

Supplementary Information for

**Ligand-tuning copper in coordination polymers for efficient electrochemical
C–C coupling**

Yang et al.

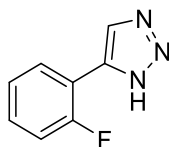
Characterisation of synthesised ligands Ln.

General data:

NMR spectra were recorded on a Bruker-400 MHz or Bruker-500 MHz spectrometer. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl_3 : $\delta\text{H} = 7.26$ ppm, $\delta\text{C} = 77.16$ ppm; $\text{DMSO}-d_6$: $\delta\text{H} = 2.50$ ppm, $\delta\text{C} = 39.52$ ppm).

Characterisation data of ligands Ln:

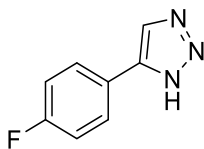
Ligand L1: 5-(2-fluorophenyl)-1H-1,2,3-triazole (oF-PhTA)



$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 8.22 (d, $J = 3.8$ Hz, 1H), 8.04 (t, $J = 7.7$ Hz, 1H), 7.45–7.27 (m, 3H).

$^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$) δ 160.1, 157.7, 139.4, 130.0, 129.9, 128.1, 128.0, 125.0, 125.0, 118.3, 118.1, 116.3, 116.1.

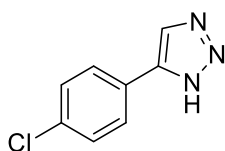
Ligand L3: 5-(4-fluorophenyl)-1H-1,2,3-triazole (pF-PhTA)



$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 11.7 (br s, 1H), 7.93 (s, 1H), 7.82–7.79 (m, 2H), 7.17–7.13 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.2, 161.8, 147.0, 128.1, 128.0, 126.3, 126.2, 116.3, 116.1.

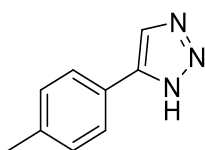
Ligand L4: 5-(4-chlorophenyl)-1H-1,2,3-triazole (pCl-PhTA)



¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.95 (s, 0H), 7.81–7.74 (m, 1H), 7.43 (d, J = 8.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 162.8, 134.5, 129.2, 129.1, 128.9, 127.4, 36.6, 31.6.

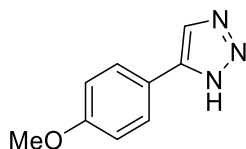
Ligand L5: 5-(*p*-tolyl)-1H-1,2,3-triazole (*p*Me-PhTA)



¹H NMR (400 MHz, DMSO-*d*₆) δ 8.28 (s, 1H), 7.75 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 2.32 (s, 3H).

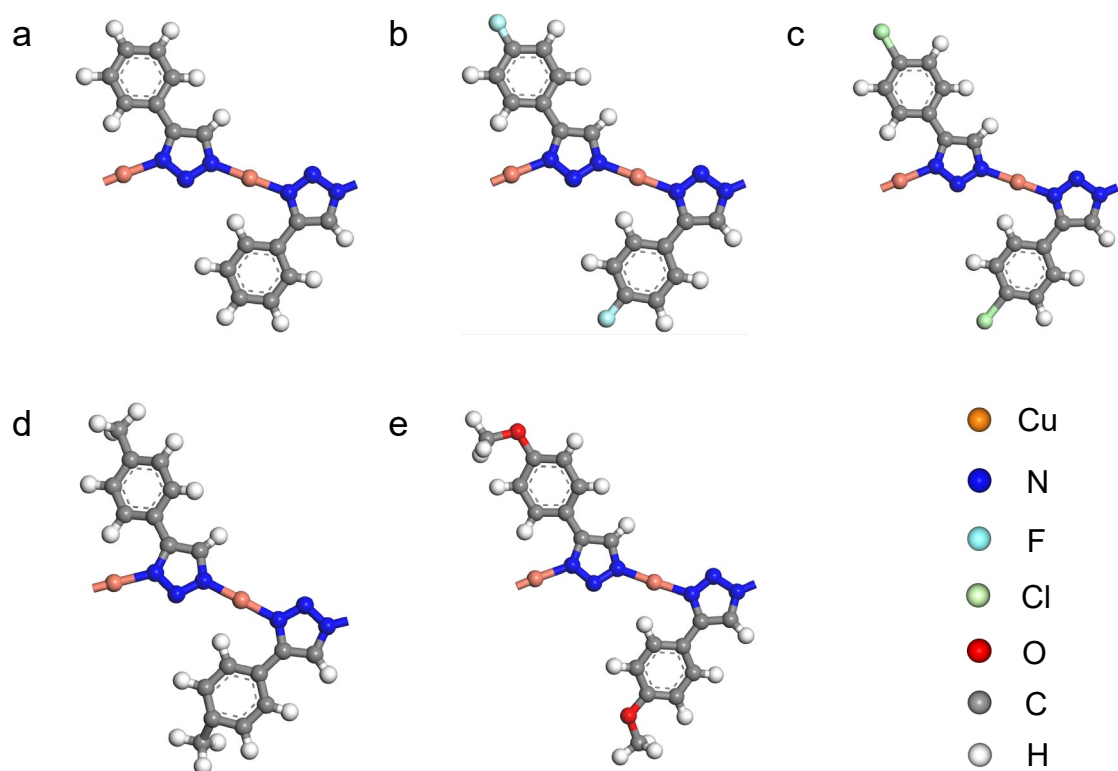
¹³C NMR (101 MHz, DMSO-*d*₆) δ 137.5, 129.5, 129.3, 127.5, 127.2, 125.5, 20.9.

Ligand L6: 5-(4-methoxyphenyl)-1H-1,2,3-triazole (*p*MeO-PhTA)

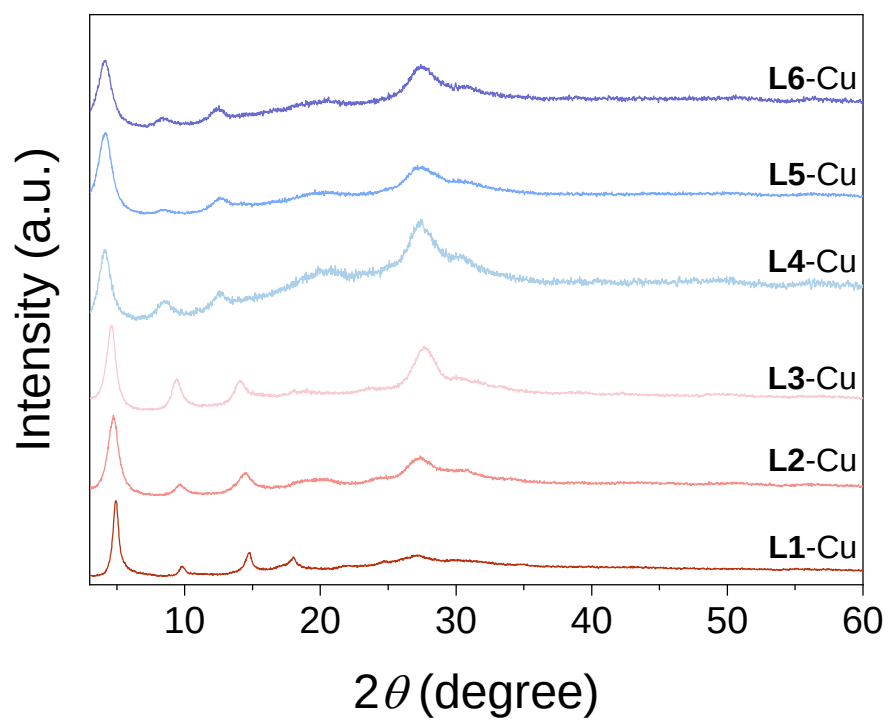


¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.74 (d, 2H, J = 8.8 Hz), 6.98 (d, 2H, J = 8.8 Hz), 3.86 (s, 3H).

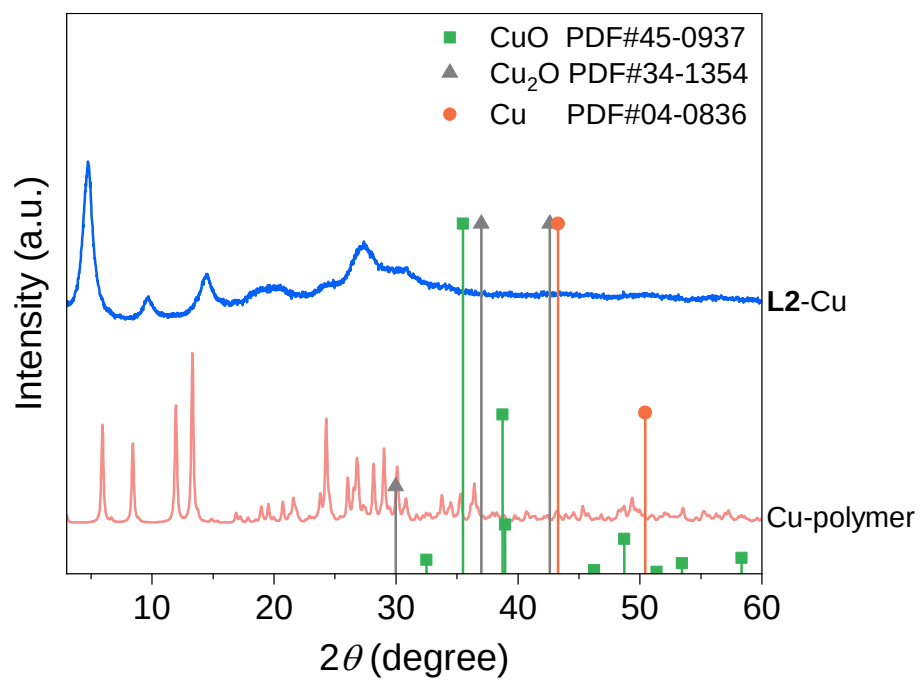
¹³C NMR (100 MHz, CDCl₃) δ 160.3, 147.2, 127.6, 122.6, 114.6, 55.



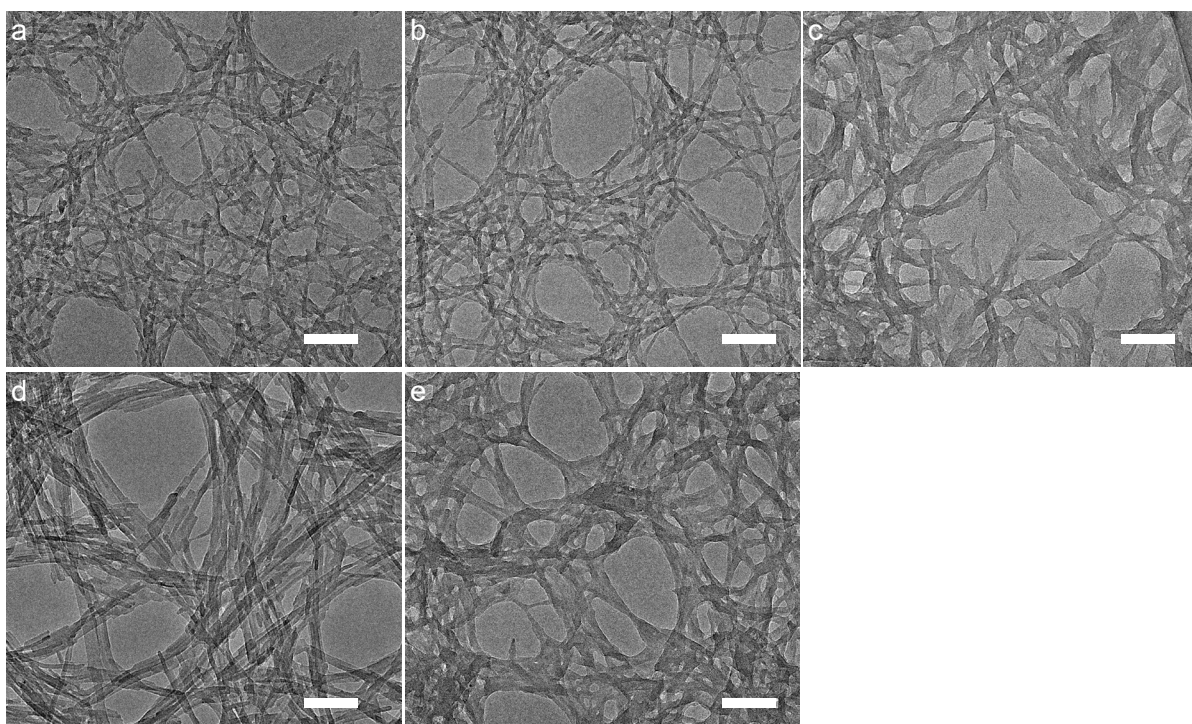
Supplementary Fig. 1 | Cu–N coordination models used for calculating Bader charge of Cu.
a, L2. b, L3. c, L4. d, L5. e, L6. The orange, blue, grey, cyan (in L3), green (in L4), and white balls represent Cu, N, C, F, Cl, and H, respectively.



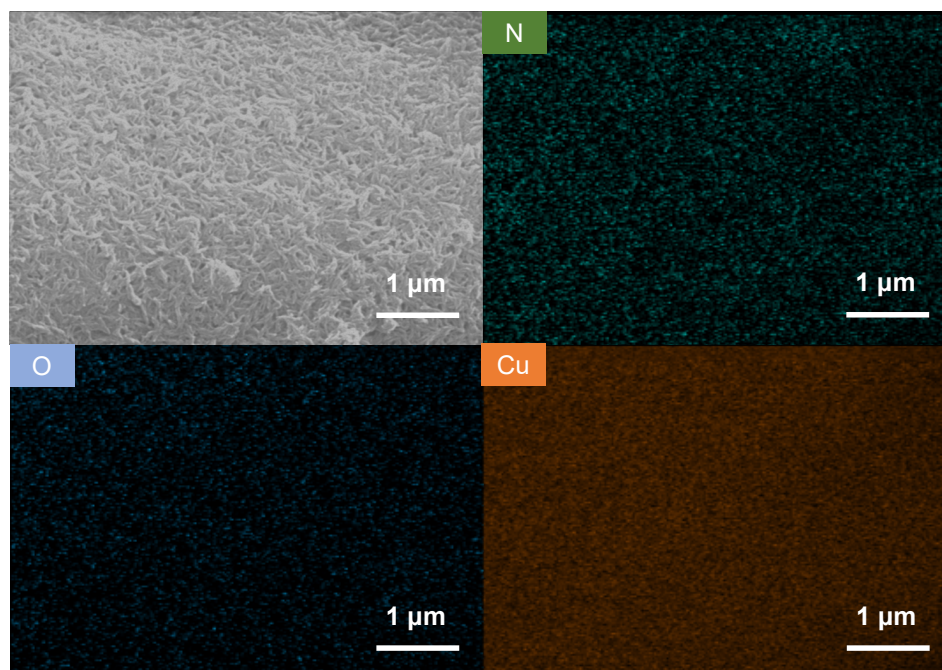
Supplementary Fig. 2 | XRD patterns of Ln-Cu.



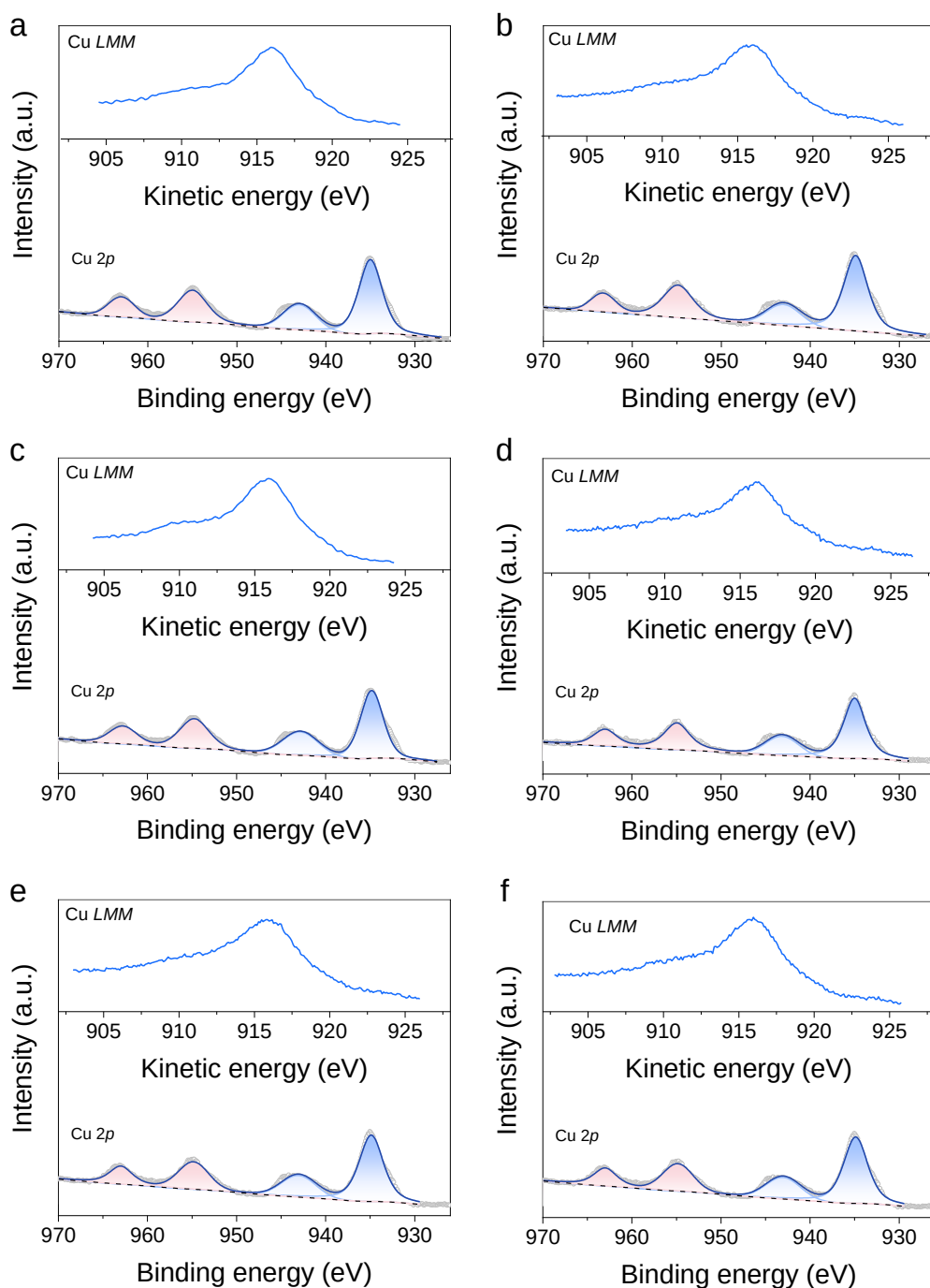
Supplementary Fig. 3 | XRD patterns of L2-Cu. The XRD patterns of Cu, Cu₂O, CuO and Cu-polymer¹ were used as references.



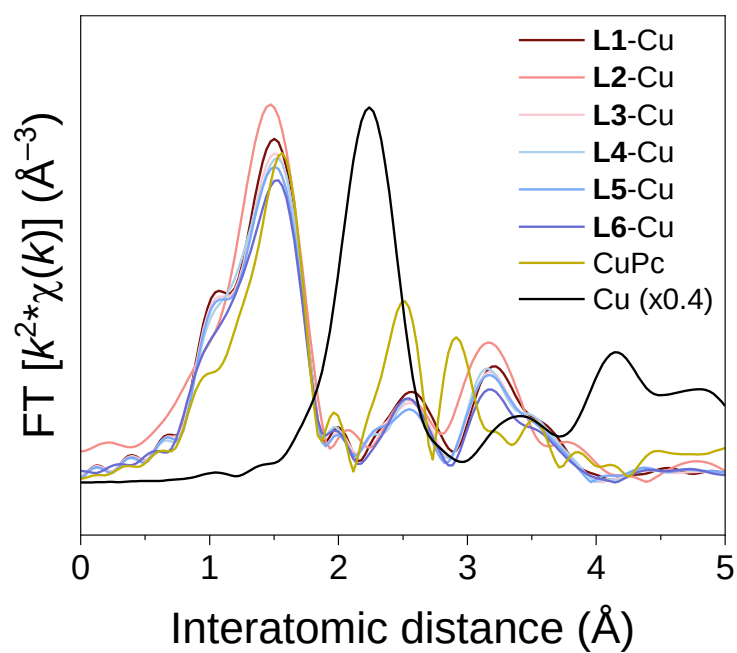
Supplementary Fig. 4 | TEM images. a, L1-Cu. b, L3-Cu. c, L4-Cu. d, L5-Cu. e, L6-Cu. Scale bar = 100 nm.



Supplementary Fig. 5 | Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS) mapping of synthesised L2-Cu, showing the uniform dispersion of Cu, N, and O in the catalyst. L2-Cu was spray-coated on the carbon paper.

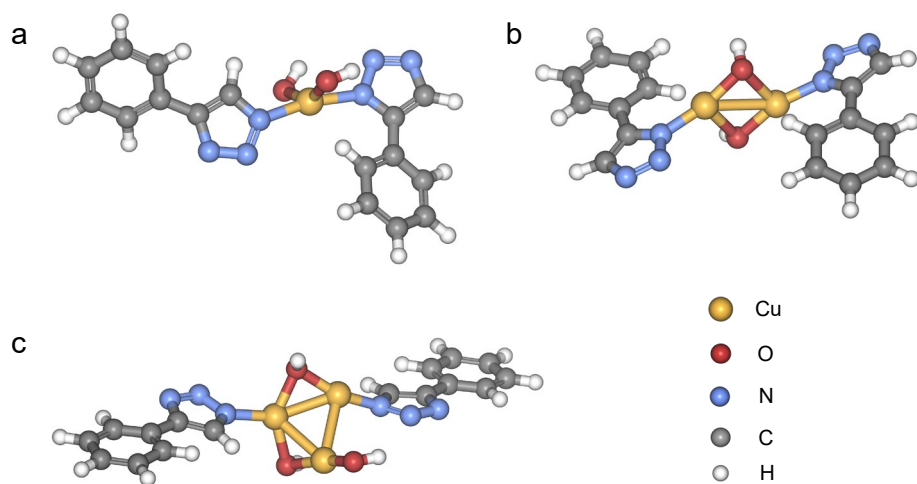


Supplementary Fig. 6 | Cu 2p XPS (bottom) and Auger Cu LMM (up) spectra of Ln-Cu. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. For XPS spectra, the peaks at about 935 eV filled in blue indicate Cu 2p_{3/2} and the peaks at about 955 eV filled in pink indicate Cu 2p_{1/2}. The peaks of ~916 eV showed a Cu oxidation state of +2.

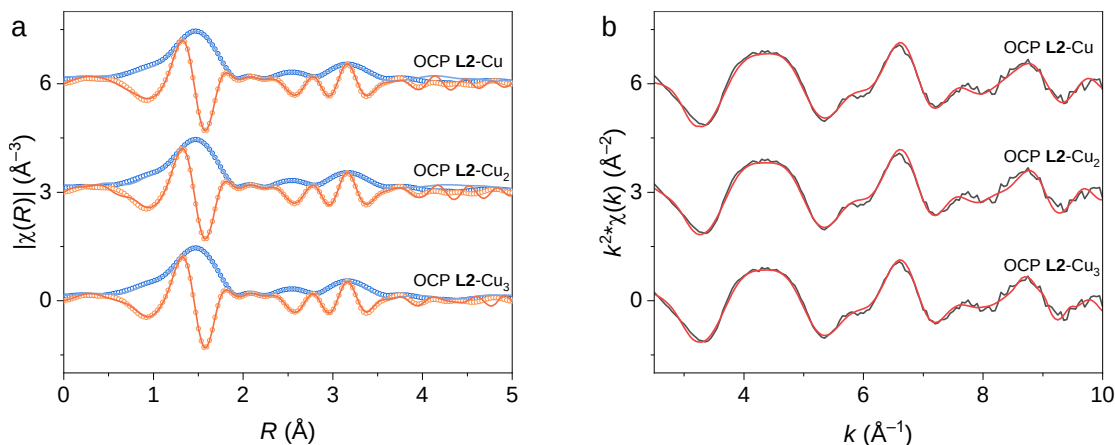


Supplementary Fig. 7 | The Fourier-transform EXAFS spectra for Ln-Cu at the Cu k-edge.

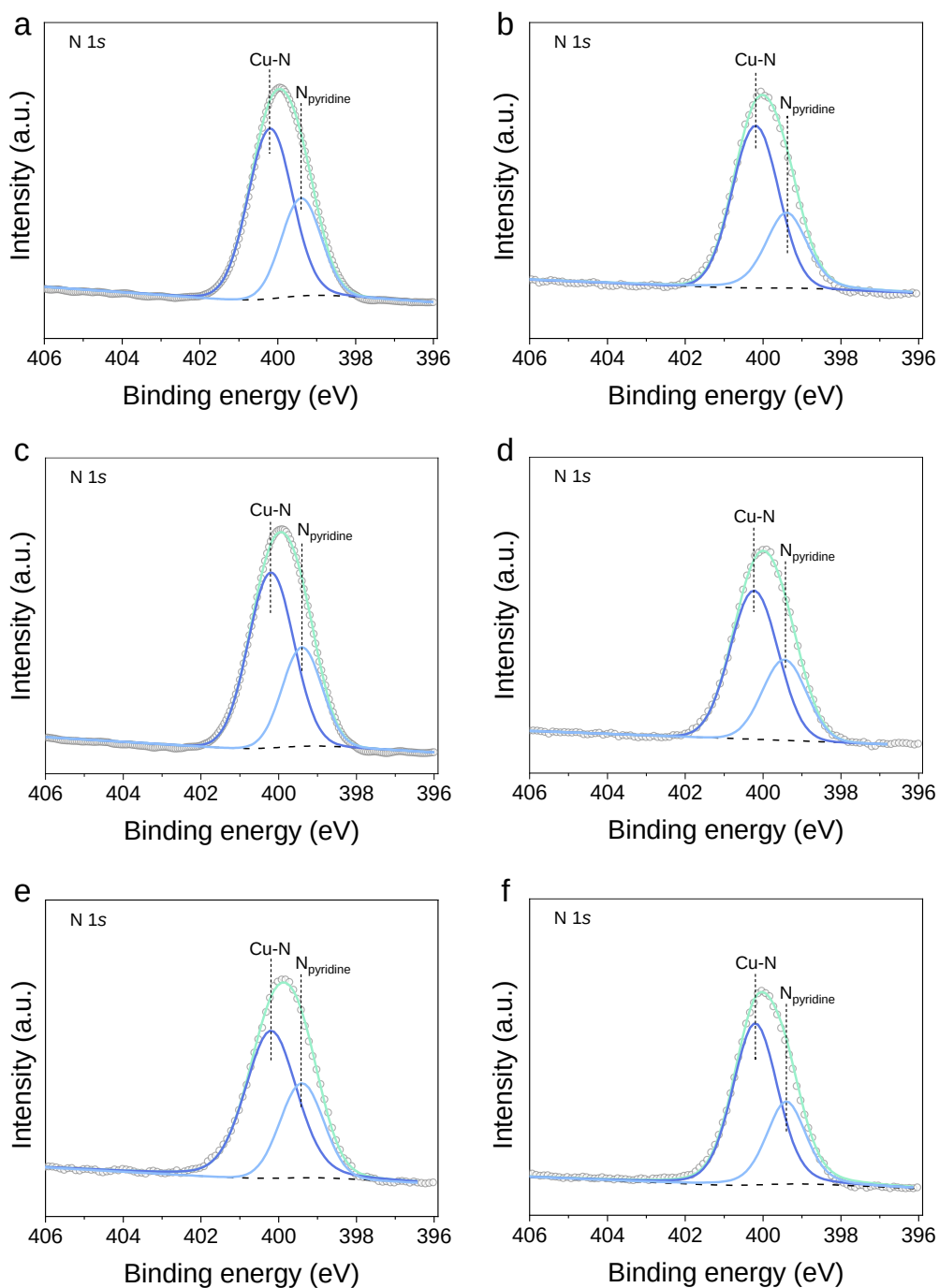
The FT-EXAFS spectra of Cu foil and CuPc were used as references.



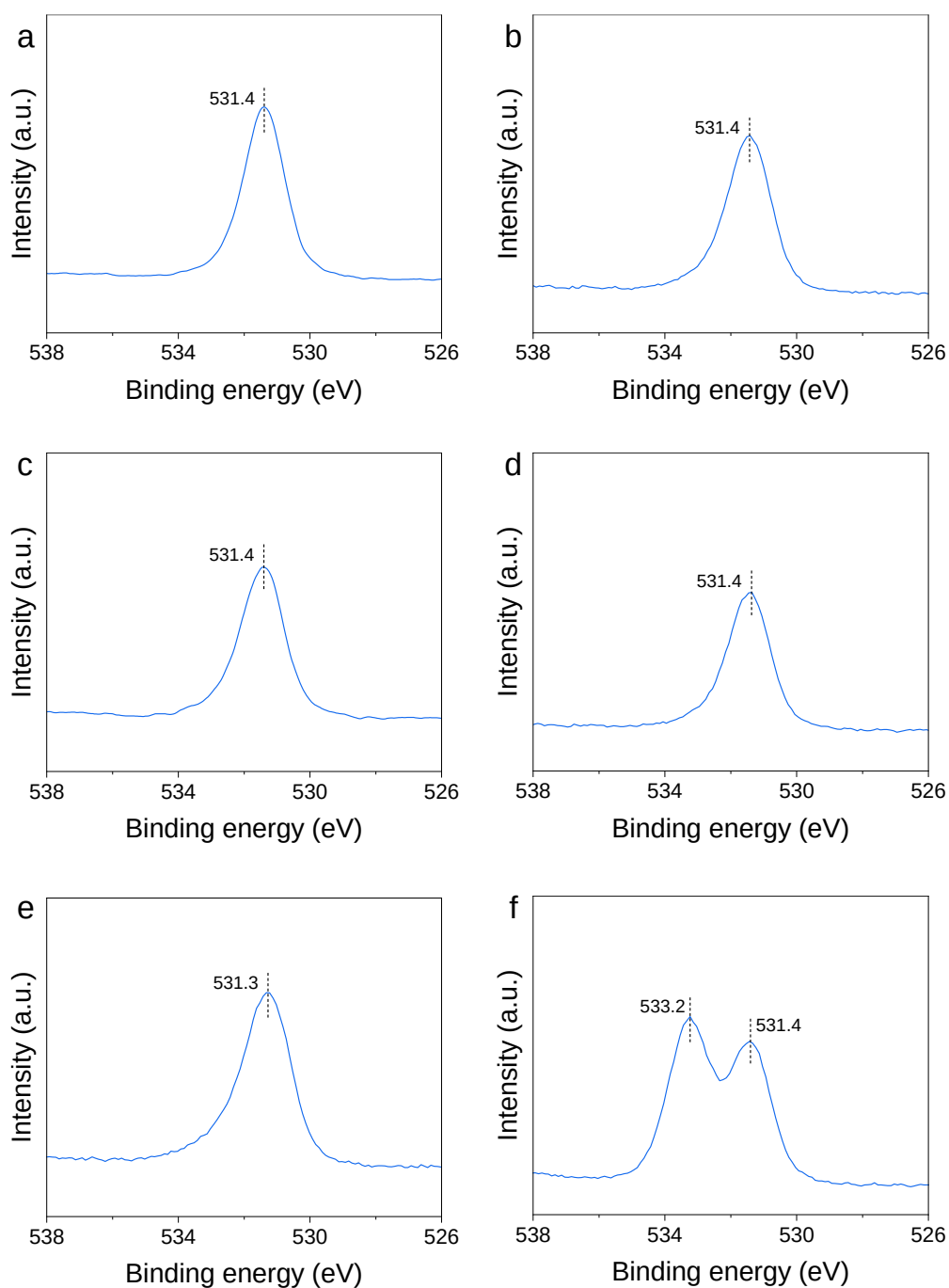
Supplementary Fig. 8 | L2-Cu (a), L2-Cu₂ (b), and L2-Cu₃ (c) models used for FT-EXAFS fitting. The orange, red, blue, grey, and white balls represent Cu, O, N, C, and H, respectively.



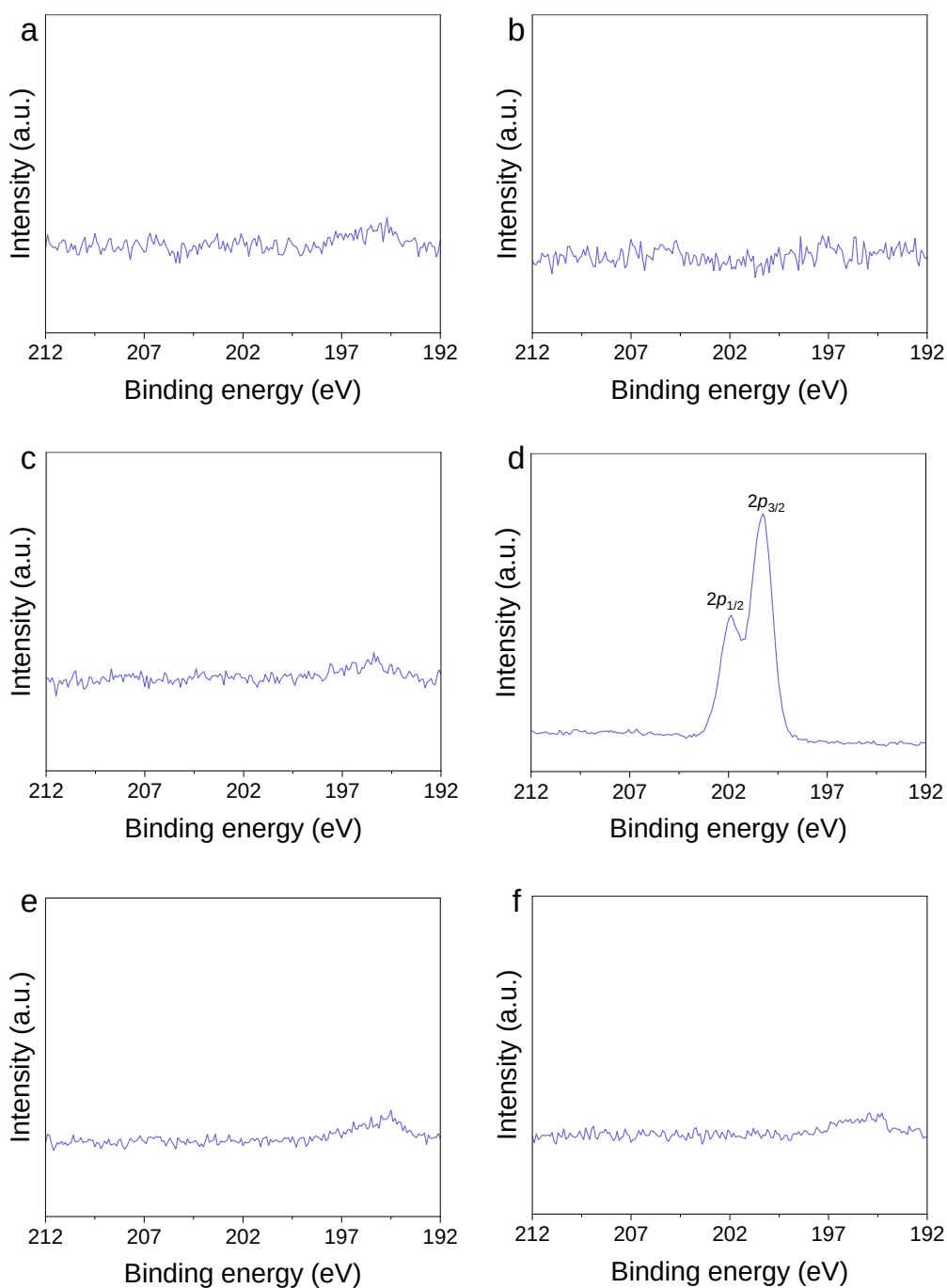
Supplementary Fig. 9 | The FT-EXAFS spectra fitting results for L2-Cu at OCP state with L2-Cu, L2-Cu₂, and L2-Cu₃ models. a, The Fourier-transform EXAFS spectra (magnitude and imaginary part) for L2-Cu at OCP state fitted with L2-Cu, L2-Cu₂, and L2-Cu₃ models at the Cu k -edge, showing the magnitude (experimental data: blue circles; fitting data: blue lines) and imaginary portions (experimental data: orange circles; fitting data: orange lines). The k -range of 2.5–10 $\text{\AA}^{-1}$ and the R -range of 0–4 $\text{\AA}$ were used for the fits. b, EXAFS spectra in k -space at the Cu k -edge. Experimental data: dark grey; fitting data: red. The fitting results showed that the Cu–Cu metal distances in L2-Cu, L2-Cu₂, and L2-Cu₃ are 3.11 $\text{\AA}$, 2.25 $\text{\AA}$, and 2.18 $\text{\AA}$, separately (Supplementary Tables 1–3). The standard Cu metal foil model indicates a Cu–Cu metal distance of 2.55 $\text{\AA}$, significantly greater than the distances in L2-Cu₂ or L2-Cu₃, suggesting an unreasonable fitting of L2-Cu catalyst using either L2-Cu₂ or L2-Cu₃ model. Besides, the fitting with L2-Cu model yielded the lowest R-factor of 0.64%, compared to 0.71% for L2-Cu₂ and 1.45% for L2-Cu₃, indicating that the L2-Cu single-site model showed the best fitting result.



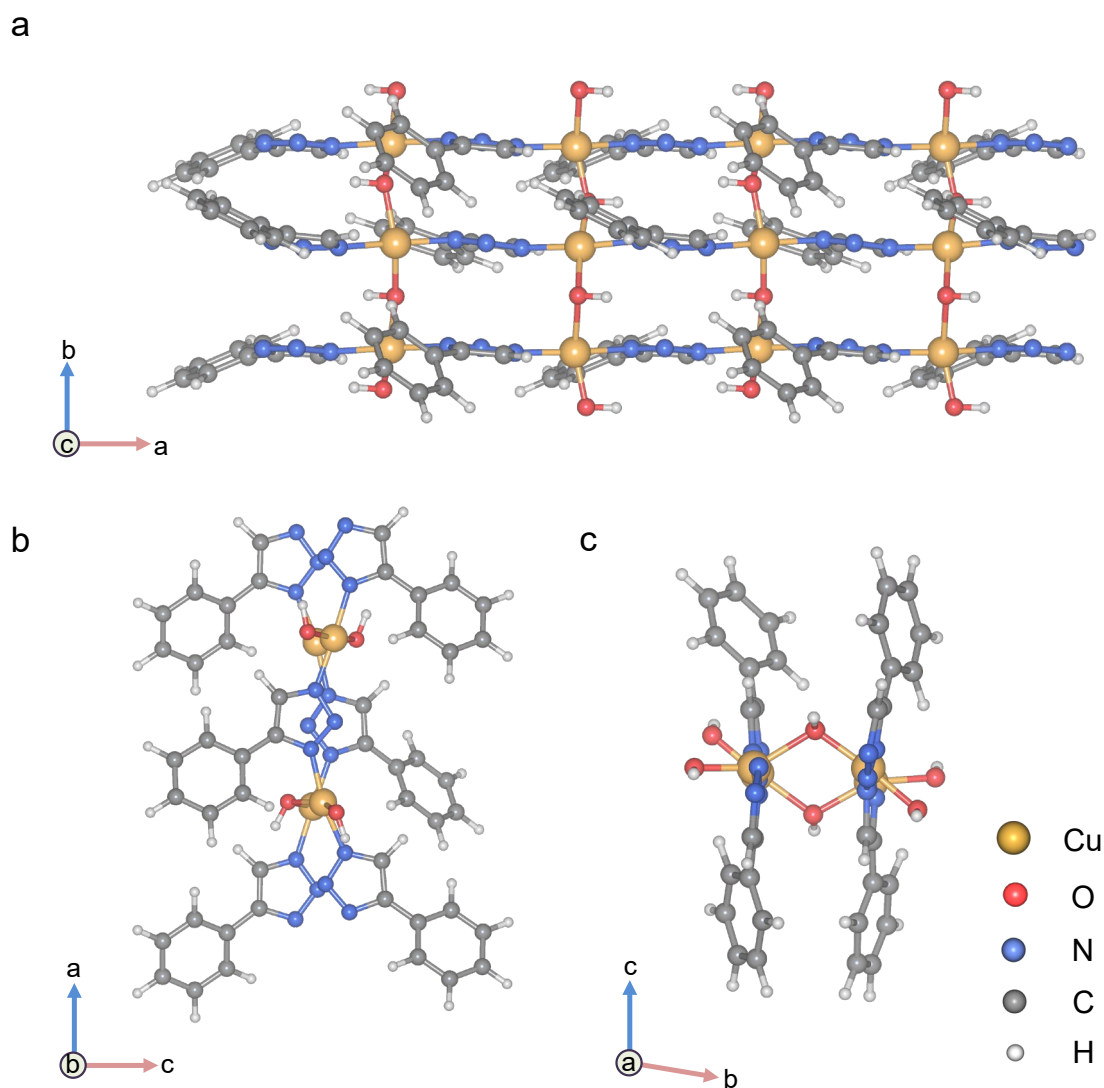
Supplementary Fig. 10 | N 1s XPS spectra of Ln-Cu. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. N 1s spectra have been deconvoluted into Cu–N at 400.2 eV and pyridinic N at 399.4 eV.²



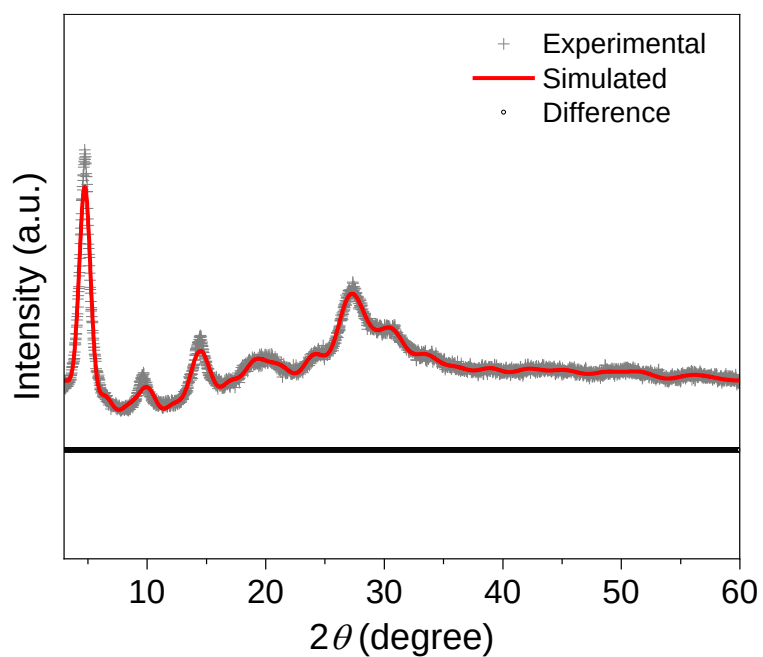
Supplementary Fig. 11 | O 1s XPS spectra of Ln-Cu. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The peaks at about 531.4 eV are related to the bridged –OH groups which are in the Cu–OH–Cu structure.³ The peak of 533.2 eV in **L6-Cu** indicates the –OCH₃ groups located at the ligand molecules.⁴



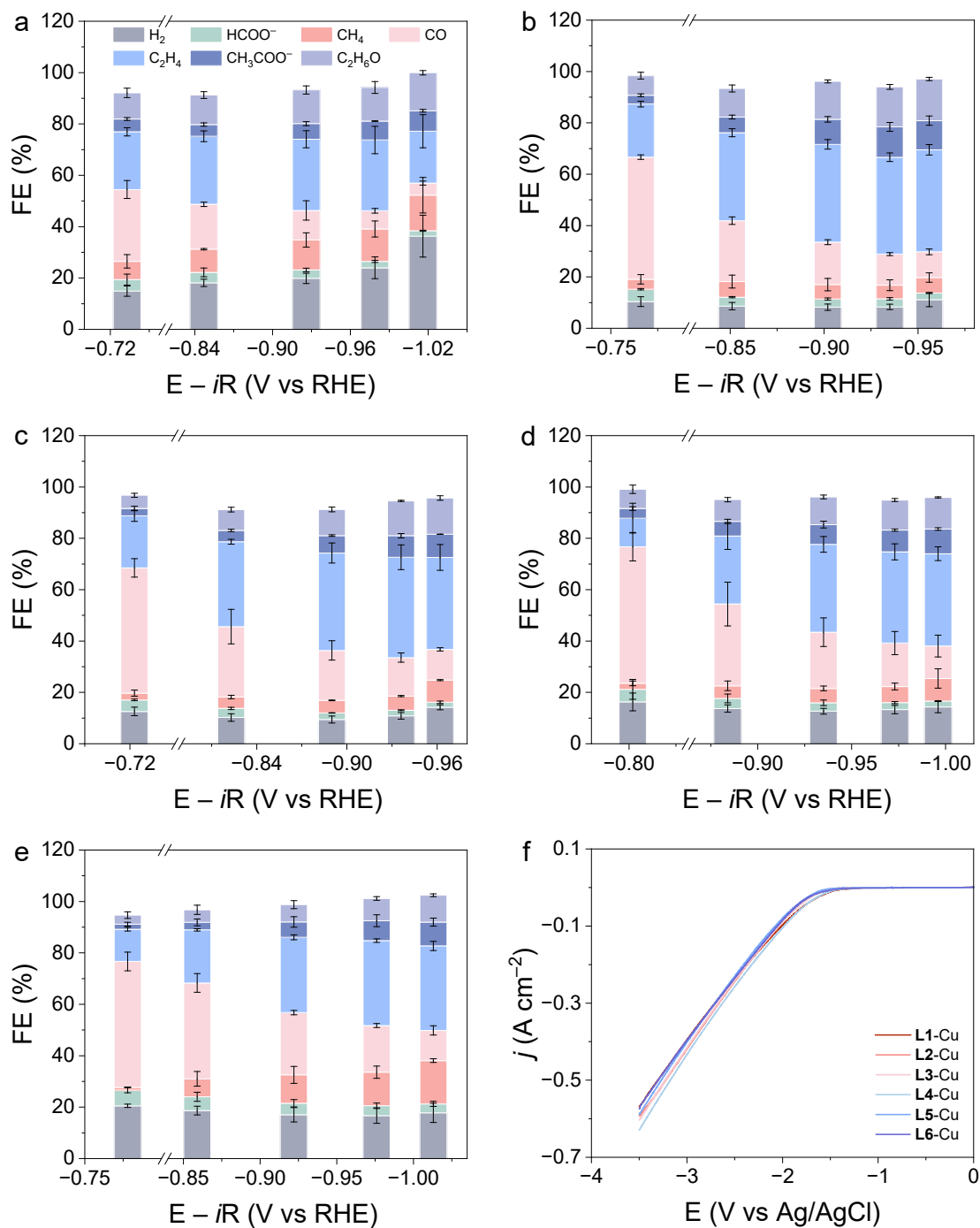
Supplementary Fig. 12 | Cl 2p XPS spectra of Ln-Cu. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. Except L4-Cu, there is no Cl existed in Ln-Cu catalysts. The Cl in L4-Cu comes from the L4 ligands.



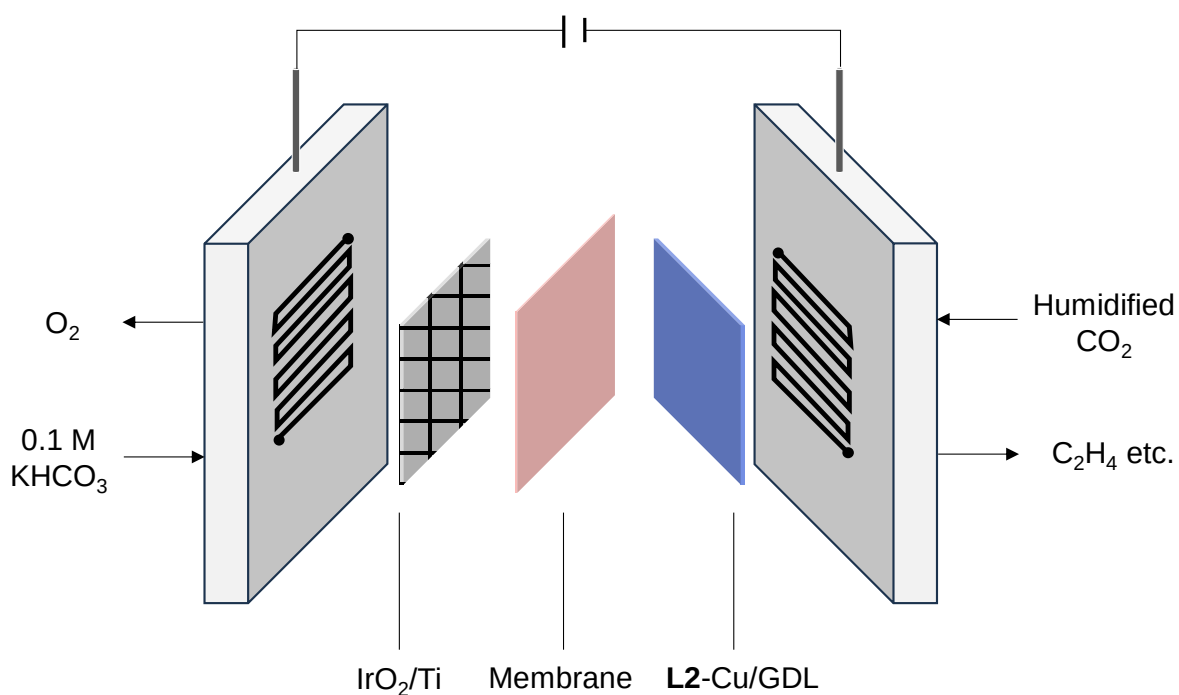
Supplementary Fig. 13 | Structure of the L2-Cu. Views from the c-axis (a), b-axis (b), and a-axis (c). The orange, red, blue, grey, and white balls represent Cu, O, N, C, and H, respectively.



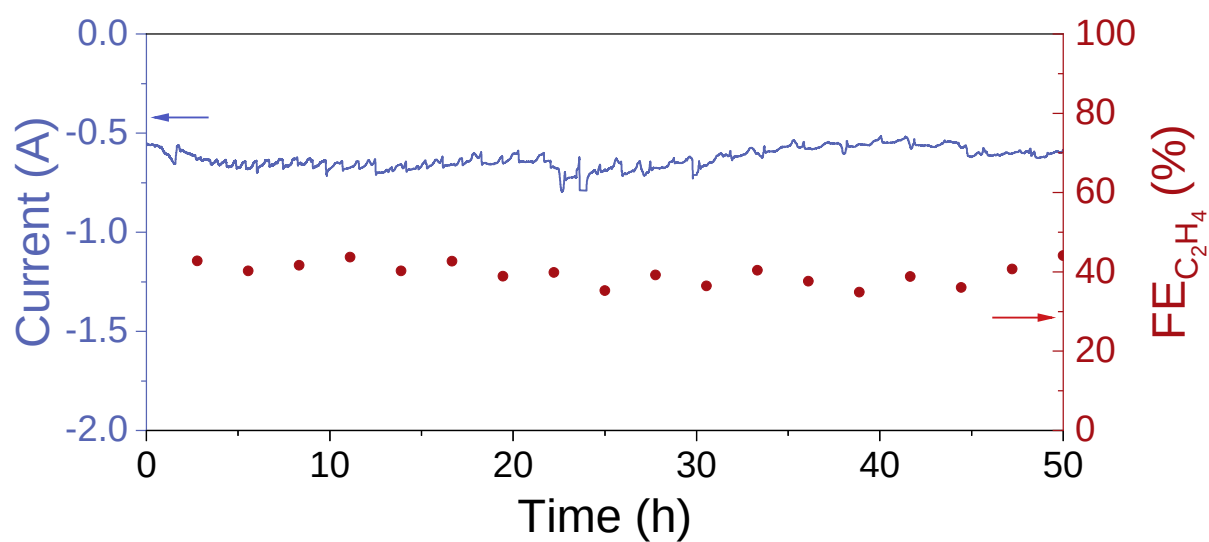
Supplementary Fig. 14 | Experimental (grey +) and simulated (red line) PXRD patterns of L2-Cu. The calculated refinement is based on the structure simulated by DFT calculations. The black circle indicates the differences between the experimental data and the refinement. The weighted-profile R factor $R_{wp} = 7.41\%$ and $\chi^2 = 2.06$.



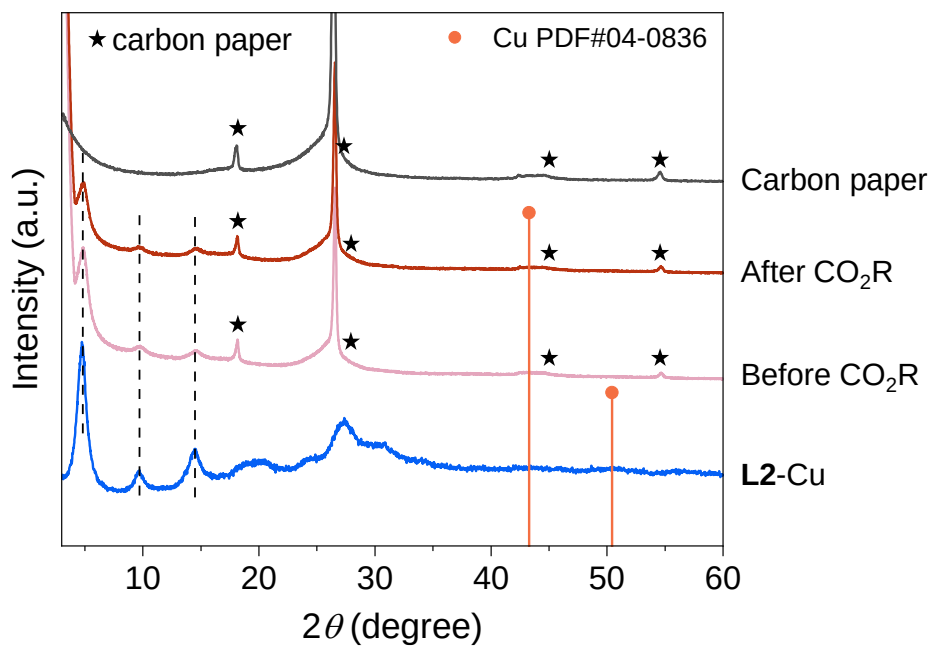
Supplementary Fig. 15 | CO₂RR performances of Ln-Cu in a flow cell. a, L1-Cu. b, L3-Cu. c, L4-Cu. d, L5-Cu. e, L6-Cu. f, non- iR corrected voltammograms for Ln-Cu catalysts The CO₂ flow rate was 20 sccm. 1 M KOH was used as the electrolyte.



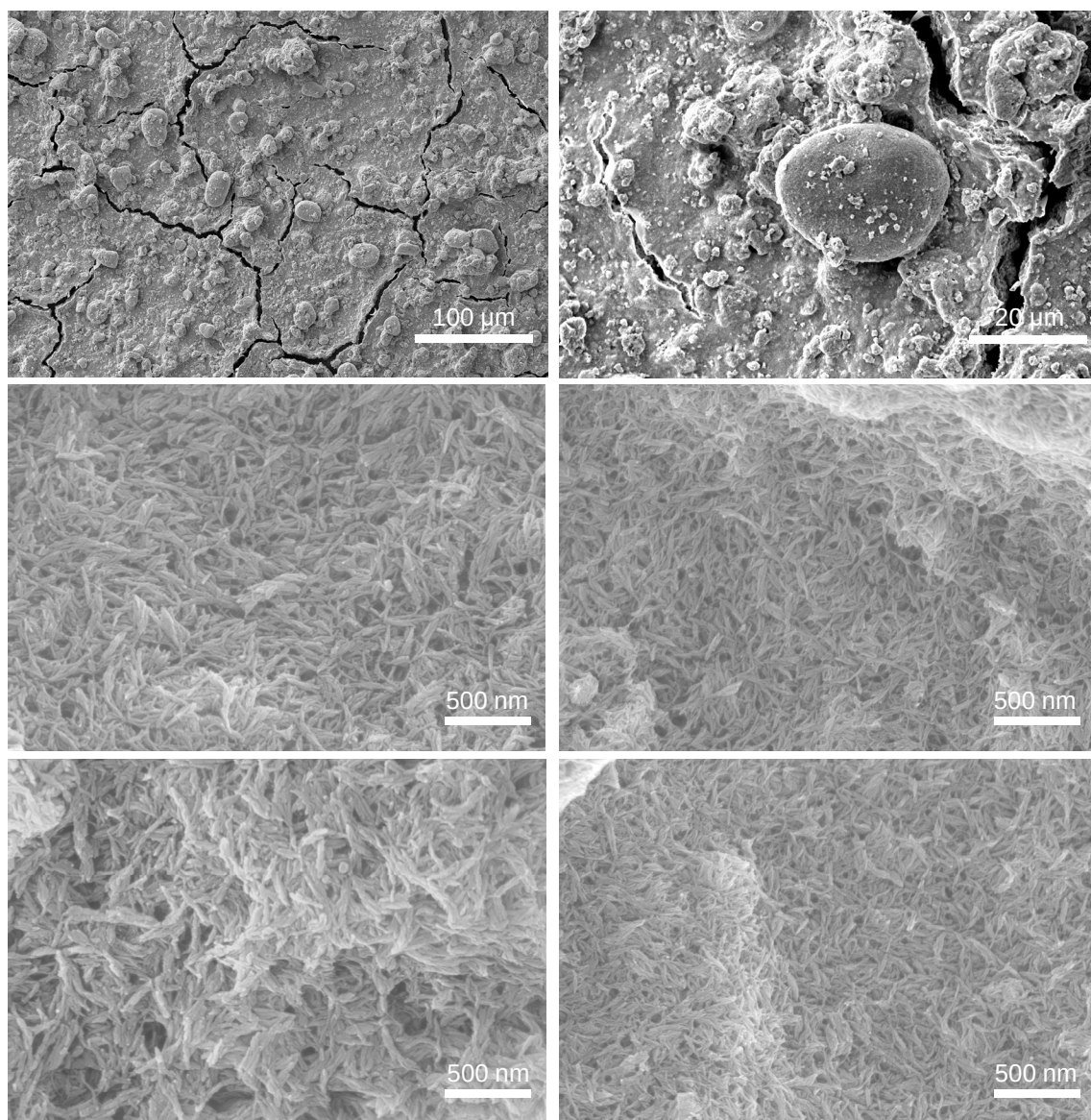
Supplementary Fig. 16 | Schematic illustration of the MEA system. The geometric area of cathode is 4 cm². Gas diffusion layer (GDE, cathode), anion exchange membrane (AEM), and IrO₂/Ti mesh (anode) were compacted tightly to form a sandwich structure. The GDE was prepared by spraying L2-Cu catalysts to the gas diffusion layer (GDL).



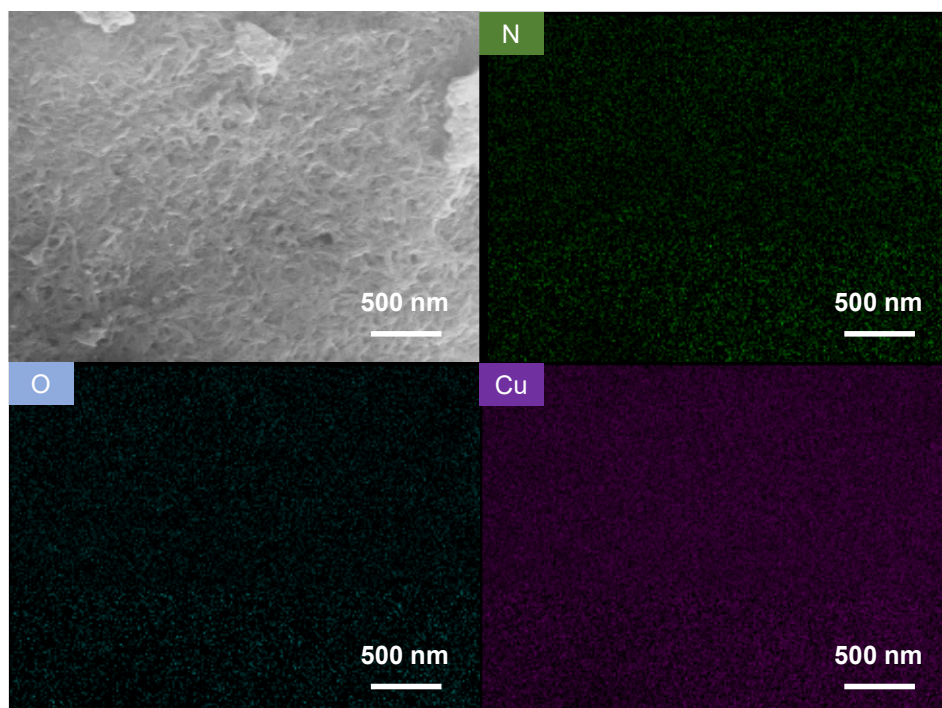
Supplementary Fig. 17 | CO₂RR performance test of L2-Cu in the MEA system.



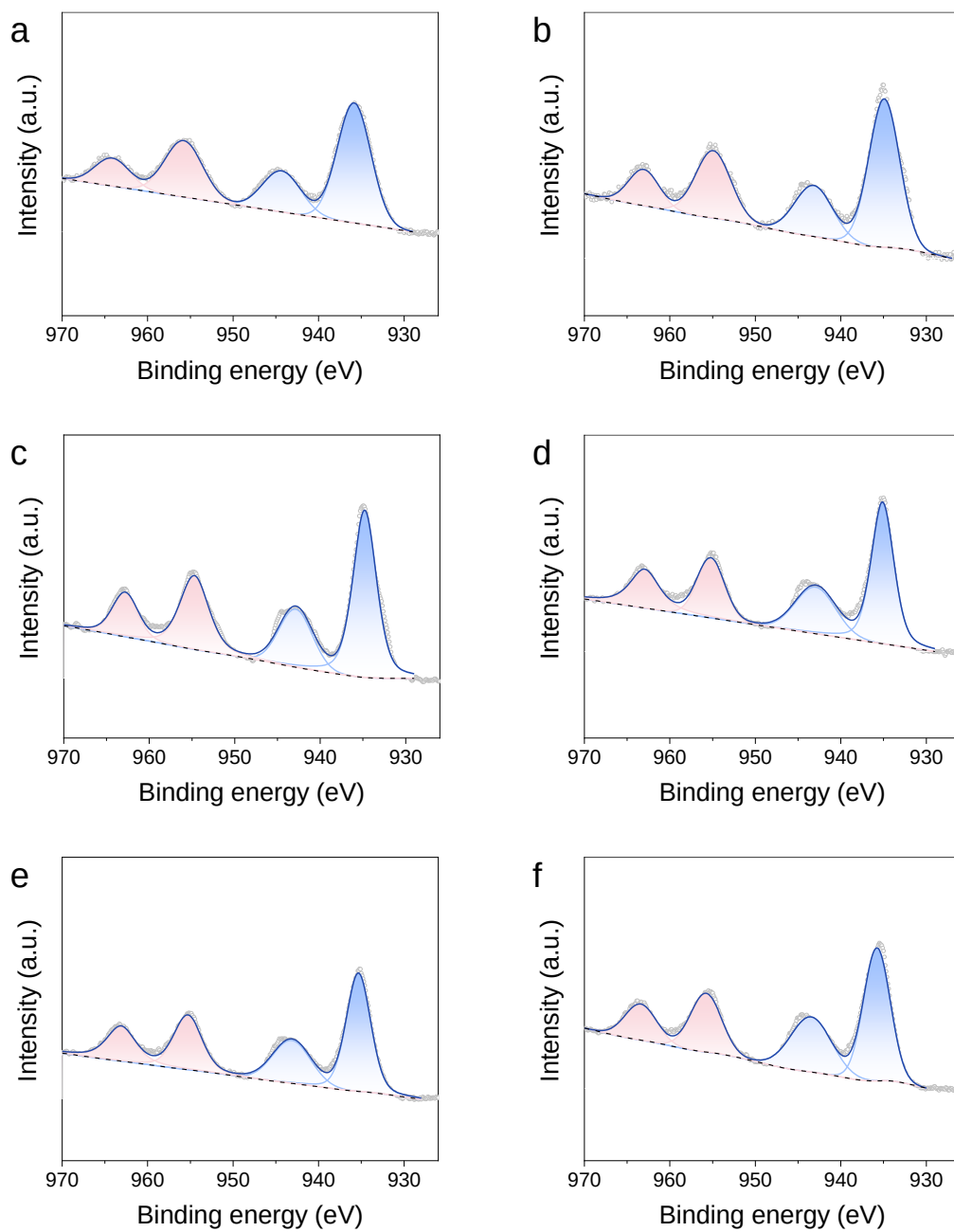
Supplementary Fig. 18 | XRD patterns of L2-Cu before and after a long-term CO₂RR performance test. L2-Cu was spray-coated on the carbon paper. The signals for carbon paper were listed by star symbols. The XRD patterns of L2-Cu after CO₂RR were collected after a galvanostatic test at -500 mA cm^{-2} for 1 hour. The specific patterns of L2-Cu located at about 5, 10, 15 degrees were maintained, and no metallic Cu patterns existed after CO₂RR, indicating the L2-Cu was not reduced to metallic copper.



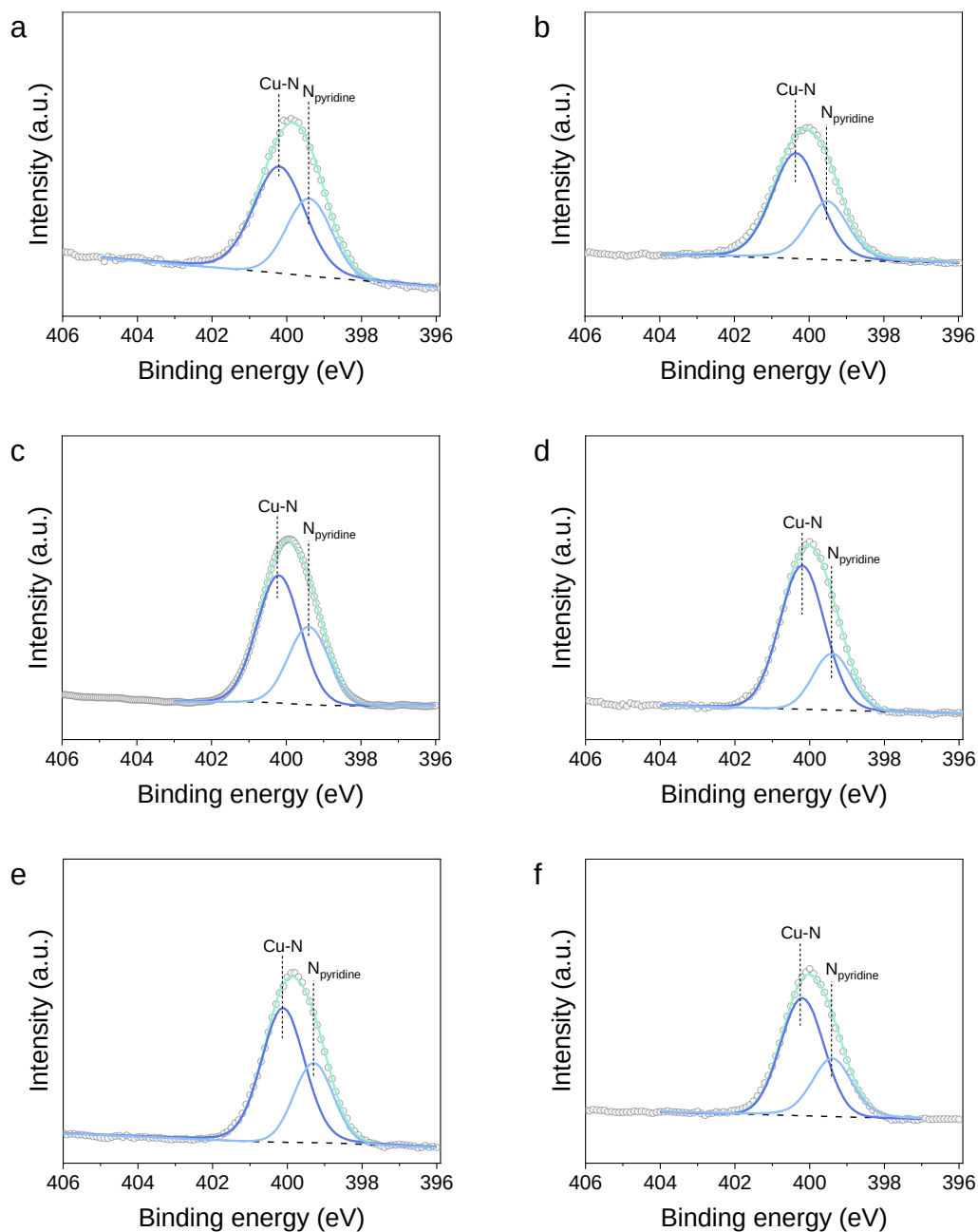
Supplementary Fig. 19 | Scanning electron microscopy (SEM) images of L2-Cu after test at – 300 mA cm⁻² for 1 hour. Several different areas were measured to show the homogeneous morphology after the CO₂RR test.



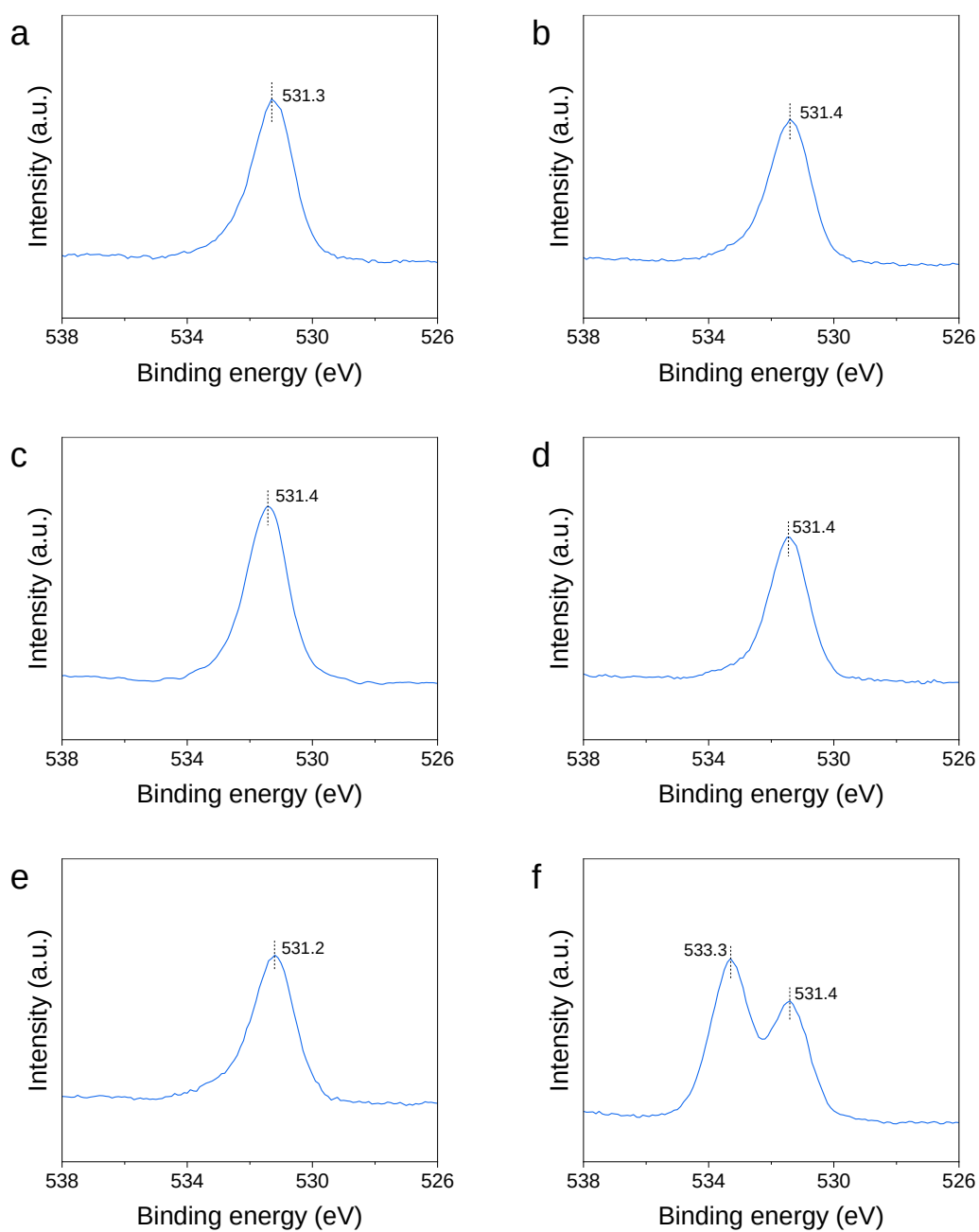
Supplementary Fig. 20 | SEM-EDS mapping of L2-Cu following CO₂RR test at -200 mA cm^{-2} for 30 minutes, showing the uniform dispersion of Cu, N, and O in the catalyst after CO₂RR.



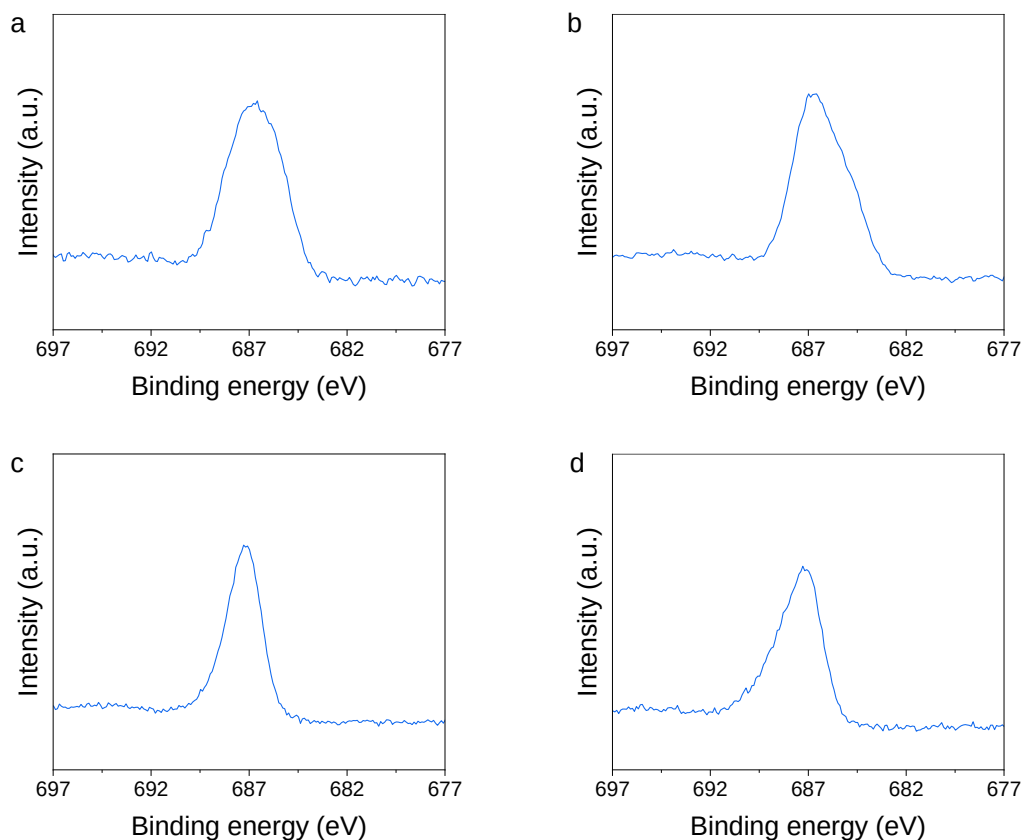
Supplementary Fig. 21 | Cu 2p XPS spectra of Ln-Cu after CO₂RR. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The peaks at ~935 eV (Cu 2p_{3/2}) and ~955 eV (Cu 2p_{1/2}) showed no change compared to as-prepared Ln-Cu in **Supplementary Fig. 6.**



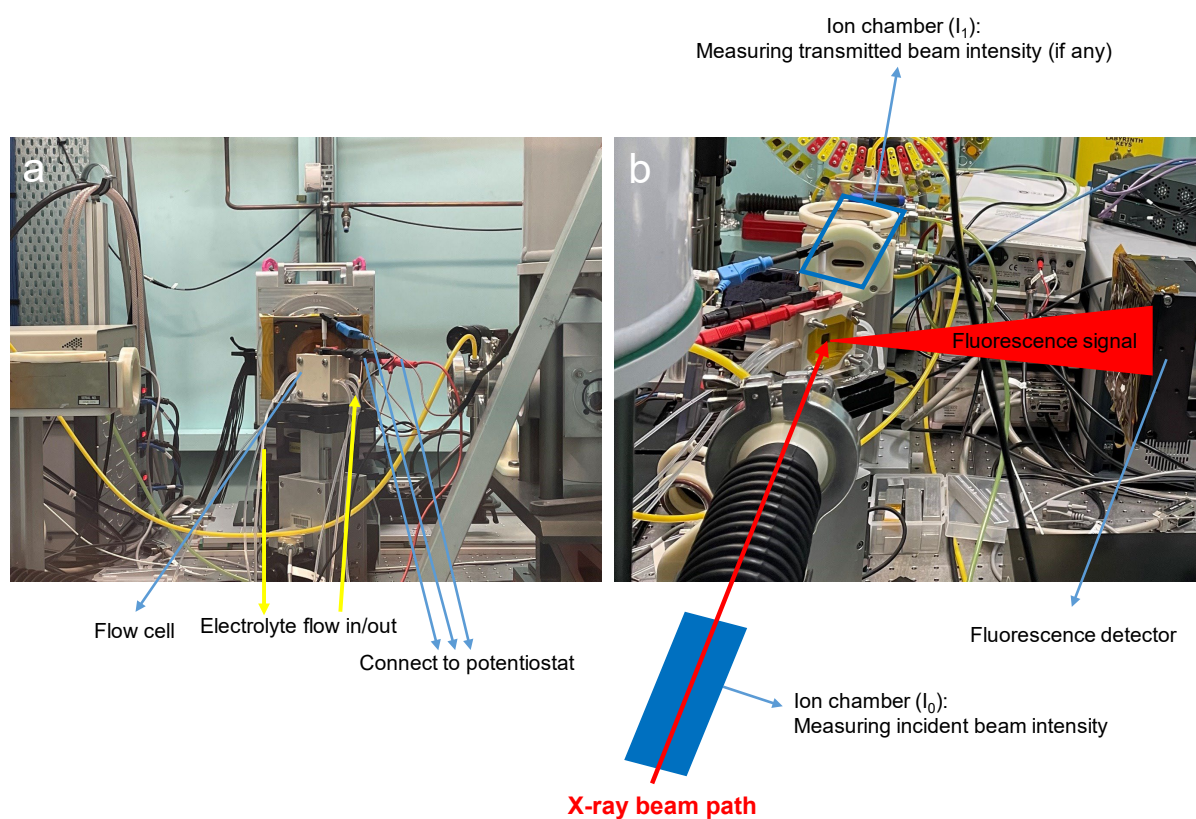
Supplementary Fig. 22 | N 1s XPS spectra of Ln-Cu after CO₂RR. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The peaks at 400.2 eV (Cu–N) and 399.4 eV (pyridinic N) showed no change compared to as-prepared Ln-Cu in **Supplementary Fig. 10.**



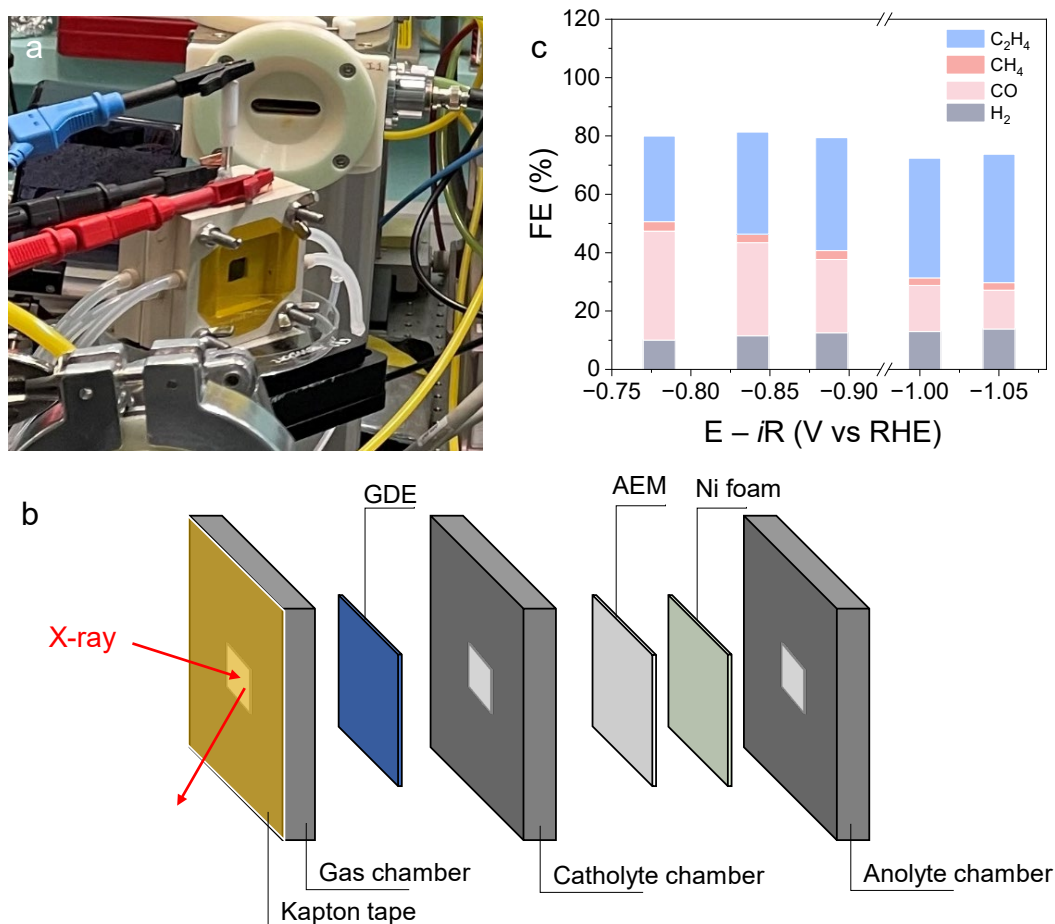
Supplementary Fig. 23 | O 1s XPS spectra of Ln-Cu after CO₂RR. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The peaks at ~531.4 eV (–OH) and 533.3 eV (–OCH₃) were consistent with as-prepared Ln-Cu in **Supplementary Fig. 11.**



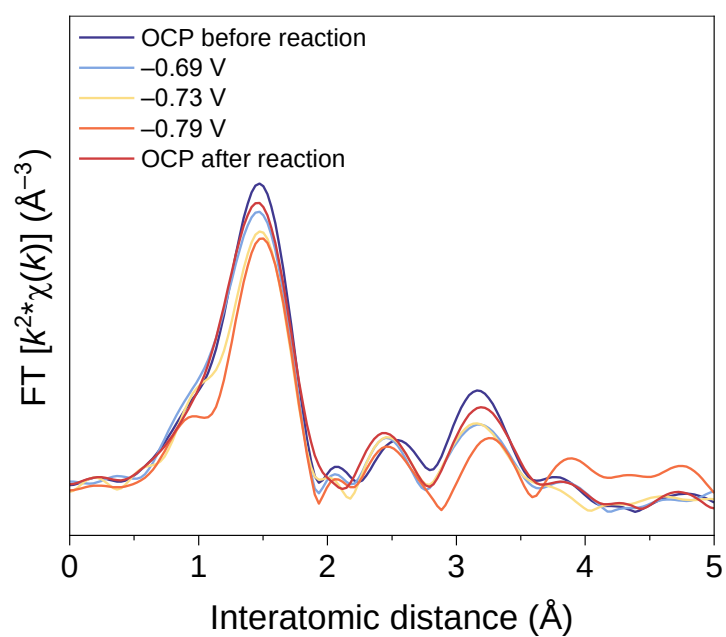
Supplementary Fig. 24 | F 1s XPS spectra of Ln-Cu before and after electrolysis. a, L1-Cu before CO₂RR. b, L1-Cu after CO₂RR. c, L3-Cu before CO₂RR. d, L3-Cu after CO₂RR. The catalysts were coated on carbon paper without Nafion solution to eliminate the influence of F from Nafion.



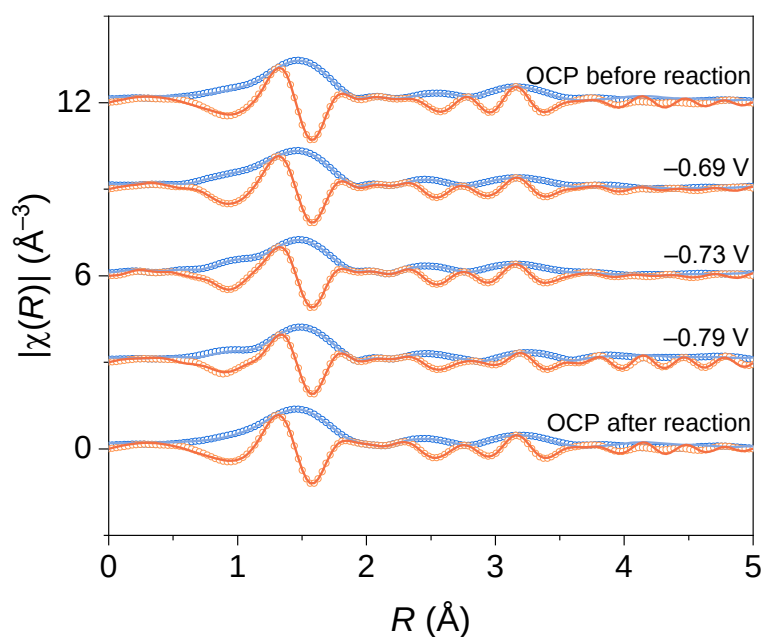
Supplementary Fig. 25 | The photograph of *operando* XAFS experiments in operation. a, Front view. b, side view. The yellow arrows show the electrolyte flow direction. The red arrows show the beam path.



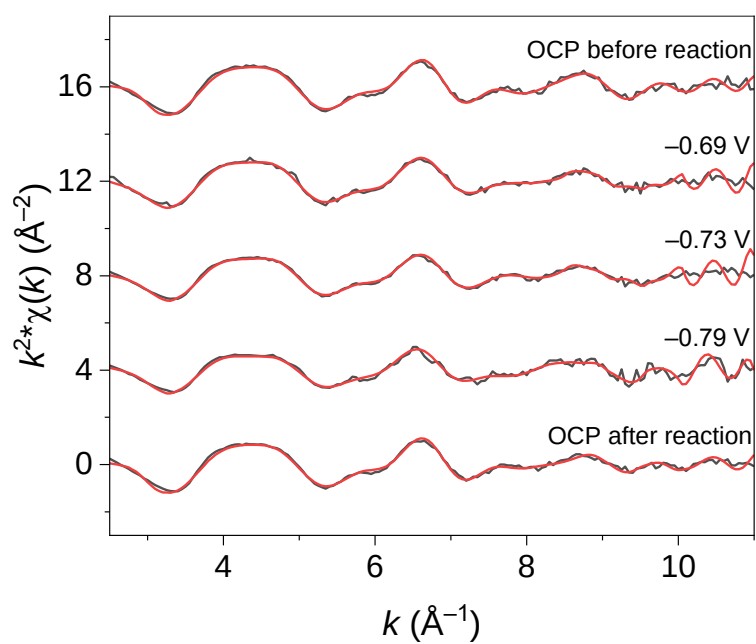
Supplementary Fig. 26 | The cell configuration of XAS cell and CO₂RR performance during *operando* XAS test. a, The photograph of *operando* XAFS experiments in operation. b, The detailed schematic of the XAS flow cell. c, The CO₂RR performance of L2-Cu performed in the XAS flow cell.



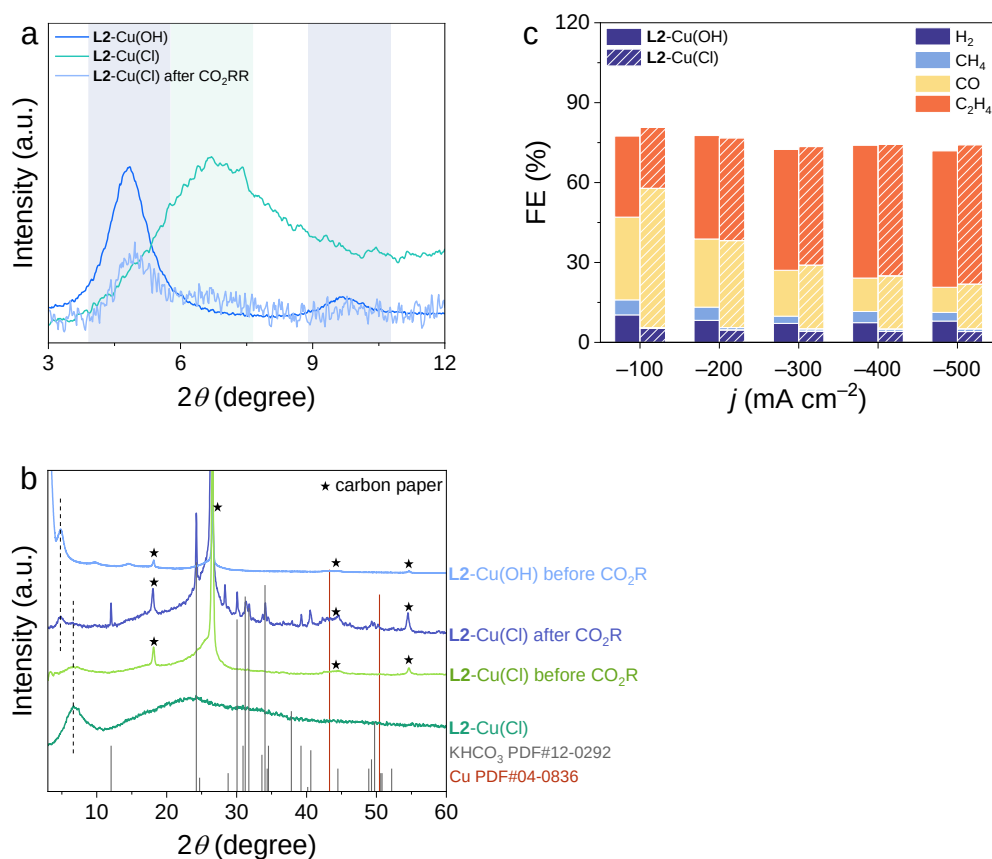
Supplementary Fig. 27 | *Operando* Fourier-transform EXAFS spectra for L2-Cu at the Cu k -edge.



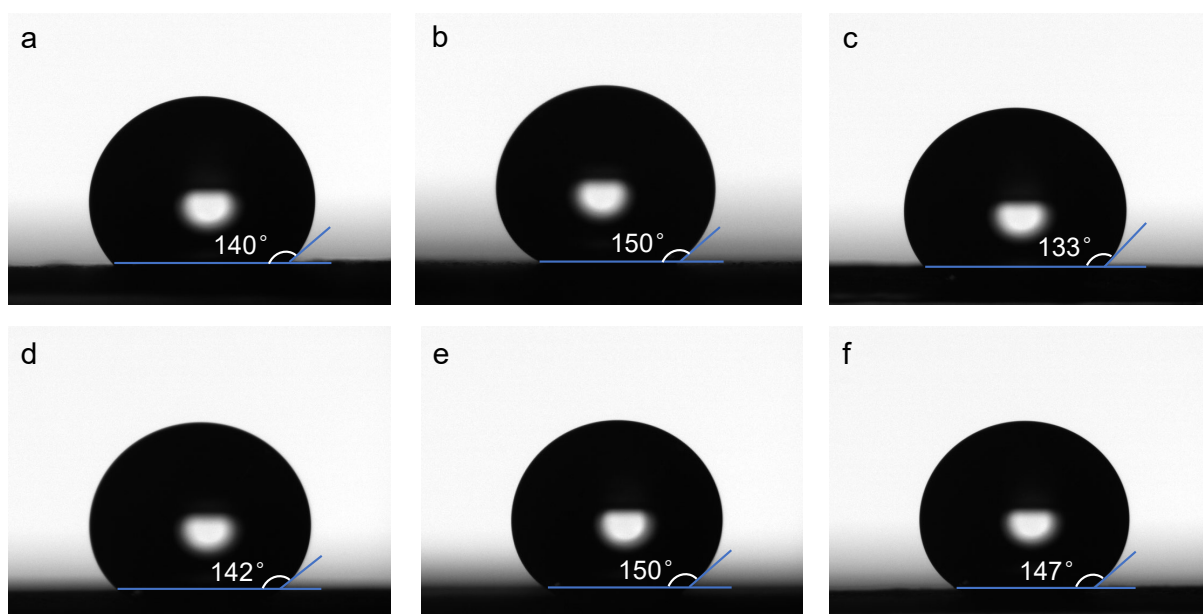
Supplementary Fig. 28 | The *operando* Fourier-transform EXAFS spectra (magnitude and imaginary part) for L2-Cu at the Cu k -edge, showing the magnitude (experimental data: blue circles; fitting data: blue lines) and imaginary portions (experimental data: orange circles; fitting data: orange lines) of Fourier transforms of the data. The k -range of 2.5–11 $\text{\AA}^{-1}$ and the R -range of 0–4 $\text{\AA}$ were used for the fits. EXAFS spectra and fits in k -space are provided in **Supplementary Fig. 29**. The corresponding fitting results are shown in **Supplementary Tables 1 and 8–11**.



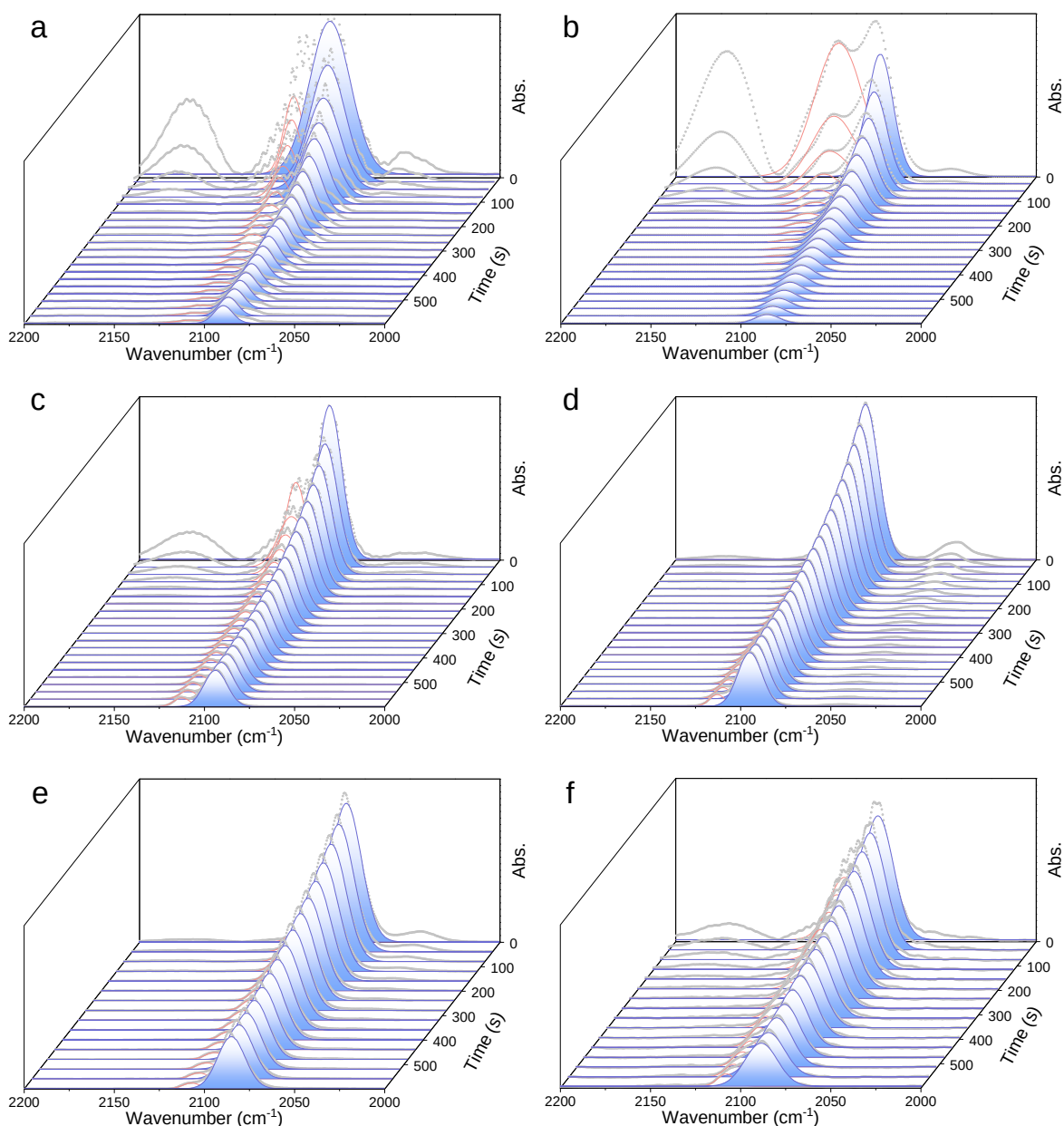
Supplementary Figure 29 | EXAFS spectra and fits in k -space at the Cu k -edge. Experimental data: dark grey; fitting data: red. Corresponding XANES and Fourier-transform EXAFS are shown in **Fig. 3d** and **Supplementary Fig. 28**.



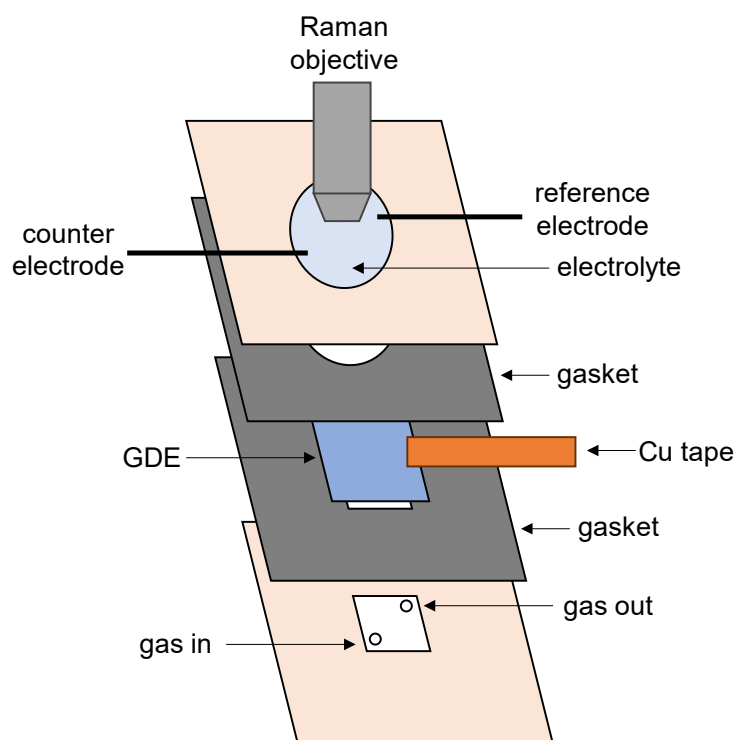
Supplementary Fig. 30 | The ligand exchange of L2-Cu exhibited in XRD patterns. a, The transformation from L2-Cu(Cl) to L2-Cu(OH). b, XRD patterns of L2-Cu(Cl) after CO₂RR. c, CO₂RR performance of L2-Cu(Cl) in 1 M KOH electrolyte. L2-Cu(OH) indicates the original L2-Cu catalysts where the bridged group is –OH. L2-Cu(Cl) has similar structure as L2-Cu(OH) where the bridged group is changed into Cl. L2-Cu(Cl) was synthesised using the same method as L2-Cu(OH), while the NaOH was replaced by hydrochloric acid solution to adjust the solution pH of 3. L2-Cu(Cl) performed in CO₂RR with 1 M KOH as the electrolyte at current densities from –100 mA cm⁻² to –500 mA cm⁻². At the beginning, L2-Cu(Cl) showed some differences from L2-Cu(OH) in the FE of CO and ethylene at –100 mA cm⁻². With the test going, these two catalysts gradually exhibited similar CO₂RR performances. Besides, after reacting for 1 hour at a current density of –300 mA cm⁻², the XRD patterns of L2-Cu(Cl) shaded in green disappeared, while new XRD patterns emerged in blue shaded area which can be ascribed to L2-Cu(OH). This solid-to-solid transformation based on ligand exchange suggests the stable structure frameworks coordinated by triazoles. Besides, no XRD patterns of metallic Cu were found in L2-Cu(Cl) after CO₂RR, suggesting that the transient ligand exchange of bridged groups did not lead to reconstruction of Ln-Cu catalysts.



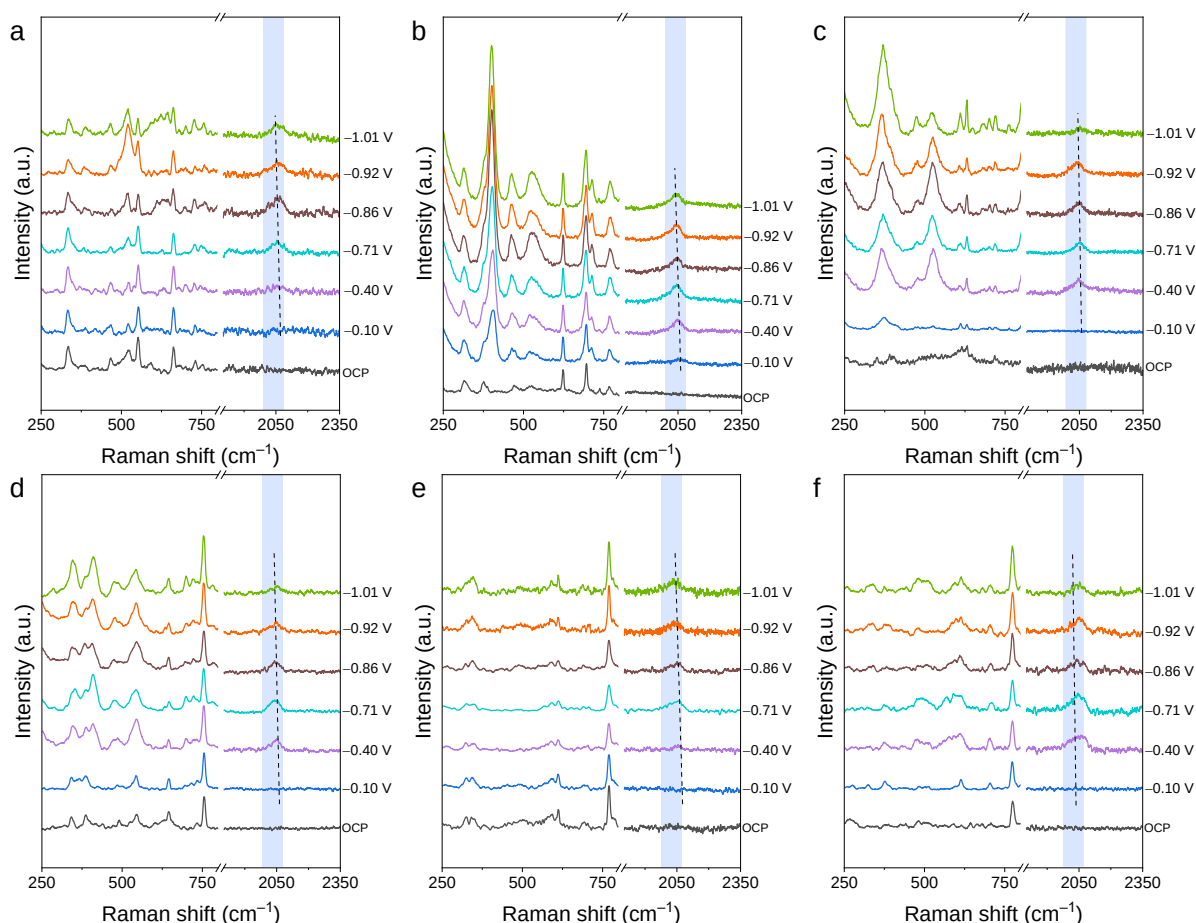
Supplementary Fig. 31 | Contact angles of the GDE loaded with Ln-Cu catalysts. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The GDE preparation process was detailed in *Methods*. The droplets shown in the figure were 1 M KOH solution.



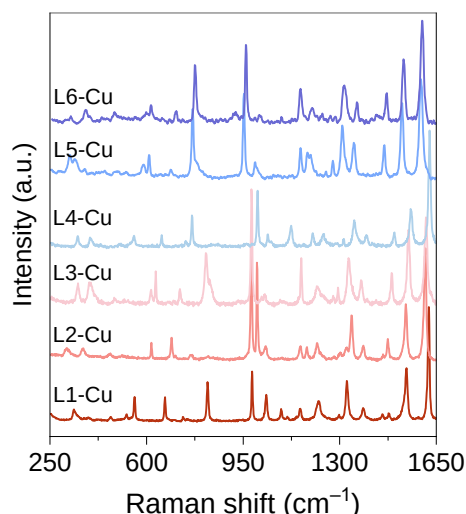
Supplementary Fig. 32 | CO-DRIFT spectra of Ln-Cu. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The spectra were collected when Ar gas was used to purge the catalysts for the removing of atmospheric CO gas. The bands at 2,085–2,095 cm⁻¹ in DRIFT spectra, where the area was filled with gradient blue, were assigned to the adsorbed CO on **Ln**-Cu catalysts. The absorbance area was normalised in the range of 0–600 seconds and used to draw the CO decay curve in Fig. 5d.



Supplementary Fig. 33 | Schematic illustration of the electrochemical cell for *in-situ* Raman measurements. A water immersion objective (Olympus x60 water immersion lens (NA 1.0, WD 2.0 mm)) and a 785 nm laser were used. An Ag/AgCl (saturated KCl) electrode and a Pt wire were used as the reference and counter electrodes, respectively.

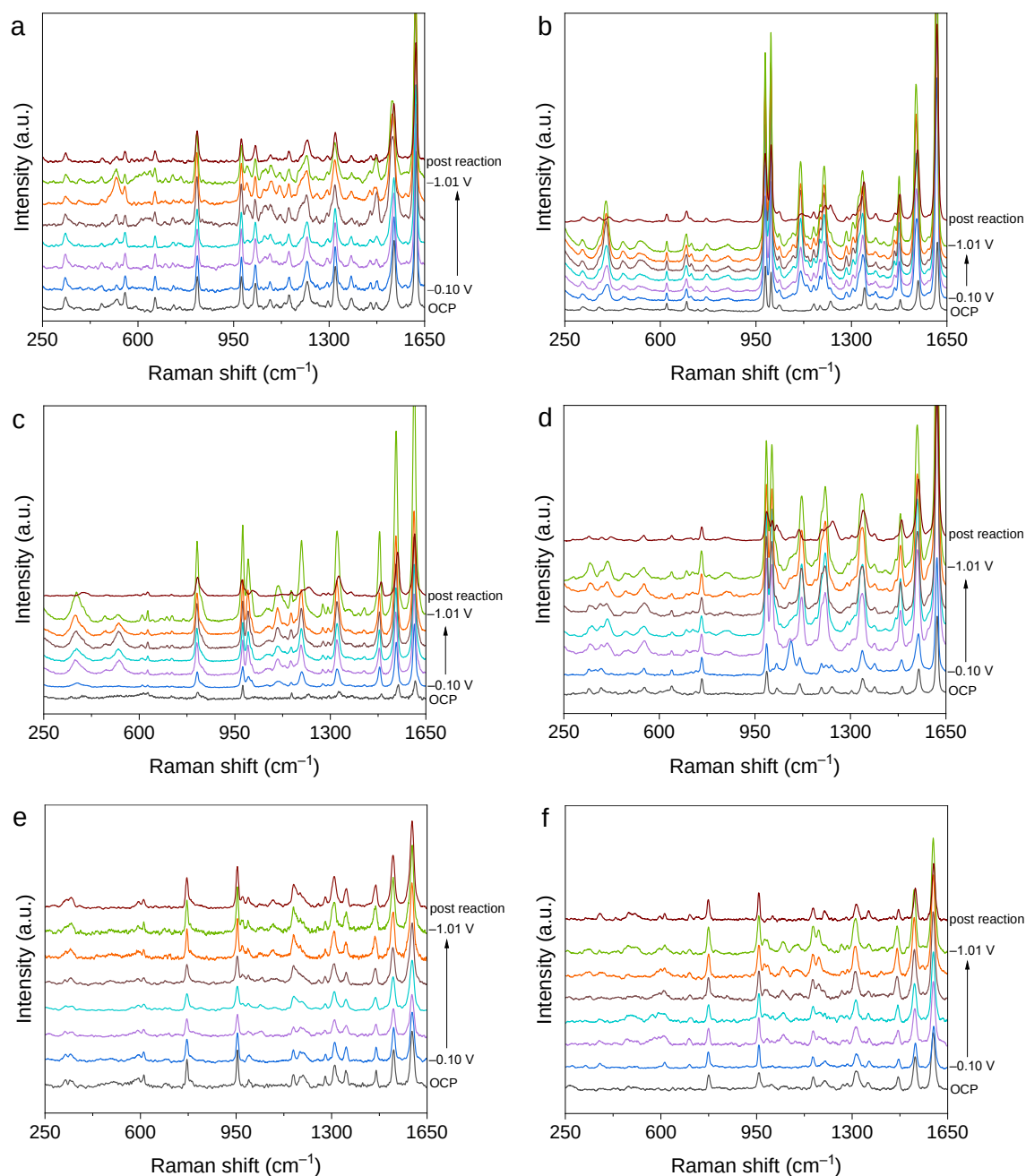


Supplementary Fig. 34 | *In-situ* Raman spectra of Ln-Cu during CO₂RR. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The *in-situ* Raman spectroscopy was conducted in a flow cell using 0.5 M KOH as the electrolyte with CO₂ flow rate of 5 sccm. The potentials in figures are $E - iR$. Only *CO_{atop} species at $\sim 2,050\text{ cm}^{-1}$ was detected on **Ln-Cu** catalysts, indicating the single-site nature of the catalysts.⁵ The *CO peak intensity increased initially and then decreased, attributed to the consumption of *CO at high applied potentials. The weak signals were caused by the interference of ligand molecules existed in the catalysts and lack of localised surface plasmon resonance (LSPR) effect, which is common in metallic Cu-based catalysts.⁶

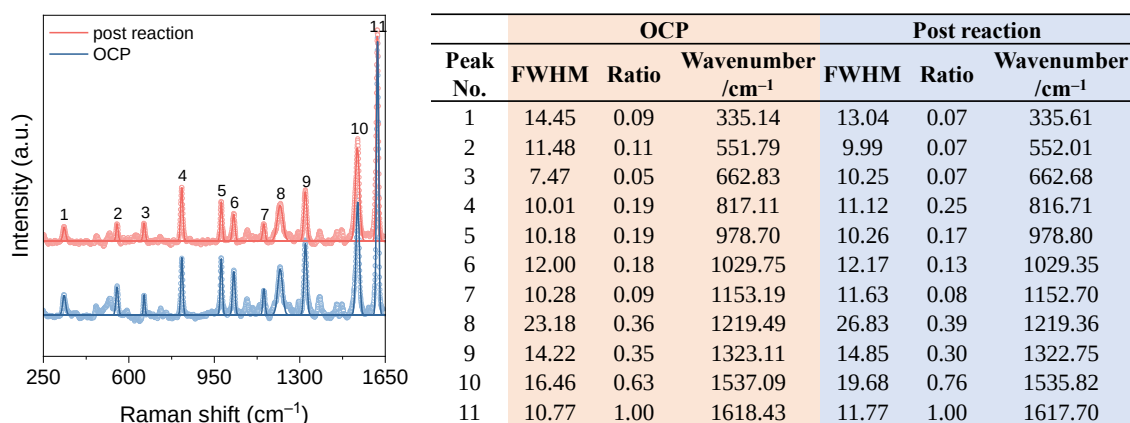


Observed frequency (cm ⁻¹)	Vibrational assignments
1610 vs	[ν CC + δ HCC] in benzene
1538 s	ν C _b C _t + ν NC in triazole + ν CC in benzene
1474 w	δ HCN + δ HCC
1456 vw	ν NC in triazole
1385 w	ν NC in triazole + δ HCN
1342 m	δ HCC + δ HCN
1218 m	ν CC in benzene + ν CC in triazole
1181 w	ν CC in triazole
1158 w	δ HCC
1031 w	ν NN in triazole
1000 vs	[ν CC + ν HCC] in benzene
980 vs	ν NC in triazole
691 m	τ HCCC
617 m	δ CCC
370 w	τ benzene
310 w	δ CCC + δ CCN

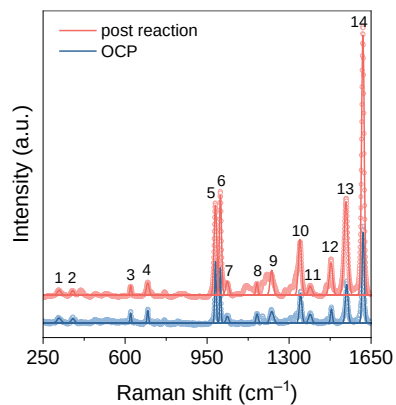
Supplementary Fig. 35 | *Ex-situ* Raman spectra of Ln-Cu and the peak assignment. The peak assignment is listed based on **L2-Cu**.^{7,8} It is worth noting that the corresponding peaks in other **Ln-Cu** materials may exhibit slight shifts due to the presence of different substituents. Additionally, these substituents may generate corresponding vibrations, such as aromatic ν CF (556 cm⁻¹) in **L1-Cu** and ν CF (616 cm⁻¹) in **L3-Cu**,⁹ aromatic ν CCl (761 cm⁻¹) in **L4-Cu**,¹⁰ ν C–OCH₃ (1,158 cm⁻¹) in **L6-Cu**.¹¹ Abbreviations in the table: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; ν , stretching; δ , in-plane bending; τ , torsion.



Supplementary Fig. 36 | *In-situ* Raman spectra of Ln-Cu during CO₂RR. a, L1-Cu. b, L2-Cu. c, L3-Cu. d, L4-Cu. e, L5-Cu. f, L6-Cu. The peaks at 250–1,650 cm⁻¹ correspond to the vibrational modes of molecular structures in Ln-Cu.¹² The post-reaction spectra indicate the retention of ligands after *in-situ* Raman test. The peaks at ~520 cm⁻¹, ~1,010 cm⁻¹ and ~1,060 cm⁻¹ can be ascribed to Cu–OH, HCO₃⁻ and CO₃²⁻ signals.^{13,14} The potentials in figures are E – iR.

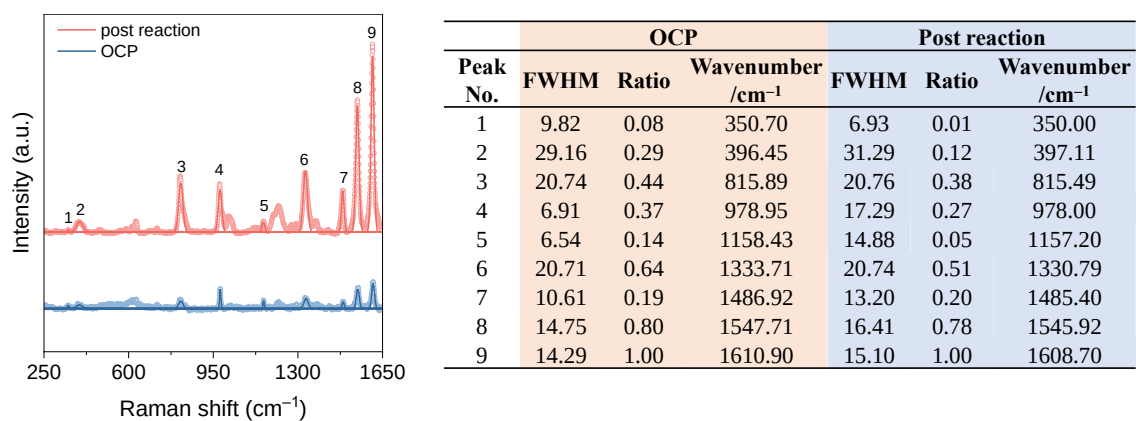


Supplementary Fig. 37 | The comparison of Raman spectra of L1-Cu between OCP state and post reaction state. The peak areas were normalized by the area of the highest peak at ~1,600 cm⁻¹ (same normalized method for Supplementary Figs. 38–42).

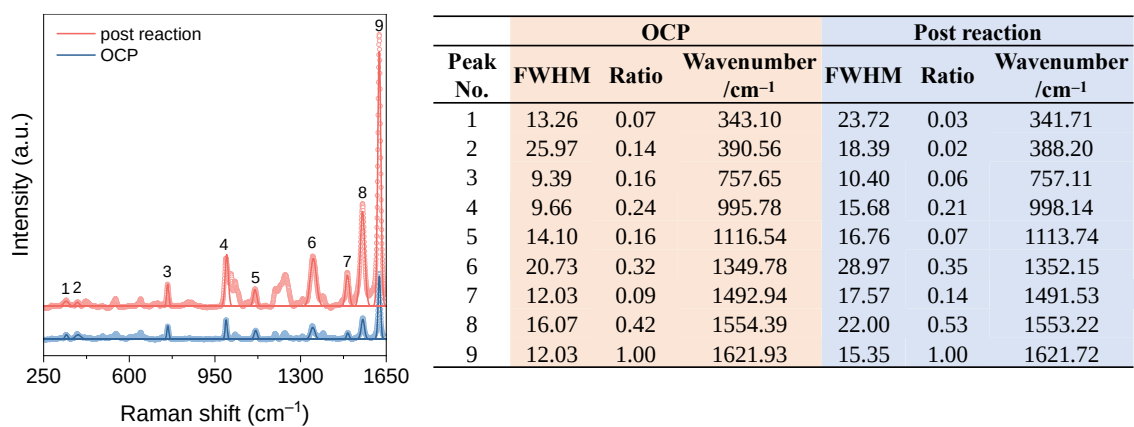


Peak No.	OCP			Post reaction		
	FWHM	Ratio	Wavenumber /cm ⁻¹	FWHM	Ratio	Wavenumber /cm ⁻¹
1	20.02	0.09	317.99	17.57	0.02	318.53
2	16.64	0.07	377.41	14.40	0.02	376.40
3	6.76	0.07	623.85	8.07	0.02	624.04
4	7.48	0.09	696.83	13.51	0.05	696.75
5	7.66	0.47	985.90	13.66	0.35	985.59
6	6.26	0.34	1006.70	11.30	0.32	1006.99
7	12.84	0.09	1036.66	15.62	0.06	1036.19
8	10.57	0.09	1163.56	10.13	0.04	1162.81
9	18.22	0.20	1226.01	15.31	0.11	1225.69
10	12.72	0.37	1349.31	15.73	0.25	1346.23
11	16.13	0.14	1390.34	17.89	0.04	1390.22
12	9.48	0.13	1480.91	16.77	0.15	1478.86
13	13.37	0.51	1546.00	19.24	0.51	1542.96
14	11.08	1.00	1616.44	13.42	1.00	1615.07

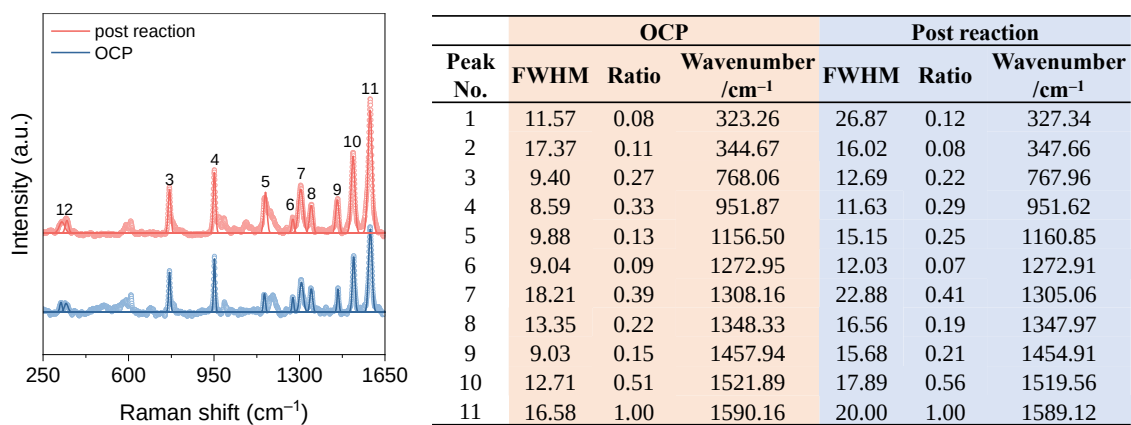
Supplementary Fig. 38 | The comparison of Raman spectra of L2-Cu between OCP state and post reaction state.



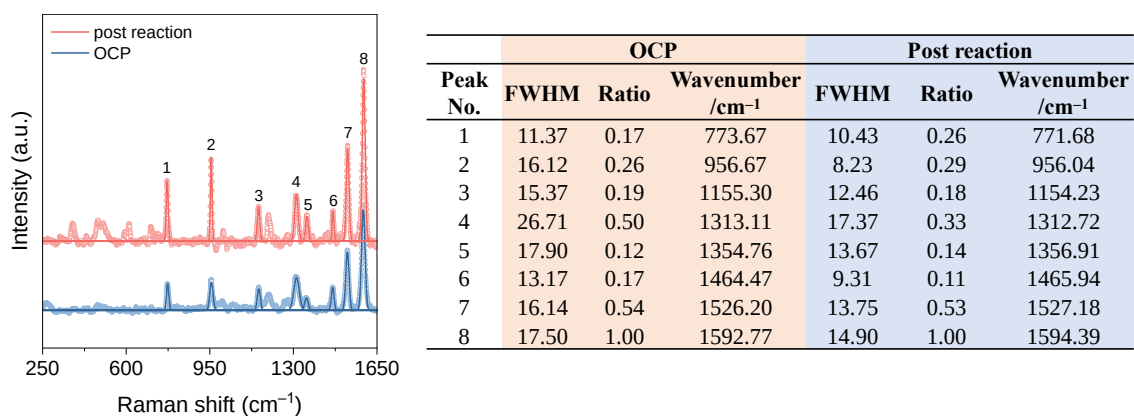
Supplementary Fig. 39 | The comparison of Raman spectra of L3-Cu between OCP state and post reaction state.



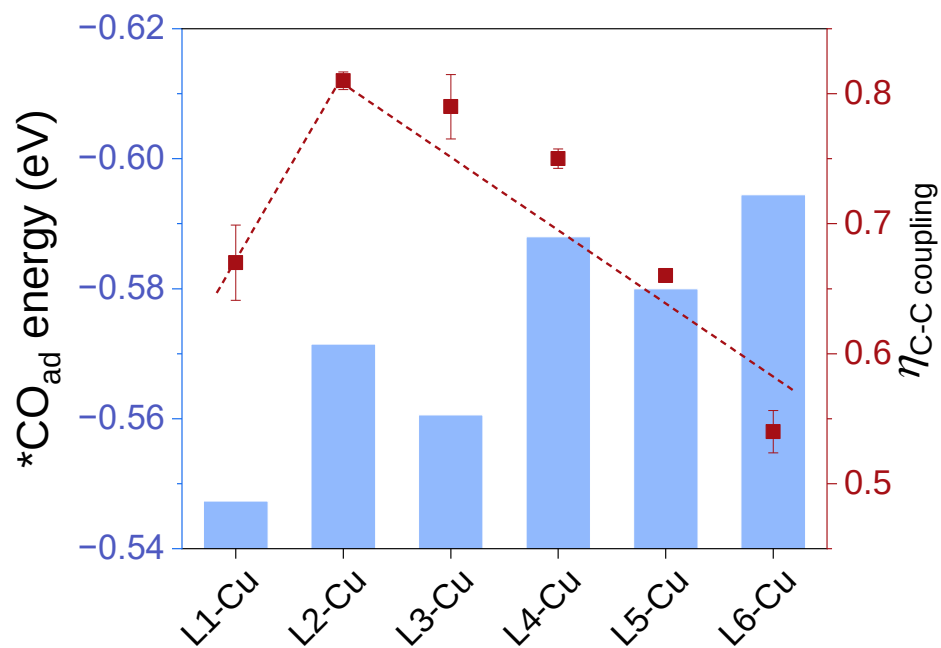
Supplementary Fig. 40 | The comparison of Raman spectra of L4-Cu between OCP state and post reaction state.



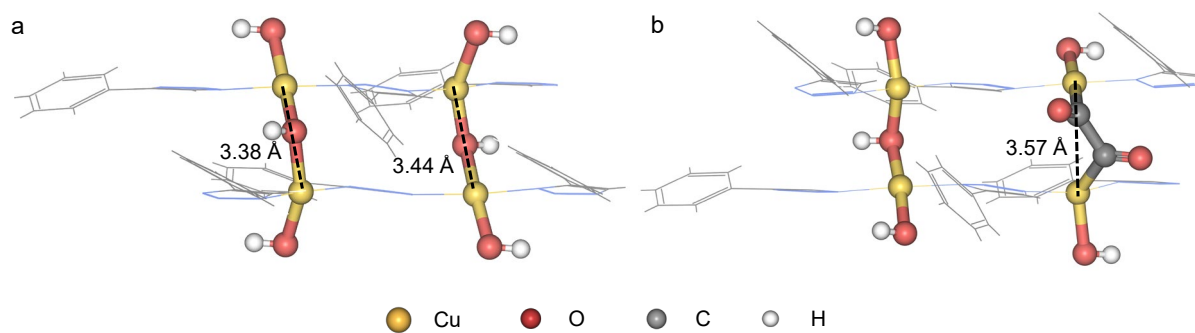
Supplementary Fig. 41 | The comparison of Raman spectra of L5-Cu between OCP state and post reaction state.



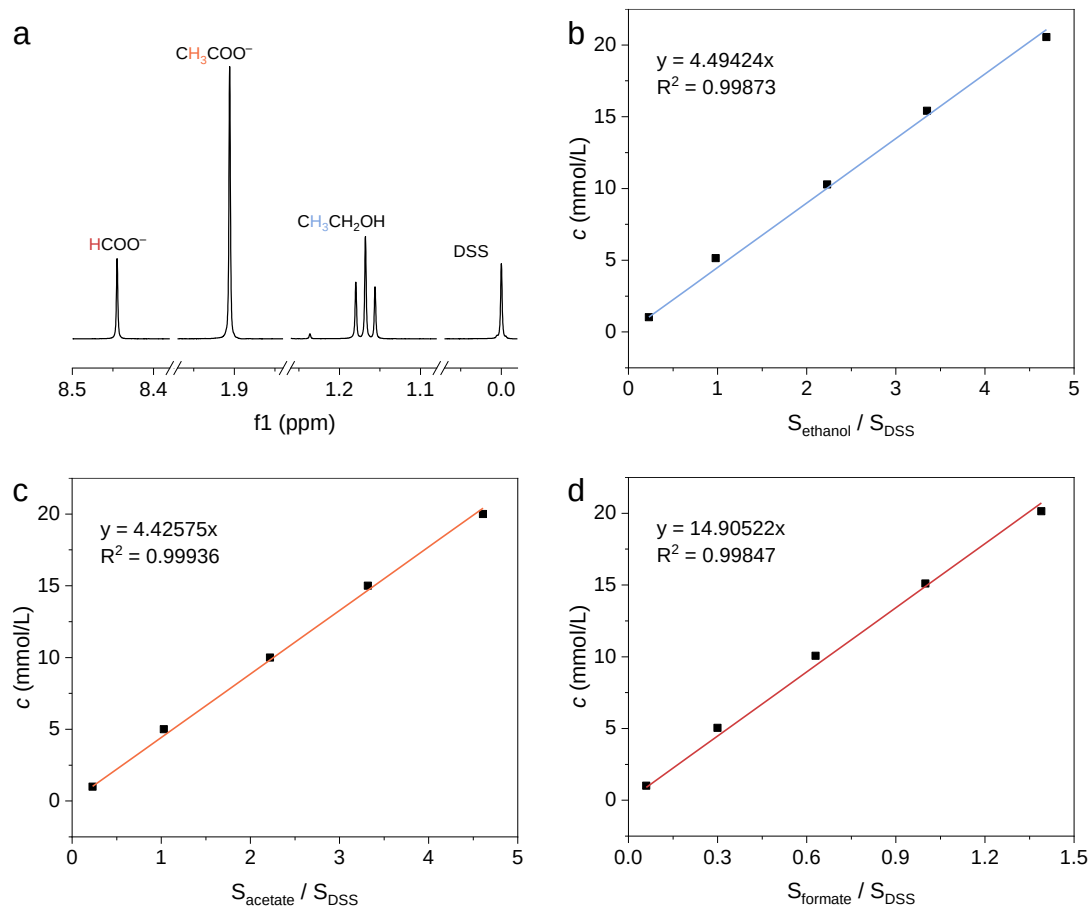
Supplementary Fig. 42 | The comparison of Raman spectra of L6-Cu between OCP state and post reaction state.



Supplementary Fig. 43 | The relationship between *CO_{ad} energy (blue bars) and the trend of η_{C-C} coupling (red-brown plots) at $E - iR = -0.93$ V vs RHE.



Supplementary Fig. 44 | DFT-predicted *OCCO configuration on L2-Cu and Cu-Cu distance before (a) and after (b) *CO adsorption. The yellow, red, and white balls represent Cu, O, and H, respectively. The L2 ligands were displayed in wires.



Supplementary Fig. 45 | ^1H -NMR spectrum of liquid products and calibration plots. **a**, ^1H -NMR spectrum for ethanol (1.17 ppm), acetate (1.91 ppm) and formate (8.44 ppm). **b**, Calibration plot for ethanol measured in 1 M KOH electrolyte. **c**, Calibration plot for acetate measured in 1 M KOH electrolyte. **d**, Calibration plot for formate measured in 1 M KOH electrolyte. 6 mmol L $^{-1}$ of 3-trimethylsilyl-1-propane sulfonic acid sodium salt (DSS) was used as an internal standard to quantify the concentration of each liquid product.

Supplementary Table 1 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu under OCP state before CO₂RR using L2-Cu model. Data range $k = 2.5\text{--}11 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
L2-Cu at OCP	Cu–O	2.00±0.06	1.83±0.12	1.2±0.4	0.00297±0.00371	0.64%
	Cu–N	2.00±0.06	1.99±0.01	1.2±0.4	0.00604±0.00386	
	Cu–N	2.05±0.23	2.88±0.07	1.2±0.4	0.01202±0.00585	
	Cu–C	2.03±0.21	3.16±0.15	1.2±0.4	0.0150±0.01146	
	Cu–C	1.02±0.11	3.35±0.24	1.2±0.4	0.03102±0.00644	
	Cu–Cu	2.06±0.33	3.11±0.27	1.2±0.4	0.00906±0.00411	
	Cu–C	1.02±0.12	3.22±0.19	1.2±0.4	0.03088±0.01241	
	Cu–N	1.02±0.11	3.37±0.36	1.2±0.4	0.02305±0.03155	
	Cu–N	1.01±0.09	4.09±0.25	1.2±0.4	0.02610±0.02044	
	Cu–C	2.02±0.20	4.28±0.37	1.2±0.4	0.02313±0.01972	

Supplementary Table 2 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu under OCP state before CO₂RR using L2-Cu₂ model. Data range $k = 2.5\text{--}10 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
L2-Cu ₂ at OCP	Cu-O	1.01±0.03	1.77±0.02	3.1±2.3	0.01406±0.00456	0.71%
	Cu-O	1.01±0.03	1.90±0.01	3.1±2.3	0.01938±0.00501	
	Cu-N	1.02±0.06	2.05±0.11	3.1±2.3	0.02199±0.00261	
	Cu-Cu	1.04±0.11	2.25±0.27	3.1±2.3	0.01110±0.01034	
	Cu-N	1.03±0.11	2.44±0.41	3.1±2.3	0.02092±0.01236	
	Cu-C	1.01±0.07	2.92±0.05	3.1±2.3	0.01448±0.00589	
	Cu-N	1.00±0.05	4.17±0.17	3.1±2.3	0.03350±0.00430	
	Cu-N	1.01±0.06	4.03±0.06	3.1±2.3	0.03038±0.00391	
	Cu-C	1.01±0.05	4.34±0.24	3.1±2.3	0.03171±0.00441	

Supplementary Table 3 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu under OCP state before CO₂RR using L2-Cu₃ model. Data range $k = 2.5\text{--}10 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
L2-Cu ₃ at OCP	Cu-N	1.00±0.02	1.96±0.11	1.4±6.6	0.03009±0.01000	0.71%
	Cu-O	1.00±0.02	1.78±0.07	1.4±6.6	0.02176±0.00933	
	Cu-Cu	1.00±0.02	2.18±0.29	1.4±6.6	0.02252±0.01545	
	Cu-Cu	1.00±0.03	2.43±0.24	1.4±6.6	0.02204±0.02644	
	Cu-N	1.00±0.03	2.61±0.19	1.4±6.6	0.03177±0.02290	
	Cu-C	1.00±0.03	2.38±0.44	1.4±6.6	0.03067±0.04030	
	Cu-O	1.00±0.12	2.90±0.32	1.4±6.6	0.00937±0.08337	
	Cu-O	0.98±0.28	3.68±0.18	1.4±6.6	0.00678±0.11241	
	Cu-N	0.99±0.03	4.16±0.25	1.4±6.6	0.03508±0.01269	
	Cu-C	1.01±0.03	4.33±0.37	1.4±6.6	0.03208±0.01307	
	Cu-N	0.99±0.03	4.01±0.31	1.4±6.6	0.03263±0.01412	

Supplementary Table 4 | Atomic ratio measured by XPS.

Catalysts	Atomic Ratio of N:Cu	Atomic Ratio of O:Cu
L1-Cu	2.92	1.05
L2-Cu	2.91	1.16
L3-Cu	2.97	1.11
L4-Cu	3.05	1.21
L5-Cu	2.61	1.01
L6-Cu	2.67	2.27 ^a

^aThe double atomic ratio of O:Cu in **L6-Cu** derives from both –OH groups and CH₃O– groups.

Supplementary Table 5 | Summary of the amount of Cu in Ln-Cu measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Cu (wt.%)^a	Theoretical Value	ICP-AES
L1-Cu	26.18	27.57
L2-Cu	28.28	28.27
L3-Cu	26.18	30.70
L4-Cu	24.52	24.82
L5-Cu	26.62	25.13
L6-Cu	24.95	N.A. ^b

^a mass percentage.

^b **L6-Cu** cannot be dissolved in aqua regia.

Supplementary Table 6 | Element analysis of Ln-Cu.

Cu (wt.%)^a	Theoretical Value	Elemental Analysis
L1-Cu	26.18	29.38
L2-Cu	28.28	28.43
L3-Cu	26.18	26.22
L4-Cu	24.52	24.33
L5-Cu	26.62	25.95
L6-Cu	24.95	23.99

^a mass percentage.

Supplementary Table 7 | The mass percentage of Cu in L2-Cu before and after CO₂RR. The results were determined by SEM-EDS mapping.

Catalyst	Cu (wt. %) ^a
L2-Cu before CO₂RR	29.8
L2-Cu after CO₂RR	29.0

^amass percentage.

Supplementary Table 8 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu at –0.69 V using L2-Cu model. Data range $k = 2.5\text{--}11 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
–0.69 V	Cu–N	2.00±0.03	2.05±0.05	3.7±1.9	0.00907±0.00223	0.30%
	Cu–C	1.00±0.02	1.93±0.06	3.7±1.9	0.00791±0.00357	
	Cu–O	1.00±0.02	1.78±0.25	3.7±1.9	0.00514±0.00771	
	Cu–O	0.99±0.03	3.05±0.22	3.7±1.9	0.01910±0.00594	
	Cu–N	0.99±0.03	2.92±0.01	3.7±1.9	0.01492±0.00303	
	Cu–C	1.00±0.04	2.34±0.58	3.7±1.9	0.01487±0.00359	
	Cu–C	1.98±0.11	3.30±0.27	3.7±1.9	0.02531±0.00776	
	Cu–N	1.00±0.03	3.45±0.38	3.7±1.9	0.02918±0.00564	
	Cu–C	0.99±0.04	3.50±0.36	3.7±1.9	0.03207±0.00325	
	Cu–Cu	1.00±0.03	3.25±0.01	3.7±1.9	0.02085±0.00349	
	Cu–C	1.00±0.04	3.41±0.05	3.7±1.9	0.03777±0.01946	

Supplementary Table 9 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu at −0.73 V using L2-Cu model. Data range $k = 2.5\text{--}11 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
−0.73 V	Cu–N	2.00±0.03	2.06±0.06	4.4±2.4	0.01410±0.00788	0.24%
	Cu–C	1.00±0.01	1.94±0.05	4.4±2.4	0.01089±0.00382	
	Cu–O	1.00±0.01	1.79±0.24	4.4±2.4	0.00630±0.00536	
	Cu–O	1.00±0.02	2.93±0.10	4.4±2.4	0.02093±0.01543	
	Cu–N	1.00±0.02	3.09±0.18	4.4±2.4	0.01932±0.00656	
	Cu–C	0.99±0.04	2.38±0.53	4.4±2.4	0.01038±0.00777	
	Cu–C	1.98±0.13	3.39±0.35	4.4±2.4	0.01953±0.00897	
	Cu–N	1.01±0.02	3.47±0.40	4.4±2.4	0.02127±0.01652	
	Cu–C	1.00±0.45	3.46±0.32	4.4±2.4	0.01568±0.00327	
	Cu–Cu	1.01±0.02	3.27±0.01	4.4±2.4	0.02247±0.01078	
	Cu–C	1.01±0.02	3.44±0.03	4.4±2.4	0.01650±0.00690	
	Cu–Cu	1.03±0.09	3.90±0.33	4.4±2.4	0.00650±0.00747	

Supplementary Table 10 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu at –0.79 V using L2-Cu model. Data range $k = 2.5\text{--}11 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
–0.79 V	Cu–N	2.01±0.06	1.97±0.02	4.7±3.0	0.00501±0.00991	0.77%
	Cu–C	1.04±0.19	2.16±0.16	4.7±3.0	0.00248±0.00921	
	Cu–O	1.00±0.05	1.82±0.21	4.7±3.0	0.00358±0.00366	
	Cu–O	1.08±0.12	2.86±0.03	4.7±3.0	0.01793±0.00593	
	Cu–N	1.09±0.13	3.06±0.15	4.7±3.0	0.02924±0.00222	
	Cu–C	1.09±0.13	3.21±0.28	4.7±3.0	0.03324±0.03535	
	Cu–C	2.19±0.37	3.31±0.27	4.7±3.0	0.02514±0.00585	
	Cu–N	1.08±0.12	3.51±0.44	4.7±3.0	0.03591±0.00941	
	Cu–C	1.09±0.12	3.60±0.47	4.7±3.0	0.03693±0.00580	
	Cu–Cu	1.09±0.12	3.34±0.08	4.7±3.0	0.02749±0.00520	
	Cu–C	1.08±0.12	3.46±0.01	4.7±3.0	0.03816±0.00467	
	Cu–Cu	1.07±0.17	3.69±0.12	4.7±3.0	0.00985±0.00522	

Supplementary Table 11 | Interatomic distances and coordination numbers determined by EXAFS analysis of L2-Cu under OCP after CO₂RR using L2-Cu model. Data range $k = 2.5\text{--}11 \text{ \AA}^{-1}$, amplitude reaction factor $S_0^2 = 0.8$, bond distance $R = 0\text{--}4 \text{ \AA}$. CN: Coordination numbers. ΔE : The inner potential shift. σ^2 : The Debye-Waller factor. First shell: yellow lines; Second shell: blue lines; Third shell: green lines.

	Scatter path	CN	$R \text{ (\AA)}$	$\Delta E \text{ (eV)}$	$\sigma^2 \text{ (\AA}^2\text{)}$	R-factor
OCP after reaction	Cu–O	2.00±0.05	1.82±0.13	1.2±1.3	0.00407±0.00675	0.57%
	Cu–N	2.00±0.06	1.99±0.01	1.2±1.3	0.00741±0.00635	
	Cu–N	2.02±0.20	2.87±0.08	1.2±1.3	0.01192±0.00750	
	Cu–C	2.03±0.16	3.22±0.22	1.2±1.3	0.02749±0.00735	
	Cu–C	1.01±0.07	3.28±0.17	1.2±1.3	0.02960±0.00648	
	Cu–Cu	2.03±0.16	3.10±0.28	1.2±1.3	0.01217±0.00671	
	Cu–C	1.02±0.14	3.05±0.36	1.2±1.3	0.01810±0.01012	
	Cu–N	1.01±0.07	3.37±0.36	1.2±1.3	0.03094±0.00464	
	Cu–N	1.01±0.08	4.11±0.26	1.2±1.3	0.02602±0.01044	
	Cu–C	2.02±0.17	4.29±0.37	1.2±1.3	0.02336±0.00552	

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