

Supporting Information

Constructing Cu⁰/Cu⁺ interfaces on Cu-based MOFs derivatives to promote the adsorption stability of intermediates in the process of CO₂ electroreduction to C₂ products

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***In situ* ATR-FTIR instruments**

In this study, *in situ* ATR-FTIR tests were performed in a commercially available spectroelectrochemical cell with a three-electrode configuration. First, 20 μL of catalyst ink (1 mg/mL) was uniformly dripped onto the surface of the gold-film electrode and dried at room temperature, and this operation was repeated after it was allowed to dry. Then, the prepared loaded catalyst electrode was used as the working electrode, and the Pt wire and saturated Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. *In situ* ATR-FTIR tests were carried out on a Nicolet Is50 Fourier Transform Infrared Spectrometer equipped with a spectroscopic component VeeMAX III from PIKE, USA and a liquid nitrogen cooled IR spectrometer detector. The spectroelectrochemical cell was connected to a CHI 660E electrochemical analyzer for electrochemical measurements. Prior to the *in situ* tests, the working electrode to be tested was first electrically reduced in CO_2 -saturated 0.1 M KHCO_3 at -0.9 V (relative to Ag/AgCl) for 20 min. background spectra were recorded without applying any potentials or adding any catalysts in order to eliminate the effect of the gold layer. Subsequently, *in situ* spectra of the catalyst-loaded electrodes were recorded at a gradient voltage of -0.5 ~ -1.5 V. To reduce the effect of CO_2 and water vapor, CO_2 drumming was stopped during the *in situ* test. The spectral resolution was 4 cm^{-1} and each spectrum was scanned 10 times.

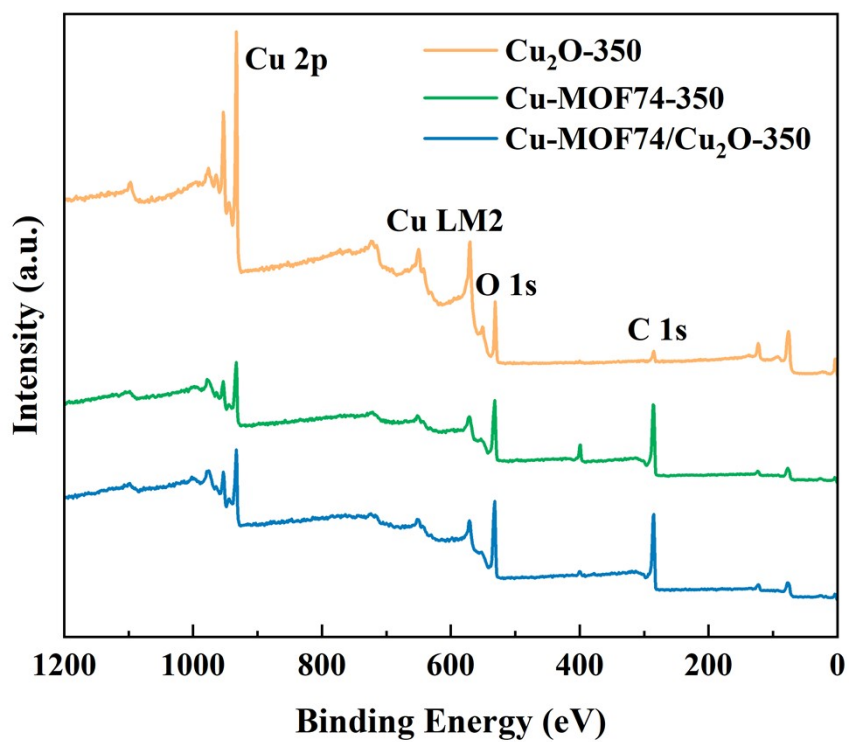


Fig. S1. XPS full spectra of Cu₂O-350, Cu-MOF74-350, and Cu-MOF74/Cu₂O-350.

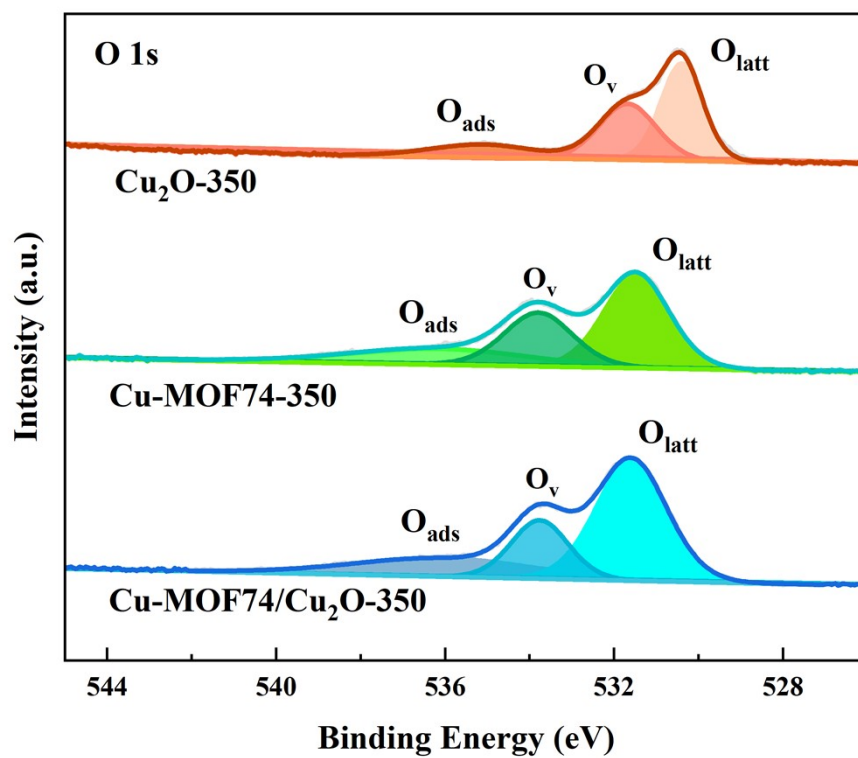


Fig. S2. O 1s XPS spectra of Cu₂O-350, Cu-MOF74-350, and Cu-MOF74/Cu₂O-350.

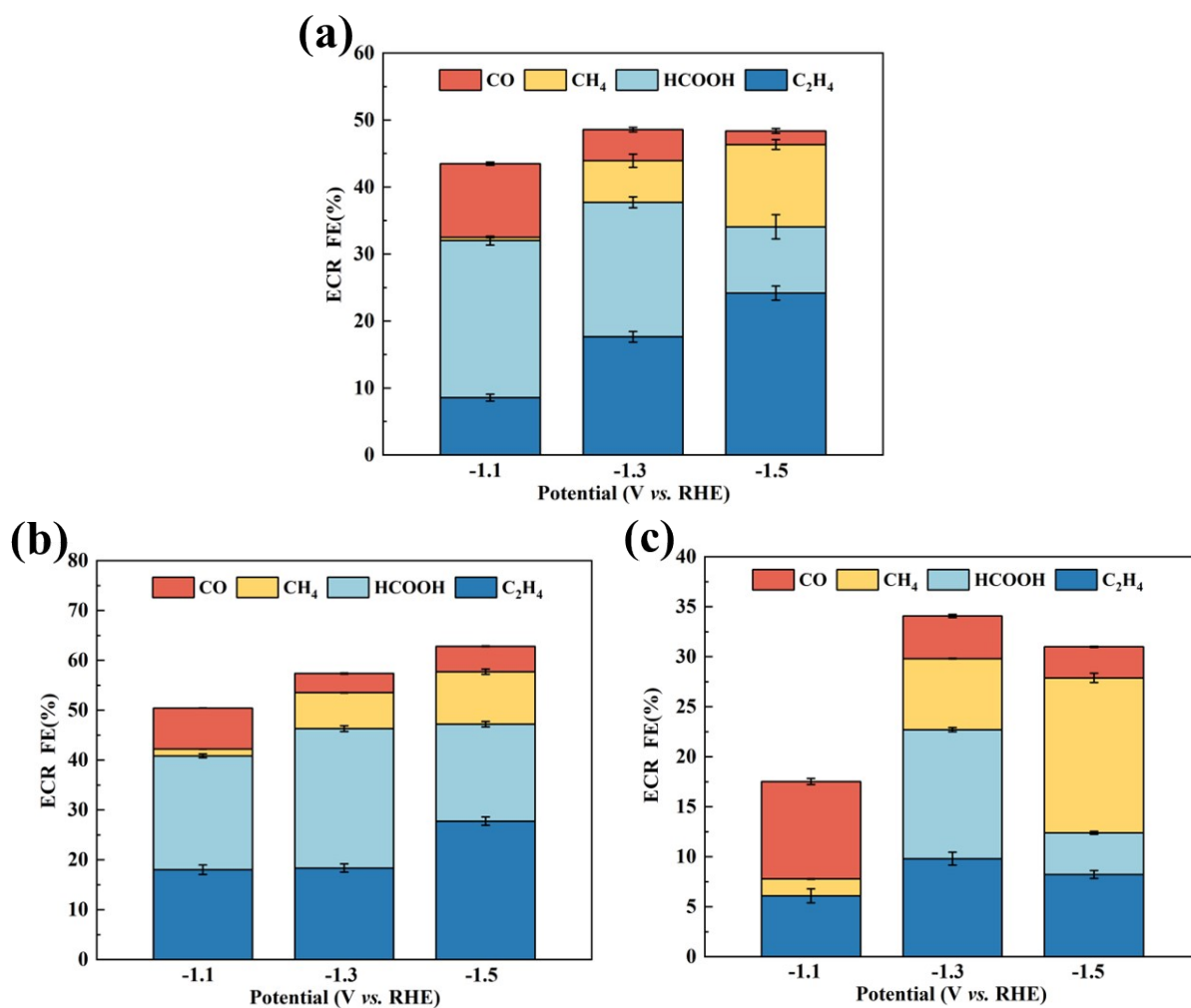


Fig. S3. Selectivity of CO₂RR products measured in 0.1 M KHCO₃ electrolyte under an applied bias of -1.3 V for (a) Cu-MOF74/Cu₂O, (b) Cu-MOF74/Cu₂O-250, (c) Cu-MOF74/Cu₂O-450.

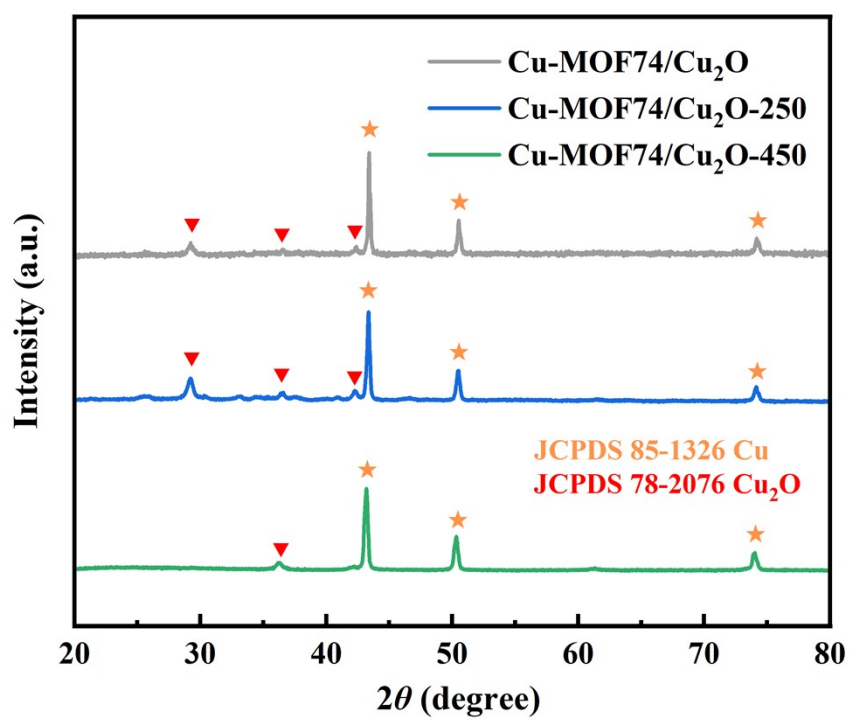


Fig. S4. XRD spectra of Cu-MOF74/Cu₂O, Cu-MOF74/Cu₂O-250 and Cu-MOF74/Cu₂O-450.

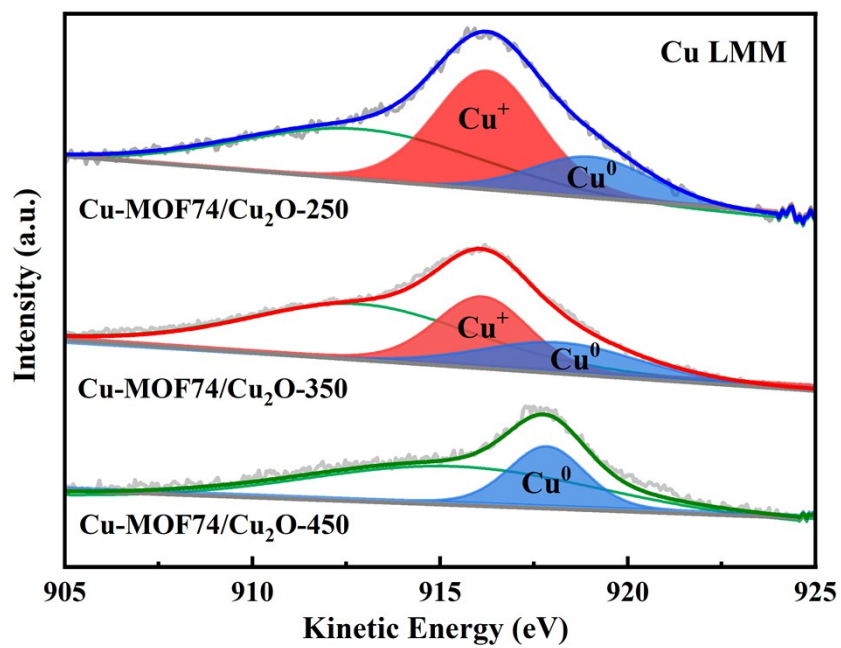
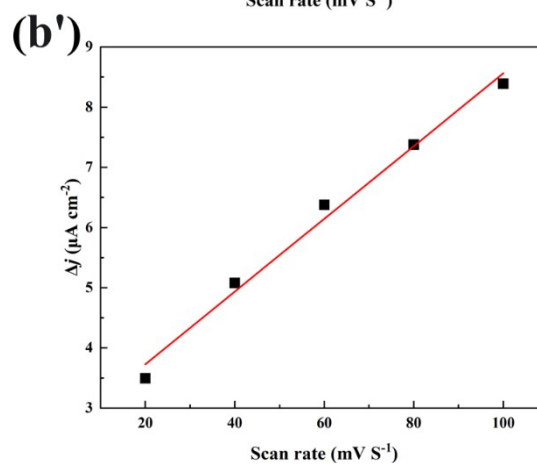
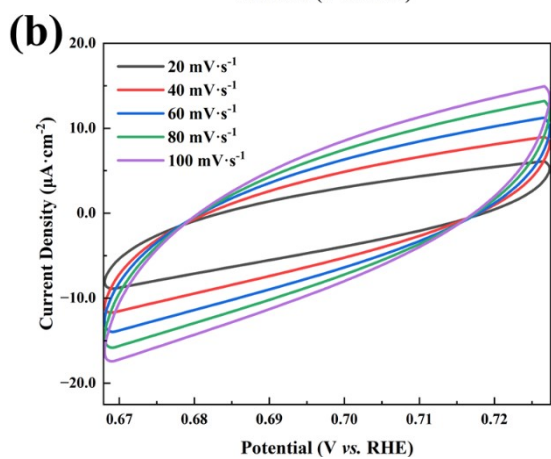
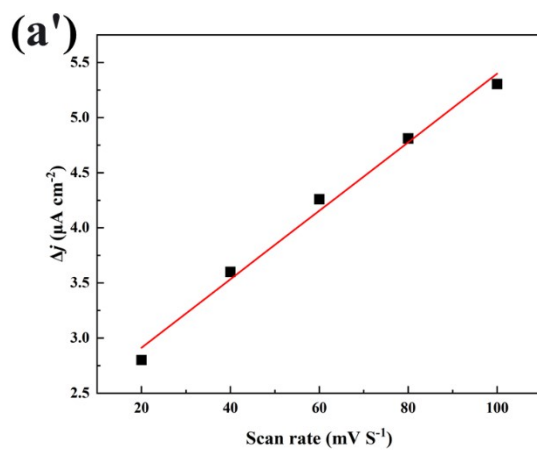
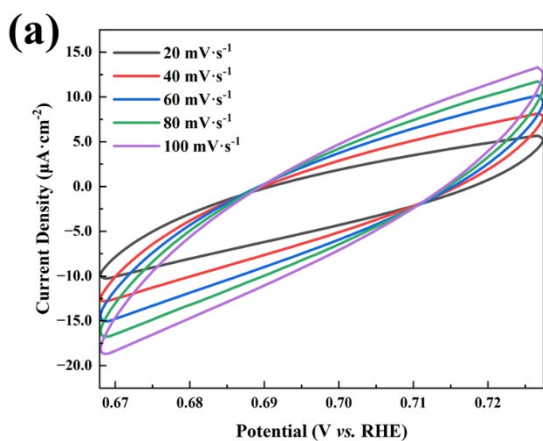


Fig. S5. Cu LMM spectra of Cu-MOF74/Cu₂O-250, Cu-MOF74/Cu₂O-350, and Cu-MOF74/Cu₂O-450.



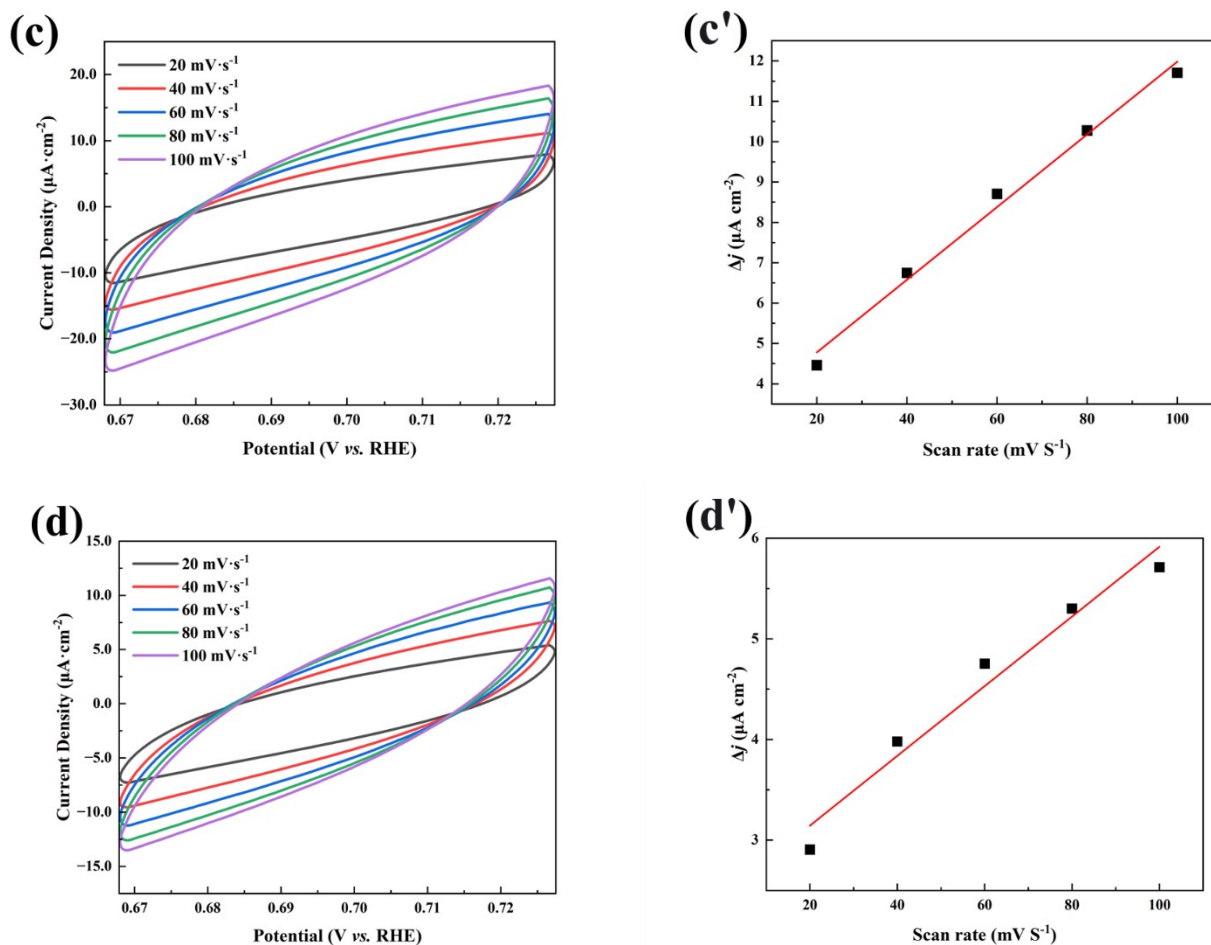


Fig. S6. CV curves at different scan rates of 20-100 $\text{mV}\cdot\text{s}^{-1}$ for (a) Cu-MOF74/Cu₂O, (b) Cu-MOF74/Cu₂O-250, (c) Cu-MOF74/Cu₂O-350, (d) Cu-MOF74/Cu₂O-450 and the corresponding double-layer capacitance (C_{dl}).

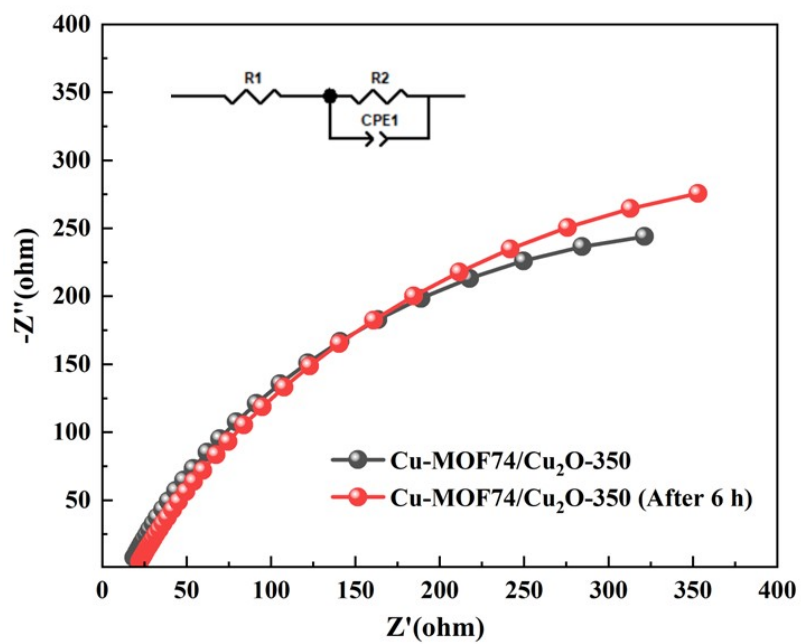


Fig. S7. Nyquist plots of Cu-MOF74/Cu₂O-350 before and after 6 hours of continuous reaction.

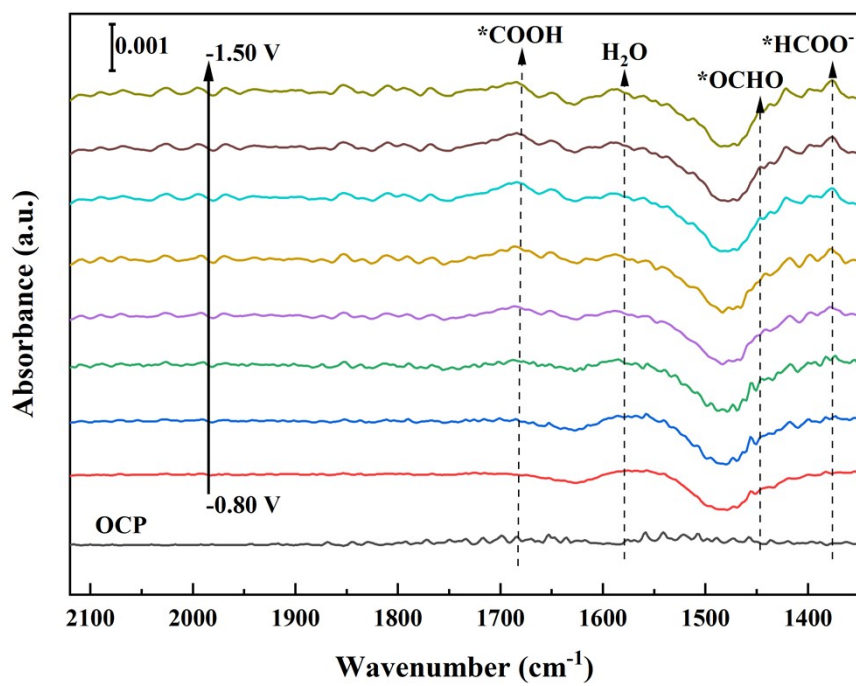


Fig. S8. *In situ* infrared spectra of Cu-MOF74-350 under different biases.

Table S1. Proportion of oxygen species on the surfaces of Cu₂O-350, Cu-MOF74-350, and Cu-MOF74/Cu₂O-350.

Sample	O _v %	O _{latt} %	O _{ads} %
Cu ₂ O-350	36.35	46.73	16.92
Cu-MOF74-350	28.92	48.00	23.08
Cu-MOF74/Cu ₂ O-350	22.08	55.99	21.93

Table S2. Specific surface area measurements of Cu-MOF74-350 and Cu-MOF74/Cu₂O-350.

Sample	BET specific surface area m ² /g	Average pore diameter nm	Total pore volume mL/g
Cu-MOF74-350	106.88	9.99	0.41
Cu-MOF74/Cu ₂ O-350	59.98	16.62	0.18

Table S3. Comparison of CO₂RR performance with other copper-based electrocatalysts.

Catalyst	Electrolyte	Potential /(V vs. RHE)	FE%(C ₂ H ₄)	Ref.
Cu porphyrin	0.5 M KHCO ₃	-0.976	17%	[1]
Cu phthalocyanine	0.5 M KCl	-1.7	25%	[2]
HKUST-1 + Cu nanoparticle	0.5 M NaHCO ₃	-2.0	12%	[3]
Cu ₂ O/NRGO	0.1 M KHCO ₃	-1.4	19.7%	[4]
Cu ₂ O/ILGS-100	0.1 M KHCO ₃	-1.15	31.1%	[5]
3% SnO ₂ -CuO NS	0.5 M KHCO ₃	-1.0	22.0%	[6]
Fe-TCPP@Cu	0.5 M KHCO ₃	-1.17	33.42%	[7]
Cu- MOF74/Cu₂O- 350	0.1 M KHCO₃	-1.30	32.48%	This work

References

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