Efficient Electroreduction of CO$_2$ to C$_{2+}$ Products on CeO$_2$ modified CuO

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Experimental Section

Chemicals and materials: Cerium(III) Nitrate (Ce(NO$_3$)$_3$, ≥ 99.0%), Copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, ≥ 99.0%), potassium hydroxide (KOH, ≥ 85%) and sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS, 99%) were purchased from Sigma-Aldrich. Ammonium hydroxide (NH$_3$·H$_2$O, 65% ~ 68%), sodium hydroxide (NaOH, ≥ 99.0%) and Ni foam were purchased from Sinopharm Chemical Reagent Co. Ltd. D$_2$O (98%). Ni foam was purchased from Beijing Innochem Science & Technology Co. Ltd. All the chemicals were used as received. N$_2$ (99.999%) and CO$_2$ (99.999%) were provided by Beijing Analytical Instrument Company. Deionized water was used in the experiments.

Synthetic procedures for CCX and CeO$_2$. CC0 was synthesized in a facile way according to a literature method. First, 1 g Cu(NO$_3$)$_2$·3H$_2$O were dissolved in 100 mL deionized water, followed by the addition of 30 mL 0.15 M NH$_3$·H$_2$O to obtain the blue solution with a constant stirring. Then about 8 mL 1 M NaOH solution was dropped into the solution to adjust the pH value to 10, and kept stirring for 30 minutes. After centrifugation, precipitates were collected and dried in a vacuum freeze drying oven for 24 h. The dried samples were then annealed at 600 °C for 2 h, while the temperature was rapidly risen from ambient temperature to 600 °C in 18 minutes. The different CCX were prepared by the same method except Cu(NO$_3$)$_2$·3H$_2$O is replaced by the mix Ce(NO$_3$)$_3$ and Cu(NO$_3$)$_2$·3H$_2$O (the molar ratios of Ce and Cu were 1%, 5%, 10% 15%, 20% and 30%). The CeO$_2$ was prepared by the same method except Cu(NO$_3$)$_2$·3H$_2$O is replaced by Ce(NO$_3$)$_3$.

Characterization of the materials. The SEM and TEM characterizations were carried out using a HITACHI S-4800 and JEOL JEM-2100 equipped with EDS, respectively. The operando X-ray adsorption spectroscopy (XAS) measurements were performed using a modified flow cell at the 1W1B, 1W2B beamline at Beijing Synchrotron Radiation Facility (BSRF).

Preparation of electrodes. To construct the cathode electrode, a catalyst slurry that contained 5 mg of obtained catalysts, 1 mL of methanol and 20 µL of Nafion ionomer solution (5 wt% in H$_2$O) was first mixed and sonicated for 30 min. Then, the catalyst slurry (0.2 mL) was slowly drop cast onto a PTFE membrane (Fuel Cell Store) under vacuum to achieve a catalyst loading of ~1.0 mg cm$^{-2}$. Ni foam were used anode electrode.

Electrochemical study. Electrochemical studies were conducted in an electrochemical flow cell which including a gas chamber, a cathodic chamber, and an anodic chamber, as reported in our previous work. An anion exchange membrane (FumasepFAA-3-PK-130) was used to separate the anodic and cathodic chambers, and an Ag/AgCl electrode and Ni foam were used as the reference and counter electrodes, respectively. The electrolysis was
conducted using a CHI-660e electrochemical workstation equipped with a high current amplifier CHI 680c. The measured potentials after \(iR\) compensation (3.6 ohm was used) were rescaled to the RHE by \(E\) (versus RHE) = \(E\) (versus Ag/AgCl) + 0.209 V + 0.0591V/pH \(\times\) pH. For performance studies, 1 M KOH was used as the electrolyte, and it was circulated through the cathodic and anodic chambers using peristaltic pumps at a rate of 20 mL min\(^{-1}\). The flow rate of CO\(_2\) gas through the gas chamber was controlled to be 20 sccm using a digital gas flow controller. The KIE experiment was conducted in the 1 M KOH solution, in which H\(_2\)O was replaced by D\(_2\)O.

**Product analysis.** The gaseous product of electrochemical experiments was collected using a gas bag (the first bag was collected from the 10th minute at every applied potential and each bag was collected for 15 minutes) and analyzed by gas chromatography (GC, HP 4890D), which was equipped with TCD detector using argon as the carrier gas. The liquid product was analyzed by \(^1\)H NMR (Bruker Advance III 400 HD spectrometer) in deuterioxide.

**Calculations of Faradaic efficiencies of gaseous and liquid products**

**Calculations of Faradaic efficiencies of Liquid products:** After electrolysis, a certain amount of internal standard solution was added to the electrolyte as the internal standard. Because the concentration of internal standard was known, the moles of liquid products can be calculated from integral areas and calibration curves. To accurately integrate the products in NMR analysis, two standards located in different regions were used in NMR analysis. 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 μL catholyte after the reaction was mixed with 100 μL 6 mM DSS solution, 100 μL 200 mM phenol and 200 μL D\(_2\)O, and then analyzed by \(^1\)H NMR (Bruker Advance III 400 HD spectrometer).

The Faradaic efficiency of liquid product is:

\[
FE= \frac{\text{moles of product}}{Q/nF} \times 100\%
\]

(Q: charge (C); F: Faradaic constant (96485 C/mol); n: the number of electrons required to generate the product)

**Calculations of Faradaic efficiencies of Gaseous products.** From the GC peak areas and calibration curves for the TCD detector, we can obtain the V % of gaseous products. Since the flow rate of the outlet was monitored to be constant, the moles of gaseous products can be calculated. The Faradaic efficiency of gaseous product is:

\[
FE= \frac{\text{moles of product}}{Q/nF} \times 100\%
\]

(Q: charge (C); F: Faradaic constant (96485 C/mol); n: the number of electrons required to generate the product)

**Electrochemical impedance spectroscopy (EIS) study.** The EIS measurement was carried out in 1 M KOH at an open circuit potential (OCP) with an amplitude of 5 mV of \(10^{-1}\) to \(10^6\) Hz.
Double-layer capacitance ($C_{dl}$) measurements. The catalyst was dropped on the 6mm glass carbon electrode (GCE) as the work electrode. The electrochemical active surface area is proportional to $C_{dl}$ value. $C_{dl}$ was determined by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammogram (CV). The CV ranged from -0.43 V to -0.53 V vs. RHE. The $C_{dl}$ was estimated by plotting the $\Delta j$ ($j_a-j_c$) at -0.48 V vs. RHE against the scan rates, in which the $j_a$ and $j_c$ are the anodic and cathodic current density, respectively. The scan rates were 20, 30, 40, 50, 60, 80, 100 and 120 mV s$^{-1}$.

**In-situ Raman measurements.** In-situ Raman measurements were carried out using a Horiba LabRAM HR Evolution Raman microscope in a modified flow cell (purchased from Gaossunion Technology Co., Ltd.). A 785-nm laser was used and signals were recorded using a 20 s integration and by averaging two scans. The catalysts were firstly detected as the “pre” line in Fig. 3d and 3E to confirm the structure properties after the pre-electrolysis, and the corresponding lines were amplified to exhibit the signal of Cu$_2$O. The $iR$ compensation was conducted in the operando XAS experiment at each potential, and a 15-minute electrolysis was conducted to gain the steady state before the collection of Raman spectra with constantly flowed gaseous CO$_2$.

**XAFS measurements**

The X-ray absorption find structure spectra data (Fe K-edge) were collected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF, operated at 2.5 GeV with a maximum current of 250 mA). The data were collected in fluorescence excitation mode using a Lytle detector. All samples were pelletized as disks of 13 mm diameter with 1mm thickness using graphite powder as a binder.

Operando XAS measurements were conducted in a custom-designed flow cell as our previous reports. Catalysts were filtered on the PTFE membrane as the working electrode and 1 M KOH was used as the electrolyte. The saturated KCl Ag/AgCl electrode was chosen as the reference electrode and the Ni foam was used as the counter electrode. The $iR$ compensation was conducted in the operando XAS experiment at each potential, and a 15-minute electrolysis was conducted to gain the steady state before the collection of XAS spectra with constantly flowed gaseous CO$_2$.

The acquired EXAFS data were processed according to the standard procedures using the Athena and Artemis implemented in the IFEFFIT software packages. The fitting detail is described below:

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the $\chi(k)$ data of were Fourier transformed to real (R) space using a hanning windows ($dk=1.0$ Å$^{-1}$) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central
atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

The following EXAFS equation was used:

$$\chi(k) = \sum_j \frac{N_j S_o^2 F_j(k)}{k R_j^2} \exp[-2k^2 \sigma_j^2] \exp[-2\lambda(k)] \sin[2k R_j + \phi_j(k)]$$

$S_o^2$ is the amplitude reduction factor, $F_j(k)$ is the effective curved-wave backscattering amplitude, $N_j$ is the number of neighbors in the $j^{th}$ atomic shell, $R_j$ is the distance between the X-ray absorbing central atom and the atoms in the $j^{th}$ atomic shell (backscatterer), $\lambda$ is the mean free path in Å, $\phi_j(k)$ is the phase shift (including the phase shift for each shell and the total central atom phase shift), $\sigma_j$ is the Debye-Waller parameter of the $j^{th}$ atomic shell (variation of distances around the average $R_j$). The functions $F_j(k)$, $\lambda$, and $\phi_j(k)$ were calculated with the ab initio code FEFF8.2.

The obtained $S_o^2$ was fixed in the subsequent fitting. Since the composition of the sample is known, we fixed the interatomic distance (R) of CuO, Cu and Cu$_2$O in the fitting process. While the coordination number N, Debye-Waller factor $\sigma^2$, and the edge-energy shift $\Delta E_0$ were allowed to run freely. P1 represents the percentage of CuO in the total content; P2 represents the percentage of Cu in the total content; P3 ($P_3 = 1 - P_1 - P_2$) represents the percentage of Cu$_2$O in the total content.

Computational Method

**Computational Method.** Spin-polarized DFT calculations were performed with periodic super-cells under the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional for exchange-correlation and the ultrasoft pseudopotentials for nuclei and core electrons. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 30 Ry and the charge-density cutoff of 300 Ry. The Fermi-surface effects were treated by the smearing technique of Methfessel and Paxton, using a smearing parameter of 0.02 Ry. The models we use in this paper were hybrid structures with Cu and Cu$_2$O joint by respective (111) surfaces, with Cu$_2$O(111) located underneath 3 and 2 layered Cu(111) to simulate different content of Cu(I) (Fig. S25). For such hybrid structures, the lattice of Cu is remained to its optimized value while that of Cu$_2$O is compressed by 20%. To study the role of CeO$_2$, a cluster of CeO$_2$ was built on the surface (Fig. S25). All of the structure optimizations were proceeded at the supercells of 4x4’s Cu(111), while the transition state calculations for CeO$_2$ associated structure were also done under 4x8’s supercell. For all of the structures, only the first layer of the substrates was allowed to relax. The convergence criteria were set as $10^{-3}$ Ry/Bohr of Cartesian force components acting on each atom and $10^{-5}$ Ry of total energy. The Brillouin-zones were sampled with a 1×1×1 k-point mesh. The PWSCF codes
contained in the Quantum ESPRESSO distribution\textsuperscript{3} were used to implement the calculations.

The transition state (TS) calculation involved the CO\textsuperscript{*} protonation step to generate CHO\textsuperscript{*} (RS3) on structures with and without CeO\textsubscript{2}. Specifically, to get the saddle points and minimum energy paths (MEPs), we first used normal elastic band (NEB) method with 5 images, then interpolated with 2 images around the structure with highest energy achieved, and restarted the calculation with climbing image nudged method (CI-NEB).\textsuperscript{4} The quasi-Newton method was employed to optimize the transition-state images from the NEB calculations until a maximum force less than 0.015 Ry/Å was achieved.

**The details for composing the free energy diagram:**

The reactions associated in this paper are

\[
\text{CO}^* + \text{CO}^* \rightarrow \text{CO}^*\text{CO} \quad (\text{RS1})
\]

\[
\text{CO}^* + \text{H}_2\text{O} + e^{-} \rightarrow \text{COH}^* + \text{OH}^- \quad (\text{RS2})
\]

\[
\text{CO}^* + \text{H}_2\text{O} + e^{-} \rightarrow \text{CHO}^* + \text{OH}^- \quad (\text{RS3})
\]

\[
\text{CHO}^* + \text{CHO}^* \rightarrow \text{CHO}^*\text{CHO} \quad (\text{RS4})
\]

\[
\text{COH}^* + \text{COH}^* \rightarrow \text{COH}^*\text{COH} \quad (\text{RS5})
\]

For proton donation associated reaction, the free energy were calculated via the computational hydrogen electrode method proposed by Norskov et al.\textsuperscript{5} The adsorption energy for adsorbates X\textsuperscript{*} is defined by

\[
\Delta E_{X^*} = E_{X^*}^{DFT} - E_{X^*}^{DFT}
\]

Where \( E_{X^*}^{DFT} \) and \( E_{X^*}^{DFT} \) are the DFT based total energy of the structures with and without X\textsuperscript{*} adsorption. The zero point energy for the adsorbates are not involved, which has been considered negligible based on the calculations in previous report.\textsuperscript{6}
Supplementary Figure

Fig. S1. (a-e) The SEM images of CC0, CC1, CC5, CC10, CC15, CC30.
Fig. S2. (a-e) The TEM images of CC0, CC1, CC5, CC10, CC15, CC30.
**Fig. S3.** The first cycle of CV on CC20 in 1 M KOH electrolyte in a flow cell during CO$_2$RR, and the orange column represents the reduction of CuO to Cu.
Fig. S4. A typical $^1$H NMR spectrum of liquid products after electrolysis at -1.07 V (vs RHE) over CC20.
Fig. S5. The $^1$H NMR plot of the liquid products after electrolysis at -1.07 V (vs RHE) using $^{13}$CO$_2$ as gas source.
Fig. S6. (a-e) The FE of products for CC1, CC5, CC10, CC15, CC30 at various applied potentials in CO$_2$RR.
Fig. S7. The distribution of products over CC20 at various applied potentials in CO$_2$RR.
Fig. S8. The distribution of products over CC0 at various applied potentials in CO$_2$RR.
**Fig. S9.** The comparison for the FE of H$_2$ (a), formate (b), ethanol (c) and n-propanol (d) on CC0 and CC20 at various applied potentials in CO$_2$RR.
Fig. S10. The comparison for the FE of C$_2$H$_4$ on CC0 and CC20 at various applied potentials in CO$_2$RR.
Fig. S11. The comparison for the FE of CO on CC0 and CC20 at various applied potentials in CO$_2$RR.
Fig. S12. (a) The current density and (b) faradaic efficiency of products on CeO$_2$ at various applied potentials in CO$_2$RR.
**Fig. S13.** The long-term stability test in 1 M KOH with the CO$_2$ flow rate as 20 scm at -1.12 V (vs RHE) on CC20.
Fig. S14. (a-e) The TEM images of CC0, CC1, CC5, CC10, CC15, CC30 after the electrochemical test.
Fig. S15. (a) The TEM, (b) HR-TEM images and (c) EDS spectra of CC20 after the long-term stability test.
Fig. S16. The HR-TEM images of CC0 after the electrochemical test.
**Fig. S17.** The XRD patterns for CC0 and CC20 on PTFE membranes after CO$_2$RR, the orange column represents the corresponding peak of Cu(111).
Fig. S18. (a, c, e, g, i, j, l) The cyclic voltammetry at various scan rates (20, 30, 40, 50, 60, 80, 100, 120 mV s\(^{-1}\)) over CC0, CC1, CC5, CC10, CC15, CC20, CC30; (b, d, f, h, k, m) the charging current density differences plotted against the scan rates over CC0, CC1, CC5, CC10, CC15, CC20, CC30.
Fig. S19. Nyquist plots for different electrodes in CO\textsubscript{2}-saturated 1 M KOH electrolyte.
**Fig. S20.** *Operando* Cu K-edge extended XAFS oscillation function $k^3 w(k)$ at various applied potentials for CC20.
Fig. S21. (a) Operando XANES, (b) the corresponding extended XAFS oscillation function $k^3 w(k)$, and (c) Fourier transforms of $k^3$-weighted EXAFS data at Cu K-edge at various applied potentials over CC0.
Fig. S22. The ratios of Cu species [Cu(0), Cu(I) and Cu(II)] at various applied potentials over CC20.
**Fig. S23.** The ratios of Cu species [Cu(0), Cu(I) and Cu(II)] at various applied potentials over CC0.
**Fig. S24.** The EXAFS data fitting results of CC0 at various applied potentials.
Fig. S25. The EXAFS data fitting results of CC20 at various applied potentials.
**Fig. S26.** *In-situ* electrochemical spectral cell for SERS test.
Fig. S27. (a) Top views of the Cu-M, Cu-L and CeO$_2$/Cu-L. Blue balls, yellow balls, red balls, gray balls and white balls stand for Cu, Ce, O, C and H, respectively.
Fig. S28. Top view of (a) *CO, (b) *CO-*CO, (c) *O*CCO, (d) O*CCHO, (e) *CHO, (f) *OHCCCHO*, (g) *COH, (h) *COH*COH on the Cu-M. Blue balls, red balls, gray balls and white balls stand for Cu, O, C and H, respectively.
**Fig. S29.** Side view of (a) *CO, (b) *CO-*CO, (c) O*CCO, (d) O*CCHO, (e) *CHO, (f) OHCCHO*, (g) *COH, (h) *COH*COH on the Cu-M.
**Fig. S30.** Top view of (a) *CO, (b) *CO-*CO, (c) *O*CCO, (d) O*CCHO, (e) *CHO, (f) *OHCC*H*, (g) *COH, (h) *COH*COH on the Cu-L.
Fig. S31. Side view of (a) *CO, (b) *CO- *CO, (c) *O*CCO, (d) O*CCHO, (e) *CHO, (f) *OHCCCHO*, (g) *COH, (h) *COH*COH on the Cu-L.
**Fig. S32.** Top view of (a) *CO, (b) *CO-*CO, (c) *OCCO*, (d) O*CCHO, (e) *CHO, (f) *OHCCCHO*, (g) *COH, (h) *COH*COH on the CeO$_2$/Cu-L. Blue balls, yellow balls, red balls, gray balls and white balls stand for Cu, Ce, O, C and H, respectively.
**Fig. S33.** Side view of (a) *CO, (b) *CO-*CO, (c) *OCO*, (d) O*CCHO, (e) *CHO, (f) *OHCH*, (g) *COH, (h) *COH*COH on the CeO2/Cu-L.
**Fig. S34.** (a, b, c) Side views of the key states in the hydrogenation of *CO into *CHO in the presence of H₂O* on Cu-M, Cu-L and CeO₂/Cu-L. Blue balls, yellow balls, red balls, gray balls and white balls stand for Cu, Ce, O, C and H, respectively.
Fig. S35. (a, b, c) Reaction energy diagram for the CO$_2$RR to describe the possible C-C coupling step from *CO on Cu-M, Cu-L and CeO$_2$/Cu-L after applying a -0.5 V bias potential (vs RHE). (d, e, f) Reaction energy diagram for *CO hydrogenation to *COH on Cu-M, Cu-L and CeO$_2$/Cu-L after applying a -0.5 V bias potential (vs RHE).
Fig. S36. (a, b, c) Reaction energy diagram for the CO$_2$RR to describe the possible C-C coupling step from *CO on Cu-M, Cu-L and CeO$_2$/Cu-L after applying a -1.12 V bias potential (vs RHE). (d, e, f) Reaction energy diagram for *CO hydrogenation to *COH on Cu-M, Cu-L and CeO$_2$/Cu-L after applying a -1.12 V bias potential (vs RHE).
**Fig. S37.** KIEs of H/D in CO\textsubscript{2}RR to ethylene in 1 M KOH (D\textsubscript{2}O) with the CO\textsubscript{2} flow rate as 20 sccm and hydrogen evolution performance under a nitrogen atmosphere in 1 M KOH at -1.02 V versus RHE on CC20 and CC0.
## Supplementary Tables

**Table 1.** The Comparison of C$_2$+ products in CO$_2$RR on various Cu-based catalysts.

| Samples                | E (V) vs. RHE | $\text{FE}_{\text{C}_2^+}$ (%) | $j_{\text{C}_2^+}$ (mA cm$^{-2}$) | References |
|------------------------|---------------|-------------------------------|----------------------------------|------------|
| CC20                   | -1.12         | 75.2                          | 913.2                            | This work  |
| NGQ/Cu-nr              | -0.9          | 80.4                          | 226.81                           | S2         |
| Cu-KI                  | -1.09         | 72.58                         | 29.03                            | S7         |
| FeTPP[Cl]/Cu           | -0.82         | 85                            | 257.04                           | S8         |
| Cu-CO$_2$              | -0.71         | 90                            | 519.3                            | S9         |
| CuAg wire              | -0.7          | 85                            | 255                              | S10        |
| F-Cu                   | -0.89         | 80                            | 1280                             | S6         |
| Nanoporous Cu          | -0.67         | 62                            | 404.86                           | S1         |
| Dealloyed Cu           | -1.8 ~ -2.1   | 75                            | 450                              | S11        |
| I-modified Cu          | -0.9          | 80                            | 31.2                             | S12        |
| Reconstructed Cu       | -1.8          | 77                            | 346.5                            | S13        |
| 100-cycle Cu           | -0.963        | 60.5                          | 41                               | S14        |
| OBC                    | -1            | 45                            | 44.7                             | S15        |
| Cu nanocubes           | -0.8          | 60                            | 44.4                             | S16        |
| Multihollow Cu$_2$O    | -0.61         | 75                            | 267±13                           | S17        |
| 3D-CIBH                | -0.91         | 91.7                          | 1210                             | S18        |
Table 2. Structural parameters extracted from the EXAFS fitting for CC0. ($S_0^2=0.85$)

| Sample | Scattering pair | P   | CN  | $\sigma^2 (10^{-3}\text{Å}^2)$ | $\Delta E_0 (\text{eV})$ | R factor |
|--------|----------------|-----|-----|-------------------------------|--------------------------|----------|
| OCP    | Cu-O(CuO)      | P1=1.0 | 1.7 | 4.4                           | -3.4                     | 0.01     |
|        | Cu-Cu(CuO)     |      | 4.2 | 4.6                           | 3.1                      |          |
|        | Cu-Cu (Cu foil)| P2=0  | /   | /                             | /                        | /        |
|        | Cu-O (Cu$_2$O) | P3=0  | /   | /                             | /                        | /        |
|        | Cu-Cu (Cu$_2$O)|      | /   | /                             | /                        | /        |
| -0.62 V| Cu-O(CuO)      | P1=0.75 | 1.7 | 4.9                           | -3.4                     | 0.01     |
|        | Cu-Cu(CuO)     |      | 4.1 | 5.2                           | 3.1                      |          |
|        | Cu-Cu (Cu foil)| P2=0.15 | 10  | 5.3                           | 4.0                      | 0.02     |
|        | Cu-O (Cu$_2$O) | P3=0.05 | 2.3 | 5.2                           | -3.6                     | 0.01     |
|        | Cu-Cu (Cu$_2$O)|      | 2.1 | 5.3                           | 4.2                      |          |
| -0.82 V| Cu-O(CuO)      | P1=0.2 | 1.6 | 5.2                           | -3.4                     | 0.01     |
|        | Cu-Cu(CuO)     |      | 3.9 | 5.3                           | 3.1                      |          |
|        | Cu-Cu (Cu foil)| P2=0.65 | 11.5 | 5.6                           | 4.0                      | 0.01     |
|        | Cu-O (Cu$_2$O) | P3=0.15 | 2.4 | 5.5                           | -3.6                     | 0.01     |
|        | Cu-O (Cu$_2$O) |      | 2.2 | 5.7                           | 4.2                      |          |
| -1.02 V| Cu-O(CuO)      | P1=0.15 | 1.7 | 5.5                           | -3.4                     | 0.01     |
|        | Cu-Cu(CuO)     |      | 4.0 | 5.9                           | 3.1                      |          |
|        | Cu-Cu (Cu foil)| P2=0.66 | 11.2 | 7.0                           | 4.0                      | 0.02     |
|        | Cu-O (Cu$_2$O) | P3=0.21 | 3.0 | 6.1                           | -3.6                     | 0.01     |
|        | Cu-O (Cu$_2$O) |      | 3.0 | 6.5                           | 4.2                      |          |

$S_0^2$ is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); $\sigma^2$ is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); $\Delta E_0$ is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.
Table 3. Structural parameters extracted from the EXAFS fitting for CC20. ($S_0^2=0.85$)

| Sample  | Scattering pair     | $P$  | CN      | $\sigma^2(10^{-3}\text{Å}^2)$ | $\Delta E_0$(eV) | R factor |
|---------|---------------------|------|---------|--------------------------------|------------------|----------|
| OCP     | Cu-O(CuO)           | P1=1 | 1.8     | 4.4                            | -3.4             | 0.01     |
|         | Cu-Cu(CuO)          |      | 4.3     | 4.6                            | 3.1              |          |
|         | Cu-Cu (Cu foil)     | P2=0 | /       | /                              | /                | /        |
|         | Cu-O (Cu$_2$O)      | P3=0 | /       | /                              | /                | /        |
|         | Cu-Cu (Cu$_2$O)     |      | /       | /                              | /                | /        |
| -0.62 V | Cu-O(CuO)           | P1=0.7| 1.7    | 4.9                            | -3.4             | 0.01     |
|         | Cu-Cu(CuO)          |      | 4.3     | 5.3                            | 3.1              |          |
|         | Cu-Cu (Cu foil)     | P2=0.19| 10     | 5.1                            | 4.0              | 0.02     |
|         | Cu-O (Cu$_2$O)      | P3=0.11| 2.4   | 5.2                            | -3.4             | 0.01     |
|         | Cu-Cu (Cu$_2$O)     |      | 2.1     | 5.3                            | 4.2              |          |
| -0.82 V | Cu-O(CuO)           | P1=0.27| 1.8   | 5.0                            | -3.4             | 0.01     |
|         | Cu-Cu(CuO)          |      | 4.0     | 5.4                            | 3.1              |          |
|         | Cu-Cu (Cu foil)     | P2=0.37| 10     | 6.3                            | 4.1              | 0.02     |
|         | Cu-O (Cu$_2$O)      | P3=0.36| 3.0   | 5.8                            | -3.4             | 0.01     |
|         | Cu-O (Cu$_2$O)      |      | 2.8     | 6.1                            | 4.2              |          |
| -1.02 V | Cu-O(CuO)           | P1=0.13| 1.7   | 5.2                            | -3.4             | 0.01     |
|         | Cu-Cu(CuO)          |      | 4.0     | 5.7                            | 3.1              |          |
|         | Cu-Cu (Cu foil)     | P2=0.41| 10     | 6.8                            | 4.1              | 0.01     |
|         | Cu-O (Cu$_2$O)      | P3=0.46| 3.5   | 6.1                            | -3.4             | 0.01     |

$S_0^2$ is the amplitude reduction factor; CN is the coordination number; $R$ is interatomic distance (the bond length between central atoms and surrounding coordination atoms); $\sigma^2$ is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); $\Delta E_0$ is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.
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