# **Electronic Supplementary Information**

## Identifying the Optimal Oxidation State of Cu for Electrocatalytic

### CO<sub>2</sub>-to-C<sub>2+</sub> Products

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#### **Experimental Section**

**Materials:** The commercial Cu foils (0.01 mm in thickness) and Nafion N-117 membrane (0.180 mm thick,  $\geq 0.90$  meg/g exchange capacity) were obtained from Alfa Aesar China Co., Ltd. The phosphoric acid (85 wt%), KHCO<sub>3</sub> (AR, 99.5%) and 1,4-bezenedicarboxylic acid (1,4-H<sub>2</sub>BDC, 99%) were purchased from Sinopharm Chem. Reagent Co., Ltd. N<sub>2</sub> (99.999%) and CO<sub>2</sub> (99.999%) were provided by Beijing Analytical Instrument Company. Deionized water was used in the experiments.

**Electrode preparation.** The commercial Cu foil was used as working electrode. Before used, the Cu foils (0.5 cm×2 cm) were cleaned with acetone and ultrapure water in an ultrasonic bath, then electropolished in 85 wt% phosphoric acid at 2.0 V vs. Ag/AgCl for 500 s. Electropolished Cu foils were washed with deionized water, then dried with nitrogen.

The  $Cu_xC_yO_z$  electrode was fabricated via a pulse electrochemical method with two steps in 0.1 M KHCO<sub>3</sub>-potassium benzenedicarboxylate (K<sub>2</sub>BDC) aqueous solution, including in situ electrodeposition of Cu complex on Cu foil at E<sub>a</sub> (1.25 V vs. RHE) for 3 s and in situ electroreduction of the Cu complex to obtain  $Cu_xC_yO_z$  at E<sub>c</sub> (-1.0 V vs. RHE) for 5 s, and this procedure was repeated for 80 cycles. The  $Cu_xC_yO_z$  electrode with different oxidation state of Cu were prepared by changing the E<sub>a</sub> (E<sub>a</sub>=1.0 V, 1.25 V, 1.4 V, and 1.6 V vs. RHE, respectively).

**Characterization of the electrocatalysts.** The scanning electron microscope (SEM) and highresolution transmission electron microscopy (HR-TEM) characterizations were carried out using a HITACHI S-4800 and JEOL JEM-2100F, equipped with EDS. X-ray diffraction (XRD) analysis of the samples were performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-K $\alpha$  radiation at the scan speed was 10° min<sup>-1</sup>.

**Operando Characterization.** XPS study was performed on the Thermo Scientific ESCALab 250Xi using a 200W Al-K $\alpha$  radiation. In the analysis chamber, the base pressure was about  $3 \times 10^{-10}$  mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. In order to detect accurately the valence state of Cu, quasi-operando XPS was carried out with the samples processed in a glove box. After electrolysis, the gas-tight H-cell was transferred into the glove box immediately. Since the catholyte is always saturated with CO<sub>2</sub> during the reaction process, the electrodes in the solution are in an isolation state from air. In the glove box, we took out the electrode from the H-cell, soaked it in Ar gas-saturated acetone

solution, then took the electrode out, dried it with ear washing balls. The obtained electrode plate was cut into  $5 \times 5$  mm and glued on a support. The support could be evacuated into vacuum to prevent the samples to be oxidized by the air. The electrodes were not exposed to air during the whole process of our operation.

The XES data was performed at beamline 4W1B of the Beijing synchrotron Radiation Facility, and electron storage ring was operated at 2.5 GeV with current of 250 mA. A polychromatic beam (pink beam) with an incident X-ray energy of 5 or 10-18 keV was used, and the photon flux was on the order of  $10^{13}$  phs/s. The beam spot-size (FWHM) was focused down to 50 µm by a polycapillary half-lens. The K $\beta$  XES data were collected by means of a multiscriptal energy-dispersive spectrometer based on the von Hamos geometry. The 2D spectra were recorded using a Pilatus 100K detector with a pixel size of  $172 \times 172 \ \mu\text{m}^2$ . The XES spectra were normalized with respect to their total area using the range 8890-8920 eV.

The XAS measurements were carried out on the beamline 1W1B station of the Beijing Synchrotron Radiation Facility. A water-cooled Si (111) double-crystal monochromator (DCM) was utilized to monochromatize the X-ray beam. The electron storage ring of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. The XAS data of Cu K-edge were obtained in the energy range from -200 to 1000 eV in transmission mode. Cu foil, Cu<sub>2</sub>O, and CuO were used as references. All collected spectra were analyzed using Athena and Artemis program within the Ifeffit package.

**Electrocatalytic CO<sub>2</sub> reduction.** The experiments were performed in a gas-tight H-cell separated by a Nafion 117 membrane. A three-electrode configuration was used: Cu foil working electrode, Pt gauze counter electrode, and Ag/AgCl reference electrode. Both working electrode and counter electrode compartments were filled with 30 mL of electrolyte. The working electrode compartment was purged continuously with CO<sub>2</sub> (20 mL·min<sup>-1</sup>) by a mass flow controller. The electrolyte was 0.1 M KHCO<sub>3</sub>-0.1 M potassium benzenedicarboxylate (K<sub>2</sub>BDC). And all the anolyte was 0.1 M KHCO<sub>3</sub>. All potentials were measured against Ag/AgCl with a constant *iR* compensation and were converted to the reversible hydrogen electrode (RHE) using the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + 0.059 V × pH. Throughout the paper, the selectivity data reported correspond to an average of at least three different measurements collected under the same experimental conditions, and the error bars represent the standard deviation.

**Product analysis.** The gaseous product of electrochemical experiments was collected using a gas bag and analyzed by gas chromatography (GC, HP 4890D), which was equipped with TCD detectors using argon as the carrier gas.

The Faraday efficiency of gas products was calculated as indicated below: [S1,S2]

$$i_{partial} = V \times \text{flow rate} \times \frac{nFp_0}{RT_0} \times \frac{t_{anodic} + t_{cathodic}}{t_{cathodic}}$$
 (1)

$$FE = \frac{i_{partial}}{i_{total}} \times 100 \tag{2}$$

(V: the volume concentration of gas products obtained based on a previous calibration of the GC; n: the number of transferred electrons for a certain product;  $i_{total}$ : a steady-state current (mA); F = 96485 ((A×s)/mol);  $p_0 = 1.013$  (bar);  $T_0=298$  (K); R = 8.314 (J/(mol×K)).  $t_{anodic}$  represents the duration of the oxidation phase and  $t_{cathodic}$  the duration of the CO<sub>2</sub> electroreduction phase.

The liquid product was analyzed by <sup>1</sup>H NMR (Bruker Avance III 400 HD spectrometer) in deuteroxide with phenol and sodium 2, 2-dimethyl-2-silpentane-5-sulfonate (DSS) as internal standards. The sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS) was the reference for n-propanol, ethanol and acetic acid. And the phenol was the reference for formate. 400  $\mu$ L catholyte after the reaction was mixed with 100  $\mu$ L 6 mM DSS solution, 100  $\mu$ L 200 mM phenol and 200  $\mu$ L D<sub>2</sub>O, and then analyzed by <sup>1</sup>H NMR.

The Faraday efficiency of liquid products was calculated as indicated below:

$$i_{partial} = \frac{C_{liquid} \times V \times n \times F}{t}$$
(3)

$$FE = \frac{i_{partial}}{i_{total}} \times 100 \tag{4}$$

( $C_{liquid}$ : the concentration of liquid products (mol/L); V: the volume of catholyte (L); n: the number of transferred electrons for a certain product; t: the electrolysis time (s),  $i_{total}$ : the steady-state current (mA); F = 96 485 ((A×s)/mol))

### **Supplementary Figures and Tables**



Fig. S1 The quasi in situ XPS signals of Cu  $2p_{3/2}$  of Cu for Cu foil, Cu complex, and  $Cu_xC_yO_z$ .



Fig. S2. Cu K-edge Fourier transform of the EXAFS spectra of the Cu complex,  $Cu_xC_yO_z$  and the reference samples.



Fig. S3. SEM images of  $Cu_xC_yO_z$  prepared under different conditions (A,  $E_a=1.0$  V, B,  $E_a=1.4$  V, C,  $E_a=1.6$  V vs. RHE,  $t_a=3$  s,  $E_c=-1.0$  V vs. RHE,  $t_c=5$  s).



**Fig. S4.** Cu K-edge Fourier transform of the EXAFS spectra of the  $Cu_xC_yO_z(0.41)$  electrodes that reacted in (A) Route (1) and (B) Route (2) for different time, respectively.



**Fig. S5.**  $CO_2RR$  products distribution and current density (*j*) of  $Cu_xC_yO_z(0.41)$  electrode in the KHCO<sub>3</sub> electrolyte with different K<sup>+</sup> concentrations at -1.0 V vs. RHE for 2 h.



Fig. S6.  $CO_2RR$  products distribution of  $Cu_xC_yO_z(0.41)$  electrode in (A) Route (3) (E<sub>a</sub>=1.25 V vs. RHE, t<sub>a</sub>=3 s; E<sub>c</sub>=-1.0 V vs. RHE, t<sub>c</sub>=50 s) and (B) Route (4) (E<sub>c</sub>=-1.0 V vs. RHE) for 2 h.



Fig. S7. SEM images of  $Cu_xC_yO_z(0.41)$  after reaction in route (1) with different electrolysis conditions ( $E_c = -1.0$  V vs. RHE,  $t_c = 50$  s,  $E_a = 1.25$  V vs. RHE,  $t_a = 1$  s, 2 s, 3 s and 4 s, respectively) for 0.5 h.

As shown in Fig. S7, when the  $t_a$  is extended and  $t_c$  keeps unchanged, more  $Cu^{2+}$  can be provided to interact with negatively charged carboxylate ligands to form Cu complex during each pulse cycle. It can be converted into more  $Cu_xC_yO_z$  catalyst with lower oxidation state of Cu when the  $E_c$  was applied.



**Fig. S8.** (A) The current density (*j*), (B) FE for  $C_{2+}$  products, and (C) FE for  $C_1$  products and  $H_2$  over the  $Cu_xC_yO_z(0.41)$  electrodes after reaction in route (1) for 2 h with different electrolysis conditions.

The oxidation state of Cu in the  $Cu_xC_yO_z$  catalyst can significantly affect the  $CO_2RR$  catalytic performance. As shown in Fig. S8, when the  $t_a$  is shorter or longer, more C1 products and H<sub>2</sub> was detected, indicating that the  $Cu_xC_yO_z$  catalyst with appropriate oxidation state of Cu can promote the pathway towards  $C_{2+}$  products formation. When  $t_a=3$  s and  $t_c=50$  s, the formed  $Cu_xC_yO_z$  catalyst showed the best  $CO_2$ -to- $C_{2+}$  performance.



Fig. S9. SEM images of  $Cu_xC_yO_z(0.41)$  after reaction in route (1) with different electrolysis conditions ( $E_a = 1.25$  V vs. RHE,  $t_a = 3$  s,  $E_c = -1.0$  V vs. RHE,  $t_c = 10$  s, 50 s, 100 s and 150 s, respectively) for 0.5 h.



**Fig. S10.** (A) The current density (*j*), (B) FE for  $C_{2+}$  products, and (C) FE for  $C_1$  products and  $H_2$  over the  $Cu_xC_yO_z(0.41)$  electrodes after reaction in route (1) for 2 h with different electrolysis conditions.



Fig. S11. SEM images of the  $Cu_xC_yO_z(0.41)$  electrodes after reaction in route (1) ( $E_a$ = 1.25 V vs. RHE,  $t_a$  = 3 s;  $E_c$ = -1.0 V vs. RHE,  $t_c$  = 50 s) in 0.1 M KHCO<sub>3</sub> with different concentrations of K<sub>2</sub>BDC (0.05 M, 0.1 M, and 0.2 M) for 0.5 h.



**Fig. S12.** (A) The current density (*j*), (B) FE for  $C_{2+}$  products, and (C) FE for  $C_1$  products and  $H_2$  over  $Cu_x C_y O_z(0.41)$  electrodes after reaction in Route (1) ( $E_a$ = 1.25 V vs. RHE,  $t_a$  = 3 s;  $E_c$ = -1.0 V vs. RHE,  $t_c$  = 50 s) for 2 h in 0.1 M KHCO<sub>3</sub> with different concentrations of K<sub>2</sub>BDC (0.05 M, 0.1 M, and 0.2 M).

It can be found that the amount of  $Cu_xC_yO_z$  catalyst regenerated on the electrode surface increased depending on the concentration of K<sub>2</sub>BDC (Fig. S11), which affected the content of Cu<sup>+</sup> and Cu<sup>0</sup> in the Cu<sub>x</sub>C<sub>y</sub>O<sub>z</sub> catalyst, and thus affecting the CO<sub>2</sub>-to-C<sub>2+</sub> performance (Fig. S12). Both the lower or higher concentration of K<sub>2</sub>BDC in the electrolyte can promote the formation of C1 and H<sub>2</sub> products, when the concentration of K<sub>2</sub>BDC was 0.1 M, the Cu<sub>x</sub>C<sub>y</sub>O<sub>z</sub> catalyst showed the best CO<sub>2</sub>-to-C<sub>2+</sub> performance.



Fig. S13. SEM images of  $Cu_xC_yO_z(0.41)$  after reaction in (A, B) Route (1) and (C, D) Route (2) at different time, respectively.



**Fig. S14.** Dependence of current density (*j*) on time of the (A)  $Cu_xC_yO_z(0.20)$ , (B)  $Cu_xC_yO_z(0.47)$ , and (C)  $Cu_xC_yO_z(0.59)$ .

Element	Weight%	Atomic%
Cu	86.72	57.91
С	7.80	27.56
0	5.48	14.53
Totals	100.00	100.00

Table S1 The EDS results of  $Cu_x C_y O_z$ .

Samples	Pristine Cu	E <sub>a</sub> =1.0 V	E <sub>a</sub> =1.25 V	E <sub>a</sub> =1.4 V	E <sub>a</sub> =1.6 V	Cu <sub>2</sub> O
E <sub>0</sub>	8979	8979.28	8979.56	8979.65	8979.81	8980.37
δ	0	0.20	0.41	0.47	0.59	1

**Table S2**  $E_0$  and corresponding oxidation states ( $\delta$ ) of Cu.

 $E_0$ : the copper K-edge energy shift of different samples;  $\delta$ : the corresponding average valence state of Cu

The calculation method for quantifying the average valence state of Cu is referred to the previous study.<sup>[S3,S4]</sup> To give a direct comparison of the oxidation state of Cu in the  $Cu_xC_yO_z$  catalysts, we acquired the Cu oxidation state as a function of Cu K-edge energy shift, the relation is expressed as  $\delta$ =E<sub>0</sub>\*0.72993-6554.04147. According to the above calculation method, the Cu oxidation state was +0.20, +0.41, +0.47 and +0.59, when the applied E<sub>a</sub> was 1.0 V, 1.25 V, 1.4 V, and 1.6 V vs. RHE, respectively.

#### References

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