Supporting Information

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Enhanced Electrocatalytic CO\textsubscript{2} Reduction to C\textsubscript{2+} Products by Adjusting the Local Reaction Environment with Polymer Binders

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1. Supporting Figure S1-24
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Characterization of the oxide catalyst

**Figure S1.** SEM images of the highly porous catalyst copper oxide, acquired at different magnifications. Scale bar for a) 20 µm b) 1 µm c) 500 nm.
Figure S2. HR-TEM images of different grains and analysis of their d-spacing. Scale bar: 2 nm. A line was drawn perpendicularly to the crystal plane and a profile plot of the grey scale is shown. The d-spacing was determined by analyzing the distance between two adjacent grey intensity peaks. Determination of d-spacing base on grey intensity level of the crystal planes and d) the corresponding HR-TEM images of different grains of as-synthesized CuO. Scale bar: 2 nm.
**Figure S3.** Chemical formula of PAA, Nafion and FEP.
Figure S4. SEM image and elemental maps of a) Cu-Nafion and b) Cu-FEP. The dispersions of Cu-Nafion and Cu-FEP were drop-casted onto a glassy carbon surface. The distribution of the polymer can be well indicated by the elemental map of Cu and F.
Figure S5. TEM images of the polymer layer coated on the CuO surface. a) Cu-PAA. b) Cu-Nafion. c) Cu-FEP. Scale bar: 20 nm.
Electrochemical performance

**Equation S1** Calculations of the partial current density and the faradaic efficiency (FE) for gas products

\[ \text{Partial current density} = \frac{\text{measured concentration} \times F \times z \times \text{pressure} \times \text{CO}_2 \text{ flow rate}}{R \times T} \]

\[ FE = \frac{\text{measured concentration} \times F \times z \times \text{pressure} \times \text{CO}_2 \text{ flow rate}}{I_{\text{total}} \times R \times T} \]

**Equation S2** Calculations of the partial current density and the faradaic efficiency (FE) for liquid products

\[ \text{Partial current density} = \frac{\text{measured molarity} \times F \times z \times \text{pressure} \times \text{CO}_2 \text{ flow rate}}{t} \]

\[ FE = \frac{\text{measured molarity} \times F \times z \times \text{pressure} \times \text{CO}_2 \text{ flow rate}}{I_{\text{total}} \times t} \]
Figure S6. $^1$H NMR spectrum for a prepared solution used for calibration curve and a sample from CuO-FEP after 800 s of reaction under –400 mA.cm$^{-2}$. 
Table S1. Chemical shift of the liquid products in NMR measurements

| Product  | Chemical shift |
|----------|----------------|
| n-propanol | 0.77           |
| Ethanol   | 1.06           |
| Acetate   | 1.87           |
| Acetone   | 2.1            |
| Methanol  | 3.23           |
| Formate   | 8.33           |
Figure S7. Faradaic efficiencies towards all CO$_2$RR products of (a)(b) Cu-PAA, (c)(d) Cu-Nafion, and (e)(f) Cu-FEP. (g)(h) Bare Cu.
Figure S8. Faradaic efficiencies towards a) C₁ and C₂⁺ products, b) C₁ products and c) Ratio of FE for C₂⁺/C₁ products of the Cu-polymer catalysts with respect to the potential, in the H-cell, with 0.1 M KHCO₃ as the electrolyte.
**Figure S9.** a) Partial current densities of $\text{H}_2$ and b) $\text{C}_2\text{H}_4$ of the three Cu-polymer catalysts with respect to the potential, obtained in the H-cell, with 0.1 M KHCO$_3$ as the electrolyte.
Figure S10. (a) Product distribution and current density of Cu-FEP at three different loadings of FEP. Obtained in H-cell, at -1.1 V vs RHE, in 0.1 M KHCO₃. (c) A typical TEM image of the Cu-FEP sample with 0.8 mg FEP/ mg catalyst.
Figure S11. Morphology of the catalyst after 1 h electrolysis of CO$_2$, at -1.1 V vs RHE, in 0.1 M KHCO$_3$. (a-c) Cu-PAA, (d-f) Cu-Nafion, (g-i) Cu-FEP. Scale bar: (a)(d)(g) 1 µm, (b)(e)(h) 100 nm, (c)(f)(i) 10 nm.
Figure S12. Water contact angle (CA) measurements of the three coated surfaces after 1 h electrolysis of CO$_2$, at -1.0 V vs RHE, in 0.1 M KHCO$_3$. 
Figure S13. Stability of a) Cu-PAA and b) Cu-Nafion over 10 h of electrolysis of CO$_2$, at -0.8 V vs RHE, in 0.1 M KHCO$_3$. 

Figure S14. Activity and product selectivity of the CO2RR towards H2 and C2+ products as a function of the hydrophilicity for 5 polymers, acquired in a) H-cell at -1.1 V vs RHE in 0.1 M KHCO3, and b) flow cell at -0.71 V vs RHE in 0.1 M KOH.
Figure S15. Product distributions of the Cu-polymer catalysts in a flow cell, with 1.0 M KOH as an electrolyte at a CO$_2$ flow rate of 110 mL/min. (a)(b) Cu-PAA, (c)(f) Cu-Nafion, and (e)(f) Cu-FEP. Lines are added to guide the eyes.
Figure S16. FE of H₂ of the three Cu-polymer catalysts with respect to the potential, obtained in the flow cell, with 1.0 M KOH as the electrolyte.
Figure S17. K$_2$CO$_3$ accumulates at the backside of the GDE of Cu-PAA after CO$_2$ electrolysis reaction.
Figure S18. a) Activity and product selectivity of the CO$_2$RR towards H$_2$ and C$_2$+ products as a function of the hydrophilicity, acquired at around -0.64 V vs RHE, for spray-coated Cu-PAA, Cu-Nafion and Cu-FEP. b) Partial current densities for C$_2$+ products of the three Cu-polymer catalysts with respect to the potential, obtained in the flow cell, with 1.0 M KOH as the electrolyte.
Figure S19. Stability of a) Cu-PAA over 10 h of electrolysis of CO$_2$, at 50 mA.cm$^{-2}$ in 1.0 M KOH and b) Cu-Nafion, and c) Cu-FEP over 15 h of electrolysis of CO$_2$, at 200 mA.cm$^{-2}$ in 1.0 M KOH. The increasing trend of C$_2$H$_4$ FE for Cu-Nafion and Cu-FEP can be due to the decrease of potential. And the decreased potential may originate from the change of Cu structure, electrode conductivity, or accumulation of K$_2$CO$_3$. 
Figure S20. Morphology of the catalyst after 15 min electrolysis of CO$_2$, at 50 mA.cm$^{-2}$, in 1.0 M KOH. (a-c) Cu-PAA, (d-f) Cu-Nafion, (g-i) Cu-FEP. Scale bar: (a)(d)(g) 1 µm, (b)(e)(h) 100 nm, (c)(f)(i) 10 nm.
Figure S21. Morphology of the Cu-binder catalysts after stability test in the flow cell. a) SEM image of Cu-PAA (the signal of C from the microporous layer does not allow to interpret the elemental maps of Cu and C for Cu-PAA). b) SEM image and its corresponding elemental maps of Cu and F for Cu-Nafion, and c) Cu-FEP. Scale bar: 1µm.
**Table S2.** Comparison of the catalysts, electrochemical performance and reactions conditions between this work and previous publications in H-cell

| Position in Figure 6 | References | FE C_{2+} (%) | Current density (mA/cm²) | Potential (V vs RHE) | Electrolyte |
|----------------------|------------|---------------|--------------------------|----------------------|-------------|
| A                    | 5wt%-PTFE-coated Cu nanoarrays[^1] | 34 | 18 | -1.1 | 0.1M KHCO₃ |
| B                    | Nafion-coated CuO nanowires[^2] | 26 | 25 | -1.3 | 0.1M KHCO₃ |
| C                    | 8.1-μm-length Cu NW arrays[^3] | 28 | 4 | -1.1 | 0.1M KHCO₃ |
| D                    | Electropolished Cu wire[^4] | 40 | 12.6 | -1.1 | 0.1M KHCO₃ |
| E                    | Oxide-derived nanostructured Cu wire[^4] | 49 | 12 | -1.1 | 0.1M KHCO₃ |
| F                    | Alkanethiol-treated Cu dendrites[^5] | 74 | 30 | -1.6 | 0.1M CsHCO₃ |
| G                    | 3.6 um Cu₂O film deposited on Cu[^6] | 50.6 | 35 | -0.99 | 0.1M KHCO₃ |
| H                    | Cu₂O nanocubes decorated with 3 at% Ag[^7] | 60 | 13 | -1 | 0.1M KHCO₃ |
| I                    | ^18O enriched OD Cu catalysts[^8] | 60 | 10.9 | -1 | 0.1M KHCO₃ |
| J                    | 44 nm-Cu nanocubes[^9] | 55 | 2 | -1.1 | 0.1M KHCO₃ |
| K                    | Ag_{55}Cu_{45} foam[^10] | 41.2 | 30.5 | -1.1 | 0.5M KHCO₃ |
| L                    | Electropolished Cu(111[^11]) | 10 | 3 | -1 | 0.1M KHCO₃ |
| M                    | Cu-Sustainion covered with Nafion[^12] | 80 | 20.5 | -1.15 | 0.1M CsHCO₃ |
| N                    | ZnO/CuO[^13] | 31.8 | 48.6 | -1.15 | 0.1M KHCO₃ |
| O                    | Fragmented Cu-Based NP/C[^14] | 17 | 74 | -1.1 | 0.1M KHCO₃ |
| CuO-FEP[^15] this work | 52 | 37.4 | -1.1 | 0.1M KHCO₃ |
Table S3. Comparison of the catalysts, electrochemical performance and reactions conditions between this work and previous publications in flow-cell

| Position in Figure 6 | References | FE C$_{2+}$ (%) | Current density (mA.cm$^{-2}$) | Potential (V vs RHE) | Electrolyte |
|----------------------|------------|-----------------|-------------------------------|----------------------|-------------|
| P                    | Electrodeposited hydrophobic Cu-nanoneedles electrode$^{[15]}$ | 64 | 438 | -0.68 | 1.0 M KOH |
| Q                    | Cu particles and Nafion$^{[15]}$ | 25.3 | 398 | -0.75 | 1.0 M KOH |
| R                    | Unsupported Cu$_2$O nanocubes$^{[16]}$ | 59 | 300 | -1.02 | 1.0 M KHCO$_3$ |
| S                    | Cu nanodendrites$^{[17]}$ | 57 | 298 | -2 | 0.1M KBr |
| T                    | Cu nanoparticles, prepared by solvent-based method$^{[18]}$ | 46 | 430 | -0.58 | 1.0 M KOH |
| U                    | Thermal annealed Cu oxide nanowires$^{[19]}$ | 36 | 300 | -0.6 | 1M KOH |
| V                    | Wet chemical oxidized Cu oxide nanowires$^{[19]}$ | 38 | 300 | -0.6 | 1M KOH |
| W                    | Cu$_2$O nanoparticle, dropcasted GDE$^{[20]}$ | 32 | 300 | -0.93 | 1M KHCO$_3$ |
| X                    | Cu$_2$O nanoparticle, airbrushed GDE$^{[20]}$ | 75.5 | 300 | -0.85 | 1M KHCO$_3$ |
| Y                    | B-doped CuO$^{[21]}$ | 60 | 137 | -0.625 | 1.0 M KOH |
|                      | CuO-FEP$^{[\text{this work}]}$ | 77 | 800 | -0.76 | 1.0 M KOH |
Figure S22. Operando Raman spectrum of the three Cu-polymer catalysts, Raman shift ranges from 1700 to 2200 cm\(^{-1}\). From bottom to top: initial OCP, -0.4 to -0.9 V vs RHE, final OCP. Raman spectrum is acquired at 60s after the chronoamperometric test starts. a) Cu-FEP. b) Cu-Nafion. c) Cu-PAA.
Figure S23. Faradaic efficiencies towards CO of Cu catalysts with the three binders with respect to the potential. Obtained in the H-cell, with 0.1 M KHCO₃ as the electrolyte.
Synthesis of Au-nanoparticles-supported on Cu

On the as-synthesized CuO support, Au is precipitated and deposited to obtain the **Au@Cu** catalyst. The synthesis proceeds as following:

1. **Neutralization of the precursor:** The precursor for Au deposition is HAuCl\(_4\).3H\(_2\)O, it is neutralized with NaOH to avoid dissolution of the CuO support. In 28.5 mL of H\(_2\)O, 1.5 mL of 0.02 M HAuCl\(_4\).3H\(_2\)O is added. The solution is stirred and heated up to 70°C and 0.01 M NaOH is added to bring the pH up to 6.

2. **Precipitation deposition:** 81 mg of CuO is added to the neutralized position and the pH is adjusted to approximately 7.5. The reaction is kept at 75°C under continuous stirring for 1h then cooled down to room temperature. The obtained solution is washed with deionized water twice, then ethanol, before freeze-fried for 72 hours.

3. **After freeze-drying,** the powder CuO-Au is calcined in air for 1 h at 300°C.
Figure S24. Performance of the as-synthesized Au@Cu-polymer catalysts. a) TEM image (Scale bar: 100 nm) and b) the particle size distribution of the Au@Cu sample without polymer binder. c) and d) Faradaic efficiency towards $C_1$ and $C_{2+}$ products of the Au@Cu-polymer catalysts, 0.1 M KHCO$_3$ in H-cell.
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