3.0 \leq k (\text{Å}^{-1}) \leq 10.0$ and $1.0 \leq R (\text{Å}) \leq 3.0$.

1 **Supplementary Table 3** | Comparison of the CO₂RR performance with those from other reported
 2 photocatalysts.

Photovoltaics	STF (%)	Cathode Anode	Reference
III-V/Si	8.33	TB-Cu_{29.6} Pt	This work
Si	6.4	Cu(OH)₂-D NiFe-LDH	27
Perovskite	5.6	CuAg IrO ₂	28
Perovskite	2.3	CuO CuO	29
Si	2.4	Cu ₂ O derived Cu IrO _x	30
III-V/Si	5.6	CuAg IrO ₂ nanotube	31

References

1. De Luna, P. *et al.* Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. *Nat. Catal.* **1**, 103–110 (2018).
2. Tang, C. *et al.* CO₂ reduction on copper's twin boundary. *ACS Catal.* **10**, 2026–2032 (2020).
3. Rehr, J. J. & Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621 (2000).
4. Newville, M. EXAFS analysis using FEFF and FEFFIT. *J. Synchrotron Radiat.* **8**, 96–100 (2001).
5. Qi, K., Chhowalla, M. & Voiry, D. Single atom is not alone: Metal–support interactions in single-atom catalysis. *Mater. Today* **40**, 173–192 (2020).
6. Baturina, O. A. *et al.* CO₂ electroreduction to hydrocarbons on carbon-supported Cu nanoparticles. *ACS Catal.* **4**, 3682–3695 (2014).
7. Gabardo, C. M. *et al.* Continuous carbon dioxide electroreduction to concentrated multi-carbon products using a membrane electrode assembly. *Joule* **3**, 2777–2791 (2019).
8. Lees, E. W. *et al.* Linking gas diffusion electrode composition to CO₂ reduction in a flow cell. *J. Mater. Chem. A* **8**, 19493–19501 (2020).
9. Akemann, W. & Otto, A. Vibrational modes of CO adsorbed on disordered copper films. *J. Raman Spectrosc.* **22**, 797–803 (1991).
10. Gunathunge, C. M. *et al.* Spectroscopic observation of reversible surface reconstruction of copper electrodes under CO₂ reduction. *J. Phys. Chem. C* **121**, 12337–12344 (2017).
11. Chen, Z. *et al.* Grain-boundary-rich copper for efficient solar-driven electrochemical CO₂ reduction to ethylene and ethanol. *J. Am. Chem. Soc.* **142**, 6878–6883 (2020).

12. Pappijn, C. A., Ruitenbeek, M., Reyniers, M. F. & Van Geem, K. M. Challenges and opportunities of carbon capture and utilization: electrochemical conversion of CO₂ to ethylene. *Front. Energy Res.* **8**, 557466 (2020).
13. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
14. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758 (1999).
15. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953 (1994).
16. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
17. Tran, R. *et al.* Surface energies of elemental crystals. *Sci. Data* **3**, 1–13 (2016).
18. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).
19. Zheng, H. *et al.* Grain boundary properties of elemental metals. *Acta Mater.* **186**, 40–49 (2020).
20. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188 (1976).
21. Feng, X., Jiang, K., Fan, S. & Kanan, M. W. A direct grain-boundary-activity correlation for CO electroreduction on Cu nanoparticles. *ACS Cent. Sci.* **2**, 169–174 (2016).
22. Li, C. W., Ciston, J. & Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **508**, 504–507 (2014).

23. Verdaguer-Casadevall, A. *et al.* Probing the active surface sites for CO reduction on oxide-derived copper electrocatalysts. *J. Am. Chem. Soc.* **137**, 9808–9811 (2015).
24. Cheng, D. *et al.* The nature of active sites for carbon dioxide electroreduction over oxide-derived copper catalysts. *Nat. Commun.* **12**, 395 (2021).
25. Gu, Z. *et al.* Efficient electrocatalytic CO₂ reduction to C₂₊ alcohols at defect-site-rich Cu surface. *Joule* **5**, 429–440 (2021).
26. Cai, J. *et al.* Highly selective electrochemical reduction of CO₂ into methane on nanotwinned Cu. *J. Am. Chem. Soc.* (2023).
27. Zhong, D. *et al.* Coupling of Cu (100) and (110) facets promotes carbon dioxide conversion to hydrocarbons and alcohols. *Angew. Chem. Int. Ed.* **60**, 4879–4885 (2021).
28. Gao, J. *et al.* Selective C-C coupling in carbon dioxide electroreduction via efficient spillover of intermediates as supported by *operando* Raman spectroscopy. *J. Am. Chem. Soc.* **141**, 18704–18714 (2019).
29. Huan, T. N. *et al.* Low-cost high-efficiency system for solar-driven conversion of CO₂ to hydrocarbons. *Proc. Natl. Acad. Sci.* **116**, 9735–9740 (2019).
30. Sacco, A. *et al.* An integrated device for the solar-driven electrochemical conversion of CO₂ to CO. *ACS Sustain. Chem. Eng.* **8**, 7563–7568 (2020).
31. Bullock, J. *et al.* Efficient solar-driven electrochemical CO₂ reduction to hydrocarbons and oxygenates. *Energy Environ. Sci.* **10**, 2222–2230 (2017).