Supplementary Information

Protecting Copper Oxidation State via Intermediate Confinement for Selective CO₂ Electroreduction to C₂⁺ Fuels

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Fig S1. Computed concentrations of CO$_2$, C$_1$, C$_2$ and C$_3$ species of samples with different number of cavities. (a) Solid model. (b-h) models with different holes (1,3,5,6,7,9,11). (i) Fragmental model. Color scale, in moles per litre.
Fig S2. Computed concentrations of CO$_2$, C$_1$, C$_2$ and C$_3$ species of samples with different cavity sizes. (a-d) models with different sizes of holes (20 nm, 30 nm, 40 nm, 50 nm). Color scale, in moles per litre.
**Fig S3.** SEM images of solid Cu$_2$O. Scale bars, 1μm (a), 200 nm (b-d).
Fig S4. Size distribution of solid Cu$_2$O. It can be seen that the particle sizes of solid Cu$_2$O mainly distribute at 160–220 nm.
Fig S5. SEM images of multi-hollow Cu$_2$O. Scale bars, 200 nm (a, d), and 300nm (b, c).
**Fig S6.** Size distribution of multi-hollow Cu$_2$O. It can be seen that the particle sizes of multi-hollow Cu$_2$O mainly distribute at 180~260 nm.
**Fig S7.** SEM images of fragmental Cu$_2$O. Scale bars, 1μm (a), 100 nm (b), 200 nm (c, d).
Fig S8. XRD patterns. It shows that the Cu$_2$O with different morphologies have the same diffraction peaks, which can be assigned to cubic Cu$_2$O (JCPDS 78-2076).
**Fig S9.** HAADF images of multi-hollow Cu$_2$O. Scale bars, 100nm (a), 50nm (b) and (c).
**Fig S10.** TEM images of solid Cu$_2$O. (a-c) Morphology images of solid Cu$_2$O. (d) HRTEM image and the corresponding SAED pattern of solid Cu$_2$O. Scale bars, 200 nm (a-c), 5 nm (HRTEM image) and 2 l/nm (SAED pattern) for (d).
Fig S11. TEM images of fragmental Cu$_2$O. (a-c) Morphology images of fragmental Cu$_2$O. (d) HRTEM image and the corresponding SAED pattern of fragmental Cu$_2$O. Scale bars, 100 nm (a-c), 5 nm (HRTEM image) and 2 Å/nm (SAED pattern) for (d).
Fig S12. BET surface area analysis. (a) Nitrogen adsorption-desorption isotherms of fragmental Cu$_2$O. (B) Nitrogen adsorption-desorption isotherms of multi-hollow Cu$_2$O. (c) Nitrogen adsorption-desorption isotherms of solid Cu$_2$O. The results show that the BET Surface areas are 19.910 m$^2$/g for fragmental Cu$_2$O, 17.975 m$^2$/g for multi-hollow Cu$_2$O, and 17.062 m$^2$/g for solid Cu$_2$O.
Fig S13. Pore size distribution curves of three types of Cu$_2$O (BJH method). It can be seen that the pore diameters of multi-hollow Cu$_2$O are mainly distributed at 5 nm, 10 nm, 20 nm, 30 nm, 40 nm and 50 nm.
Fig S14. XPS and UPS Characterizations. (a) Cu 2p XPS spectra for multi-hollow, fragmental and solid Cu$_2$O. (b) O 1s XPS spectra for multi-hollow, fragmental and solid Cu$_2$O. (c) Cu LMM spectra for multi-hollow, fragmental and solid Cu$_2$O. (d) Work function for multi-hollow, fragmental and solid Cu$_2$O.

It can be seen from the spectra that the peak positions of Cu and O of the three samples are the same: Cu 2p$_{3/2}$ appears at 932.6 eV, Cu 2p$_{1/2}$ appears at 952.5 eV, O 1s appears at 530.3 eV (Ref. 1), O absorbed on the surface of Cu$_2$O appears at 531.4 eV and Cu$^+$ appears at 570.3 eV (Ref. 2). The work functions of the three types of Cu$_2$O are 4.82 eV, 4.86 eV and 4.88 eV, respectively, in good agreement with the value observed for Cu$_2$O$^3$. 
We used the diffusion-layer-coated catalyst as cathode, nickel foam as anode and Ag/AgCl electrode as reference electrode. The cathode and anode were connected with conductive copper tape respectively so that they could connect to an external electrochemical workstation. An anion exchange membrane was placed on the other side of the reference electrode, facing the anode. As shown in the photo, the anion exchange membrane and the three electrodes were combined together using polytetrafluoroethylene spacers so that a liquid electrolyte could be introduced into the chambers between the anode and membrane, as well as the membrane and the cathode. During the CO$_2$RR process, gaseous CO$_2$ was passed through the gas chamber at the back side of the gas diffusion-layer-coated catalysts. The electrolytes (30 ml of 1M, 2 M, and 3M solution) were circulated through both the anode and cathode chambers. The electrolyte flow was kept at 20 ml min$^{-1}$. The CO$_2$ flow through cathode compartment was maintained at 24 ml min$^{-1}$. The reaction time was kept at 20 minutes.
Fig S16. Photograph of catalysts coated on hydrophobic carbon paper.
Fig S17. Effect of electrolyte concentration on Faraday efficiency on multi-hollow Cu$_2$O catalyst. It can be seen that the Faraday efficiencies of the C$_{2+}$ products reached the highest value when 2 M KOH was used.
Fig S18. Faradaic efficiencies of CO$_2$RR major products on (a) multi-hollow Cu$_2$O, (b) fragmental Cu$_2$O and (c) solid Cu$_2$O at different applied potentials in 2 M KOH.
Fig S19. Faradaic efficiencies of C$_2^+$ products on the three types of Cu$_2$O catalysts. (a) Faradaic efficiencies of n-PrOH on multi-hollow, fragmental and solid Cu$_2$O. (b) Faradaic efficiencies of EtOH on multi-hollow, fragmental and solid Cu$_2$O. (c) Faradaic efficiencies of acetate on multi-hollow, fragmental and solid Cu$_2$O. (d) Faradaic efficiencies of ethylene on multi-hollow, fragmental and solid Cu$_2$O. It can be seen that multi-hollow Cu$_2$O performs much better than fragment and solid Cu$_2$O for generating C$_2^+$ products.
Fig S20. 1H-NMR spectra. The electrolyte collected from the working electrode in a flow-cell reactor at -0.61V vs. RHE for the multi-hollow, fragmental and solid Cu$_2$O. It clearly shows that much more C$_2$+ products yield on multi-hollow Cu$_2$O.
Fig S21. BET normalized current density of $C_{2+}$ and $C_1$ products on the three types of Cu$_2$O. It shows that multi-hollow Cu$_2$O has larger current density than fragmental and solid Cu$_2$O.
Fig S22. Half-cell PCE (power conversion efficiency) of C₂, products on (a) multi-hollow, (b) fragmental and (c) solid Cu₂O. It shows that multi-hollow Cu₂O has higher PCE.
**Fig S23.** SEM image of multi-hollow Cu$_2$O after CO$_2$RR. It shows that after CO$_2$RR at −0.61 V vs RHE for 20 minutes, Cu$_2$O roughly maintains the multi-hollow morphology. Scale bar: 1μm.
Figure S24. STEM-EDX elemental mapping of multi-hollow Cu$_2$O after CO$_2$RR. Scale bar: 50 nm
Figure S25. HRTEM images of multi-hollow Cu$_2$O after CO$_2$RR. (a) TEM image of multi-hollow Cu$_2$O after CO$_2$RR. (b-c) HRTEM images of multi-hollow Cu$_2$O after CO$_2$RR. (d) The corresponding SAED pattern of multi-hollow Cu$_2$O after CO$_2$RR. It shows that Cu$_2$O phase well remains after CO$_2$RR at -0.61V vs RHE for 20 minutes. Scale bars, 50 nm (a), 5 nm (b, c), and 2 1/nm (d).
Fig S26. Photos of the operando Raman setups. (a) Photo of the cell with three-electrode system. We used an electrolytic cell with three-electrode system to obtain operando Raman spectra of Cu$_2$O as a function of reaction time at -0.61V versus RHE. Cu$_2$O catalysts were spread on the glassy carbon connecting external metal bar, which are used as working electrodes. A metal bar connecting with a platinum wire extending in the cell was used as counter electrode. An Ag/AgCl electrode was used as reference electrode. 2M KOH electrolytes were poured into the cell to immerse the three electrodes. During the CO$_2$RR process, CO$_2$ gas continued to flow into the cell, a 532 nm laser was taken as light source to shine directly on the catalyst surface, and a computer synchronously collected the Raman signals. (b) Photo of the cell with two-electrode system. We took a two-electrode system to reduce the interference of the cell thickness on the laser intensity. The diffusion-layer-coated Cu$_2$O catalysts connecting with the conductive tape were used as the working electrodes. And the nickel foam was used as counter electrode. 2M KOH electrolytes were poured into the cell to immerse the catalysts and the nickel foam. The 532 nm laser was replaced by 785 nm laser to reduce the interference caused by fluorescence. The CO$_2$RR test was performed under 60 mA cm$^{-2}$. During the CO$_2$RR process, CO$_2$ gas continued to flow into the cell, and a computer synchronously collected the Raman signals.
Fig S27. Raman spectra of Cu standard and Cu$_2$O standard. It shows that Cu$_2$O has obvious Raman signals while Cu is Raman inactive. 223, 419, 524, and 624 cm$^{-1}$ are attributed to the $2\Gamma_{12}$, $4\Gamma_{12}$, $\Gamma_{25}$, and $\Gamma_{12}^+\Gamma_{25}$ phonon modes of Cu$_2$O$^{4-6}$. 
Fig S28. Operando Raman analysis of multi-hollow Cu$_2$O. (a) Operando Raman spectra of multi-hollow Cu$_2$O as a function of reaction time at -0.61V versus RHE in 2 M KOH. (b) Operando Raman spectra of CO stretching as a function of reaction time at -0.61V versus RHE in 2 M KOH. We used the cell with three-electrode system and the 785 nm laser to perform operando Raman test in 2 M KOH. Due to instrument limitations, it took very long time to collect valid spectra from 150 cm$^{-1}$ to 2300 cm$^{-1}$. To ensure the quality of data, we collected spectra from 150 cm$^{-1}$ to 900 cm$^{-1}$, as well as from 1900 cm$^{-1}$ to 2300 cm$^{-1}$, respectively. It thus took much shorter to collect each spectrum. We took the spectra of 5 min, 10 min, 15 min and 20 min for comparison.
Fig S29. Schematic illustrates the stabilization of Cu⁺ species via confined intermediates. Compared to fragmental and solid Cu₂O, multi-hollow Cu₂O can confine intermediate to protect copper oxidation state and thus yields C₂⁺ compounds with a high production rate. White, hydrogen; Gray, carbon; Red, oxygen; Violet, copper.
References


