

Supplementary Information

Stabilization of Cu⁺ sites by amorphous Al₂O₃ to enhance electrochemical CO₂ reduction to C₂₊ products

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Experimental Section

Chemicals

Copper (II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), acetone (CH_3COCH_3), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), potassium hydroxide (KOH), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and isopropanol ($\text{C}_3\text{H}_7\text{OH}$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and Nafion D-521 dispersion (5% w/w in water and 1-propanol, ≥ 0.92 meg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Anion exchange membrane FUMA-FAA-3-PK-130 (0.11-0.13 mm thick, 1.1-1.4 meg g^{-1} exchange capacity) was obtained from FuMA-Tech. Perfluorinated resin solution containing NafionTM 1100W (~5 wt.% in lower aliphatic alcohols and water) was purchased from Sigma-Aldrich. Carbon paper-based gas diffusion layers (GDLs, Sigracet 29 BC) and nickel foam were provided by the Fuel Cell Store. CO_2 and Ar (Shanghai Chemistry Industrial Zone Pujiang Special Type Gas Co., Ltd.) had a purity of 99.999 % and were used as received.

Synthesis of $\text{Cu}_x\text{Al}_y\text{-Ox}$ electrodes

Synthesis of $\text{Cu}_x\text{Al}_y\text{-Ox}$ catalysts: The $\text{Cu}_x\text{Al}_y\text{-Ox}$ catalysts were synthesized by hydrothermal method with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as precursors. The catalyst was prepared as follows: 2.7 mmol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.3 mmol of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 16 mL of deionized water, and then added to 10 mL of 1.0 M KOH solution, and stirred continuously at room temperature until the precipitation was complete. Then, the pH was adjusted with a small amount of ammonia. After 5 minutes of continuous stirring, the solution was transferred to a hydrothermal reactor and placed in an oven at 100 °C for 18 hours. After cooling, the sample was washed with ethanol and deionized water and centrifuged at least 3 times to remove unreacted precursors and other possible impurities. Then the catalysts were dried in a vacuum oven at 60 °C overnight. After cooling to room temperature, the final product was obtained, named as $\text{Cu}_{100}\text{Al}_{7.88}\text{-Ox}$ (x and y are the mass percentages of Cu and Al, the percentage mass value of Cu (x) is set at 100.).

According to the above catalyst preparation method, bimetallic catalysts with different Cu/Al ratios ($\text{Cu}_{100}\text{Al}_{0.98}\text{-Ox}$, $\text{Cu}_{100}\text{Al}_{1.77}\text{-Ox}$, $\text{Cu}_{100}\text{Al}_{7.88}\text{-Ox}$, and $\text{Cu}_{100}\text{Al}_{137}\text{-Ox}$ catalysts) were prepared by adjusting the ratio of the precursors.

Synthesis of $\text{Cu}_x\text{Al}_y\text{-OD}$ electrodes: The $\text{Cu}_x\text{Al}_y\text{-Ox}$ electrode was treated by the

redox reaction cyclic voltammetry (CV) technique to obtain the $\text{Cu}_x\text{Al}_y\text{-OD}$ electrode. The CV was carried out in a flow cell equipped with a three-electrode system, and the anode and cathode electrolytes were both 1 M KOH. The potential ranged from 0 V to -1.98 V vs. RHE at a rate of 100 mV s^{-1} for at least 10 cycles to completely reduce the possible oxidized species.

Characterizations

Scanning electron microscopy (SEM, HITACHI S-4800) and high-magnification transmission electron microscopy (TEM, JEM-2100F) were used to characterize the morphology and structural characteristics of the samples. The composition of the catalyst was assessed on an X-ray diffractometer (XRD, Rigaku Ultima VI) and an X-ray photoelectron spectroscopy (XPS, AXIS Supra). The inductively coupled plasma (ICP) atomic emission spectrometer, model Agilent 5100 SVDV, was used to determine the relative content of Cu and Al. Synchrotron X-ray absorption spectroscopy (XAS) were performed at the Shanghai Synchrotron Radiation Facility with the BL13SSW beamline. The Cu K-edge X-ray absorption spectra of $\text{Cu}_x\text{Al}_y\text{-OD}$ electrodes were obtained, and Cu foil, Cu_2O and CuO were used as references. *In-situ* Raman measurements were performed on a Renishaw inVia Reflex Raman microscope in a modified flow cell without CO_2 by using a water immersion objective lens (63x) with a 785 nm laser, with 5 s integration and averaging 20 scans per region. The modified flow-cell setup consisted of a three-electrode setup, in which graphite rod and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively.

Electrocatalytic CO_2 reduction reaction (e CO_2RR) measurements

All electrochemical experiments were performed in a flow cell on an electrochemical workstation (CHI 660E, CH Instruments, Shanghai, China). Typically, 10 mg of catalyst and 100 μL of 5 wt% Nafion 1100W were dispersed in 1 mL of *i*-PrOH and sonicated for 20 min. Then, the resulting ink was dropped onto a 1.5 cm \times 2.5 cm piece of gas diffusion layer (GDL) to prepare the gas diffusion electrode (GDE). In the flow cell, the prepared GDEs, Ag/AgCl electrode (saturated KCl) and nickel foam electrode were employed as the working, reference and counter electrodes, respectively. The electrolyte was 1 M KOH aqueous solution. The anode chamber and cathode chamber were separated by an anionic membrane. In all measurements, we used Ag/AgCl as the reference electrode, and the potential (V vs. Ag/AgCl) was

converted to RHE using the following equation ¹:

$$E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.059 \times \text{pH}$$

Electrochemical measurements

(1) Linear sweep voltammetric (LSV) curve: The test of the LSV curve was carried out in a flow cell equipped with a three-electrode system. In the test, Ar or CO₂ was introduced with a sweep potential ranging from 0 V to -1.78 V vs. RHE at a sweep speed of 100 mV s⁻¹.

(2) Electrochemical impedance spectroscopy (EIS): The EIS measurements were carried out in CO₂-saturated 1 M KOH solution at an open circuit potential (OCP). The impedance spectra were recorded with an amplitude of 5 mV of 10⁻² to 10⁵ Hz. The data obtained from the EIS measurements were fitted by the Zview software (Version 3.1, Scribner Associates, USA).

(3) Double-layer capacitance (C_{dl}): The electrochemical surface area (ECSA) is proportional to the double-layer capacitance, and the C_{dl} of the catalytic material was determined according to the CV curve at different scanning rates, so the ECSA was evaluated. The scanning potential range of the CV curves was chosen from 0.75 V to 0.85 V vs. RHE. Scans were recorded at different scan rates with a minimum of 3 cycles in the non-Faradaic region, which included 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹ and 100 mV s⁻¹. The C_{dl} was estimated by plotting the Δj ($j_a - j_c$) at 0.80 V vs. RHE against the scan rates, where j_a and j_c were the anodic and cathodic current density, respectively ². The ECSA of the working electrodes was calculated according to the following equation: ECSA = $R_f S$, where R_f is the roughness factor and S is the actual surface area of the working electrode (in this work, $S = 1 \text{ cm}^2$). The R_f can be calculated by the relation $R_f = C_{dl}/a$, where a is the double-layer capacitance of a smooth Cu surface. Therefore, the ECSA is proportional to the C_{dl} value and can be compared via the C_{dl} value.

Quantification of products

Gaseous products were analyzed by a gas chromatograph (GC, Agilent-8890) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The volume fraction of the gaseous product was calculated from the product peak area using standard calibration curve. The theoretical molar number was calculated based on the current density and the amount of electron transfer in the

process. Liquid products were quantified by a ^1H nuclear magnetic resonance (^1H NMR) spectrometer (Bruker; Ascend 500 MHz) in D_2O with $\text{C}_6\text{H}_5\text{OH}$ (200 mM) and DMSO (5 mM) as internal standards. The solvent pre-saturation technique was implemented to suppress the water peak. The moles of a liquid product were calculated from integral areas and calibration curves. The molarity of the liquid products was calculated from the integrated area and calibration curve. After quantification, the FE of each product was calculated as follows:

$$FE_x = \frac{nzF}{Q_{total}} \times 100\%$$

(n: the molar amount of product (mol), z: number of electrons transferred to generate the target product, F: The Faraday constant (96485 C mol^{-1}), Q_{total} : the amount of charge passed through the working electrode (C).)

Supplementary Figures and Tables

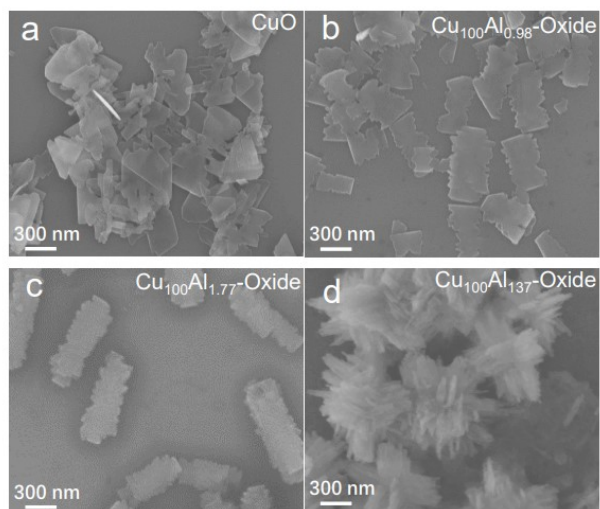


Figure S1. SEM images of (a) CuO, (b) Cu₁₀₀Al_{0.98}-Ox, (c) Cu₁₀₀Al_{1.77}-Ox, and (d) Cu₁₀₀Al₁₃₇-Ox catalysts.

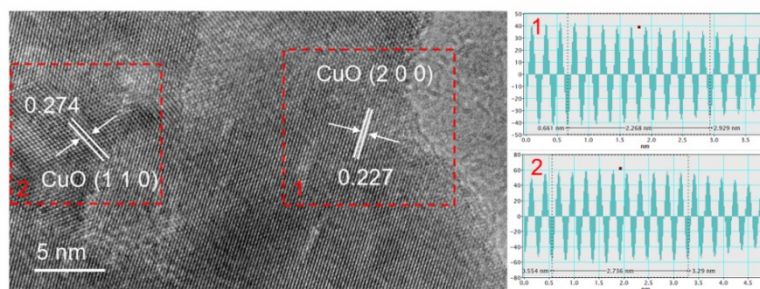


Figure S2. TEM image and intensity profiles measured from the marked area in the left HR-TEM image of the CuO catalyst.

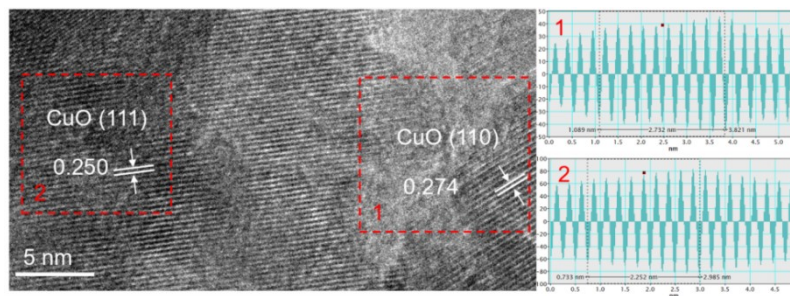


Figure S3. TEM image and intensity profiles measured from the marked area in the left HR-TEM image of the $\text{Cu}_{100}\text{Al}_{7.88}\text{-Ox}$ catalyst.

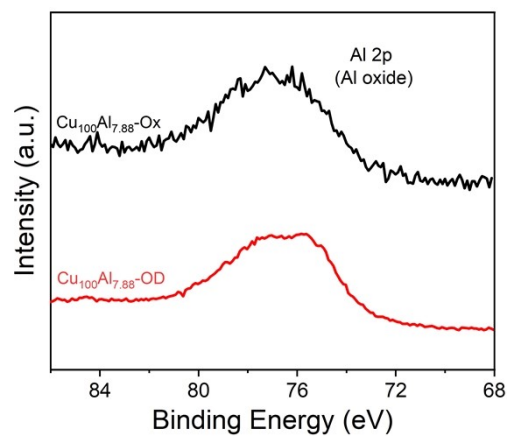


Figure S4. Al 2p XPS spectra of Cu₁₀₀Al_{7.88}-Ox catalyst before and after CV activating in CO₂-saturated 1 M KOH electrolyte.

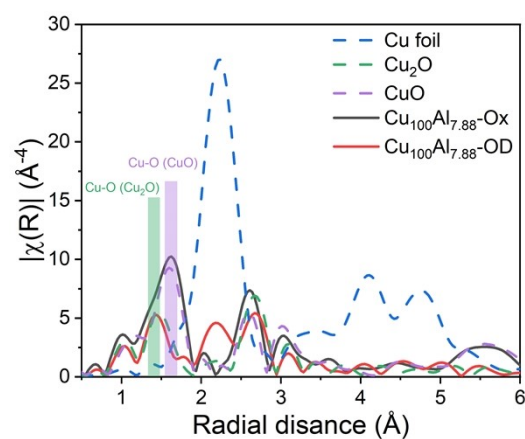


Figure S5. The k^3 -weighted Cu K edge Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) spectra of $\text{Cu}_{100}\text{Al}_{7.88}\text{-Ox}$ catalyst before and after CV activating in CO_2 -saturated 1 M KOH electrolyte.

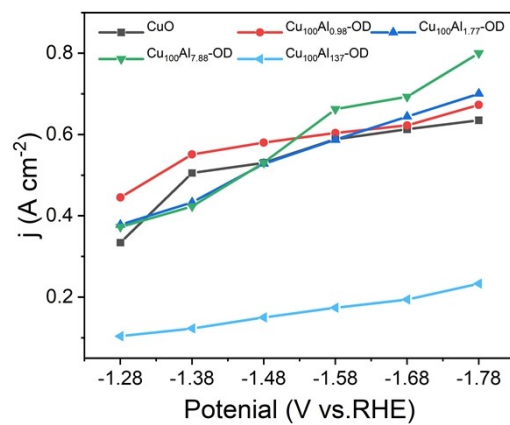


Figure S6. Current density at different potentials for $\text{Cu}_x\text{Al}_y\text{-OD}$ electrodes. Data were obtained at ambient temperature and pressure with a CO_2 stream of 20 sccm.

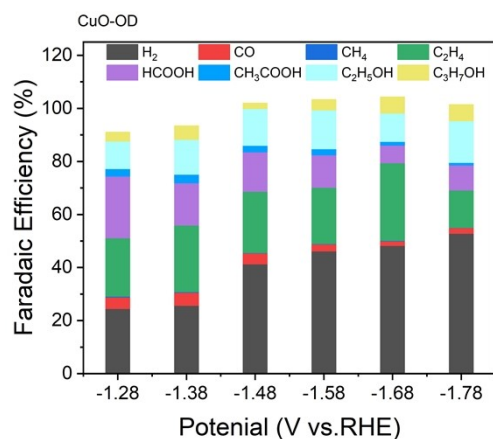


Figure S7. FE of the products over CuO-OD electrode at different applied potentials. Data were obtained at ambient temperature and pressure with a CO₂ stream of 20 sccm.

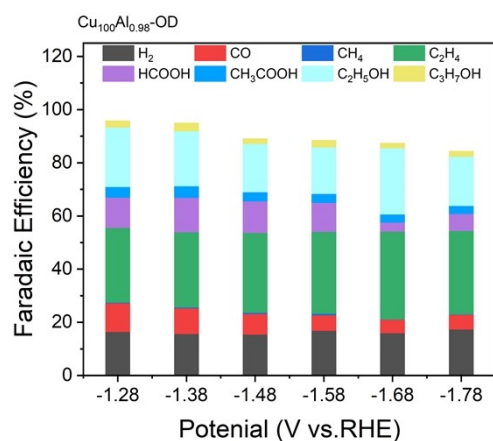


Figure S8. FE of the products over Cu₁₀₀Al_{0.98}-OD electrode at different applied potentials. Data were obtained at ambient temperature and pressure with a CO₂ stream of 20 sccm.

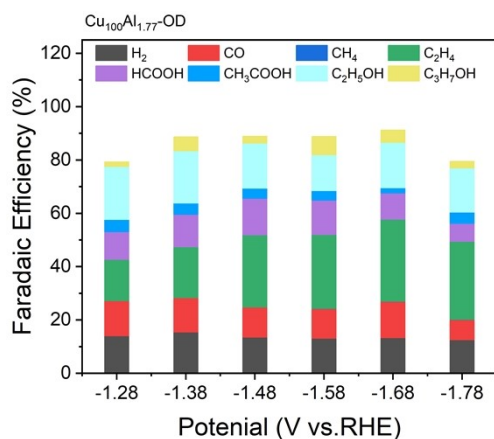


Figure S9. FE of the products over Cu₁₀₀Al_{1.77}-OD electrode at different applied potentials. Data were obtained at ambient temperature and pressure with a CO₂ stream of 20 sccm.

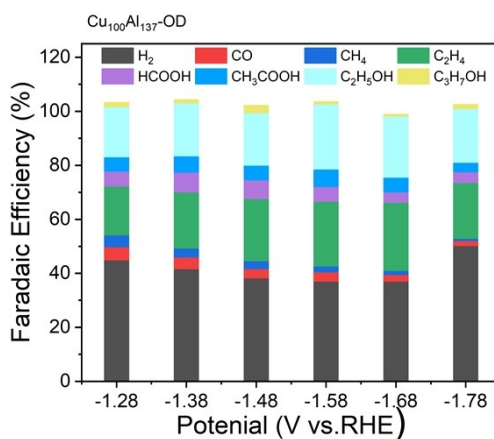


Figure S10. FE of the products over Cu₁₀₀Al_{1.37}-OD electrode at different applied potentials. Data were obtained at ambient temperature and pressure with a CO₂ stream of 20 sccm.

Supplementary Tables

Table S1. Elemental composition of the Cu and Al in investigated samples determined by ICP-OES. ($\text{Cu}_x\text{Al}_y\text{-Ox}$, x and y are the mass percentages of Cu and Al, the percentage mass value of Cu (x) is set at 100.)

Catalysts	Cu ($\mu\text{g/mL}$)	Al ($\mu\text{g/mL}$)
$\text{Cu}_{100}\text{Al}_{0.98}\text{-Ox}$	112.7	1.103
$\text{Cu}_{100}\text{Al}_{1.77}\text{-Ox}$	77.58	1.370
$\text{Cu}_{100}\text{Al}_{7.88}\text{-Ox}$	102.5	8.080
$\text{Cu}_{100}\text{Al}_{137}\text{-Ox}$	51.71	71.06

References

1. J. Shen, R. Kortlever, R. Kas, Y. Y. Birdja, O. Diaz Morales, Y. Kwon, I. Ledezma Yanez, K. J. Schouten, G. Mul and M. T. Koper, *Nat. Commun.*, 2015, **6**, 8177.
2. J. Huang, M. Mensi, E. Oveisi, V. Mantella and R. Buonsanti, *J. Am. Chem. Soc.*, 2019, **141**, 2490-2499.