## **Electronic Supplementary Information**

## for

# Multi-layered CuO/SiO<sub>2</sub> core-shell structure improves electrocatalytic CO<sub>2</sub>-to-n-propanol conversion

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#### **Experimental Section**

#### Materials

Deionized water and high-purity CO<sub>2</sub> (99.999%) were purchased from Beijing Analysis Instrument Factory. Absolute ethanol (A. R. Grade) was provided by Beijing Chemical Works. TEOS, PVP, ascorbic acid, sodium hydroxide, potassium chloride, sodium bicarbonate and copper sulfate pentahydrate (Cu(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O) were provided by Beijing InnoChem Science&Technology Co., Ltd. Nafion D-521 dispersion (5% w/w in water and 1-propanol, >0.92 meq/g exchange capacity) and Nafion N-117 membrane (0.180 mm thick,  $\geq$ 0.90 meq/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Carbon gas diffusion layer (YLS-30T) was obtained from Suzhou Sinero Technology Co. Ltd. Commercial CuO was purchased from Beijing InnoChem Science&Technology Co., Ltd.

#### Methods

#### Preparation of CuO/SiO<sub>2</sub>-n

For the synthesis of CuO/SiO<sub>2</sub>-3, 1.0 g TEOS was added into 20.0 mL ethanol/water solution (V: V=4:1) containing 1.0 mL ammonia solution under stirring for 8 h reaction. The white precipitate was collected by centrifugation, washed with ethanol and dried under vacuum at 80 °C for 12 h, thus producing SiO<sub>2</sub> spheres. 50.0 mg SiO<sub>2</sub> and 50.0 mg PVP were dispersed in 50 mL water. Then 20.0 mL  $Cu(SO_4)_2$  solution (10 mg/mL) was dispersed in the above system under stirring for 10 min. After that, 8.0 mL NaOH solution (0.2 mol/L) and 8.0 mL ascorbic acid solution (0.2 mol/L) were added to the mixture successively drop by drop. Under the action of ascorbic acid, copper-based materials are reduced to form Cu<sub>2</sub>O. After 1 h reaction, the precipitate was collected by centrifugation and washed by water/ethanol mixture. Then the solid was dispersed in the mixture of 0.5 mL ammonia and 20.0 mL ethanol/water (V/V=4:1) under stirring, followed by the addition of 20.0 mL ethanol containing 100 mg TEOS. After 8 h reaction, the solid was obtained via centrifugation and washing. Then, the obtained solid was alternately coated with Cu<sub>2</sub>O and SiO<sub>2</sub> until three layers of Cu<sub>2</sub>O species were coated. After that, the solid was immersed into 400 mL NaOH solution (10 mmol/L) at 50 °C for 10 h to etch away SiO<sub>2</sub> and obtain multi-layered hollow CuO. During this process, Cu<sub>2</sub>O may react with OH<sup>-</sup> under heating conditions. The possible chemical reactions are as follows: Cu<sub>2</sub>O + H<sub>2</sub>O = 2CuOH, CuOH + OH<sup>-</sup> = CuO+H<sub>2</sub>O. Finally, 20.0 mL TEOS ethanol solution (2.5 mg/mL) was added drop by drop into a mixture of 0.5 mL ammonia and 20 mL ethanol/water (V/V=4:1) containing 50.0 mg sample for 8 h reaction. The final solid was obtained after centrifugation, washing and drying at 85 °C for 12 h.

For the synthesis of CuO/SiO<sub>2</sub>-1, CuO/SiO<sub>2</sub>-2 and CuO/SiO<sub>2</sub>-4, their synthesis processes are roughly similar to that of CuO/SiO<sub>2</sub>-3. The only difference is that the number of CuO layer was controlled as 1, 2 and 4, respectively.

#### Characterizations

The morphology of the electrocatalyst was observed using SEM (S-4800) with a beam voltage of 5 kV. TEM, HRTEM and EDX line scan were characterized using F-200 microscope, with an acceleration voltage of 300 kV, equipped with a Bruker EDX detector. The EDX study was performed at an acquisition time of 3 min. The signal intensity distributions of copper (Cu) elements detected by EDX are key factors in determining the selection range. When scanning a certain area, if there are significant peak changes in the signal intensities of Cu elements, it indicates the presence of a different CuO layer. We used the starting and ending positions of the signal intensity peaks as the reference boundaries for the selection range of that layer. CuO/SiO<sub>2</sub>-3 was sliced into ultra-thin specimen by ultrathin slice technique and characterized on TEM (JEM-F200). XRD pattern was collected using a Bruker D8 diffractometer with Cu  $K\alpha$  radiation ( $\lambda$  = 0.15406 nm). Composition of the sample was tested on FT-IR spectra (Bruker Tensor 27 Spectrometer). The metal content in sample was investigated by inductively coupled plasma mass spectrometry (ICP-MS, Vista Axial). The porosity was determined on an Autosorb-iQ system at 77 K using liquid nitrogen as coolant. The material was activated and degassed at 150 °C for 4 h before the measurements. XPS was recorded on a PHI 5700 ESCA system using Al  $K\alpha$  X-ray radiation (1486.6 eV) for excitation. Synchrotron X-ray absorption spectroscopy (XAS) measurement was performed at 4A9B Beamline station at Beijing Synchrotron Radiation Facility (BSRF). Specific surface areas of the samples were characterized via  $N_2$  adsorption-desorption

isotherm at 77 K (ASAP 2020HD88 system).

#### **Electrochemical measurements**

4.0 mg catalyst and 40.0  $\mu$ L Nafion solution were added to 80.0  $\mu$ L methanol and 20.0  $\mu$ L water under ultrasonic dispersion for 30 min to form slurry. And then, the slurry was deposited on carbon gas-diffusion layer with size of 3.5×2 cm. Electrochemical test was conducted on electrochemical flow cell consisting of a gas chamber, a cathodic chamber and an anodic chamber. The polytetrafluoroethylene (PTFE) membrane was fixed on working electrode between the gas and cathodic chambers, with the catalyst layer facing the cathodic chamber. A proton exchange membrane was used to separate the anodic and cathodic chambers. High-purity CO<sub>2</sub> was supplied to the gas chamber at a constant flow rate of 20.0 mL min<sup>-1</sup> via a digital mass flow controller. 1.0 M KCl and 1.0 M KHCO<sub>3</sub> were used as the catholyte and anolyte circulated at a constant flow rate of 20 mL min<sup>-1</sup> through a peristaltic pump, respectively. All electrochemical tests were conducted on an Autolab PGSTAT204 instrument, with Ag/AgCl electrode and Pt piece as the reference and counter electrodes, respectively. Applied potentials were converted to RHE with *iR* compensation, according to the following formula:

#### *E*<sub>(RHE)</sub>=*E*<sub>(Ag/AgCl)</sub>+0.21 V+0.0591×pH+0.85×*iR*

where *i* is the current at each applied potential and *R* is the equivalent series solution resistance measured via electrochemical impedance spectroscopy.

#### Product analysis

After electrochemical test, 2.0 mL of the collected gas was injected into a gas chromatograph (GC, HP 4890D) to analyze gas products and determine the concentration of gas products. The liquid product was analyzed by <sup>1</sup>H NMR on a Bruker AVANCE AV III 400, in which the used electrolyte was mixed with D<sub>2</sub>O (deuterated water) as lock solvent and dimethyl sulfoxide as internal reference. After the quantification, the faradaic efficiencies (FE) of the products were calculated as follows:

 $FE = \frac{\text{amount of the product} \times n \times F}{Q} \times 100\%$ 

where n is number of moles of electrons to participate in the faradaic reaction, F is the

Faraday constant (96485 C mol<sup>-1</sup>), and Q is the amount of charge passed through the working electrode.

#### ECSA measurement

CV was performed in the same single electrochemical cell with 1.0 M KCl electrolyte at scan rates from 20 to 120 mV/s in potential window where no Faradaic process occurred. By plotting the average current j ( $j=(j_a-j_c)/2$ , where  $j_a$  and  $j_c$  are anodic and cathodic current densities, respectively) against the scan rate (mV/s), the C<sub>dl</sub> was derived from the slope. The electrochemical impedance spectroscopy (EIS) tests accompanied with a frequency range of 0.1 to 10<sup>5</sup> HZ were performed in a flow cell, which is consistent with the assembly of ECO<sub>2</sub>RR.

#### **FEM Simulation**

FEM simulation was carried out on COMSOL Multiphysics software package (https://www.comsol.com/). A multi-layer material structure model, which matches the dimensions of the experimentally fabricated one and consists of 1 to 4 layers, is constructed and immersed in an aqueous electrolyte to simulate ECO<sub>2</sub>RR into npropanol. It is reported that the cavity nanostructures are concentrated carbon intermediates through the spatial confinement effect by FEM.<sup>[1]</sup> We used FEM to examine whether CuO/SiO<sub>2</sub>-n with 1-4 shell numbers have different behaviors in confining the local diffusion of carbon intermediates during ECO<sub>2</sub>RR. First, the models of CuO/SiO<sub>2</sub>-n with 1-4 layers were established to simulate the carbon intermediate mass transport around individual catalyst. In its "Chemistry" module, four chemical species and the corresponding surface reactions were defined to simulate intermediate steps for ECO<sub>2</sub>RR. The chemical species included CO<sub>2</sub> feedstock, and CO intermediate, C2 intermediate, C3 intermediate in bulk solution and adsorbed on surface. These reactions were defined: four surface adsorption-desorption equilibrium reactions for these four chemical species, as well as three irreversible reactions for the CO<sub>2</sub> reduction into C<sub>1</sub>, the C-C coupling into C<sub>2</sub>, and the C<sub>1</sub>-C<sub>2</sub> coupling into C3. And then, the diffusion of these four species was simulated using the " Transport of Diluted Species" module according to the diffusion constants of CO<sub>2</sub>, CO,  $C_2$  and  $C_3$  in literature.<sup>[1-3]</sup> The diffusion constants of  $CO_2$ ,  $C_1$  (CO assumed),  $C_2$  ( $C_2H_4$ 

assumed) and C<sub>3</sub> (n-PrOH assumed) were taken to be  $1.80 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $1.00 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ <sup>1</sup>,  $1.23 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $1.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Reaction parameters in FEM simulation were fitted, based on the experimental data. The electrical conductivity values of the used electrolyte (1.0 M KCl aqueous solution) were sourced from the literature <sup>[4]</sup>.

#### In situ Raman measurement

It was performed on Raman spectrometer (T64000) with 785 nm laser from National Center for Nanoscience and Technology (NCNST), China. The gas diffusion layer (GDL) impregnated with the catalyst served as the working electrode and was placed within a tailor-made operando Raman cell. The electrochemical measurements were conducted by means of a potentiostat. Ag/AgCl reference electrode (3.0 M KCl) and platinum coil acted as working electrode, reference electrode and counter electrode, respectively. 20.0 mL/min CO<sub>2</sub> was continuously supplied to the gas chamber during the measurement.

#### In situ ATR-IRAS measurement

In situ ATR-IRAS was measured using Nicolet iS20 spectrometer furnished with an HgCdTe (MCT) detector and a VeeMax III (PIKE Technologies) accessory. The measurement was conducted in an electrochemical cell in which Pt-wire and Ag/AgCl acted as counter and reference electrodes, respectively. 4.0 mg of the catalyst was dispersed in a mixture of 80.0 µL methanol, 20.0 µL H<sub>2</sub>O and 40.0 µL 5 *wt.*% Nafion solution, and then sonicated for 30.0 min, then dropped on Ge prism. ECO<sub>2</sub>RR test was accompanied by spectrum collection (32 scans, 4 cm<sup>-1</sup> resolution). All spectra were subtracted with background.

Results



Fig. S1 TEM image of ultra-thin specimen of CuO/SiO $_2$ -3.



Fig. S2 FT-IR spectra of CuO/SiO<sub>2</sub>-3 and pure SiO<sub>2</sub>.

The adsorption peak at 1078 cm<sup>-1</sup> corresponds to the asymmetrical stretching vibration of Si-O-Si, which confirms the existence of SiO<sub>2</sub> in CuO/SiO<sub>2</sub>-3. The shift compared with that of pure SiO<sub>2</sub> (1097 cm<sup>-1</sup>) implies the interaction between CuO and SiO<sub>2</sub>.



Fig. S3 An enlarged view of the selected section in Fig. 2c.



Fig. S4 An enlarged view of the selected section in Fig. 2f.



Fig. S5 A typical <sup>1</sup>H NMR spectrum of liquid products over CuO/SiO<sub>2</sub>-3 at -1.65 V after  $ECO_2RR$  in flow cell.



Fig. S6 Total current density at various potentials on CuO/SiO<sub>2</sub>-3.



**Fig. S7** (a) TEM image and (b) EDX element line scan of CuO/SiO<sub>2</sub>-1, (c) TEM image and (d) EDX element line scan of CuO/SiO<sub>2</sub>-4. Scale bars: 50 nm in (a) and 200 nm in (c). During the preparation process, as the number of copper oxide layers increases (n=4), the precursor solid is not so uniformly dispersed in the solvent, so that the template and copper oxide layers of the latter layer are not so evenly distributed. Thus, the layer spacing shows an asymmetric distribution when the number of CuO layers is 4.



Fig. S8  $N_2$  adsorption-desorption isotherms of CuO/SiO<sub>2</sub>-1.



Fig. S9  $N_2$  adsorption-desorption isotherms of CuO/SiO<sub>2</sub>-2.



Fig. S10  $N_2$  adsorption-desorption isotherms of CuO/SiO<sub>2</sub>-4.



Fig. S11 Specific surface area vs. CuO layer number of CuO/SiO<sub>2</sub>-n.



**Fig. S12** (a) FE values of various products and (b) total current density at various potentials over CuO/SiO<sub>2</sub>-1.



**Fig. S13** (a) FE values of various products and (b) total current densities at various potentials over CuO/SiO<sub>2</sub>-2.



**Fig. S14** (a) FE values of various products and (b) total current densities at various potentials over CuO/SiO<sub>2</sub>-4.



**Fig. S15** Comparison of electrochemical performances of  $j_{C2+ alcohols} vs. FE_{C2+ alcohols}$  on Cu-based electrocatalysts during ECO<sub>2</sub>RR in flow cell.



**Fig. S16** CV curves with various scan rates of (a) CuO/SiO<sub>2</sub>-1, (b) CuO/SiO<sub>2</sub>-3 and (c) CuO/SiO<sub>2</sub>-4.



**Fig. S17** Double-layer capacitance of CuO/SiO<sub>2</sub>-1, CuO/SiO<sub>2</sub>-3 and CuO/SiO<sub>2</sub>-4.



**Fig. S18** Simulated concentrations and distributions of local CO,  $C_2$  and  $C_3$  intermediates of CuO/SiO<sub>2</sub>-n, (a) CuO/SiO<sub>2</sub>-1, (b) CuO/SiO<sub>2</sub>-2, (c) CuO/SiO<sub>2</sub>-3 and (d) CuO/SiO<sub>2</sub>-4. (color scale: mol m<sup>-3</sup>)



Fig. S19 C<sub>3</sub> intermediate concentration in the core region vs. shell number of CuO/SiO<sub>2</sub>-n.



Fig. S20 EDX element line scan of CuO-3.



Fig. S21  $N_2$  adsorption-desorption isotherms of CuO-3.



Fig. S22 FE values of various products at various potentials over CuO-3.



Fig. S23 n-PrOH partial current density at various potentials on CuO-3.



Fig. S24 Nyquist plots for CuO/SiO<sub>2</sub>-3 and CuO-3.



Fig. S25 Electrical equivalent circuit used for simulating experimental impedance

data.



Fig. S26 XRD pattern of CuO/SiO<sub>2</sub>-3 after  $ECO_2RR$  for 60 min at -1.65 V.



Fig. S27 Cu 2p XPS and (b) Cu LMM Auger spectrum of CuO/SiO<sub>2</sub>-3 after  $ECO_2RR$  for 60 min at -1.65 V.



Fig. S28 An enlarged view of the selected section for Cu K-edge XANES spectra of CuO/SiO<sub>2</sub>-3 after ECO<sub>2</sub>RR for 60 min at -1.65 V.



Fig. S29 i-t curve and the corresponding n-PrOH and the other products FE on  $CuO/SiO_2$ -3 at -1.65 V during continuous  $ECO_2RR$  process.



Fig. S30 XRD pattern of the CuO/SiO $_2$ -3 after ECO $_2$ RR stability test.



Fig. S31 In situ XANES spectra for the electrolysis process at -1.65 V vs. RHE.

For the CuO/SiO<sub>2</sub>-3 sample, distinct characteristic peaks were observed at approximately 8977 eV, 8987 eV, and 8997 eV (the curve labeled "0 min"). These peaks correspond to CuO. As the electrolysis process progressed, the peaks indicative of Cu<sup>2+</sup> weakened and vanished within 10 min. Concurrently, new peaks emerged at around 8982 eV, 8993 eV, and 9003 eV. These peaks correspond to the fingerprint signature of metallic Cu and became increasingly pronounced with the continuation of electrolysis.



Fig. S32. Average valence state of Cu of the obtained products in different electrolysis time.



Fig. S33 In situ Raman spectra at various potentials over CuO/SiO<sub>2</sub>-1.



Fig. S34 In situ Raman spectra at various potentials over CuO/SiO<sub>2</sub>-4.

Catalyst	Specific Surface Area (m²/g)	Pore Size (nm)	Pore Volume (cm³/g)
CuO-3	46.59	3.78	0.184
CuO/SiO₂ - 1	11.3	3.84	0.068
CuO/SiO₂ - 2	19.9	3.43	0.135
CuO/SiO₂ - 3	21.2	3.80	0.139
CuO/SiO₂ - 4	11.2	3.84	0.090

**Table S1** Comparison of the pore structure parameters of the prepared catalysts

**Table S2** Comparison of electrochemical performances for  $CO_2$  reduction to n-PrOHon Cu-based electrocatalysts in flow cell and H-type cell. The given potential is iR-corrected one for the sake of comparison.

catalyst	FE <sub>n-</sub> <sup>ргОН</sup> (%)	j <sub>n-PrOH</sub> (mA cm <sup>-2</sup> )	<i>E</i> (V <i>vs</i> . RHE)	electrolyte	cell	Ref.
Activated Cu mesh	13.1	<2	-0.9	0.5 M KHCO₃	H cell	ACS Catal. 2017, 7, 7946
Pd <sub>9</sub> Cu <sub>91</sub> catalyst	13.7	1.15	-0.65	0.5 M KHCO₃	H cell	Green Chem. 2020, 22, 6497
Cu-NC <sub>20</sub>	~10.6	1.50	-0.95	0.1 M KHCO₃	H cell	J. Phys. Chem. Lett. 2016, 7, 20
Cu-on-Cu₃N	6	1.3	-0.95	0.1 M KHCO₃	H cell	Nat. Commun. 2018, 9, 3828
Cu <sub>2</sub> O nanostructure	12.6	0.65	-0.3	0.5 M KHCO₃	H cell	ACS Appl. Mater. Interfaces 2021, 13, 39165- 39177
Hex-2Cu-O (Hex: hexaphyrin-copper complex)	18.3 ~8	2.2 ~21.0	-1.2 -0.66	0.1 M KHCO <sub>3</sub> 1M KOH	H cell flow- cell	Nat. Commun. 2022, 13, 5122
CuS <sub>x</sub> with double-sulfur vacancy	15.4 ~3.8	3.1 9.9	-1.05 -0.85	0.1 M KHCO <sub>3</sub> 1M KOH	H cell flow- cell	Nat. Commun. 2021, 12, 1580
modified Cu <sub>2</sub> S	8.0 7.0	2.5 27.9	-0.95 -0.92	0.1 M KHCO <sub>3</sub> 1.0 M KOH	H cell flow- cell	Nat. Catal. 2018, 1, 421
N-doped graphene quantum dot/Cu- derived nanoroad	~7	~20.0	-0.9	1.0 M KOH	flow- cell	Angew. Chem. Int. Ed., 2020, 59, 16459- 16464
bicontinuous Cu <sub>2</sub> O/Cu nanodomain	16.2 12.1	6.8 101.6	-1.4 -1.1	0.1 M KHCO <sub>3</sub> 1 M KOH	H cell flow- cell	Angew. Chem. Int. Ed. 2024, 63, e202405733
Cul self-pressurizing nanocatalytic capsules	25.7	155	-1.2	1 M KOH	flow- cell	Nat. Synth. 2024, 3, 891-902

CuO/SiO <sub>2</sub> -3	4.5 8.4	12.7 33.0	-1.21 -1.46	1.0 M KCl	flow- cell	This work
	15.5	94.0	-1.05			

Table S3 Comparison of electrochemical performances for  $CO_2$  reduction to  $C_{2+}$ 

catalyst	FE <sub>C2+</sub> alcohols (%)	j <sub>C2+ alcohols</sub> (mA cm <sup>-2</sup> )	electrolyte	<i>E</i> (V <i>vs.</i> RHE)	Ref.
N-doped graphene quantum dot/Cu-derived nanoroad	52.4	147.8	1.0 M KOH	-0.9	Angew. Chem. Int. Ed. 2020, 59, 16459
FeTPP[Cl]/Cu	41	124	1.0 M KHCO <sub>3</sub>	-0.82	Nat. Catal., 2020, 3, 75
Ce(OH) /Cu	42.6	128	1.0 М КОН	-0.7	Nat. Commun., 2019, 10, 5814
Defect-Site-Rich Cu Surface 67		>100	1.0 М КОН	-0.95	<i>Joule</i> 2021, 5, 429
Cu S-Cu-vacancy	31.6	126	1.0 М КОН	-0.85	Nat. Catal., 2018, 1, 421
Cu-DAT (DAT=3, 5-diamino-1,2,4- triazole)	30.8	81.2	1.0 М КНСО <sub>3</sub>	-0.69	ACS Catal., 2017, 7, 3313
CuO <sub>x</sub> @C	49	176	1.0 M KOH	-1.0	Angew. Chem. Int. Ed., 2022, 61, e2022096
Cu(B)	~46	~350	1.0 М КОН	-0.89	Nat. Commun., 2022, 13, 3754
CuO/SiO <sub>2</sub> -3	45.7	322.8	1.0 M KCI	-1.65	This work

alcohols on Cu-based electrocatalysts in flow cell.

catalyst	FE <sub>C2+</sub> (%)	j <sub>c2+</sub> (mA cm <sup>-2</sup> )	Electrolyte	E (V vs. RHE)	Ref.
N-doped graphene quantum dot/Cu-derived nanoroad	~74	208	1.0 M KOH	-0.9	Angew. Chem. Int. Ed., 2020, 59, 16459
Gd <sub>1</sub> /CuO <sub>x-0.22</sub>	81.4	444.3	1.0 M KOH	-0.8	J. Am. Chem. Soc., 2023, 145 (17), 9857- 9866
F-Cu	80	1280	1.0 M KOH	-0.89	Nat. Catal., 2020, 3, 478-487
FeTPP[Cl]/Cu	85	257	1.0 M KHCO <sub>3</sub>	-0.82	Nat. Catal., 2019, 3 (1), 75-82
quasi-graphitic C shell- coated Cu	82.3	329.2	1.0 M KOH	-0.55	Nat. Commun., 2021, 12, 3765
Cu dendrites	64	255	1.0 M KOH	-0.68	J. Am. Chem. Soc., 2021, 143, 8011-8021
Reconstructed Cu	77	346.5	3.0 M KOH	-1.80	Adv. Mater., 2018, 30, 1804867
Ce(OH) <sub>x</sub> /Cu	80.3	240.9	1.0 M KOH	-0.7	Nat. Commun., 2019, 10, 5814
CuAg wire	85.9	257.7	1.0 M KOH	-0.68	J. Am. Chem. Soc., 2018, 140, 5791-5797
CuO/SiO <sub>2</sub> -3	78.1	306.7	1.0 M KCl	-1.46	This work
	73.3	517.8	1.0 M KCl	-1.65	

Table S4 Comparison of  $ECO_2RR$ -to- $C_{2+}$  products over various reported Cu-based

electrocatalysts in flow cell.

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