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Electronic Supplementary Information for Reduction of Carbon Dioxide at a Plasmonically Active Copper–Silver Cathode

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Absorption Measurements

UV-vis total reflection measurements of dry cathodes were measured with a Shimadzu SolidSpec-3700 UV-vis-NIR spectrophotometer with an integrating sphere. A NIST-calibrated mirror was used as a reference to find the absolute reflection values, and absorption values were calculated as 100 - % reflectance (Fig. 1A and S1–S3).



Figure S1: UV-visible (UV-vis) absorbance of bare Cu nanocorals (A) as-prepared and after 1 minute of chronoamperometry (CA) at -1.0 V_{RHE} and after (B) 15, (C) 30, and (D) 45 minutes of electrochemical experiments. (E) UV-vis absorbance at 560 nm over time extracted from (A–D). All measurements were performed on the same cathode.



Figure S2: UV-visible (UV-vis) absorbance of the plasmonically active cathode (10 nm of Ag on Cu nanocorals) (A) as-prepared and after 1 minute of chronoamperometry (CA) at -1.0 V_{RHE} and after (B) 2, (C) 3, and (D) 4 days of electrochemical experiments. (E) UV-vis absorbance at 560 nm over time extracted from (A–D). The same cathode was used for the measurements performed on Day 1. Different cathodes were used for the measurements performed after 2, 3, and 4 days.



Figure S3: UV-visible (UV-vis) absorbance of Ag foil (red), 10 nm of Ag on Ag foil (orange), bare Cu nanocorals (green), and 10 nm of Ag on Cu nanocorals (blue). Different Ag foil substrates were used for each measurement. All samples were as-prepared, no electrochemistry was performed prior to the UV-vis measurement. For the 10 nm Ag on Ag foil, a 3 nm Ti layer was first deposited by electron-beam (e-beam) evaporation for adhesion.

Photocurrent Measurements

Photocurrent measurements were performed by chopping the light at 3 Hz using a Stanford Research Systems SR850 lock-in amplifier to control a ThorLabs SHB1 shutter. A square wave is produced (Fig. S4A) and the photocurrent is calculated as the difference between the current when the light is incident on the cathode and the current when the cathode is in the dark. A photocurrent is only produced through a plasmonic mechanism when an electron has sufficiently high energy to transfer to an adsorbate, and if that transfer occurs.

Linear sweep voltammetry (LSV) was performed at 5 mV s⁻¹ while chopping the light to identify the peak photocurrent voltage, -0.78 V_{RHE} (Fig. S4B). Reported photocurrent values were collected while chopping the light during chronoamperometry (CA) at -0.78 V_{RHE} for 4 minutes and averaging the photocurrent over the last 2 minutes. Depositing Ag on the Cu nanocorals more than tripled the photocurrent (Fig. S4C). The photocurrent decreased with increasing wavelength of incident light at equal photon flux (3.2 x 10^{17} photons cm⁻² s⁻¹), following the light absorbance trend measured by UV-visible spectroscopy (UV-vis) (Fig. 1A, S2, and S4D). The photocurrent increased linearly with increasing light intensity during 365 nm LED illumination at -0.78 V_{RHE} (Fig. S4E).



Figure S4: Photocurrent measurements. (A) Example of the square wave produced during chopped light experiments using the 365 nm LED. The carbon dioxide (CO₂) bubbles were stopped and the frequency set at 1 Hz to reduce the noise, resulting in a higher photocurrent. (B) Representative linear sweep voltammetry (LSV) at 5 mV s⁻¹ during 3 Hz chopping of the 365 nm LED (170 mW cm⁻²) with continuous CO₂ flow. The total current density is shown in black (left axis) and the extracted photocurrent density is shown in pink (right axis), both filtered with exponential smoothing for clarity. The peak photocurrent voltage occurred at -0.78 $V_{\rm RHE}$. The cathode had previously experienced 45 minutes of chronoamperometry (CA) at -1.0 V_{RHE} . (C) Photocurrent densities measured at -0.78 V_{RHE} using cathodes of bare Cu nanocorals and Cu nanocorals with 5, 10, and 15 nm of Ag deposited on top by electron-beam (e-beam) evaporation. Error bars represent one standard deviation of experiments performed in triplicate. (D) Photocurrent densities measured at different wavelengths of light with equal photon fluxes of 3.2×10^{17} photons cm⁻² s⁻¹ (black, left axis). The cathode had previously experienced 45 minutes of CA at -1.0 $V_{\rm RHE}$. Error bars represent one standard deviation of experiments performed in triplicate. Absorbance measured by UV-visible spectroscopy (UV-vis) was averaged over measurements performed after 0 to 120 minutes of CA at -1.0 V_{RHE} (green, right axis). (E) Photocurrent densities during 365 nm LED illumination across a range of light intensities at -0.78 $V_{\rm RHE}$. The line represents the least-squares regression line. Error bars represent one standard deviation of experiments performed in triplicate.

Cathode Fabrication

Silver (Ag) foil (Alfa Aesar 12126, 0.1 mm thick, hard, Premion 99.998%) was cut into a square with a side length of approximately 2.5 cm. The Ag foil was then wet sanded (Norton T401, 2000 grit) and polished with alumina nanoparticles (TED Pella Inc. 895-55, 0.3 µm). Subsequently, the Ag foil was rinsed with 18.2 M Ω deionized water from a Millipore system in between polishing steps. The Ag foil was then sonicated for 15 minutes in each of the following solutions: acetone, isopropanol, and Millipore water. Then the Ag foil was sonicated for 5 minutes in 0.1 M hydrochloric acid (HCl) followed by another 15 minutes of sonication in Millipore water. A 2:1 solution of 0.1 M copper(II) sulfate hydrate (CuSO₄) (Alfa Aesar 10701, Puratronic 99.999%) and 0.1 M sulfuric acid (H₂SO₄) was created with a pH of 1 to be used as the electrolyte in the electrodeposition of the Cu nanocorals.¹ A beaker cell setup was used to deposit the nanocorals with the cleaned Ag foil as the working electrode and platinum mesh (approximately 1 cm²) as both the counter and reference electrode. In order to deposit the nanocorals, -400 mA was applied to the Ag foil for 10 seconds; this high current density results in the formation of H₂ bubbles that define the nanofeature morphology.¹ The electrode was then rinsed in Millipore water and dried with compressed nitrogen. Unless otherwise noted, all cathodes in this study then had 10 nm of Ag deposited on the Cu nanocorals by electron-beam (e-beam) evaporation. A schematic and picture of the Cu–Ag cathode is shown in Fig. S5.

The Ag foil substrate will have limited influence on the plasmonic and photocurrent properties of the Cu–Ag cathode because it is a relatively flat surface. Kim et al. showed that Ag foil required intentional surface roughening through cyclic voltammetry to high anodic potentials to achieve even a small photocurrent.² Comparing the CO_2 reduction product distribution results of Gurudayal et al. (bare Cu nanocorals deposited on a Ag foil) to those of Kuhl et al. (Cu foil), the similar Faradaic efficiencies (FE) of CO demonstrate that the Ag foil substrate also has a limited impact on the catalytic activity of the Cu nanocorals.^{1,3}





Figure S5: (A) Cathode schematic and (B) cathode picture. Cu nanocorals are electrochemically deposited on a Ag foil. 10 nm of Ag is deposited by e-beam on the Cu nanocorals.

Cathode Surface Imaging

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) images are shown in Fig. 1, S6, and S7. Multiple images at different locations were taken on each cathode to ensure that presented images are representative of the entire surface.



Figure S6: Scanning electron microscopy (SEM) images of the cathode surface (A and E) as-deposited and after (B and F) 2 days, (C and G) 3 days, and (D and H) 4 days of electrochemical experiments. The scale bar in (B) applies to (A–D) and the scale bar in (F) applies to (E–H). Different cathodes were imaged for each day.



Figure S7: Energy-dispersive X-ray spectroscopy (EDS) images of the cathode surface (A) as-deposited and after (B) 2, (C) 3, and (D–E) 4 days of electrochemical experiments. The cathode surface in (E) was tilted at 60°. The scale bar in (B) applies to all of the images in this figure. Different cathodes were imaged for each day.

XRD Measurements

The crystalline structure of the cathode was analyzed by X-ray diffraction (XRD) with a Rigaku Smartlab diffractometer using Cu K α radiation. The grazing incidence angle was fixed at 0.5°, 1.0°, or 1.5° and the detector angle was scanned between 25° and 75°. Peaks were observed for Cu, Cu₂O, and Ag at all grazing incidence angles as shown in Figure S8. Both Ag and Cu are polycrystalline.



Figure S8: XRD pattern of a cathode after 1 day of electrochemical experiments. The grazing incidence angle was 0.5° (black), 1.0° (red), or 1.5° (blue).

XPS Measurements

The surface compositions were probed using X-ray photoelectron spectroscopy (XPS) acquired by a Kratos Axis Ultra spectrometer using an Al K-Alpha X-ray source ($h\nu = 1486.69 \text{ eV}$) operated at 75 W with a hemispherical electron energy analyzer (Fig. S9). Parameters used for the measurements of Ag3d3/2, Ag3d5/2, Cu2p1/2, and Cu2p3/2 were: pass energy, 20 eV; energy step size, 0.05 eV; dwell time, 300 ms; 6 scans.



Figure S9: XPS spectra of a new cathode (black) and the same cathode after 180 minutes of chronoamperometry (CA) at -1.0 V_{RHE} (red). Peaks shown are (A) Ag (3d3/2 and 3d5/2) and (B) Cu (2p1/2 and 2p3/2). The ratio of the sum of the peak areas of Ag3d3/2 and Ag3d5/2 to the peak area of Cu2p3/2 is normalized to 1 for the new cathode and decreases to 0.35 after electrolysis.

Electrochemical Measurements

0.05 M potassium carbonate (K_2CO_3) (Alfa Aesar 10838, Puratronic 99.997%) was prepared with Millipore water. Upon saturation with carbon dioxide (CO_2) the solution became 0.1 M potassium bicarbonate (KHCO₃) (pH 6.8). Electrochemical measurements were performed in a leak-tight polyether ether ketone (PEEK) compression cell described by Corson et al.⁴ CO₂ was continuously bubbled through the electrolyte at 5 sccm. A leak-free Ag/AgCl reference electrode (Innovative Instruments, Inc. LF-1) was located in close proximity to the cathode. All potentials in this study are reported versus the reversible hydrogen electrode (RHE). A thermistor (Micro Lab 103) covered with a fluorinated ethylene propylene (FEP) heat shrink cap was in contact with the catholyte. A peltier device (Ferrotec 72008/131/150B) in contact with the back of the cathode, heat sink with fan, and a proportional-integral-derivative (PID) controller maintained the catholyte at the desired set point $\pm 0.1^{\circ}$ C. An anion exchange membrane (Asahi Glass, Selemion AMV) separated the cathode and anode chambers. A platinum (Pt) foil was used as the anode. The cathode and anode were each compressed against an o-ring (Ace Seal 2-015, Kalrez 6375) exposing a 1 cm² geometric surface area.

 CO_2 was bubbled through the electrolyte for 10 minutes before the start of an electrochemical experiment

to ensure saturation. Electrochemical experiments were performed with a Biologic SP-300 potentiostat. Impedance spectroscopy was performed at the open circuit potential from 100 to 1 kHz with a 10 mV amplitude and the resulting resistance was used to apply an 85% IR correction to each electrochemical measurement. Typical resistance values ranged from 40 to 50 Ω .

The cathode was front-illuminated through a quartz window primarily using a 365 nm ultra-high-power light-emitting diode (LED) (Mightex Systems LCS-0365-48-22) with a light intensity of 170 mW cm⁻² at the surface of the cathode. Other LEDs in this study include 405 nm (Mightex Systems LCS-0405-50-22), 470 nm (Mightex Systems LCS-0470-50-22), and 525 nm (Mightex Systems LCS-0525-6022). The light intensity was measured with a Coherent PowerMax PM10 power meter.⁵

Product Measurements

The product analysis experiments were conducted in a temperature-controlled cell described by Corson et al.⁴ The gaseous products were quantified using an in-line Multiple Gas Analyzer #5 SRI Instruments gas chromatography (GC) analyzer with a 12 ft HayeSep D (divinylbenzene) column, thermal conductivity detector (TCD), flame ionization detector (FID) preceded by a methanizer, and Ar carrier gas. Each product analysis run was a single potential and temperature applied to the cell for 64 minutes with GC injections at 3, 15, 27, 39, 51, and 63 minutes with the data from 15–63 minutes averaged and reported. The concentration of each gas was calculated using a calibration curve with points from at least 3 different concentrations. Liquid products remaining in the electrolyte were analyzed using proton nuclear magnetic resonance (¹H NMR) spectroscopy on a Bruker Avance III 500 MHz magnet. Concentrations in the electrolyte were determined using phenol and dimethyl sulfoxide (DMSO) as internal standards, while using a water suppression method.³ More details on the NMR and GC analysis can be found in our previous paper.⁴ A list of all products detected in this study is shown in Table S1.

Product	Chemical Formula	Carbons	Electrons	State
Carbon Monoxide	СО	C_1	2	Gas
Formate	HCOO^{-}	C_1	2	Liquid
Methane	CH_4	C_1	8	Gas
Glycolaldehyde	$C_2H_4O_2$	C_2	8	Liquid
Acetaldehyde	C_2H_4O	C_2	10	Liquid
Ethanol	C_2H_6O	C_2	12	Liquid
Ethylene	C_2H_4	C_2	12	Gas
Ethane	C_2H_6	C_2	14	Gas
Hydroxyacetone	$C_3H_6O_2$	C_3	14	Liquid
Acetone	C_3H_6O	C_3	16	Liquid
Allyl Alcohol	C_3H_6O	C_3	16	Liquid
Propionaldehyde	C_3H_6O	C_3	16	Liquid
n-Propanol	C_3H_8O	C_3	18	Liquid

Table S1: CO_2 Reduction Products



Figure S10: Faradaic efficiencies (FE) of gaseous products demonstrating electrode stability over time. Gaseous products (A) carbon monoxide, (B) hydrogen, and (C) ethylene were measured at -0.8 $V_{\rm RHE}$ in the dark (unfilled columns) and under 365 nm LED illumination at 170 mW cm⁻² (filled columns) after

1, 2, and 3 days of cathode use for electrochemical experiments. One-way ANOVA analysis showed no statistically significant difference for any of the results over time within a confidence interval of 95%. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S11: Partial current densities of major products from -0.6 to -1.0 V_{RHE} at 22°C corresponding to the Faradaic efficiencies (FE) shown in Fig. 2. Dashed lines with unfilled symbols show results performed in the dark and solid lines with filled symbols show results performed under continuous illumination using a 365 nm LED with an intensity of 170 mW cm⁻². No points are plotted if the product was not detected. Products shown are (A) carbon monoxide, (B) hydrogen and ethylene, (C) formate and methane, and (D) ethanol. The FE and partial current densities of the minority products methanol, glycolaldehyde, acetaldehyde, ethane, hydroxyacetone, acetone, allyl alcohol, propionaldehyde, and n-propanol are shown in Fig. S12 and S13, respectively. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S12: Faradaic efficiencies (FE) of minor products from -0.6 to -1.0 V_{RHE} at 22°C. FE of (A) methanol, (B) glycolaldehyde, (C) acetaldehyde, (D) ethane, (E) hydroxyacetone, (F) acetone, (G) allyl alcohol, (H) propionaldehyde, and (I) n-propanol. Dashed lines with unfilled symbols show results performed in the dark and solid lines with filled symbols show results performed under continuous illumination using a 365 nm LED with an intensity of 170 mW cm⁻². No points are plotted if the product was not detected. Corresponding major products are shown in Fig. 2 ((FE) and S11 (partial current densities). Fig. S13 shows the partial current densities for these minor products. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S13: Partial current densities of minor products from -0.6 to -1.0 V_{RHE} at 22°C. Partial current densities of (A) methanol, (B) glycolaldehyde, (C) acetaldehyde, (D) ethane, (E) hydroxyacetone, (F) acetone, (G) allyl alcohol, (H) propionaldehyde, and (I) n-propanol. Dashed lines with unfilled symbols show results performed in the dark and solid lines with filled symbols show results performed under continuous illumination using a 365 nm LED with an intensity of 170 mW cm⁻². No points are plotted if the product was not detected. Corresponding major products are shown in Fig. 2 (Faradaic efficiencies (FE)) and S11 (partial current densities). Fig. S12 shows the FE for these minor products. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S14: Partial current densities of major products at 14, 22, and 35°C in the dark. Dashed lines with unfilled symbols show results performed at -0.6 V_{RHE} and solid lines with filled symbols show results performed at -1.0 V_{RHE} . Products shown are (A) carbon monoxide, (B) hydrogen and ethylene, (C) formate and methane, and (D) ethanol. Fig. 3 shows the Faradaic efficiencies (FE) for these major products. Ethylene and methane were not detect at any temperature at -0.6 V_{RHE} . The FE and partial current densities of the minority products methanol, glycolaldehyde, acetaldehyde, ethane, hydroxyacetone, acetone, allyl alcohol, propionaldehyde, and n-propanol are shown in Fig. S15 and S16, respectively. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S15: Faradaic efficiencies (FE) of minor products at 14, 22, and 35°C in the dark. FE of (A) methanol, (B) glycolaldehyde, (C) acetaldehyde, (D) ethane, (E) hydroxyacetone, (F) acetone, (G) allyl alcohol, (H) propionaldehyde, and (I) n-propanol. Dashed lines with unfilled symbols show results performed at -0.6 $V_{\rm RHE}$ and solid lines with filled symbols show results performed at -1.0 $V_{\rm RHE}$. No points are plotted if the product was not detected. Corresponding major products are shown in Fig. 3 (FE) and S14 (partial current densities). Fig. S16 shows the partial current densities for these minor products. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S16: Partial current densities of minor products at 14, 22, and 35° C in the dark. Partial current densities of (A) methanol, (B) glycolaldehyde, (C) acetaldehyde, (D) ethane, (E) hydroxyacetone, (F) acetone, (G) allyl alcohol, (H) propionaldehyde, and (I) n-propanol. Dashed lines with unfilled symbols show results performed at -0.6 V_{RHE} and solid lines with filled symbols show results performed at -1.0 V_{RHE}. No points are plotted if the product was not detected. Corresponding major products are shown in Fig. 3 (Faradaic efficiencies (FE)) and S14 (partial current densities). Fig. S15 shows the FE for these minor products. Error bars represent one standard deviation of experiments performed in triplicate.



Figure S17: (A) The total Faradaic efficiencies (FE) from -0.6 to -1.0 V_{RHE} at 22°C for results shown in Fig. 2 and S12. (B) The total current densities from -0.6 to -1.0 V_{RHE} at 22°C for results shown in Fig. S11 and S13. Dashed lines in (A) and (B) with unfilled symbols show results performed in the dark and solid lines with filled symbols show results performed under continuous illumination using a 365 nm LED with an intensity of 170 mW cm⁻². (C) The total FE at 14, 22, and 35°C in the dark for results shown in Fig. 3 and S15. (D) The total current densities at 14, 22, and 35°C in the dark for results shown in Fig. S14 and S16. Dashed lines in (C) and (D) with unfilled symbols show results performed at -0.6 V_{RHE} and solid lines with filled symbols show results performed at -1.0 V_{RHE} . Error bars in all plots represent one standard deviation of experiments performed in triplicate.

Plasmonic Mechanisms



Figure S18: (A) Incident light $(h\nu)$ on the cathode surface results in a collective oscillation of the electrons, a phenomenon known as localized surface plasmon resonance (LSPR). In this study, illumination of the Cu-Ag cathode during CO_2 reduction resulted in the plasmon-enhanced formation of carbon monoxide, ethylene, methane, formate, and allyl alcohol. Adapted with permission from ref. 6. Copyright 2003, American Chemical Society. Possible plasmonic mechanisms are (B) the enhancement of the local electric field or (C) a permanent or (D) temporary hot electron transfer. (B) LSPR can generate strong local electric fields which can influence the bond energy of adsorbates at the cathode surface. The electric field is expected to be maximized at the tips of the nanocorals.² (C) LSPR can also decay to form energetic electron-hole pairs. In the schematic, a hot electron is permanently transferred to an unoccupied molecular orbital (MO) of an adsorbate, where E_F is the Fermi level, E is the energy level, HOMO is the highest occupied molecular orbital of an adsorbate, and LUMO is the lowest unoccupied molecular orbital of an adsorbate. Adapted with permission from ref. 7. Copyright 2015, Springer Nature. (D) In the desorption induced by electronic transitions (DIET) mechanism, a hot electron can temporarily transfer to an unoccupied MO of an adsorbate, forming an excited metal-adsorbate complex with a different potential energy surface (PES). On this new PES, the energy of the donated charge carrier is converted to the kinetic energy of the metal-adsorbate complex. After a short time, the donated electron decays back to the metal E_F and the adsorbate returns to the ground state PES. If the energy transfer exceeds the activation barrier for desorption (E_d) , the adsorbate will leave the surface. Adapted with permission from ref. 8. Copyright 2011, Springer Nature.

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