Supporting information

Highly selective catalytic reduction of CO₂ to ethane over a petal-like

Zn(OH)₂/Cu₂₊₁O/Cu foam catalyst at low overpotentials

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S1 Experiment section

S1.1 Reagent

Copper foam (CF) was purchased from Quanzhou Yunzongcheng new material Co., LTD (China). Sodium hydroxide (NaOH, 97%), ammonium persulfate ((NH)₄S₂O₈, 98%), urea (NH₂CONH₂, \geq 99.0%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, \geq 99%), and ammonium fluoride (NH₄F, \geq 98.0%) were purchased from Aladdin. Ethanol (C₂H₅OH) was provided from Xilong scientific Co. Ltd (China). Acetone (\geq 99.5%) and hydrochloric acid (HCl, 36.0%-38.0%) were provided by commercial resources.

S1.2 Synthesis of the Zn(OH)₂/Cu₂₊₁O/CF

The synthesis of the $Zn(OH)_2/Cu_{2+1}O$ catalyst involved two steps, namely the synthesis of $Cu(OH)_2/CF$ and the fabrication of $Zn(OH)_2/Cu_{2+1}O/CF$.

S1.2.1 Synthesis of the Cu(OH)₂/CF

Initially, the copper foam $(1 \times 4 \text{ cm}^2, 0.2 \text{ mm})$ was treated in 30 mL acetone under ultrasonic treatment for 10 min, and then it was placed in 6 M HCl for 5 min to remove the impurities and oxide layer on the surface of the Cu under ultrasonic. Followed that, it was washed with deionized water and anhydrous ethanol for three times.

The obtained CF was immersed in a mixed aqueous solution containing 6.5 mmol $(NH_4)_2S_2O_8$, 125 mmol NaOH, and 50 mL distilled water for 5, 10, 15, 20, and 25 min, respectively, in which the following reaction could be conducted.

$$Cu + 4NaOH + (NH_4)_2S_2O_8 \rightarrow Cu(OH)_2 + 2Na_2SO_4 + 2NH_3 + 2H_2O_4$$

During the immersing, the solution turned to blue showing that the surface Cu on CF was dissolved into the solution, and meanwhile, Cu(OH)₂ component was formed on the CF surface. In this aspect, Cu(OH)₂/CF was obtained after washing with water and ethanol for several times.

S1.2.2 Synthesis of the Zn(OH)₂/Cu₂₊₁O/CF

The $Zn(OH)_2/Cu_{2+1}O/CF$ was prepared via a simple hydrothermal method. Typically, the obtained $Cu(OH)_2/CF$, 0.5 mmol $Zn(NO_3)_2 \cdot 6H_2O$, 5 mmol urea, and 2 mmol NH₄F were added into 30 ml deionized water under stirring. The mixture was transferred into a 50 mL stainless steel autoclave, which was placed in an oven at 120 °C for 6 h. Upon reaction completion, the obtained solid was cleaned with deionized water and ethanol for several times, and then was dried at 60 °C for 30 min, which is denoted as the $Zn(OH)_2/Cu_{2+1}O/CF$.

S1.3 Characterization of materials

A scanning electron microscopy (SEM, MAIA3 TESCAN) and a transmission electron microscopy (TEM, JEOL JEM-F200) were used for the morphology and structure characterizations. The XRD data were obtained using an X-ray diffractometer (Brock D8 Advance, Germany) with Ni-filtered Cu-K α irradiation at incidence angle from 5°-80° and a wavelength of 0.154 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos spectrometer (AXIS Ultra DLD, Al K α radiation) with a concentric hemispherical analyzer. *In situ* Raman scattering spectra (Raman, Renishaw in Via) with an excitation wavelength of 532 nm. The ion was the laser source, and the laser intensity of 1 mW was completed to further investigate the intermediates formed in the ECO₂RR measurements.

The prepared samples were subjected to X-ray absorption fine structure (XAFS) spectroscopy analysis to characterize the localized coordination environment around Cu atoms. X-ray absorption fine structure (XAFS) spectroscopy was carried out using the *RapidXAFS* 2M (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) by transmission (or fluorescence) mode at 20 kV and 20 mA, and the Si (553) spherically bent crystal analyzer with a radius of curvature of 500 mm was used for Cu . Cu standards and prepared samples were pressed and collected in transmission mode at room temperature. The data processing was performed using software Demeter 1 and then further deconvoluted by the wavelet transform (WT) method. This qualitative analysis was primarily focused on the nature of the backscattering atoms as well as the bond lengths and complemented the conventional Fourier transform (FT) analysis by connecting contributions in the EXAFS spectra to the FT peaks.

S1.4 Electrochemical CO₂ reduction reaction (ECO₂RR) measurements

ECO₂RR measurements were implemented in an H-type cell with a standard three-electrode system controlled by a CHI 660E workstation. The three-electrode configuration used a Pt net (1×1 cm²) as the counter electrode, the Ag/AgCl electrode (saturated KCl) as the reference electrode, and the catalyst material as the working electrode. Prior to the reaction, the electrolyte was purified with CO₂ for 30 min to form a CO₂-saturated solution. Linear sweep voltammetry (LSV) was performed at a scan rate of 1 mV/s. All potentials were converted to potential *vs*. RHE according to the equation:

 $E(vs. RHE) = E(vs. Ag/AgCl) + 0.196 V + 0.059 \times pH.$

Nyquist plots are obtained in the range from 100 kHz to 0.01 Hz, and the test voltage is the voltage obtained at the current density of 10 mA/cm².

The electrochemical active area (ECSA) of the material was referenced by calculating the double layer capacitance (C_{dl}) value, and CV cycle tests were performed in a 0.2 V potential window at a scan rate of 100 to 200 mV/s at a step of 20 mV/s. The linear relationship between the scanning rate and the current density was obtained, and the C_{dl} was obtained by calculating the linear slope.

The stability of the catalyst in ECO₂RR was conducted at a constant potential for three days. The obtained gas was analyzed by a gas chromatograph (FULI, GC 9790II) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The Faraday efficiency of a certain gas product was calculated based on the following equations:

$$FE = \frac{j_{target product}}{j_{total}} = \frac{nZF}{Q} \times 100\%$$

where $j_{\text{target product}}$ is the corresponding current density of the target product, j_{total} is the total current density of the reaction, n is the amount of substance that reacts to form this product, Z is the electron transfer number, F is Faraday's constant (96485 C/mol), and Q is the total amount of electric quantity in the reaction, respectively.

S1.5 In-situ Raman measurements

In-situ Raman spectra (HORIBA) was performed using a custom-built Teflon flow cell containing an optical quartz transparent window. The device was also composed of a three-electrode system. An electrolyte solution (0.1 mol/L KCl) was pumped into the cathode chamber and the anode chamber, and the cathode contained the catalyst, which was irradiated under 532 nm laser. A 50 × objective lens was used for focusing and collecting the incident and scattered laser light. The electrochemical CO₂ reduction was performed at different time from 0 to 35 min in 0.1 M KCl on $Zn(OH)_2/Cu_{2+1}O/CF$.

S1.6 DFT calculation

The density functional theory (DFT) calculations were carried out with the VASP code^[1]. The Perdew–Burke–Ernzerhof (PBE) functional within generalized gradient approximation (GGA)^[2] was used to process the exchange correlation, while the projector augmented-wave pseudopotential (PAW)^[3] was applied with a kinetic energy cut-off of 500 eV, which was utilized to describe the expansion of the electronic eigenfunctions. The vacuum thickness was set to 25 Å to minimize

interlayer interactions. The Brillouin-zone integration was sampled by a Γ -centered 5 × 5 × 1 Monkhorst–Pack k-point. All atomic positions were fully relaxed until energy and force reached a tolerance of 1 × 10⁻⁵ eV and 0.03 eV/Å, respectively. The dispersion-corrected DFT-D method was employed to consider the long-range interactions^[4].

The Gibbs free energy change (ΔG) was calculated by the computational hydrogen electrode (CHE) model as follows:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \quad (1)$$

where ΔE is the reaction energy obtained by the total energy difference between the reactant and product molecules absorbed on the catalyst surface and ΔS is the change in entropy for each reaction, ΔZPE is the zero-point energy correction to the Gibbs free energy. T represents room temperature (298.15 K).

Figures and Tables



Fig. S1 SEM images of CF.



Fig. S2 SEM images of Cu(OH)₂/CF.



Fig. S3 XRD pattern of Cu(OH)₂/CF and corresponding standard PDF cards of Cu(OH)₂ (PDF#13-0420) and Cu (PDF#04-0836).



Fig. S4 Cu 2p XPS spectrum of Cu(OH)₂/CF.



Fig. S5 SEM images of Zn(OH)₂/Cu₂₊₁O/CF samples impregated for (a-c) 5 min, (d-f) 10 min, (g-i) 20 min, and (j-k) 25 min, respectively.



Fig. S6 (a) Cu LMM spectrum of $Zn(OH)_2/Cu_{2+1}O/CF$ and (b) the K space data of Cu K-edge EXAFS for $Cu_{2+1}O$.



Fig. S7 Catalytic performances of ECO₂RR at different potentials over catalysts modified by diverse metal salts such as Zn^{2+} , Zr^{4+} , Co^{2+} , Al^{3+} , and without modification, respectively in CO₂-saturated 0.1 M KCl electrolyte .



Fig. S8 SEM image of the used $Zn(OH)_2/Cu_{2+1}O/CF$ catalyst after ECO₂RR for three days.



Fig. S9 XRD patterns of the fresh and the used $Zn(OH)_2/Cu_{2+1}O/CF$ catalyst.



Fig. S10 (a) Cu 2p, (b) Zn 2p, and (c) O 1s XPS spectra of $Zn(OH)_2/Cu_{2+1}O/CF$ sample after the three-days' ECO₂RR test.



Fig. S11 Cyclic voltammetry curves of (a) $Zn(OH)_2/Cu_{2+1}O/CF$, (b) $Cu(OH)_2/CF$, (c) $Zn(OH)_2/CF$, and (d) CF in 0.1 M KCl solution, respectively.



Fig. S12 (a) Linear sweep voltammetry curves and (b) Nyquist plots over $Zn(OH)_2/Cu_{2+1}O/CF$ synthesized by impregnating with different time (5, 10, 15, 20, and 25 min, respectively) in a CO₂-saturated 0.1 M KCl electrolyte.



Fig. S13 The dependence of Faradaic efficiency of product on the applied potential over $Zn(OH)_2/Cu_{2+1}O/CF$ catalysts impregnated for 5 min (a), 10 min (b), 20 min (c), and 25 min (d), respectively.



Fig. S14 The dependences of FE_{C2H6} (a) and total current density (b) on reaction time over $Zn(OH)_2/Cu_{2+1}O/CF$ synthesized by impregnating for 5, 10, 15, 20, and 25 min, respectively in 0.1 M KCl electrolyte at -0.3 V and -0.4 V (*vs* RHE).



Fig. S15 Current densities over $Zn(OH)_2/Cu_{2+1}O/CF$ with impregnating for 5, 10, 15, 20, and 25 min, respectively at different applied potentials.



Fig. S16 GC spectra obtained from the CO₂ electrolysis over $Zn(OH)_2/Cu_{2+1}O/CF$. Reaction conditions are similar to those of Fig. 3a at -0.3 V (*vs.* RHE).



Fig. S17 ¹H NMR spectrum of the electrolyte obtained from the ECO₂RR over $Zn(OH)_2/Cu_{2+1}O/CF$ catalyst. Reaction conditions are similar to those of **Fig. 3a** at -0.3 V (*vs.* RHE).



Fig. S18 Pictures of the *in-situ* Raman setup.



Fig. S19 Raman spectrum of $Zn(OH)_2/Cu_{2+1}O/CF$ (the red line) and *in situ* Raman spectrum after 35 min of electrochemical testing (the pink line).

Catalyst	Electrolytes	Potential (V vs. RHE)	C ₂₊ selectivity (%)	C2H6 selectivity (%)	C2 partial current density (mA cm ⁻²)	References
xFe ₂ O ₃ -N@CN	[Bmim]PF ₆ / MeCN/H ₂ O	-2.00	-	42	-32.0	[5]
Thick OD-Cu	0.1M KHCO ₃	-0.78	-	10.5	~ -7.5	[6]
CuO _x -NWF@C u-CF	0.1M KHCO ₃	-0.45	69.4	-	~ -2.0	[7]
Cu ₂ O film derived Cu	0.1 M KHCO ₃	-0.78	~25.7	8.2	~ -5.2	[8]
Iodide-derived Cu foam	0.2 M NaHCO ₃	-1.00	< 20	5.2	~ -0.9	[9]
MC-CNT/Co	0.5 M KHCO3	-0.32	~60.1	-	-5.1	[10]
Zn(OH) ₂ /Cu ₂₊₁ O/CF	0.1 M KCl	-0.3	-	67.8	-5.56	This work
Zn(OH) ₂ /Cu ₂₊₁ O/CF	0.1 M KCl	-0.5	-	25.4	-29.40	This work

Table S1. Electrocatalytic performance for CO_2 to C_2H_6 products over typical catalysts reported recently in an H-shaped cell

Table S2. EXAFS fitting parameters at the Cu and Ru K-edge ($S_0^2=0.028$)

Sample	Path	N ^a	R (Å) ^b	σ ² (Å ²) ^c	R factor
Cu foil	Cu-Cu	12*	2.54	0.0087	0.004
Cu ₂ O	Cu-O	4	1.85	0.0026	0.016
	Cu-Cu	12	3.04	0.0292	
CuO	Cu-O	4	1.97	0.0051	0.012
	Cu-O	2	2.90	0.0130	
	Cu-Cu	2	3.33	0.0001	
Cu ₂₊₁ O	Cu-O	2	3.95	0.0086	0.019
	Cu-Cu	1.6	2.55	0.0060	
	Cu-Cu	1.8	4.44	0.0028	

 N^{α} : coordination numbers. R: bond distance. σ^2 : Debye-Waller factors. R factor: goodness of fit.

*: fitting with fixed parameter.

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