Supporting Information

In Situ Oxidative Etching-Enabled Synthesis of Hollow Cu₂O Nanocrystals *f*or Efficient CO₂RR into C₂₊ Products

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Experimental Details

Materials. Copper acetate monohydrate ($C_4H_6CuO_4 \cdot H_2O$, $Cu(OAc)_2 \cdot H_2O$, 99%), copper acetylacetonate ($C_{10}H_{14}CuO_4$, $Cu(acac)_2$, 97%), ascorbic acid (AA, 99.0%), and oleylamine (OLA, C_{18} : 80-90%) were all obtained from Aladdin Chemical (Shanghai, China) and used as received. N,N-dimethylformamide (DMF, 99.5%), N,N-dimethylacetamide (DMA, >99%), methanol (AR), and ethanol (AR) were all obtained from Sinopharm (Shanghai, China) and used as received. N-Oleyl-1,3-propanediamine (OPDA, \geq 95%) was obtained from AkzoNobel and used as received. In all experiments, deionized water is used with a resistivity of 18.2 M Ω ·cm, which was prepared using an ultrapure water system (Ulupure, China).

Synthesis of $[Cu_2(OAc)_4(py)_2]$. Typically, a mixture of $Cu(OAc)_2 \cdot H_2O$ (398 mg, 0.2 mmol), pyridine (200 µL), ethanol (1.0 mL), and DMA (1.0 mL) was sealed in a Pyrex-tube (8 mL) and kept heated at 80 °C for 24 h under auto-generated pressure. After the reaction completed, the tube was naturally cooled to room temperature and green bulk crystals formed in the solution. The crystals were collected *via* filtration and dried at 50 °C in an oven overnight, prior to further use and characterization.

Standard procedure for the synthesis of hollow Cu₂O nanocrystals (HNCs). Typically, 50 mg of AA, 100 uL of oleylamine were mixed with 4.5 mL DMF in a 20-mL glass vial, which was preheated in an oil bath set at 150 °C under magnetic stirring for 10 minutes. Then, 0.5 mL of DMF solution containing 20 mg of $[Cu_2(OAc)_4(py)_2]$ was rapidly injected into the mixture. The vial was sealed and kept heated at 150 °C for 20 min, followed by bubbling oxygen gas into the reaction mixture. The reaction was allowed to proceed for another 2 h. The final product was collected by centrifugation at the rotation speed of 16,000 rpm, washed twice with toluene, and finally redispersed in toluene for further use and characterization.

Electrochemical measurements. The basic CO_2RR performance was evaluated in a threeelectrode system in a flow cell assembly. The flow cell consists of anolyte chamber, gas flow chamber and catholyte chamber. The window of the working electrode exposed was a square with an area of 0.5 cm². For the working electrode, 2 mg of catalyst was mixed with 20 µL of 5 wt% Nafion in 1 mL ethanol, and then dropped into a carbon GDL substrate with the mass loading of $\sim 1 \text{ mg} \cdot \text{cm}^{-2}$. The three-electrode system consisting of a working electrode, an Ag/AgCl reference electrode and a counter electrode (nickel foam) was used. A 3.0 M KOH solution was used as both cathode and anode electrolytes. The flow rate of the electrolyte was controlled at 50 mL min⁻¹ using a peristaltic pump. The high-purity CO₂ (99.999%) was introduced with the flow rate of 50 mL min⁻¹ controlled by a mass flow controller. All electrochemical measurements were conducted using a CHI660E electrochemical workstation (CHInstrument, China) under potentiostatic mode. All potentials (without iR correction) were converted to the reversible hydrogen electrode (RHE) scale as:

$E(vs. RHE) = E(vs Ag/AgCl) + 0.197 V + 0.0591 \times pH$

CO₂RR product analysis. Gas products were injected into a gas chromatograph (GC, Panna A60) after CO₂RR. The GC was equipped with a thermal conductivity detector for analyzing H₂, and a flame ionization detector for analyzing CO, CH₄ and C₂H₄ signals, while calibrated by using standard gas (Dalian special gases CO., LTD) before measurements. Liquid products were quantified by 1H NMR (400 MHz Bruker Avance III HD) through a water suppression mode, in which 100 μ L of the catholyte was prepared with 10 μ L dimethyl sulfoxide (DMSO, the internal standard solution), 90 μ L D₂O and 400 μ L H₂O. The Faradaic efficiencies (FE) of the gas and liquid products were calculated as:

$$FE_{gas} (\%) = \left(\frac{Q_{gas}}{Q_{total}}\right) * 100\% = \frac{N * F * v * c * \rho_o}{60 * jRT_o} * 100\%$$

Where N is the number of transferred electrons for target products, Faraday constant F=96485 C mol⁻¹, v is the gas flow rate measured by a flow meter, c is the volume concentration of gas products (CO, CH₄, C₂H₄ or H₂), pressure $p_0=1.01\times10^5$ Pa, gas constant R=8.314 J mol⁻¹ K⁻¹, temperature T₀=298.15 K, j means the total recorded current.

On the other hand, the concentration of formate, ethanol, acetate and n-propanol was elucidated by its NMR peak area relative to the internal standard. And the FE_{liquid} was determined as bellow:

$$FE_{liquid} (\%) = \left(\frac{Q_{liquid}}{Q_{total}}\right) * 100\% = n * N * F/(j * t) * 100\%$$

Here, n is the moles of liquid product in the cathodic compartment, N is electron transfer number, $F = 96485 \text{ C mol}^{-1}$, t is the reaction time, j is the recorded current. The partial current density under different applied potentials was determined by multiplying corresponding Faradaic efficiency of each component and total geometric current density.

Instrumentation. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and EDX-STEM mapping images were obtained using a TALOS F200X (FEI, USA) microscope operated at 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were obtained using a Zeiss Ultra60 microscope operated at 12 kV. The crystalline structures were analyzed with a MiniFlex600 X-ray diffractometer (XRD, Rigaku). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Fisher Scientific KALPHA XPS with monochromatic Al K_a radiation (*hv*=1486.6 eV). All extinction spectra were recorded using a T9 dual-beam UV-vis-NIR spectrometer (PERSEE, China). Inductively coupled plasma analysis was conducted on an ICAP-5000 inductively coupled plasma optical emission spectrometer (Focused Photonics Instrument, China).

Computational methods. All the simulations are implemented in CASTEP code.¹ We have employed plane-wave DFT+U² on the GGA-PBE level.³ As reported in the previous study, the value of U = 7 eV is applied to the Cu 3d states in the present work. The Cu₂O surface is modeled as a periodic slab with five layers, with the bottom two layers fixed, while the rest of the atoms are allowed to change freely during all the calculations. The vacuum gap is set to be 12 Å to avoid the interaction between the periodic slabs and the cutoff energy is set to 450 eV. We sample (1 × 1) supercells with $5 \times 5 \times 1$ mesh of k-points. The criteria for energy and maximum force convergence utilized are 10^{-5} eV/atom and 0.01 eV/Å. It should be noted that the above settings and parameters have been proved in literature to be sufficient for the periodic slab calculations.⁴ The transition states (TSs) are located by utilizing the linear and quadratic synchronous transit (LST/QST) method.5



Figure S1. The molecular structure of $[Cu_2(OAc)_4(py)_2]$. (Data were collected on Bruker Smart Apex II diffractometer equipped with a graphite-monochromated Mo K α radiation (λ =0.71073 Å at 296 K) by using ω -2 θ scan technique. The structures were solved by direct methods using SHELX-97 and refined using full-matrix least-squares techniques on F^2 with SHELXL-97 program. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, and the hydrogen atoms were located on the calculated positions and refined isotropically.)



Figure S2. XRD patterns of products formed at the time point during *in situ* oxidative etchingenabled synthesis of Cu_2O HNCs.



Figure S3. Wide XPS spectra of products formed at the time point during *in situ* oxidative etchingenabled synthesis of Cu₂O HNCs: a) 10 min, b) 30 min, c) 60 min, and d) 120 min.



Figure S4. a) High-resolution Cu 2p spectra and b) Cu LMM XPS spectra of products formed at the time point during *in situ* oxidative etching-enabled synthesis of Cu₂O HNCs.



Figure S5. UV-vis extinction spectra of products formed at the time point during *in situ* oxidative etching-enabled synthesis of Cu₂O HNCs.



Figure S6. HAADF-STEM image of Cu₂O HNCs.



Figure S7. EDS spectrum of Cu_2O HNCs. The atomic ratio of Cu:O was determined to be 67.1:32.9.



Figure S8. a) Elemental line-scan profile and b) HAADF-STEM image of an individual Cu_2O HNC particle. The green arrow dictates the measured region.



Figure S9. Effect of oleylamine on product morphology. SEM images of products synthesized *via* the standard procedure, except that a, b) the volume of oleylamine was tuned to a) 20 μ L and b) 500 μ L, respectively; c) oleylamine was replaced by OPDA.



Figure S10. Effect of etchant on product morphology. SEM images of products synthesized *via* the standard procedure, except that the gaseous oxygen was replaced by a) $Fe(acac)_3$ and b) H_2O_2 .



Figure S11. Effect of ligand on product morphology. SEM images of products synthesized *via* the standard procedure, except that a, b) the Cu precursor was replaced by a) $Cu(acac)_2$ and b) $Cu(OAc)_2$, c) $Cu(OAc)_2$ + pyridine (addition in step 1), and d) $Cu(OAc)_2$ + pyridine (addition in step 2), respectively.



Figure S12. LSV curves of Cu_2O HNCs and Cu SNCs catalysts with a scan rate of 50 mV/s in flow cells with 3 M KOH electrolyte and CO_2 gas.



Figure S13. Reduction potential dependent FEs of H_2 for electrochemical CO₂RR on Cu₂O HNCs and Cu SNCs catalysts.



Figure S14. Reduction potential dependent FEs of C_1 (CO, methane, formate) for electrochemical CO_2RR on Cu_2O HNCs and Cu SNCs catalysts.



Figure S15. FE_{C2+} of a) ethylene, b) ethanol; c) acetate; d) n-propanol for electrochemical CO_2RR on Cu_2O HNCs and Cu SNCs catalysts.

Cu based catalyst	FE _{C2+} (%)	<i>j</i> _{C2+} (mA cm ⁻²)	Ref.
Cu _{vac} -on-Cu ₂ S	60.0	240.0	Nat. Catal. 2018 ⁶
F-Cu	84	672	Nat. Catal. 2020 ⁷
Electro-redeposited copper	54	161	<i>Nat. Catal.</i> 2018 ⁸
Porous Cu	61.9	404	<i>Adv. Mater.</i> 2018 ⁹
Cu500Ag1000	50.0	160.0	Joule. 2020 ¹⁰
Multi-Cu ₂ O	75.2	257	J. Am. Chem. Soc. 2020 ¹¹
Cu(OH) ₂ -D	87	217	Angew. Chem. Int. Ed. 2021 ¹²
Cu/GDL	80.4	120.6	J. Am. Chem. Soc. 2021 ¹³
Cu-P1	72.0	312.0	Nat. Catal. 2021 ¹⁴
GB-Cu	73.1	103.6	J. Am. Chem. Soc. 2020 ¹⁵
CuS/Cu-V	52.8	211.2	Nat. Catal. 2018 ¹⁶
Cu nanoparticle	46	197.8	J. Power Sources. 2016 ¹⁷
Cu ₃ -Br	55.0	330.9	Angew. Chem. Int. Ed. 2021 ¹⁸
Cu ₂ O HNCs	75.9	540.0	This work

Table S1. Comparison of optimized C_{2+} products from various Cu catalysts in follow-cell system.

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