

Supporting Information

Operando X-ray Absorption Spectroscopic Studies of Carbon

Dioxide Reduction Reaction in a Modified Flow Cell

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Experimental Section

Preparation of a sputtered Cu on PTFE substrate: Cu with a thickness of 300 nm was sputtered on a PTFE substrate (pore size of 450 nm) using a pure Cu target (99.99%) with an Ar flow rate of 3 mtorr at a DC power of 30 Watts in a magnetron sputtering system. The base pressure is below 5×10^{-6} torr, acquired using a turbomolecular pump.

Synthesis of a sprayed Cu(OH)₂ on PTFE substrate: 15 mmol of Cu(NO₃)₂ was dissolved into 30.0 ml of deionized (DI) water. 30 ml of 1.0 M KOH was added dropwise under vigorous stirring. The precipitates were centrifuged with water three times and methanol one time and dried under vacuum at room temperature. The 4 mg of Cu(OH)₂ was mixed with 16 μ L of Nafion solution (~5 wt%) and 200 μ L of methanol. This dispersed ink was sprayed onto a PTFE substrate with a size of 5 \times 5 cm and an area loading of 1 mg cm⁻².

Characterization: Microstructure was collected by field-emission scanning electron microscopy (FESEM, JEOL, JSM-6500F). The crystallization of materials was assessed using a Bruker D8 Advance X-ray diffraction (XRD) analyzer with Cu K α radiation ($\lambda = 1.5406$ Å). X-ray absorption spectroscopy (XAS) including X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) of Cu K-edge were collected in fluorescence mode using a Lytle detector at the BL17C and BL44A beamline in NSRRC. The data were processed through Athena software from the IFEFFIT package for analyzing XANES and EXAFS. The pre-edge baseline was subtracted and the spectra was normalized to the post-edge. EXAFS analysis was conducted using a Fourier transform on k^2 -weighted EXAFS oscillations to evaluate the contribution of each bond pair to the Fourier transform peak. REX2000 software using ab initio-calculated phases and amplitudes from the program FEFF 8.2 was used for EXAFS fitting. The k -range and R -range for the k^2 -weighted Fe K-edge EXAFS are 3.5-11⁻¹ Å and 1.2-2.9 Å, respectively. Cu-Cu path was adopted for structural fitting. Fitted structural parameters from k^2 weighted EXAFS oscillations were also shown in this figure. N: coordination number; R: interatomic distance; σ^2 : the EXAFS Debye–Waller factor. Wavelet analyses were performed in Matlab R2020.

Electrochemical measurement: Electrochemical properties were investigated using a Biologic VSP-3e potentiostat in a flow cell reactor using a gas diffusion electrode (GDE) as the working electrode (WE), nickel foam as the counter electrode (CE), and a saturated Ag/AgCl electrode as the reference electrode (RE). The WE and CE were separated by an anion exchange membrane. An aqueous solution of 1.0 M KOH was used as the electrolyte, and the flow rate of CO₂ was 50 sccm. The working area of electrodes was 1.0 cm² for each experiment. The

gaseous products were evaluated via gas chromatography (Agilent 8860) equipped with a thermal conductivity detector and a flame ionization detector.

Operando XAS measurement: *Operando XAS* was carried out in the same conditions as electrochemical testing using the designed flow cell with an opening sealed by Kapton tape in the gas chamber. X-ray was allowed to transmit through the tape and electrolyte, so that the signal of X-ray absorption spectroscopy would be collected in total-fluorescence-yield mode at the BL17C and BL44A beamline.

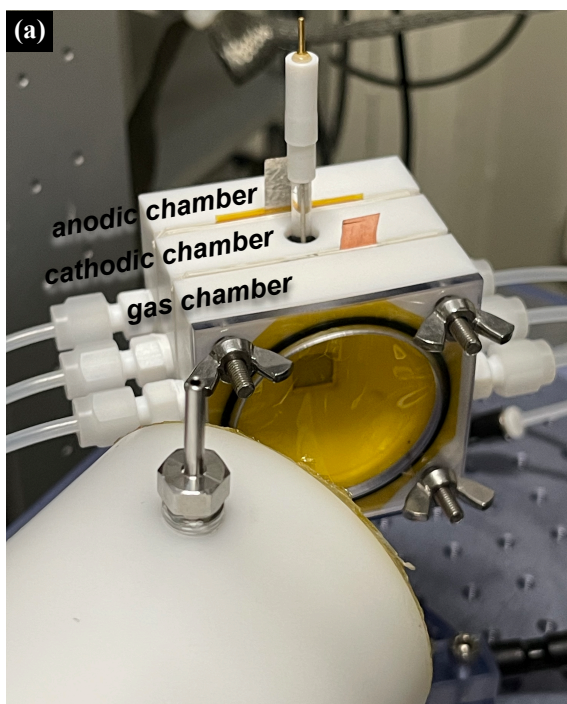


Figure S1. Comparison of the flow cell for (a) the *operando* X-ray absorption spectroscopy and (b) the typical electrochemical measurement.

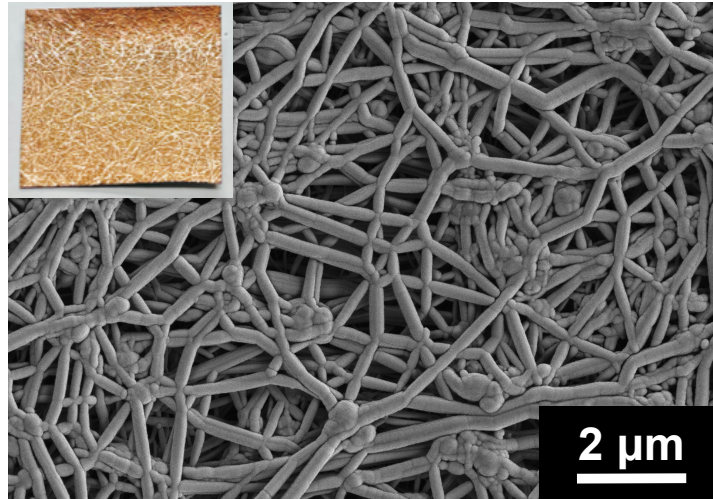


Figure S2. Microstructure of a sputtered Cu on the PTFE substrate. The inset figure shows the digital photograph of the gas diffusion electrode.

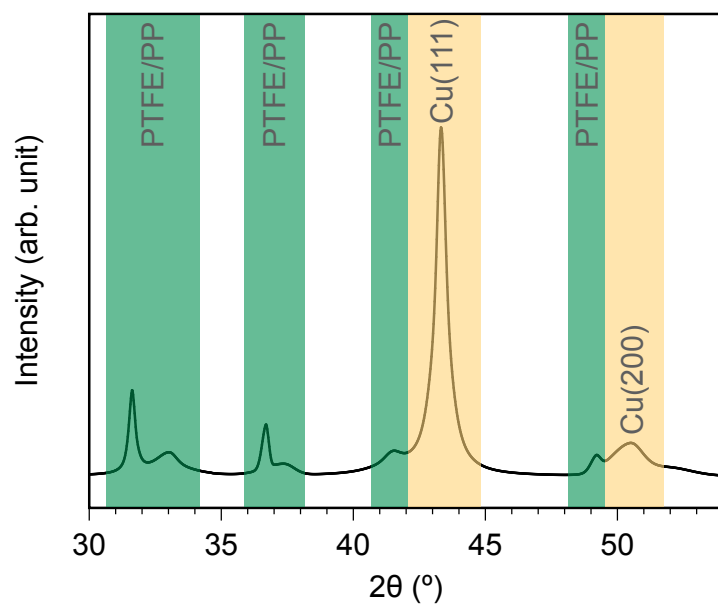


Figure S3. XRD pattern of a sputtered Cu on the PTFE substrate.

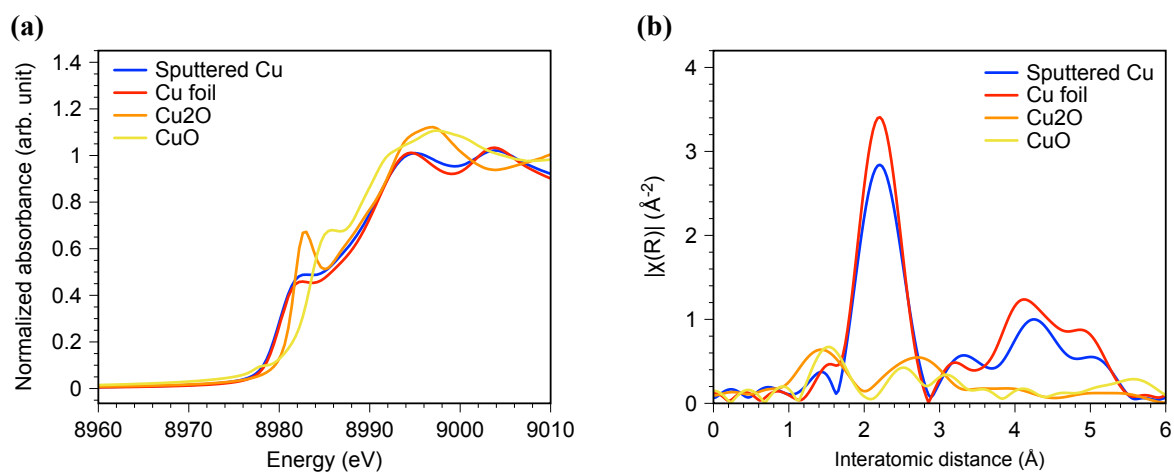


Figure S4. (a) Cu K-edge XANES spectra of a sputtered Cu on the PTFE substrate. The standard of Cu foil, Cu₂O, and CuO showed the edge position of Cu⁰, Cu⁺, and Cu²⁺. (b) Cu K-edge EXAFS spectra of a sputtered Cu on the PTFE substrate.

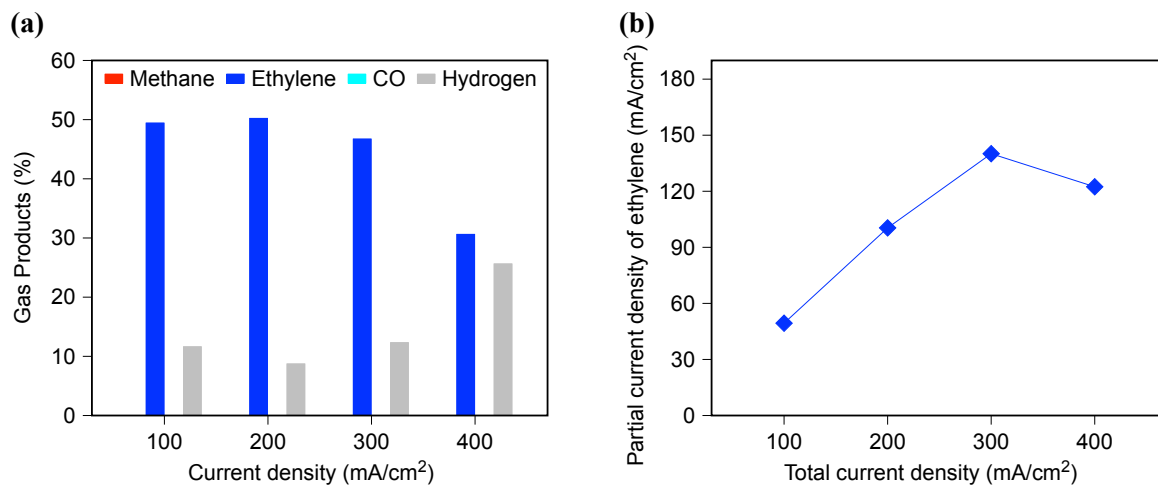


Figure S5. (a) Faradaic efficiency and (b) partial current to ethylene of a sputtered Cu on the PTFE substrate at various currents for CO₂RR.

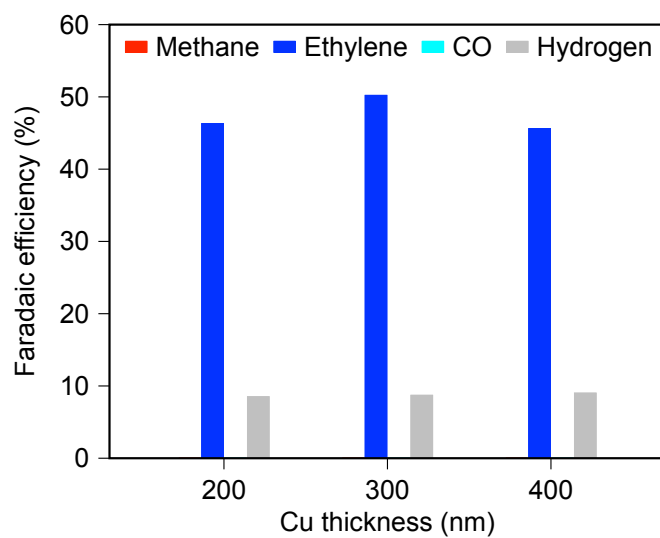


Figure S6. (a) Faradaic efficiency and (b) partial current to ethylene of the sputtered Cu on the PTFE substrate with different thicknesses for CO₂RR. It shows that the optimized thickness of the sputter Cu is 300 nm for ethylene production.

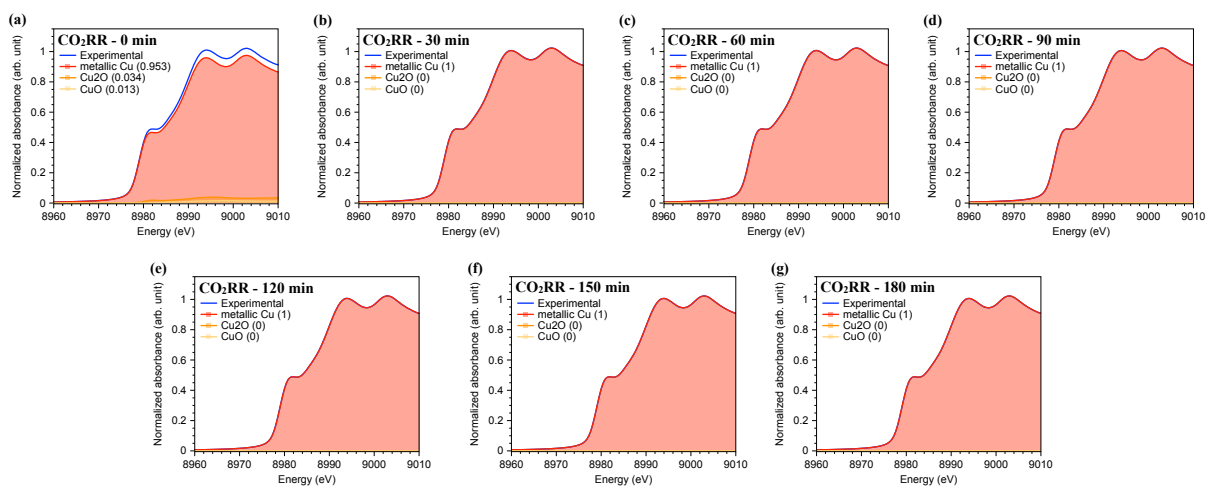


Figure S7. Linear combination fitting of the operando spectra for a sputtered Cu on the PTFE substrate at (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, and (g) 180 min during CO₂RR.

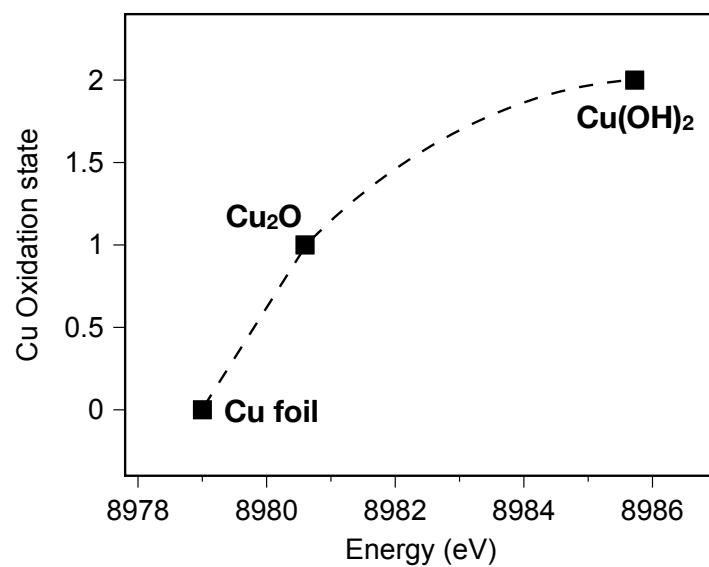


Figure S8. Correlation between the Cu oxidation state and the energy position of standard samples (Cu foil, Cu₂O, and Cu(OH)₂) obtained by zero point of the second derivatives of the XANES spectra.

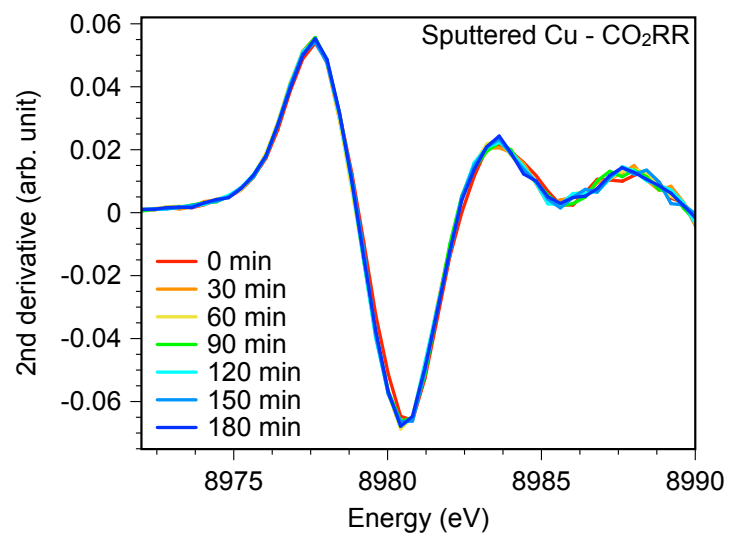


Figure S9. Second derivatives of the operando XANES spectra for the sputtered Cu during CO₂RR.

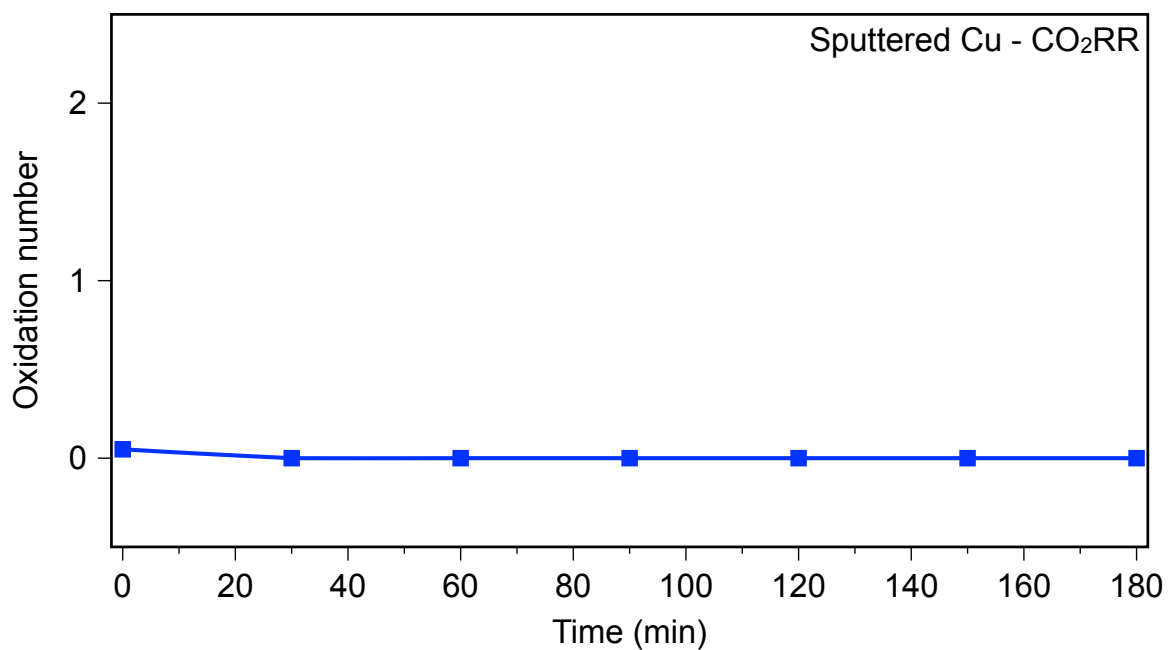


Figure S10. Investigation of Cu oxidation state for the sputtered Cu during CO₂RR. Initially, the oxidation number of the sputtered Cu was nearly zero. During the reaction, the sputtered Cu stayed in the pure metallic state.

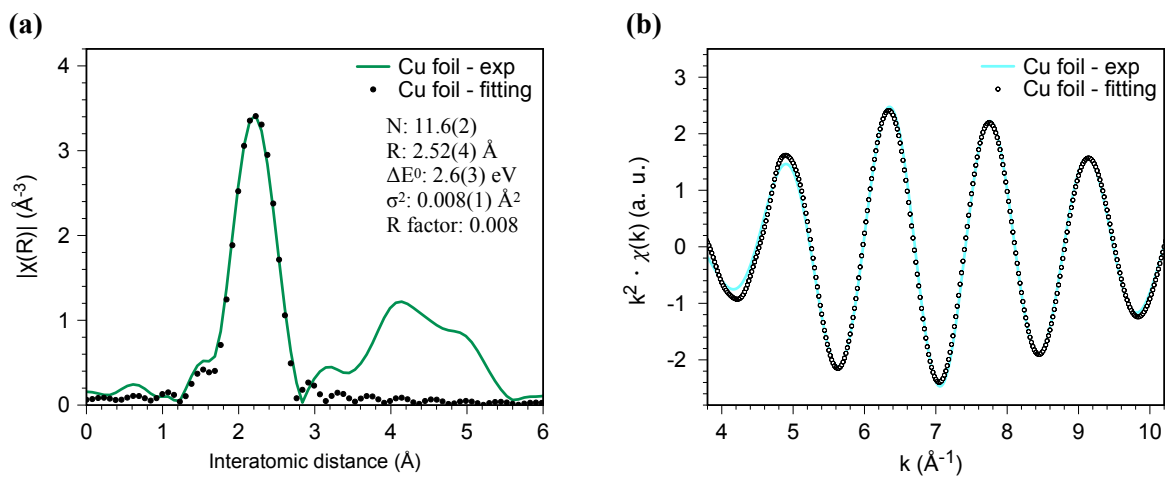


Figure S11. EXAFS fitting results of a metallic Cu foil in R and k space. The coordination number of the Cu foil is close to 12, which is the ideal coordination number for the metallic Cu.

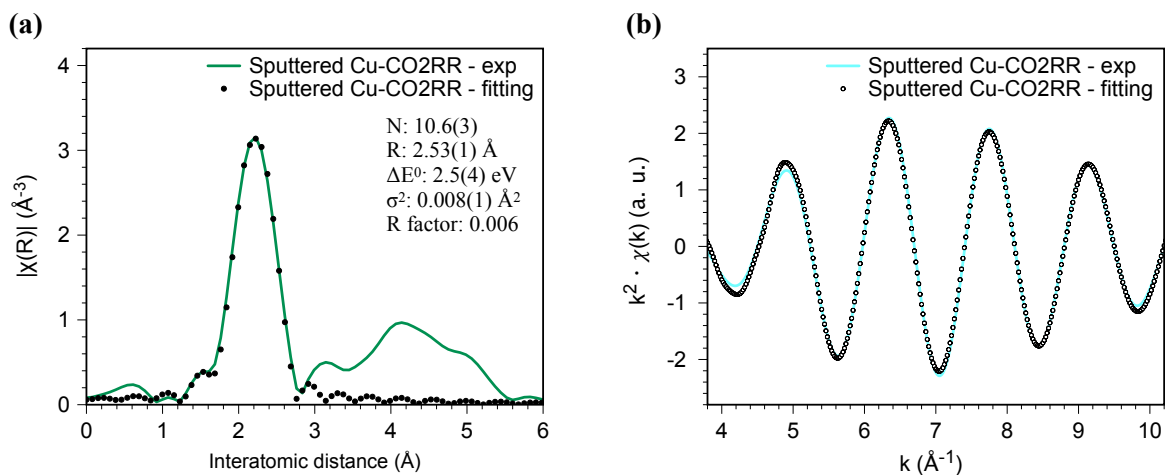


Figure S12. EXAFS fitting results of the sputtered Cu at the continuous operation of 180 minutes in R and k space. The coordination number of the sputtered Cu is lower than the Cu foil. It indicates that the grain size of the sputtered Cu is still smaller than the Cu foil.

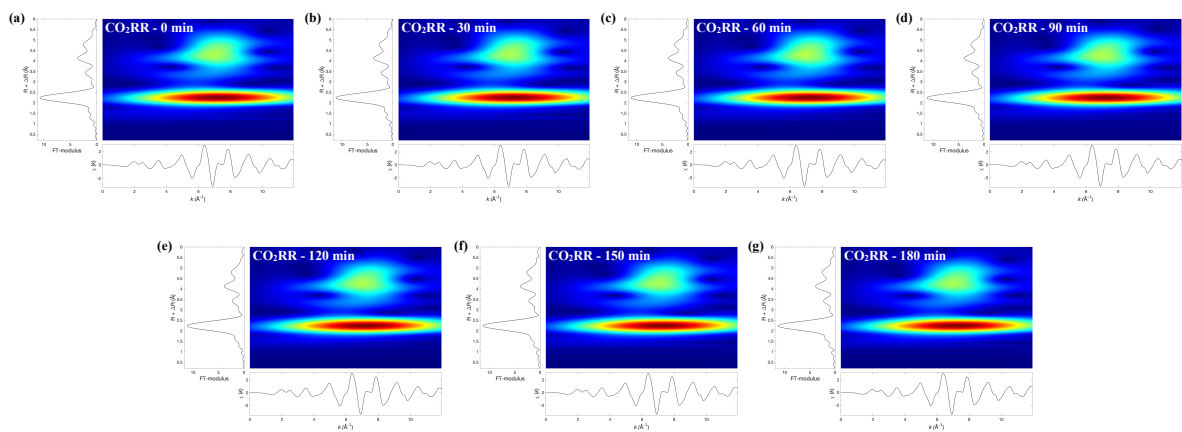


Figure S13. Wavelet analysis of the operando spectra for a sputtered Cu on the PTFE substrate at (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, and (g) 180 min during CO₂RR.

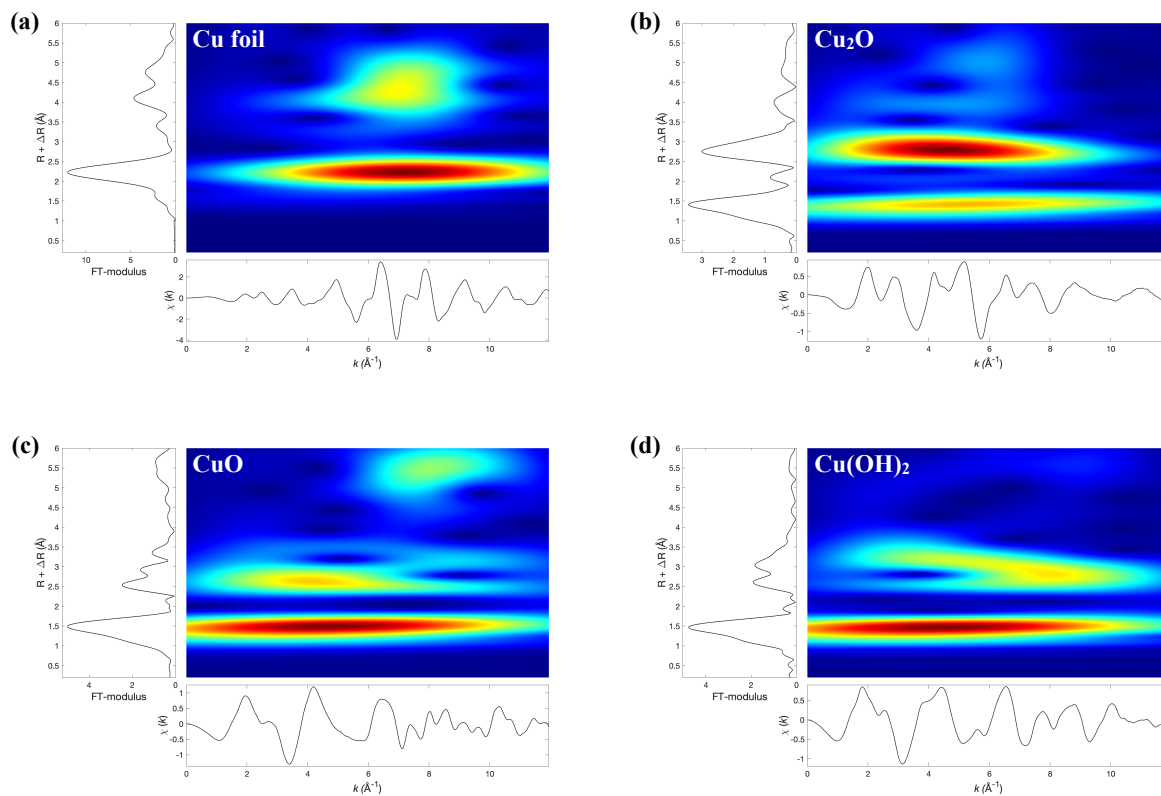


Figure S14. Wavelet analysis of standard samples (Cu foil, Cu_2O , and $\text{Cu}(\text{OH})_2$).

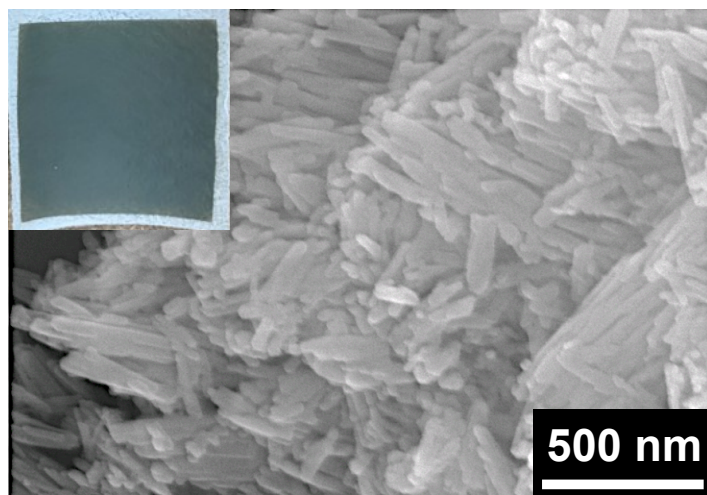


Figure S15. Microstructure of the synthesized Cu(OH)₂. The inset figure shows the digital photograph of the gas diffusion electrode.

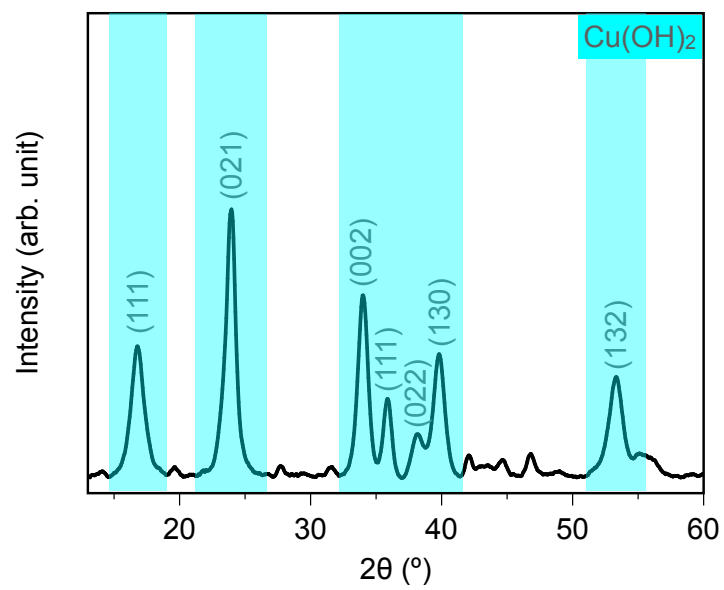


Figure S16. XRD pattern of the synthesized $\text{Cu}(\text{OH})_2$.

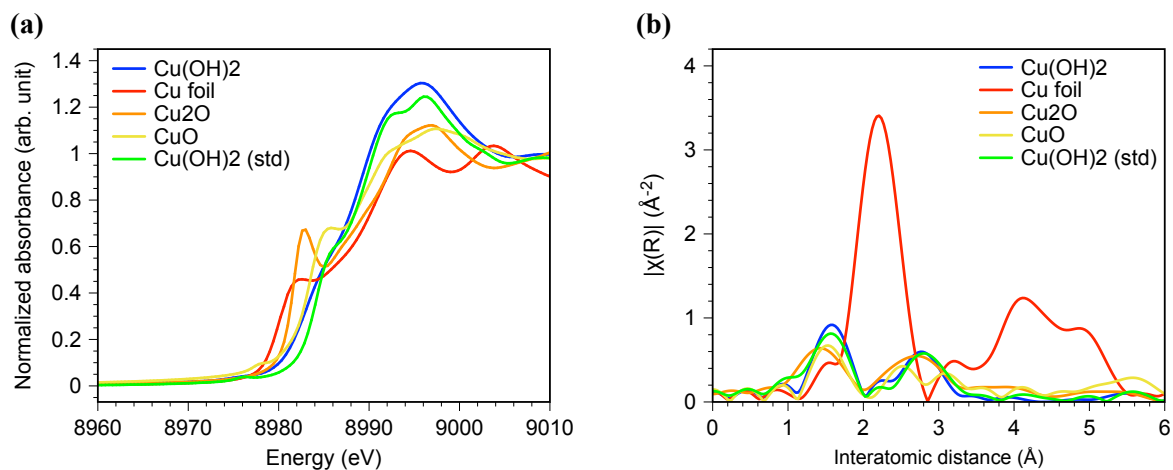


Figure S17. (a) Cu K-edge XANES spectra of the sprayed Cu(OH)₂ on the PTFE substrate. The standard of Cu foil, Cu₂O, and CuO showed the edge position of Cu⁰, Cu⁺, and Cu²⁺. (b) Cu K-edge EXAFS spectra of a sputtered Cu on the PTFE substrate.

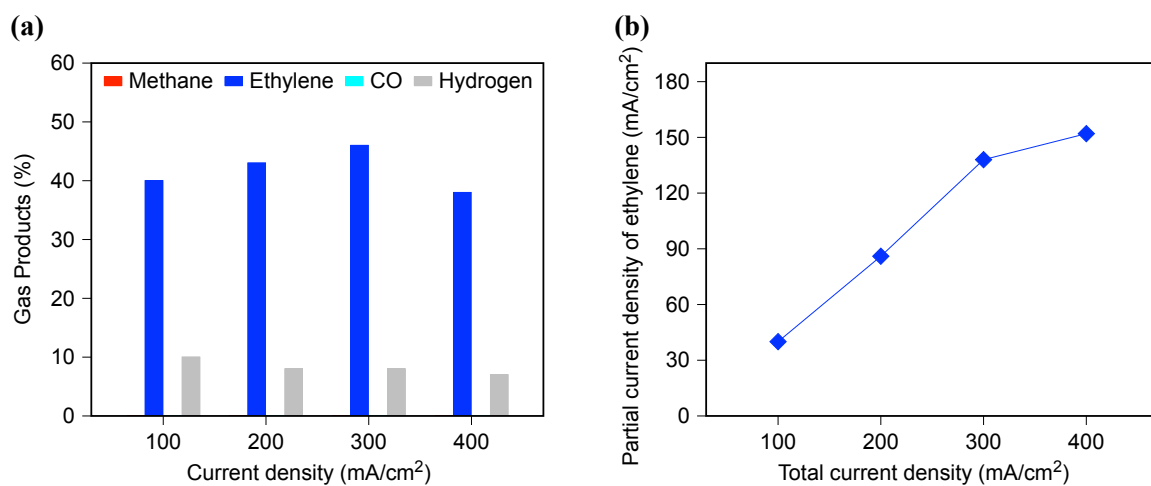


Figure S18. (a) Faradaic efficiency and (b) partial current to ethylene of the sprayed $\text{Cu}(\text{OH})_2$ on the PTFE substrate at various currents for CO_2RR .

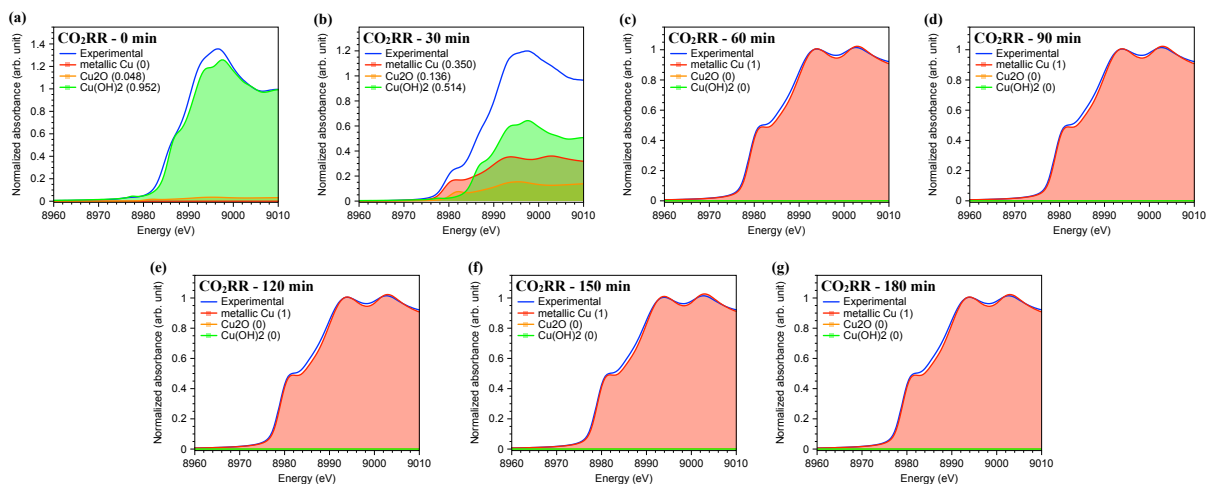


Figure S19. Linear combination fitting of the operando spectra for the sprayed Cu(OH)_2 on the PTFE substrate at (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, and (g) 180 min during CO_2RR .

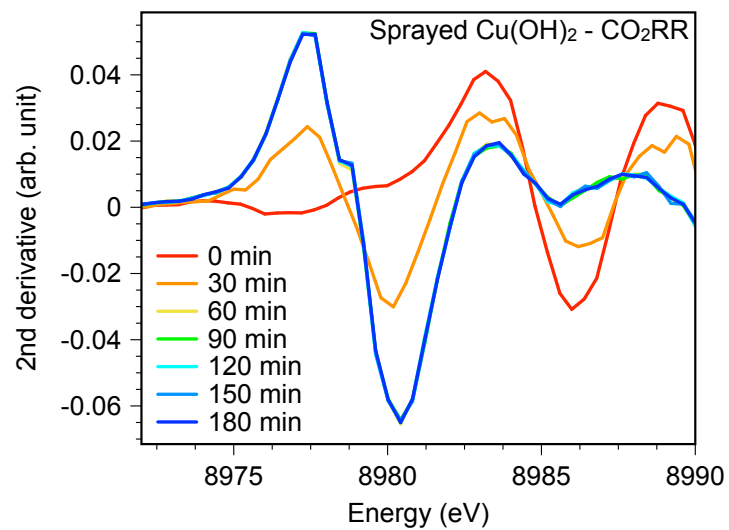


Figure S20. Second derivatives of the operando XANES spectra for the sprayed Cu(OH)₂ during CO₂RR.

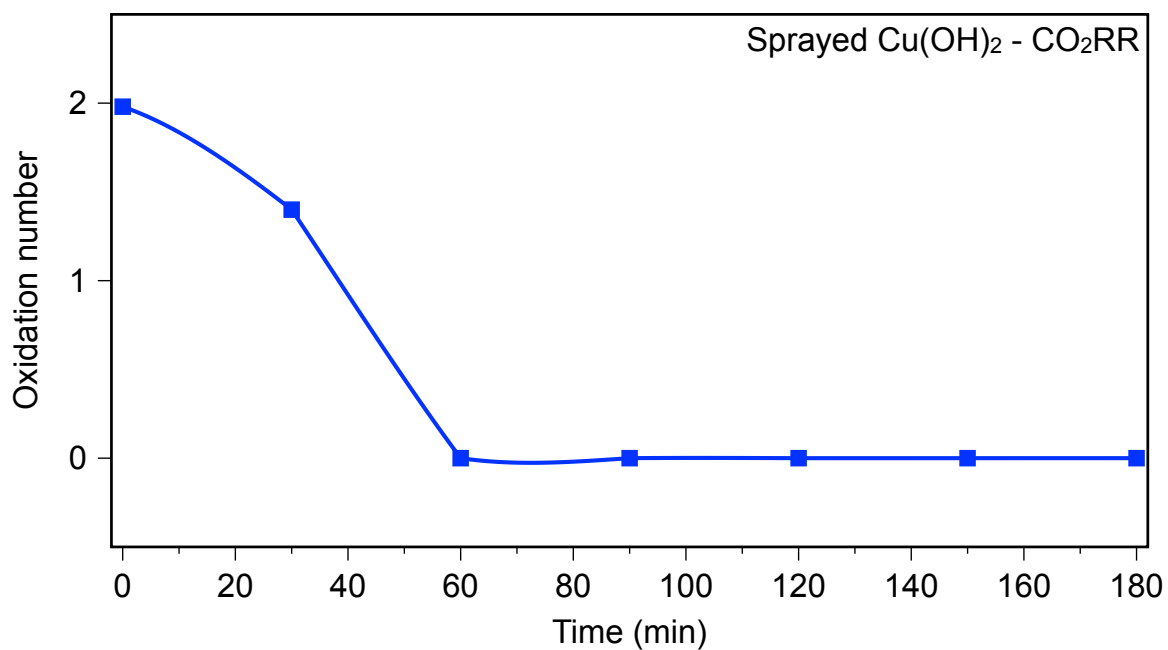


Figure S21. Investigation of Cu oxidation state for the sprayed Cu(OH)₂ during CO₂RR. Initially, the oxidation number of the sprayed Cu(OH)₂ was nearly +2. After 30 min of continuous CO₂RR, the oxidation number decreased to +1.4, corresponding to the considerable amounts of Cu(OH)₂ and Cu₂O in the sample. Cu(OH)₂ converted into the pure metallic state, leading to the zero valence after one hour.

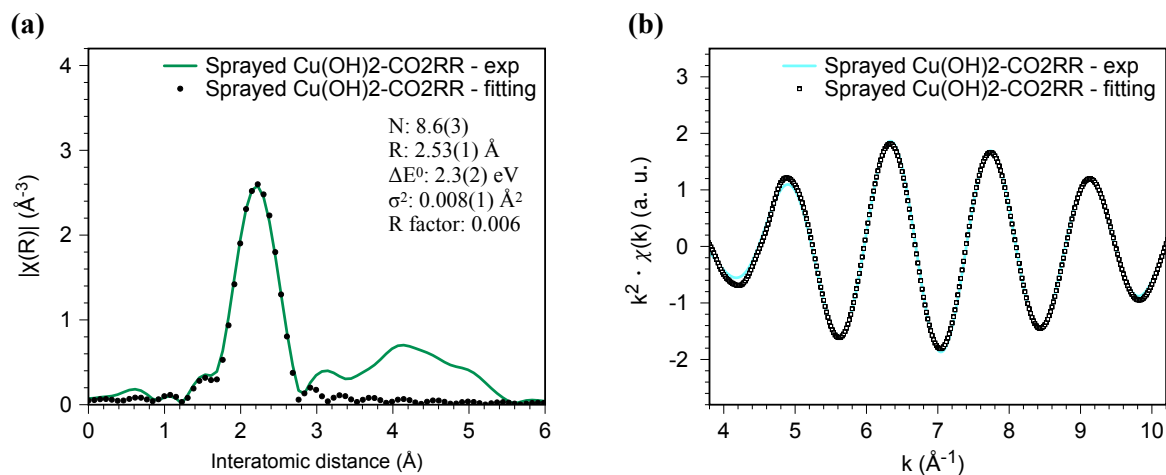


Figure S22. EXAFS fitting results of the sprayed $\text{Cu}(\text{OH})_2$ at the continuous operation of 180 minutes in R and k space. The coordination number of the sprayed $\text{Cu}(\text{OH})_2$ is significantly lower than the Cu foil and Sputtered Cu. It suggests that the aggregated size of $\text{Cu}(\text{OH})_2$ due to the electrochemical reduction was relatively small and did not become larger with the reaction time.

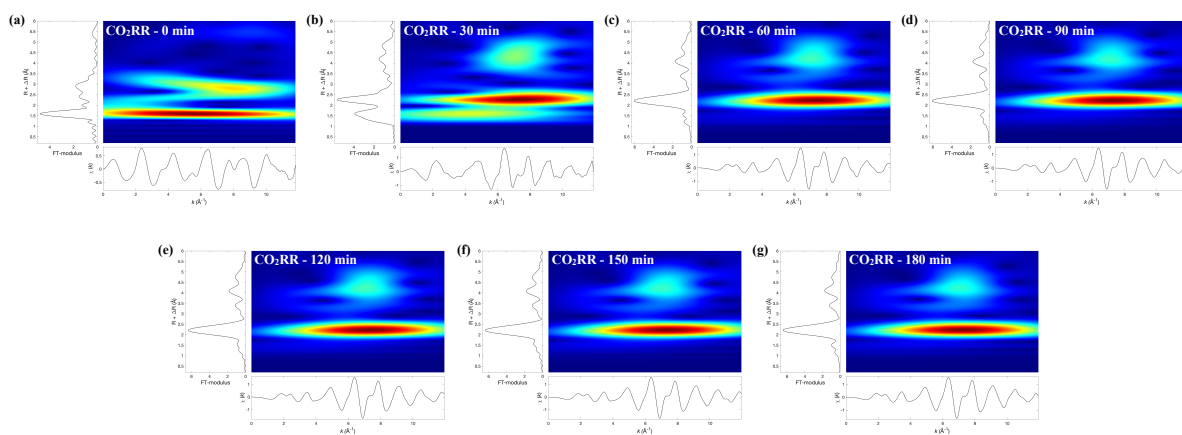


Figure S23. Wavelet analysis of the operando spectra for the sprayed $\text{Cu}(\text{OH})_2$ on the PTFE substrate at (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, and (g) 180 min during CO_2RR . The initial state matches the standard sample $\text{Cu}(\text{OH})_2$, shown in Figure S14. After 30 min of continuous CO_2RR , the signal mainly comes from $\text{Cu}(\text{OH})_2$ and metallic Cu, while the signal of Cu_2O is too faint to be observed. Metallic Cu dominates the wavelet signal after one hour.