

Electronic Supporting Information

The Spatial Distribution of Cobalt Phthalocyanine and Copper Nanocubes Controls the Selectivity towards C₂ Products in Tandem Electrocatalytic CO₂ Reduction

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Experimental Section

Chemicals and Materials. All chemicals were used as received, with no further purification. Tri-n-octylphosphine oxide (TOPO, 99%), copper(I) bromide (CuBr, 99.999%), oleylamine (OLAM, 70%), toluene (anhydrous, 99.8%), cobalt phthalocyanine (β -form, dye content 97 %, CoPc), carbon black (Sigma Aldrich < 500 nm), Nafion (5 wt %), cobalt (II) chloride (AnhydroBeads™, -10 mesh, 99.9% trace metals basis), 29H,31H-phthalocyanine (β -form, 98%) and N,N-dimethylformamid (anhydrous, 99.8%, DMF) were purchased from Sigma-Aldrich. K₂CO₃ (99+ %) was purchased from Acros. Glassy carbon electrodes (2.5 x 2.5 x 0.3 cm Sigradur G) were purchased from Hochttemperatur-Werkstoffe GmbH (HTW). SIGRACET 39BC gas diffusion electrodes were purchased from the Fuel Cell Store.

Synthesis of Cu_{cub}. Cu cubes were synthesized following the procedure introduced in our previous work.¹ TOPO (24 mmol, 9.37 g) was first mixed with OLAM (117ml) in a three-neck 250 ml flask equipped with reflux condenser and internal thermocouple temperature controller and degassed under vacuum with vigorous magnetic stirring at room temperature. CuBr (5 mmol, 0.71 g) was then added to the solution under nitrogen flow. The resulting solution was rapidly heated to 260 °C and held at reflux at this temperature for 1 h before letting it cool down to room temperature. The solution was then transferred to a glove box and divided into, 6 × 50 mL centrifuge tubes. Hexane (22.5 ml) was added to each tube and then centrifuged at 6000 rpm for 10 min. The precipitate was recovered in a minimal amount of hexane, an equal amount of ethanol was added, and then the resulting solution was centrifuged for an additional 10 min at 6000 rpm. The precipitate was finally recovered with toluene and stored in a glove box. The Cu concentration of the Cu cube stock solution was measured by ICP-OES, as described below. Typically, a Cu cube stock solution with a concentration of 0.06 mM was obtained.

Synthesis of the tandem catalysts.

The tandem catalysts were synthesized using the procedures illustrated in Scheme S1, with details described below.

Ligand-stripping. Before the electrochemical testing, it was necessary to remove the native ligands on Cu cubes to avoid possible interference with the catalytic activity. A mild-solvent washing method is effective for this purpose.¹ Specifically, the desired amount of Cu_{cub} (typically 7 μl that contains 26.6 μg of copper) from the Cu stock solution was precipitated via centrifugation after addition of the same volume of acetone. The supernatant was discarded and the precipitate was dissolved in 7 μl of toluene. These steps were repeated 3 times and then the resulting precipitate was dissolved in the desired amount of toluene for the ink preparation.

CoPc-Cu_{cub}/C. 400 μL of CoPc dissolved in DMF (0.3 mg/20 mL, 0.026 mM) was added to the Cu cubes (26.6 μg dispersed in 5 μL of toluene) and sonicated for 1 min. The obtained mixture was kept in the glove box overnight to allow adsorption of the CoPc on the Cu_{cub}. The solution was then centrifuged at 13300 rpm for 5 min. The supernatant was discarded and the precipitate was re-dispersed in DMF and centrifuged to remove excess not adsorbed molecules. Then tandem catalyst was washed via reprecipitation in toluene to remove DMF traces. The final precipitate was re-dispersed in 5 μL toluene and was used for the electrode preparation.

The catalyst inks were prepared by thorough mixing via sonication of the prepared **CoPc-Cu_{cub}** with 40 μL of carbon black suspension (Carbon black suspension: 2.5 mg of carbon black were dispersed in 980 μL of isopropanol and 20 μL Nafion and sonicated for 1 h).

For the loading experiments in **Figure S4**, 200 μL and 100 μL of CoPc dissolved in DMF (0.3 mg/20 mL, 0.026 mM) were added to the Cu cubes (26.6 μg dispersed in 5 μL of toluene). The washing and ink preparation process was the same as the typical 400 μL sample described above.

CoPc-C/Cu_{cub}. A CoPc-C stock solution was prepared as it follows. First, 0.3 mg of CoPc were dissolved in 20 mL of DMF to produce a CoPc solution with a concentration of 0.026 mM. Then, 1.25 mL of this solution were added to 5 mL isopropanol solution containing 0.625 mg of carbon black. The obtained mixture was sonicated for 30 min and then stirred at room temperature for 24 h. Subsequently, the mixture was centrifuged and the precipitate was washed via sequential centrifugation/dissolution steps in DMF. The precipitate consisted of carbon black saturated with CoPc while the supernatant, appearing light blue due to the presence of unabsorbed CoPc, was discarded. Finally, the carbon black loaded with the CoP was re-dispersed in isopropanol (0.25 mL) and 5 μL Nafion were added to obtain the final stock solution used for the electrochemical measurements (stock **CoPc-C**).

The catalyst inks for electrocatalysis were prepared by mixing Cu_{cub} (26.6 μg dispersed in 5 μL of toluene) with 40 μL of the stock **CoPc-C**.

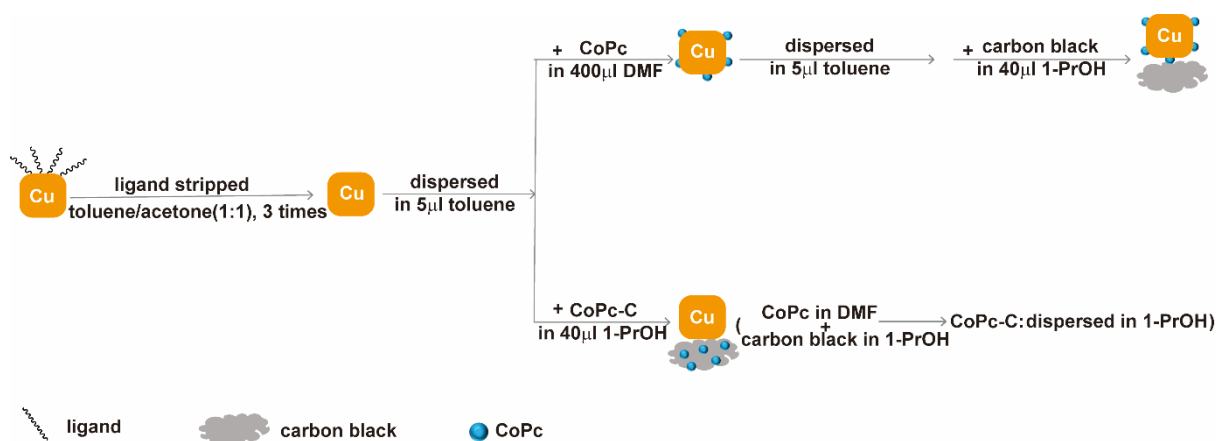
For the loading experiments in **Figure S4**, 20 μL, 10 μL and 5 μL of the stock **CoPc-C** were mixed with the Cu_{cub} (26.6 μg dispersed in 5 μL of toluene) and additional 20 μL, 30 μL and 35 μL of carbon black suspension were added respectively to keep the same total amount of carbon.

Pc-Cu_{cub}/C. The synthesis procedure of **Pc-Cu_{cub}** is the same as **CoPc-Cu_{cub}** except that the CoPc was replaced by the Pc ligand. 400 μL of Pc dissolved in DMF (0.3 mg/20 mL, 0.029 mM) were added to the Cu cubes (26.6 μg dispersed in 5 μL of toluene) and sonicated for 1 min. Then, the solution was kept in the glove box overnight. Before testing, the mixture was centrifuged and the precipitate was also washed with DMF and toluene to remove any free Pc. Finally, the precipitate was re-dispersed in 5 μL of toluene for testing. Catalyst inks for electrocatalysis were prepared by thoroughly mixing **Pc-Cu_{cub}** in 5 μL toluene and 40 μL carbon black suspension.

Co-Cu_{cub}/C. Electrodeposition method was chosen for synthesis of **Co-Cu_{cub}** catalyst, as the process did not require any external reagent and, hence, maintained a clean surface for the subsequent CO₂RR process. 400 μL of CoCl₂ dissolved in DMF (0.035 mg/20 mL, 1.35 mM) were added to the Cu cubes (26.6 μg dispersed in 5 μL of toluene) and sonicated for 1 min. The obtained mixture was kept in the glove box overnight to allow adsorption of the CoCl₂ on the Cu_{cub}. Before testing, the mixture was centrifuged and the precipitate was also washed with DMF and toluene to remove any free CoCl₂. The inks for electrodeposition were prepared by thoroughly mixing CoCl₂-Cu_{cub} in 5 μL toluene and 40 μL carbon black suspension.

To prepare the Co-Cu_{cub}/C working electrode, the CoCl₂-Cu_{cub}/C ink was first drop-casted on the glassy carbon plates within a circular area of 1.33 cm². Then, the material was reduced at 0

V vs RHE in 0.1 M KHCO₃ electrolyte. The reduction process required the flow of 5.1 C of charge. Finally, the Co-Cu_{cub}/C electrode was washed with Milli-Q H₂O and was then used for the subsequent CO₂RR process in fresh 0.1 M KHCO₃ electrolyte.



Scheme S1. Schematic of the procedure to prepare CoPc-Cu_{cub}/C and CoPc-C/Cu_{cub}.

Material characterization.

Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai-Spirit at 120 kV. The as-synthesized materials were drop-casted on a copper TEM grid (Ted Pella, Inc.) prior to imaging. High-angle annular darkfield scanning TEM (HAADF-STEM) images and X-ray energy dispersive (EDX) elemental maps were acquired on a FEI Tecnai- Osiris at 200 kV. SEM images were acquired on a FEI Teneo, using an inlens (Trinity) detector and EDX detector.

Attenuated total reflectance Fourier transform infrared spectroscopy was performed using a Perkin Elmer Spectrum 100 instrument.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed on an Agilent 5100 model to determine the solution concentration of synthesized Cu cubes. The sample solution was prepared by digesting overnight in 70% ICP grade HNO₃ followed by opportune dilution with DI water to obtain a 2% acid content needed for the analysis.

Electrocatalytic Measurements.

H-cell: Catalyst inks were drop-cast within a circular area of 1.33 cm² on glassy carbon electrodes, which were used as the working electrodes. Platinum foil and an Ag/AgCl electrode (leak free series, Innovative Instruments, Inc.) were used as the counter electrode and reference electrode, respectively. A Selemion AMV anion exchange membrane was used to separate the anodic and cathodic compartments. Before loading electrocatalysts, the glassy carbon substrates were typically polished using a 0.05 μm Al₂O₃, followed by rinsing with Milli-Q water and ultrasonication in acetone 2× for 5 min each. Electrocatalytic measurements were performed with a potentiostat (Biologic SP-300) in a custom-built gas tight three electrode cell for 60 minutes in a CO₂-saturated 0.1 M KHCO₃ as the electrolyte.

Gas-fed Flow-cell: The utilized electrolyzer possesses a geometry similar to those reported in literature and was previously used in our group.² The electrodes were prepared by air brushing the catalyst inks on the micro-porous layer of a Sigracet BC39 GDL with area of 1.33 cm², where the total loading was 20 times scaled up compared to the loading of the H-cell, which is 400 μg/cm² of Cu_{cub} and around 20 nmol/cm² of CoPc per electrode. An Ag/AgCl electrode (leak free series, Innovative Instruments, Inc.) were used as the reference electrode as well, and anionic exchange membrane (Fumasep FAB-PK-130) was interposed between the anolyte and the catholyte compartments, as counter electrode a nickel mesh (Mc Master–Carr, 100x100 mesh size) was used.

Products analysis.

For the analysis of gaseous products, a gas chromatograph (GC 8610C, SRI instruments) equipped with a HayeSep D porous polymer column, thermal conductivity detector, and flame ionization detector was used. Ultra-high purity N₂ (99.999%) was used as a carrier gas. The concentration of gaseous products was determined using calibration curves from standard gas mixtures. For liquid product analysis, high-performance liquid chromatography (HPLC) was carried out on an UltiMate 3000 instrument from Thermo Scientific. 5 mM H₂SO₄ was used as the eluent for the HPLC measurements. During electrolysis, CO₂ (99.999 %, Carbagas) was constantly bubbled through the electrolyte to prevent depletion of CO₂ in the electrolyte and to allow continuous analysis of gaseous products via the GC.

Results Section

Table S1. CoPc adsorbed on the Cu_{cub} or carbon black for the CoPc-Cu_{cub} and CoPc-C calculated from ICP-OES repeated on three different samples.

Sample	Cu	CoPc	Cu loading on electrode	CoPc loading on electrode	
	(ppm)	(ppm)	(μg)	(μg)	(nmol/cm^2)
CoPc-Cu	0.27 ± 0.06	0.08 ± 0.03	27 ± 7	0.8 ± 0.3	1.1 ± 0.4
CoPc-C	0	0.07 ± 0.04	0	0.7 ± 0.4	0.9 ± 0.5

Determination of the molecular catalyst loading from ICP-OES: The CoPc-Cu_{cub} tandem catalyst and the dried CoPc-C (40 μL), prepared as described above, were collected from the working electrode and digested overnight in 285 μL , 70% ICP grade HNO₃ followed by dilution with DI water to obtain a 10 mL, 2% acid content needed for the analysis.

Calculation of the ratio between the number of CoPc molecules and of the number of Cu_{Cub} in CoPc-Cu_{cub}

The total number of Cu_{cub} can be calculated as it follows, and corresponds to 3.4×10^{10}

$$N_{\text{number of Cu cube}} = \frac{N_{\text{total Cu atom}}}{N_{\text{Cu atom in each Cu cube}}}$$

$$N_{\text{total Cu atom}} = \frac{m_{\text{Cu loading}}}{MW_{\text{Cu}}} \times N_A,$$

$$N_{\text{Cu atom in each Cu cube}} = N_{\text{number of atoms per unit cell}} \times \frac{V_{\text{Cu cube}}}{V_{\text{per unit cell}}}$$

$$= 4 \times \frac{a_{\text{length}}^3}{a_{\text{lattice parameter}}^3}$$

The total number of CoPc can be calculated as it follows and corresponds to 8.5×10^{14}

$$N_{number\ of\ CoPc} = \frac{m_{CoPc\ loading}}{MW_{CoPc}} \times N_A$$

Cu loading: (26.6 ± 6.5) μg ; MW_{Cu} : 63.5 g/mol; Lattice parameter of Cu: 3.61 Å; Edge length of the Cu_{Cub} : 36 ± 2 nm (from statistical analysis on 100 particles in TEM images); CoPc loading: (0.81 ± 0.30) μg ; MW_{CoPc} : 571.5 g/mol.

Calculation of the surface coverage of CoPc on the Cu_{cub} in CoPc- Cu_{cub}

$$\text{Surface Coverage}_{CoPc\ on\ Cu\ cube} = \frac{\text{Total Surface Area}_{CoPc}}{\text{Total Surface Area}_{Cu\ cube}}$$

If we assume the planar CoPc as a square, we can approximate the length of molecule to be 1.2×10^{-9} m. ³

Based on their calculated total numbers, the total surface area of CoPc is $(12.4 \pm 4.4) \times 10^{-4}$ m², while the total surface area of Cu_{cub} is $(7.4 \pm 1.8) \times 10^{-4}$ m².

Thus, the calculated surface coverage is around 1.7. If precisely one monolayer of CoPc was present on the Cu_{cub} , the coverage should be equal or less than 1. The higher coverage may be due to either measurement errors (ICP, size, etc) or the CoPc self-stacking on the surface.

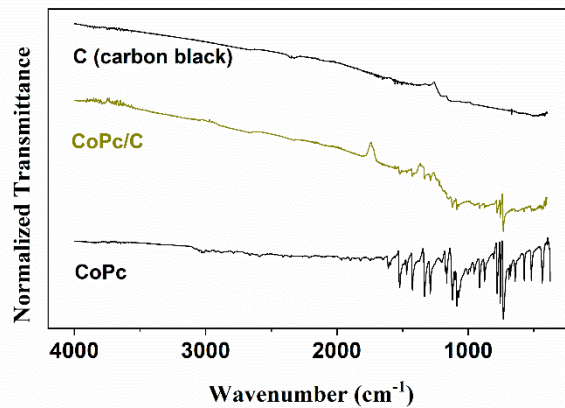


Figure S1. FT-IR spectra of carbon black, CoPc/C and CoPc measured as films.

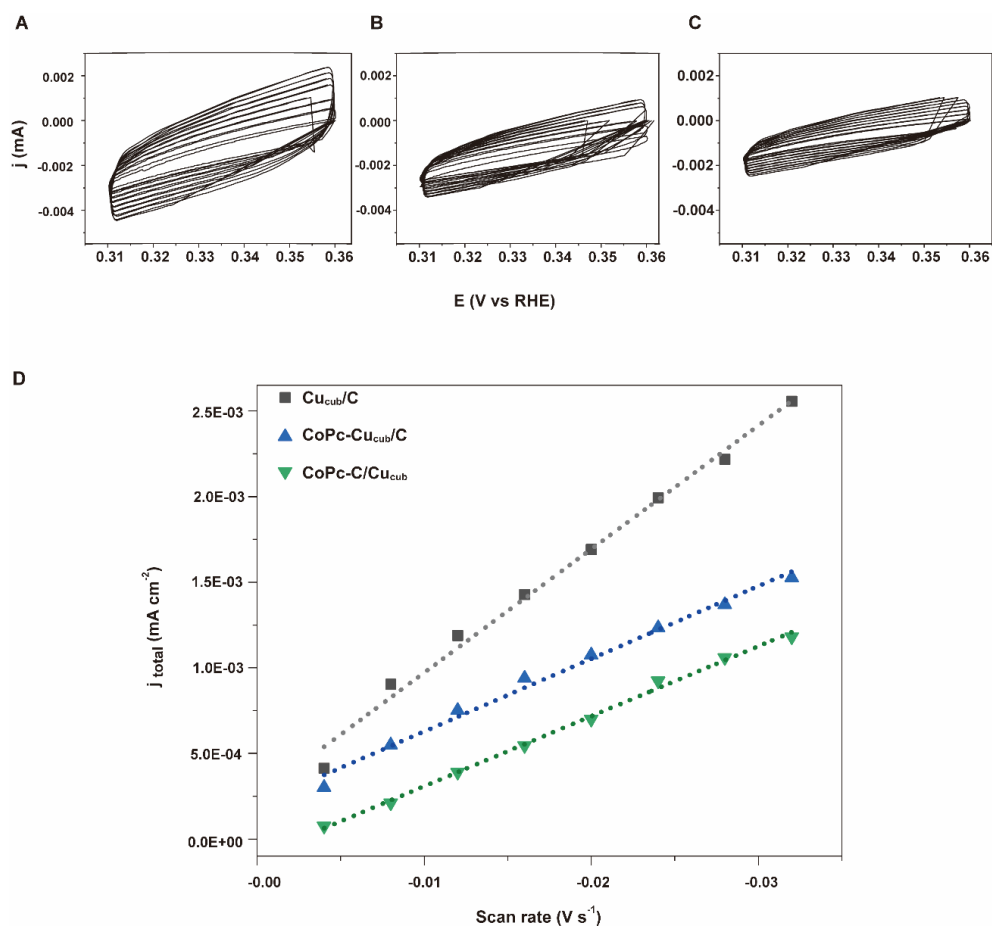


Figure S2. Representative examples of cyclic voltammograms used to determine the capacitance and the electrochemically active surface areas (ECSAs) for samples. (a) $\text{Cu}_{\text{cub}}/\text{C}$, (b) $\text{CoPc-Cu}_{\text{cub}}/\text{C}$, (c) $\text{CoPc-C}/\text{Cu}_{\text{cub}}$ and (d) j_{total} plotted against the scan-rate to determine the sample capacitance. The j_{cathodic} and j_{anodic} values at 0.325 V vs RHE were taken to calculate j_{total} .

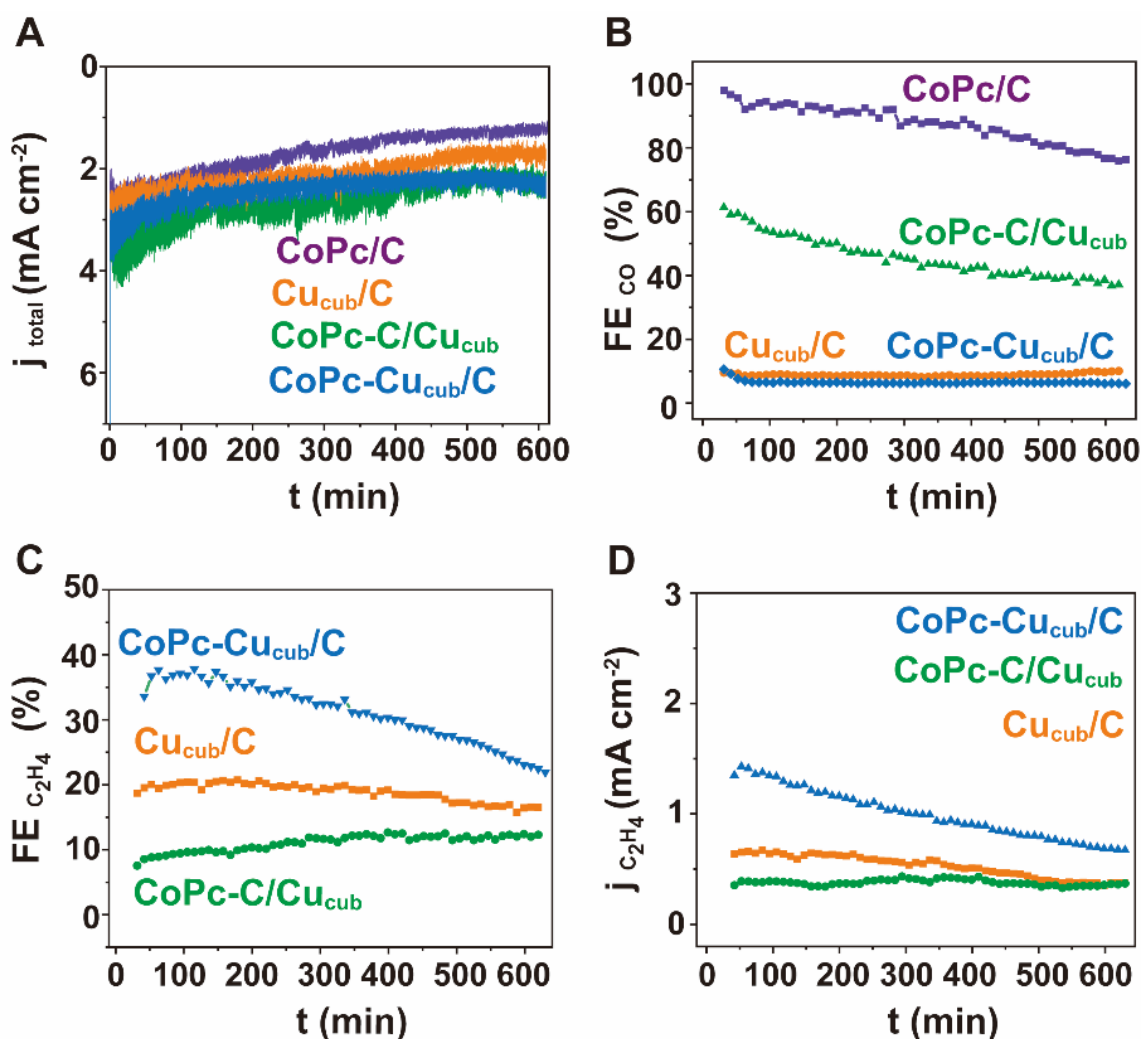


Figure S3. (A) Total current density, (B) FE_{CO} , (C, D) $FE_{C_2H_4}$ and $j_{C_2H_4}$ for CoPc/C, CoPc-Cu_{cub}/C, CoPc-C/Cu_{cub} and Cu_{cub}/C. CO₂RR was performed at -1.05 V vs RHE for 10 hours in the H-cell using 0.1 M KHCO₃ as the electrolyte. The loading of Cu_{cub} was 20 $\mu\text{g}/\text{cm}^2$ and the loading of CoPc anchored on Cu_{cub} and on carbon was 1.1 nmol/cm^2 and 0.9 nmol/cm^2 , respectively.

We note that the performance of CoPc-Cu_{cub}/C slightly decrease over time. Considering that the Cu_{cub}/C are rather stable under these conditions, one possible explanation is the detachment of the CoPc over time from the Cu_{cub}. However, this hypothesis remains to be verified in future work.

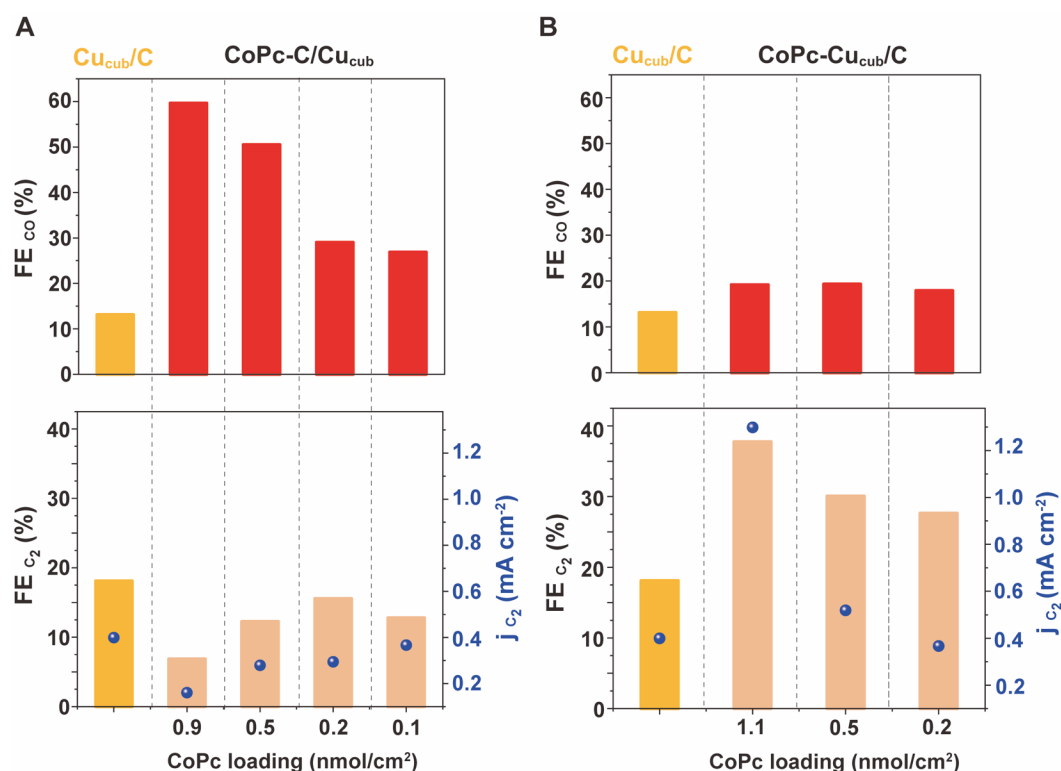


Figure S4. (A) FE_{CO} , FE_{C_2} and j_{C_2} at different CoPc loadings for the CoPc-C/Cu_{cub} catalysts. The loading of Cu_{cub} was kept constant at 20 $\mu\text{g}/\text{cm}^2$ and a different amount of CoPc-C was mixed with the Cu_{cub} to obtain a CoPc loading of 0.9 nmol/cm², 0.5 nmol/cm², 0.2 nmol/cm² and 0.1 nmol/cm². (B) FE_{CO} , FE_{C_2} and j_{C_2} at different CoPc loadings for the CoPc-Cu_{cub}/C catalysts. The loading of Cu_{cub} was kept constant at 20 $\mu\text{g}/\text{cm}^2$ and a different amount of CoPc was anchored on Cu_{cub} to obtain a CoPc loading of 1.1 nmol/cm², 0.5 nmol/cm² and 0.2 nmol/cm². All experiments were performed in an H-cell at -1.0 V vs RHE in 0.1 M KHCO₃.

In the CoPc-C/Cu_{cub}, the FE_{CO} decreases with decreasing CoPc loading. The FE_{C_2} remains below that of pure Cu, however it does increase as the loading of the CoPc decreases, probably because less Cu sites are passivated by the CoPc.

In the CoPc-Cu_{cub}/C, the FE_{CO} remains quite constant at different CoPc loading. The FE_{C_2} remains always higher than that of pure Cu but decreases with decreasing CoPc loading. This different behavior compared to the CoPc-C/Cu_{cub} can be explained in relation to the tandem process itself. The higher CoPc loading generates higher CO local concentration, which implies higher *CO surface coverage and more C-C coupling, thus higher FE_{C_2} and j_{C_2} . As the loading decreases, less CO and lower *CO surface coverage are generated which lower FE_{C_2} and j_{C_2} , and probably progressively lower CO is consumed, which results in the FE_{CO} remaining quite constant with the CoPc loading.

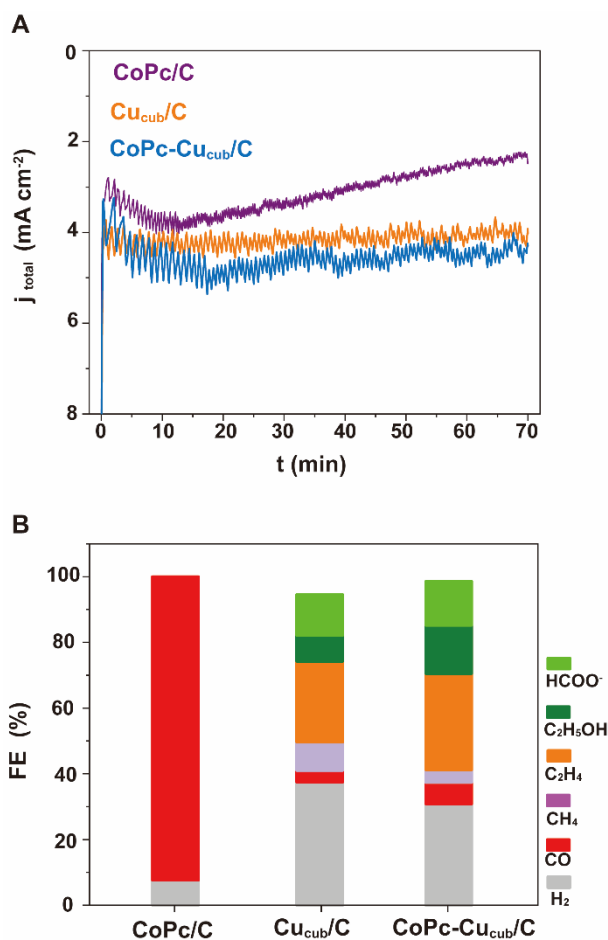


Figure S5. (A) Total current density and (B) total FEs for CoPc/C, Cu_{cub}/C and CoPc-Cu_{cub}/C at -1.15 V vs RHE with CO₂ saturated aqueous 0.1 M KHCO₃ as the electrolyte. The loading of Cu_{cub} was 20 μg/cm² and the loading of CoPc anchored on Cu_{cub} was 1.1 nmol/cm².

As expected, FE_{CH₄} starts to increase for the bare Cu_{cub} compared to the value at -1.05 V vs RHE reported in Fig. 4. The addition of CoPc in CoPc-Cu_{cub}/C does still promote C-C coupling with a similar enhancement factor but the FE_{C₂} decreases (40% at -1.15V vs RHE vs 48% at -1.05 V vs RHE).

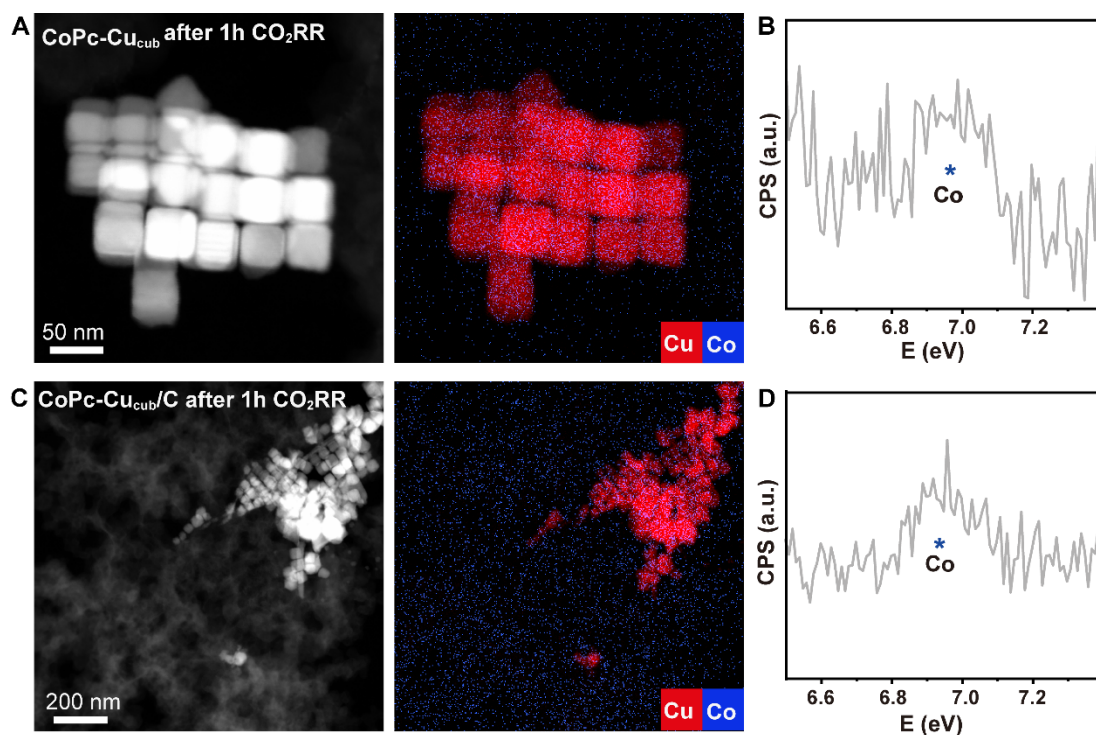


Figure S6. (A, C) HAADF-STEM images and corresponding EDX elemental maps, along with (B, D) EDX spectra for CoPc-Cu_{cub}/C (A, B) and CoPc-C/Cu_{cub} (C, D) after CO₂RR. The EDX maps show the spatial distributions of Cu (red) and Co (blue). The carbon is the low contrast material in (C) and is not coloured for the sake of clarity. The EDX spectra report the intensity of the Co signals in the map, which correspond to the Cu_{cub} in (A) and to the carbon in (C). These CO₂RR measurements were performed in an H-cell configuration using 0.1 M KHCO₃ as the electrolyte at -1.05 V vs RHE for 1 h.

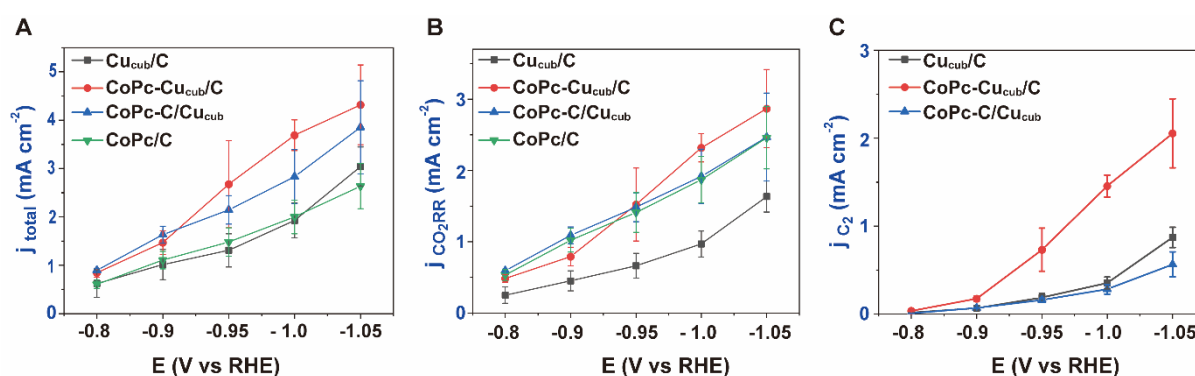


Figure S7. (A) Total current density, (B) CO₂RR partial current density and (C) C₂ products partial current density as a function of potential for CoPc/C, CoPc-Cu_{cub}/C, CoPc-C/Cu_{cub} and Cu_{cub}/C systems for CO₂RR.

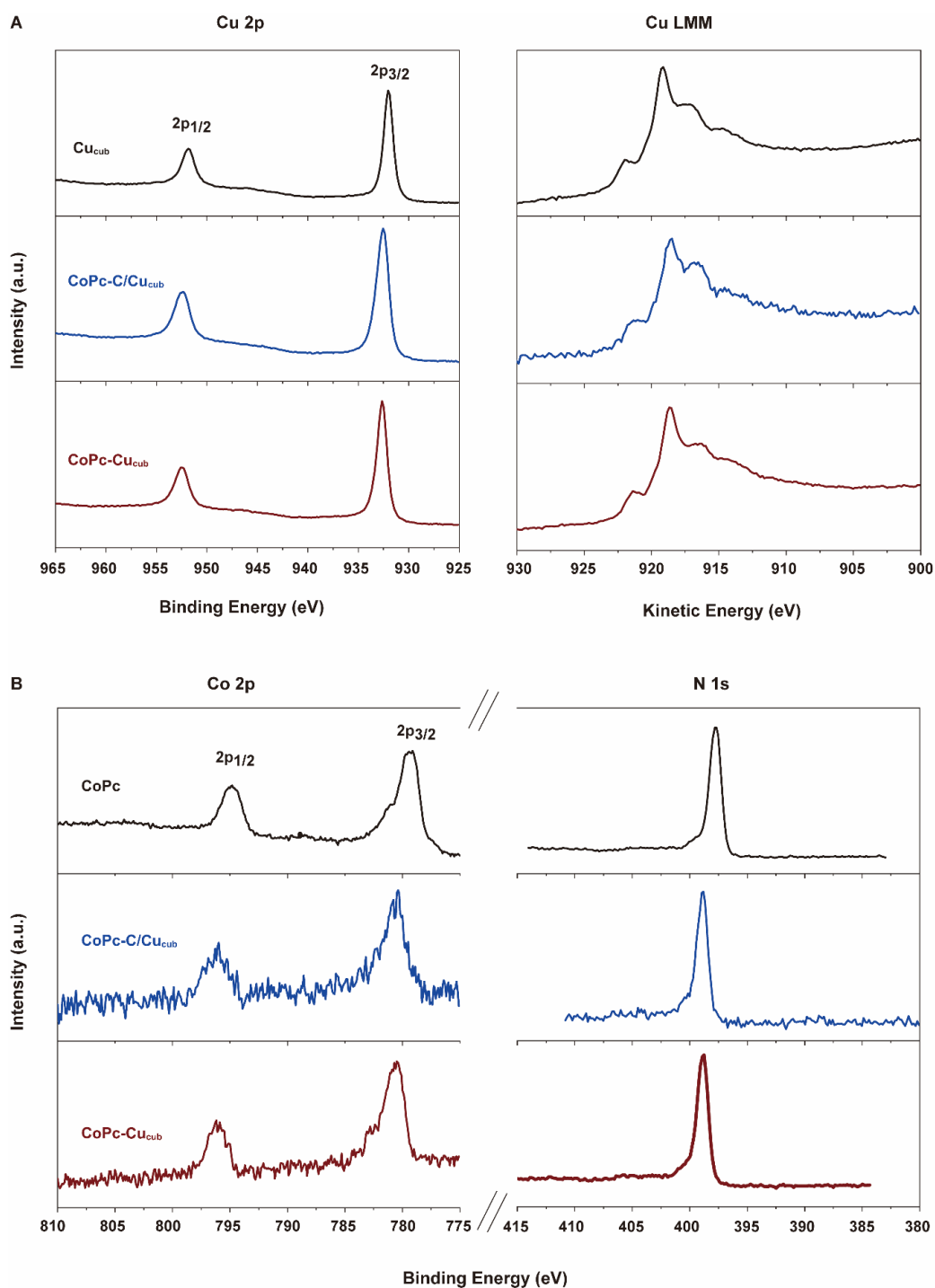


Figure S8. XPS spectra of (a) the Cu 2p and Cu LMM regions of Cu_{cub} , $\text{CoPc-Cu}_{\text{cub}}$ and $\text{CoPc-C/Cu}_{\text{cub}}$ and (b) Co 2p and N1s regions of CoPc for CoPc, $\text{CoPc-Cu}_{\text{cub}}$ and $\text{CoPc-C/Cu}_{\text{cub}}$ systems.

Table S2. Summary of key Cu data for those studied films. Here, $\Delta\alpha_{\text{Cu}}$ is the modified Auger parameter and is independent of instrument calibration, where $\Delta\alpha_{\text{Cu}} = E_{\text{k}}(\text{Cu LMM}) + E_{\text{b}}(\text{Cu } 2p_{3/2})$. Larger values of $\Delta\alpha_{\text{Cu}}$ correspond to higher Cu^0 content.

samples	B.E. $\text{Cu}2p_{3/2} / \text{eV}$	K.E. $\text{Cu}2p_{1/2} / \text{eV}$	$\Delta\alpha_{\text{Cu}} / \text{eV}$
Cu_{cub}	932.045	919.132	1851.18
$\text{CoPc-C/Cu}_{\text{cub}}$	932.413	918.506	1850.92
$\text{CoPc-Cu}_{\text{cub}}$	932.596	918.644	1851.24

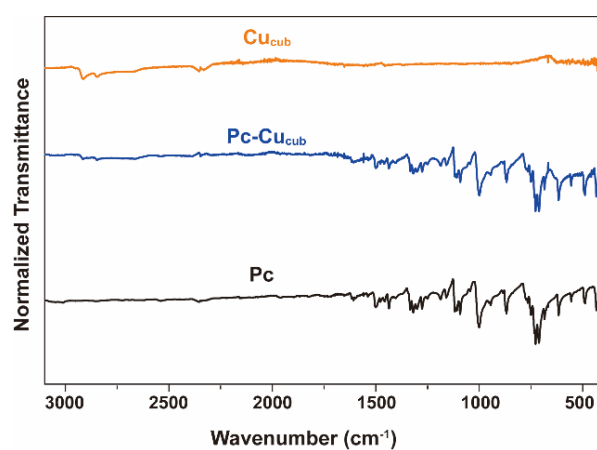


Figure S9. FT-IR spectra of ligand-stripped Cu_{cub} , $\text{Pc-Cu}_{\text{cub}}$ and Pc ligand measured as films.

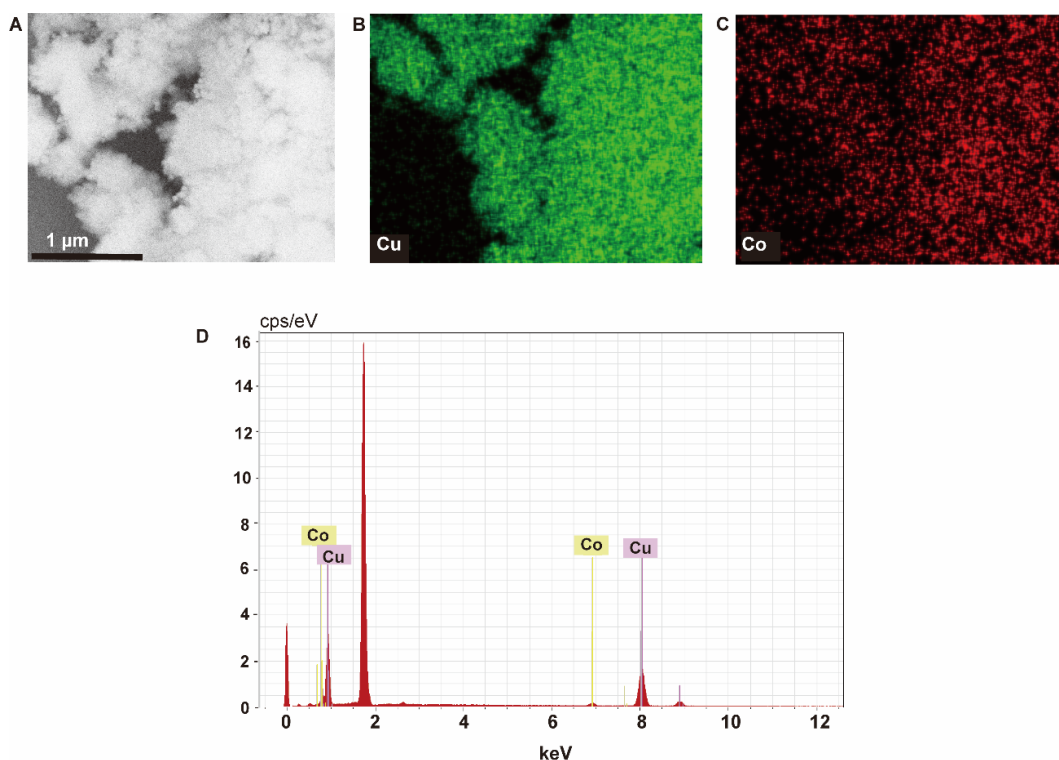


Figure S10. SEM-elemental mapping images of Co-Cu_{cub}. (A) SEM image, (B) X-ray mapping of elemental Co (light green) and (C) Cu (red), and (D) EDX spectrum of Co-Cu_{cub}.

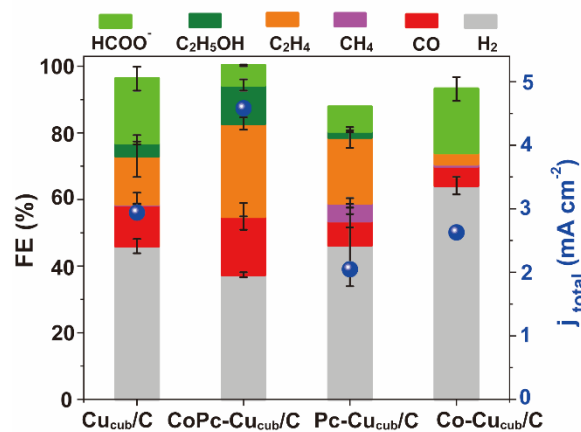


Figure S11. FEs for gaseous products (H₂, CO, CH₄, C₂H₄) and the main liquid products (i.e., formate, C₂H₅OH) in the bar plots for Cu_{cub}/C, CoPc-Cu_{cub}/C, Pc-Cu_{cub}/C and Co-Cu_{cub}/C systems in an H-cell system using 0.1 M KHCO₃ as the electrolyte at -1.0 V vs RHE. The suppression of the total current by the Pc can be due to poisoning of active sites and the variation of products distribution is consistent with functionalization effects of the Cu surface by organic molecules.⁴ The effect of Co is difficult to interpret at this stage.

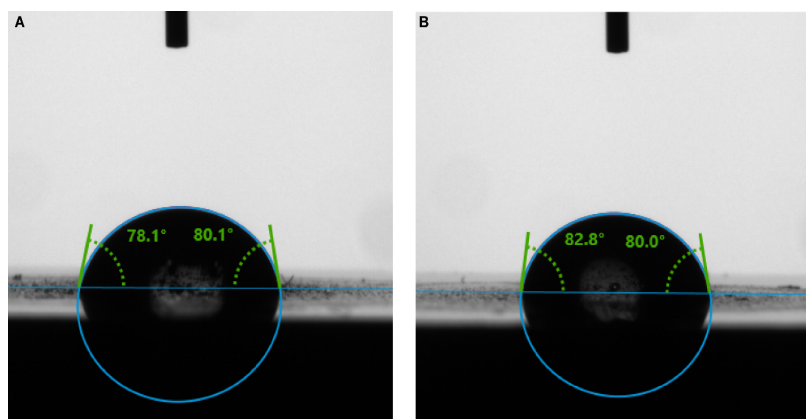


Figure S12. Water contact angle measurements for (A) CoPc-C/Cu_{cub} and (B) CoPc-Cu_{cub}/C deposited on glassy carbon electrodes used in the CO₂RR experiments. The measured contact angles are written on the images in green. While increase of hydrophobicity has been attributed to suppression of HER,^{1,5} no significant difference in wettability is observed here.

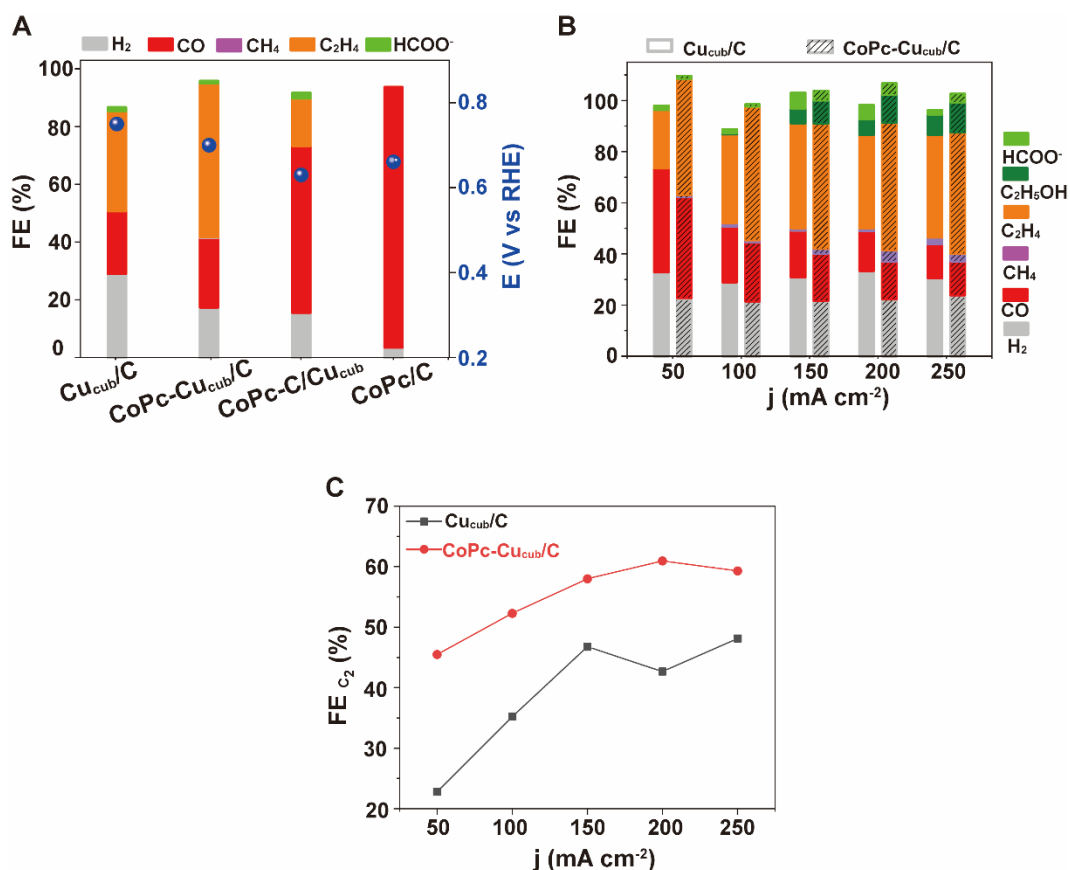


Figure S13. CO₂RR measurements in a gas-fed flow-cell using 1 M KHCO₃ as electrolyte. (A) FEs for gaseous products (H₂, CO, CH₄, C₂H₄) and the main liquid products (HCOO⁻, C₂H₅OH) for Cu_{cub}/C, CoPc-Cu_{cub}/C, CoPc/C-Cu_{cub} and CoPc/C at 100 mA/cm². (B) FEs for gaseous products (H₂, CO, CH₄, C₂H₄) and the main liquid products (HCOO⁻, C₂H₅OH) and (C) FEs for C₂ products for Cu_{cub}/C and CoPc-Cu_{cub}/C at various current densities. The loading of Cu_{cub} was 400 μg/cm² and the loading of CoPc anchored Cu_{cub} or carbon was 22 nmol/cm² and 19 nmol/cm², respectively.

References

- 1, J. Pankhurst, P. Iyengar.; V, Okatenko.; R, Buonsanti. Copper nanocrystal morphology determines the viability of molecular surface functionalization in tuning electrocatalytic behavior in CO₂ reduction, *Inorg. Chem.*, 2021, **60**, 6939.
- 2, G. L. De Gregorio, T. Burdyny, A. Loiudice, P. Iyengar, W. A. Smith, R. Buonsanti, Facet-dependent selectivity of Cu catalysts in electrochemical CO₂ reduction at commercially viable current densities. *ACS Catalysis*, 2020, **10**, 4854–4862.
- 3, M. K. Engel, K. R. K. Hokoku, Single-crystal and solid-state molecular structures of phthalocyanine complexes. *Kawamura Rikagaku Kenkyusho Hokoku*, 1997, **8**(11).
- 4, D-H Nam, P. De Luna, A. Rosas-Hernández, E. H. Sargent et al. Molecular enhancement of heterogeneous CO₂ reduction. *Nat. Mater.*, 2020, **19**, 266–276.
- 4, A. K. Buckley, M. Lee, T. Cheng, R. V. Kazantsev, D. M. Larson, W. A. Goddard III, F. D. Toste, F. M. Toma, Electrocatalysis at Organic-Metal Interfaces: Identification of Structure-Reactivity Relationships for CO₂ Reduction at Modified Cu Surfaces. *J. Am. Chem. Soc.*, 2019, **141**, 7355-7364.