

Supporting Information

Selective Electrochemical Reduction of Carbon Dioxide to Ethylene and Ethanol on Copper (I) Oxide Catalysts

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S1. Preparation and Characterization of Cu₂O Films

S1.1. Film Preparation

Cu₂O layers were electrodeposited onto polished Cu discs from an aqueous electrolyte consisting of 0.3 M CuSO₄ (99 %, GCE), 3.2 M NaOH (99 %, Chemicob) and 2.3 M Lactic Acid (>90 %, VWR).¹ The plating solution was prepared by diluting lactic acid with water (18.2 MΩ, Millipore) to give the required concentration. CuSO₄ was then added. After dissolution of the CuSO₄, the solution was cooled and stirred in an ice bath, and NaOH was slowly added. The electrolyte was then heated in a water bath at 60 °C and stirred at 500 rpm. Galvanostatic deposition of Cu₂O at a constant current density of -1.82 mA/cm² was carried out under these conditions. Cu₂O films with various thicknesses were obtained by varying the deposition time.

S1.2. Determination of the Thicknesses of the Cu₂O Films

Copper discs deposited with Cu₂O layers were cleaved, and their cross-sections were imaged by scanning electron microscopy (Figure S1). The thickness of the Cu₂O films was found to be linearly dependent on the deposition time (Figure S2). The cross-sections of the two thinnest Cu₂O films (deposition time 60 s and 150 s) could not be sharply imaged using the SEM. Hence, their thicknesses were estimated by extrapolation using Figure S2. The thicknesses of the prepared films are summarized in Table S1.

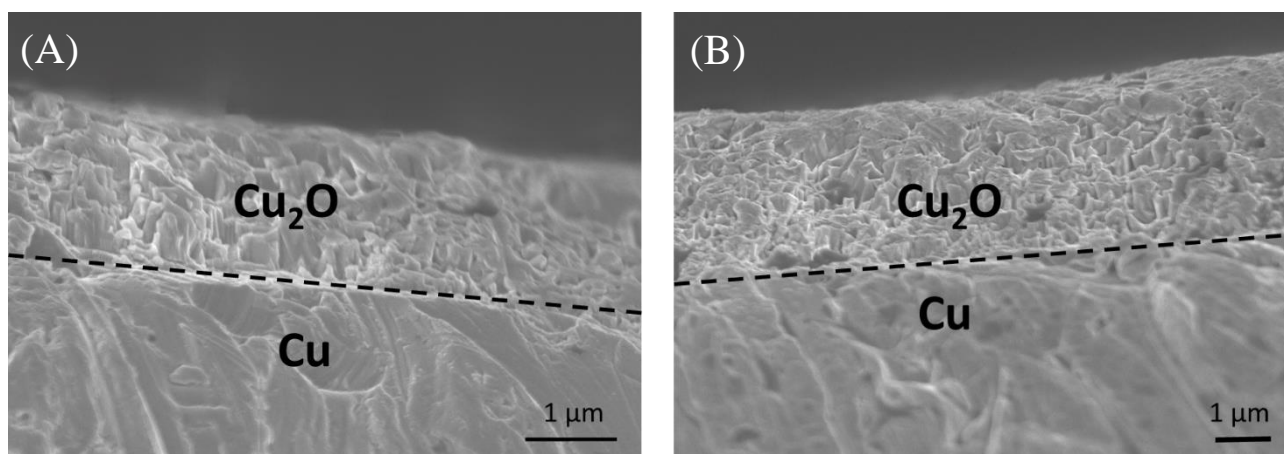


Figure S1. Cross-section of Cu₂O films deposited on Cu substrates. Time of deposition of Cu₂O film: (A) 10 min and (B) 20 min.

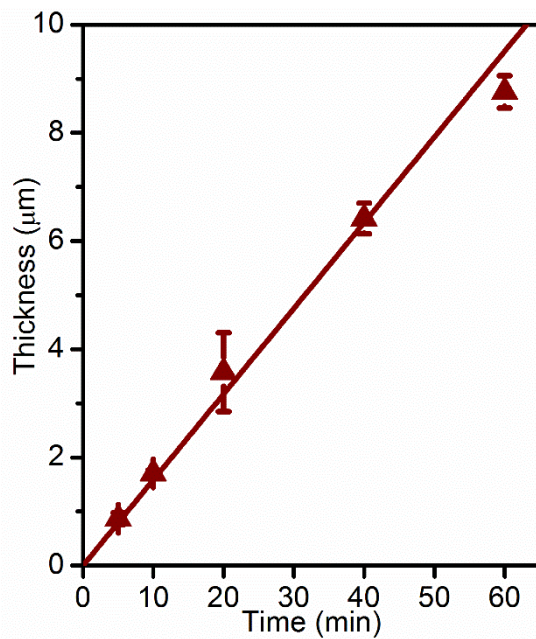


Figure S2. Plot showing the thickness of the deposited Cu₂O films as a function of deposition time.

Table S1. Thickness of the deposited Cu₂O layers.

Time of deposition (min)	Thickness (μm) obtained from each measurement					Average (μm)
	1	2	3	4	5	
1						0.2 ^a
2.5						0.4 ^a
5	0.77	0.88	1.05	0.79	0.84	0.9
10	1.78	1.70	1.74	1.64	1.68	1.7
20	2.81	2.77	4.29	4.09	3.92	3.6
40	6.48	6.05	6.39	6.33	6.84	6.4
60	9.21	8.74	8.86	8.49	8.49	8.8

^aThe thickness of the two thinnest films were estimated using the calibration plot presented in Figure S2.

S1.3 Surface Area Characterization.

The electrochemically active surface areas of the catalysts were measured using the method described by Kanan et al.² The catalysts were first reduced at -0.99 V vs. RHE for 4200 seconds in 0.1 M KHCO₃. Their surface areas were then estimated through double layer capacitance measurements in 0.1 M HClO₄. Cyclic voltammetry curves were recorded from 0-200 mV vs. RHE at scan rates from 20-300 mV/s. The capacitive current densities were plotted as a function of the scan rate, which gave a linear plot. The ratio of the slope/29 gives the roughness factor of the surface. The surface roughness factor for the electropolished Cu surface is defined as 1. The roughness factors of the catalysts are presented in Table S2.

Table S2. Double layer capacitance of the four catalysts and their respective roughness factors.

Catalyst	Capacitance	Roughness factor
Electropolished Cu	29 $\mu\text{F}/\text{cm}^2$	1
0.2 μm Cu ₂ O	42 $\mu\text{F}/\text{cm}^2$	1.5
1.7 μm Cu ₂ O	136 $\mu\text{F}/\text{cm}^2$	4.7
3.6 μm Cu ₂ O	159 $\mu\text{F}/\text{cm}^2$	5.5
8.8 μm Cu ₂ O	329 $\mu\text{F}/\text{cm}^2$	11.3

S2. Raman Spectroscopy

S2.1. Schematic Diagram of the Raman Spectroscopy System

A schematic diagram and photograph of the Raman spectroscopy system and the electrochemical cell is shown in Figure S3.

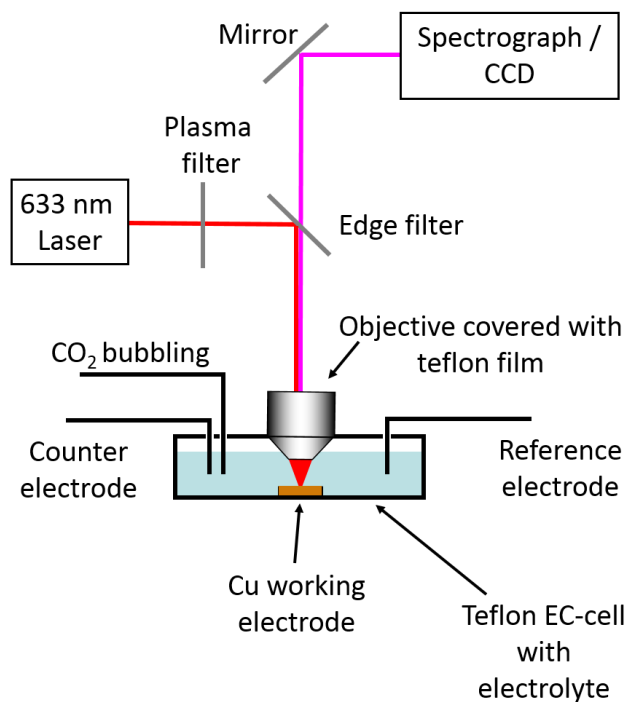


Figure S3. Schematic diagram and photograph of the electrochemical Raman spectroscopy system. The laser is not shown in the photograph.

S2.2. Raman Spectroscopy of 1.7 μm Film during CO₂ Reduction at -0.59 V

In-situ Raman spectroscopy was performed on a 1.7 μm Cu₂O film during CO₂ reduction at -0.59 V (Figure S4). Cu₂O, as evidenced by its Raman bands at 147, 218, 526 and 624 cm⁻¹, was detected at the start of the CO₂ reduction (at 0 sec). 30 seconds after a cathodic potential of -0.59 V was applied, the Cu₂O peaks disappeared and peaks at 276 and 365 cm⁻¹ appeared. We note that the 276 cm⁻¹ peak was not observed in the Raman spectrum taken at -0.99 V (Figure 2K). This difference could be due to a different type of intermediately reduced Cu oxides being formed at -0.59 V. The Raman spectra of copper oxide being reduced during a potentiodynamic scan also exhibit different features at different potentials.^{3,4} The Cu₂O film reduced to Cu metal from 200 seconds onwards.

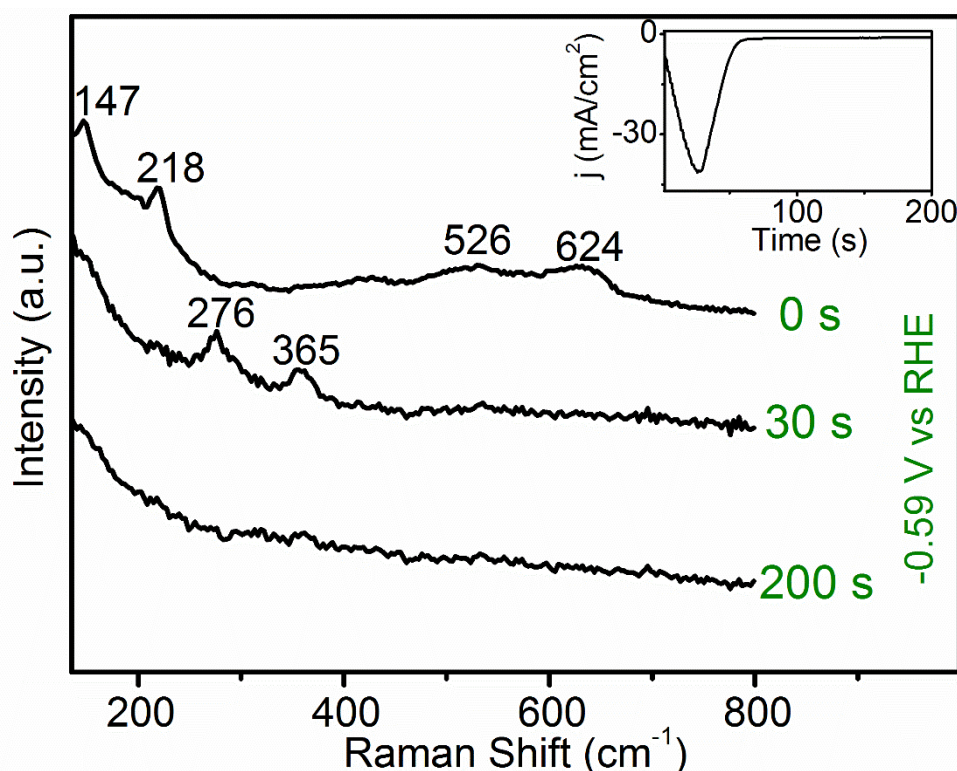


Figure S4. In-situ Raman spectra and corresponding chronoamperogram (inset) of a 1.7 μm film during CO₂ reduction at -0.59 V in 0.1 M KHCO₃.

S3. The pH of Electrolytes

The electrolytes used in this work were saturated with the required gas for 10 min. Their pH values were then measured with a pH meter (MP220, Mettler Toledo) and listed in Table S3.

Table S3. The pH values of electrolytes saturated with different gases.

Electrolyte + gas	pH
0.1M KHCO ₃ + Ar	8.81
0.1M KHCO ₃ + CO	8.81
0.1M KHCO ₃ + CO ₂	6.79
Phosphate buffer + CO ₂	6.73

S4. NMR Identification and Quantification of Liquid Products

2 mL of catholyte was syringed out from the electrochemical cell after 70 min of CO₂ electroreduction. It was then mixed with 100 μL internal standard, which consisted of 25 mM phenol (99.5%, Scharlau) and 5 mM dimethyl sulfoxide (DMSO, 99.9%, Quality Reagent Chemical). 250 μL of this mixture was further mixed with 350 μL D₂O (99.96 % D, Cambridge Isotope Lab), and transferred to a NMR sample tube.⁵ ¹H NMR spectroscopy was performed with a 300 MHz spectrometer (Avance 300, Bruker). The water suppression method was used. Each spectrum is an average of 100 continuous scans. A typical NMR spectrum is shown in Fig. S5. Very weak signals belonging to isopropanol and acetate were also detected occasionally. These products were not quantified as the intensities of the signals were below the limits of quantification

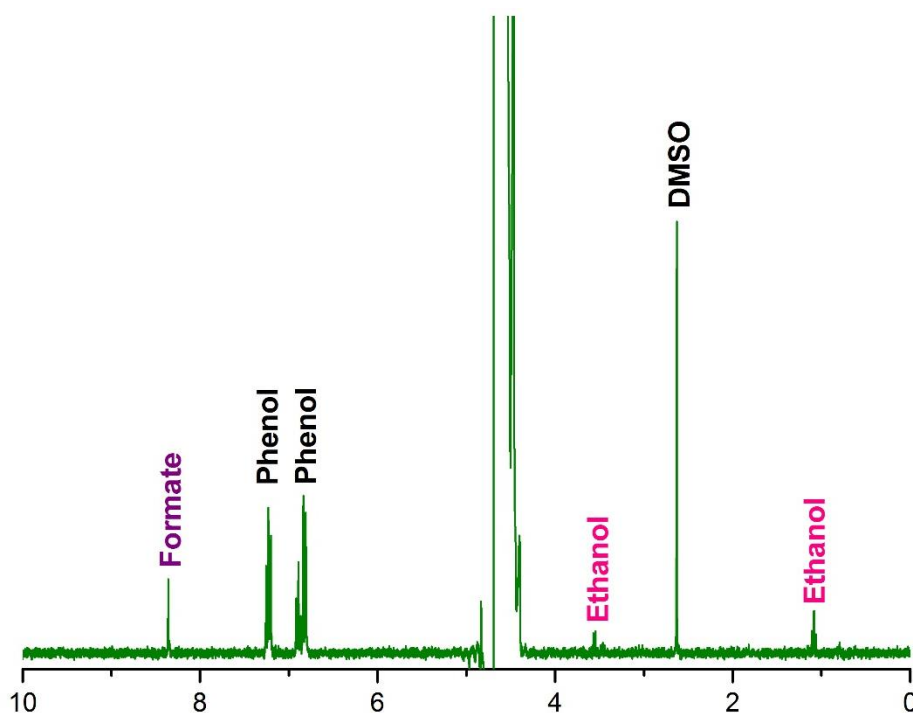


Figure S5. NMR spectra of the KHCO₃ catholyte after 4200s of CO₂ reduction on a 1.7 μm thick Cu₂O film. Potential applied=-0.99 V

The peaks were quantified by integrating the area below it. The relative peak area can be calculated as follows:

$$\text{Relative peak area ratio (ethanol)} = \frac{\text{Triplet peak area at 1.1 ppm (ethanol)}}{\text{Singlet peak area at 2.6 ppm (DMSO)}}$$

$$\text{Relative peak area ratio (formate)} = \frac{\text{Singlet peak area at 8.3 ppm (formate)}}{\text{Triplet peak area at 7.2 ppm (phenol)}}$$

The concentration of these two products were obtained using the calibration curves shown in Figure S6. The calibration curves were made by measuring standard solutions of ethanol and formate.

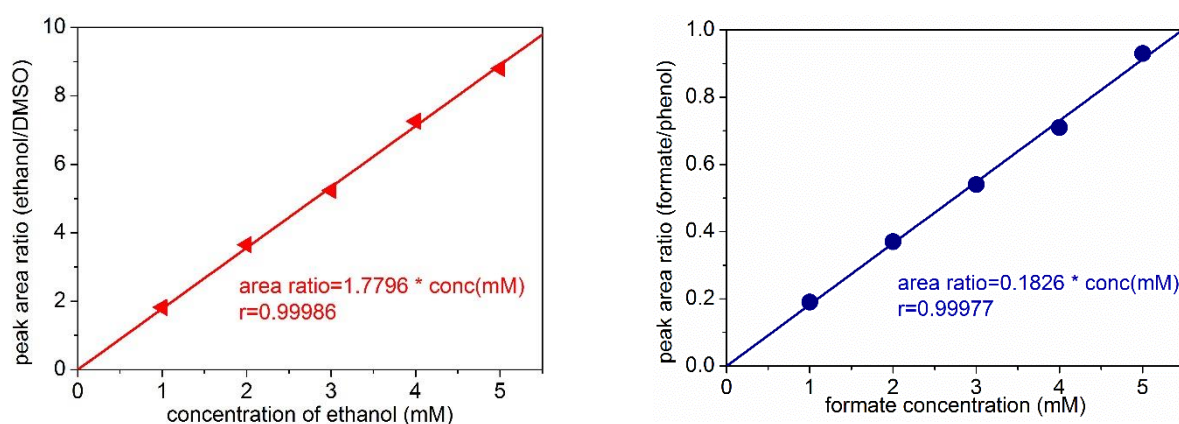


Figure S6. Calibration curves for ethanol (left hand side, DMSO as internal standard) and formate (right hand side, phenol as internal standard).

Control experiments were done to prove that all the liquid and gas products are from CO₂ reduction. No products could be detected from the cathodic compartment in the absence of applied potentials on the working electrode (Figure S7).

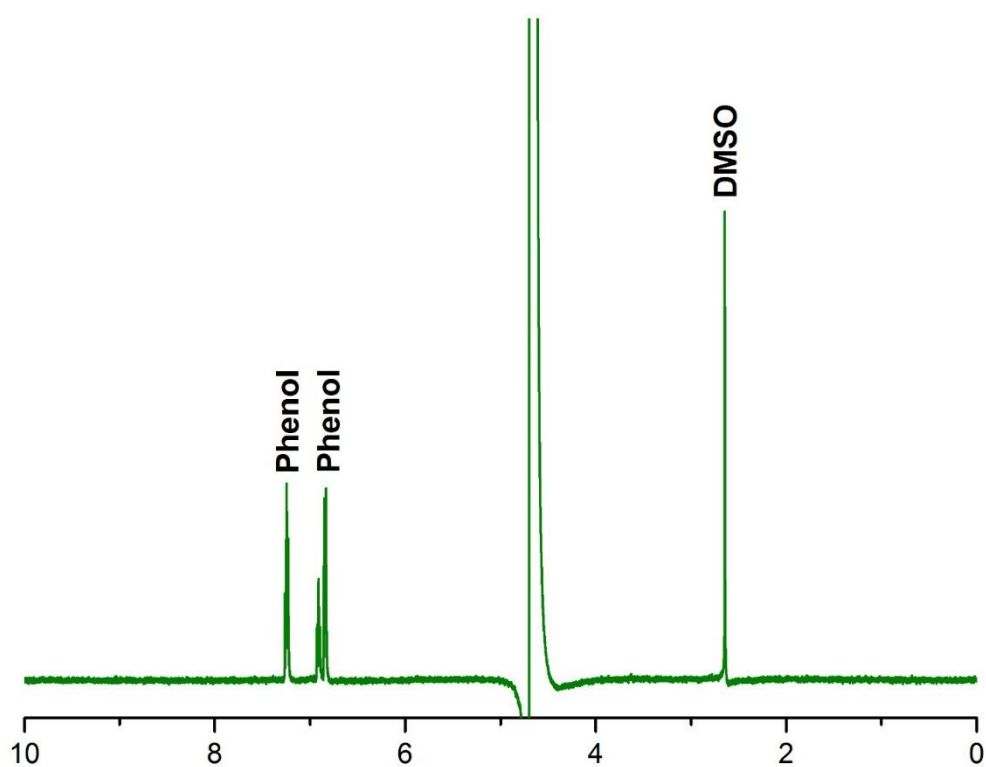


Figure S7. NMR spectrum of the KHCO_3 catholyte in the absence of applied potentials on the working electrode.

S5. Calculations of Faradic Efficiencies of Gaseous and Liquid Products.

A representative set of electrochemical, GC and NMR data obtained from a 3.6 μm thick Cu_2O film at -0.99 V vs. RHE is shown in Table S4.

Table S4. Representative data obtained from a 3.6 μm thick Cu_2O film at -0.99 V vs. RHE.

Vial	Time (s)	Current (mA)	Amount (mol ppm) in each vial					Relative area ^a	
			CH_4	C_2H_4	CO	H_2	C_2H_6	HCOO^-	$\text{C}_2\text{H}_5\text{OH}$
1	200	13.325	2.957	146.525	5.051	3569.306	0.552		
2	869	12.809	3.071	261.857	11.330	2181.950	0.840		
3	1538	14.110	3.922	316.006	14.652	1789.413	0.735		
4	2207	14.137	4.422	334.399	17.689	1838.560	0.719	0.25	1.50
5	2876	13.138	5.275	354.561	19.558	2053.391	0.720		
6	3545	12.279	5.056	274.725	22.243	2029.043	0.672		

^a Relative peak area is defined in page S9.

Faradic efficiencies of gaseous products

The volume of the sample loop (V_0) for hydrocarbons in our gas chromatograph is 1 cm^3 and the flow rate of the gas is $v = 20 \text{ cm}^3/\text{min}$. The time it takes to fill the sample loop is:

$$t = \frac{V_0}{v} = \frac{1 \text{ cm}^3}{20 \text{ cm}^3/\text{min}} = 0.05 \text{ min} = 3 \text{ s} \quad (1)$$

According to the ideal gas law, under ambient temperature of 26 °C, the amount of gas in each vial

($V_0 = 1 \text{ cm}^3$) is:

$$n = \frac{P \times V_0}{R \times T} = \frac{1.013 \times 10^5 \text{ Pa} \times 1 \times 10^{-6} \text{ m}^3}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 299.150 \text{ K}} = 4.073 \times 10^{-5} \text{ mol} \quad (2)$$

The number of electrons required to form 1 molecule of CH_4 , C_2H_4 , CO or C_2H_6 are respectively 8, 12, 2 or 14. Take **Vial 3** and the calculation of C_2H_4 as an example. The number of electrons (N_{ethylene}) needed to get x_0 ppm of ethylene is:

$$N_{\text{ethylene}} = x_0 \times n \times N_A \times 12 e = 316.006 \times 10^{-6} \times 4.073 \times 10^{-5} \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times 12 e = 9.298 \times 10^{16} e \quad (3)$$

At the injection time to fill up vial 3, the recorded current is $I_0 = 14.110 \text{ mA}$ (this data is obtained from the chronoamperogram). Total number of electrons (N_{total}) measured during this sampling period:

$$N_{\text{total}} = \frac{I_0 \times t}{e} = \frac{14.110 \times 10^{-3} \text{ A} \times 3 \text{ s}}{1.602 \times 10^{-19} \text{ C/e}} = 2.642 \times 10^{17} e \quad (4)$$

Hence, the faradic efficiency of ethylene is (3)/(4):

$$FE = \frac{N_{\text{ethylene}}}{N_{\text{total}}} \times 100 \% = \frac{9.298 \times 10^{16}}{2.642 \times 10^{17}} \times 100 \% = 35.19 \% \quad (5)$$

Faradic efficiency of liquid products:

Take the calculation of **C₂H₅OH** as an example, the calculation of ethanol is calculated based on the calibration curve. According to Table S4 and Figure S6, the ratio is $r_{ethanol} = 1.50$ and the slope of calibration curve is $k_{ethanol} = 1.7796 \text{ mM}^{-1}$. Thus, the concentration of ethanol in the catholyte ($C_{ethanol}$) is:

$$C_{ethanol} = \frac{r_{ethanol}}{k_{ethanol}} = \frac{1.50}{1.7796 \text{ mM}^{-1}} = 8.429 \times 10^{-4} \text{ mol/L} \quad (6)$$

The volume of catholyte is $V=10 \text{ cm}^3$. The number of electrons required to form 1 molecule of C_2H_5OH is 12. Hence, number of electrons required to produce ethanol during the entire CO_2 electroreduction reaction is:

$$N_{ethanol} = C_{ethanol} \times V \times N_A \times 12 e = 8.429 \times 10^{-4} \text{ mol/L} \times 10 \times 10^{-3} \text{ L} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times 12 e = 6.091 \times 10^{19} e \quad (7)$$

From the chronoamperogram, $Q_0=56.66 \text{ C}$. Hence, the total number of electrons measured:

$$N_{total} = \frac{Q_0}{e} = \frac{56.66 \text{ C}}{1.602 \times 10^{-19} \text{ C/e}} = 3.537 \times 10^{20} e \quad (8)$$

Hence, the faradic efficiency of ethanol is (7)/(8):

$$FE = \frac{N_{ethanol}}{N_{total}} \times 100\% = \frac{6.091 \times 10^{19} e}{3.537 \times 10^{20} e} \times 100\% = 17.22\% \quad (9)$$

Calculations are repeated for all other products, and their faradic efficiencies are presented in Table S5. To ensure that the reported data is from a system under equilibrium condition, only the 3rd - 6th GC measurements were used in the data analysis (see Figure S8).

Table S5. Faradic efficiencies of products obtained from CO₂ reduction on a 3.6 μm thick Cu₂O film at -0.99 V vs. RHE.

Vial	Faradic Efficiencies (%)							
	CH ₄	C ₂ H ₄	CO	H ₂	C ₂ H ₆	HCOO ⁻	C ₂ H ₅ OH	Total
1	0.23	17.28	0.10	70.15	0.08			
2	0.25	32.12	0.23	44.61	0.12			
3	0.29	35.19	0.27	33.21	0.10			
4	0.33	37.17	0.33	34.06	0.09	4.66	17.22	
5	0.40	42.41	0.39	40.93	0.10			
6	0.43	35.16	0.47	43.28	0.10			
Average (3-6)	0.36	37.48	0.37	37.87	0.10	4.66	17.22	98.06

The faradic efficiencies of all the liquid and gas products should add to 100%. However, this value more commonly fluctuates around it.^{6,7} Discrepancies could be due to slight changes in the pressure of the sampling loops while they were being filled up, which affects the calculation of the faradic efficiencies. Application of more negative potentials also leads to larger and more fluctuating currents due to gas bubbling and errors induced by the IR compensation. A less-than-accurate measured current will also affect the calculated faradic efficiencies.

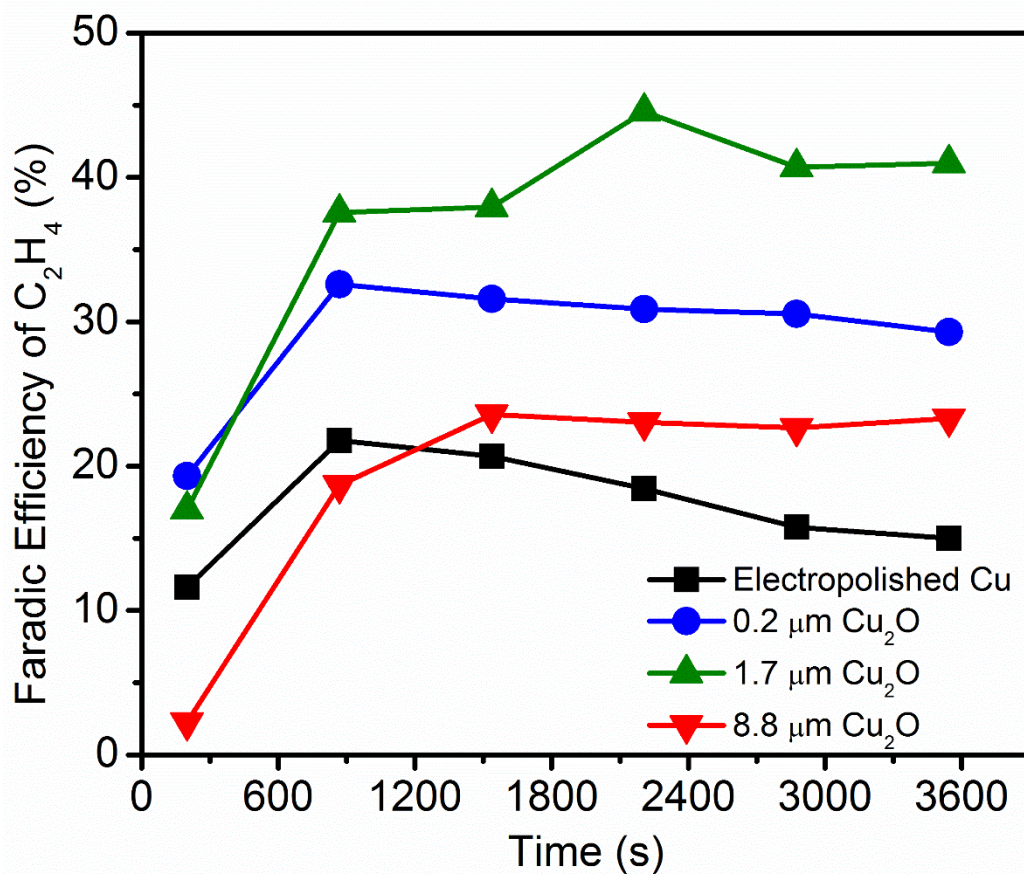


Figure S8. Faradic efficiency of C₂H₄ during 4200 seconds of CO₂ reduction on four catalysts at -0.99 V. About 25 min is needed for the products to achieve steady state concentrations.

S6. SEM Images of Cu₂O Surfaces

SEM images of other two Cu₂O films before and after reduction are shown in Figure S9.

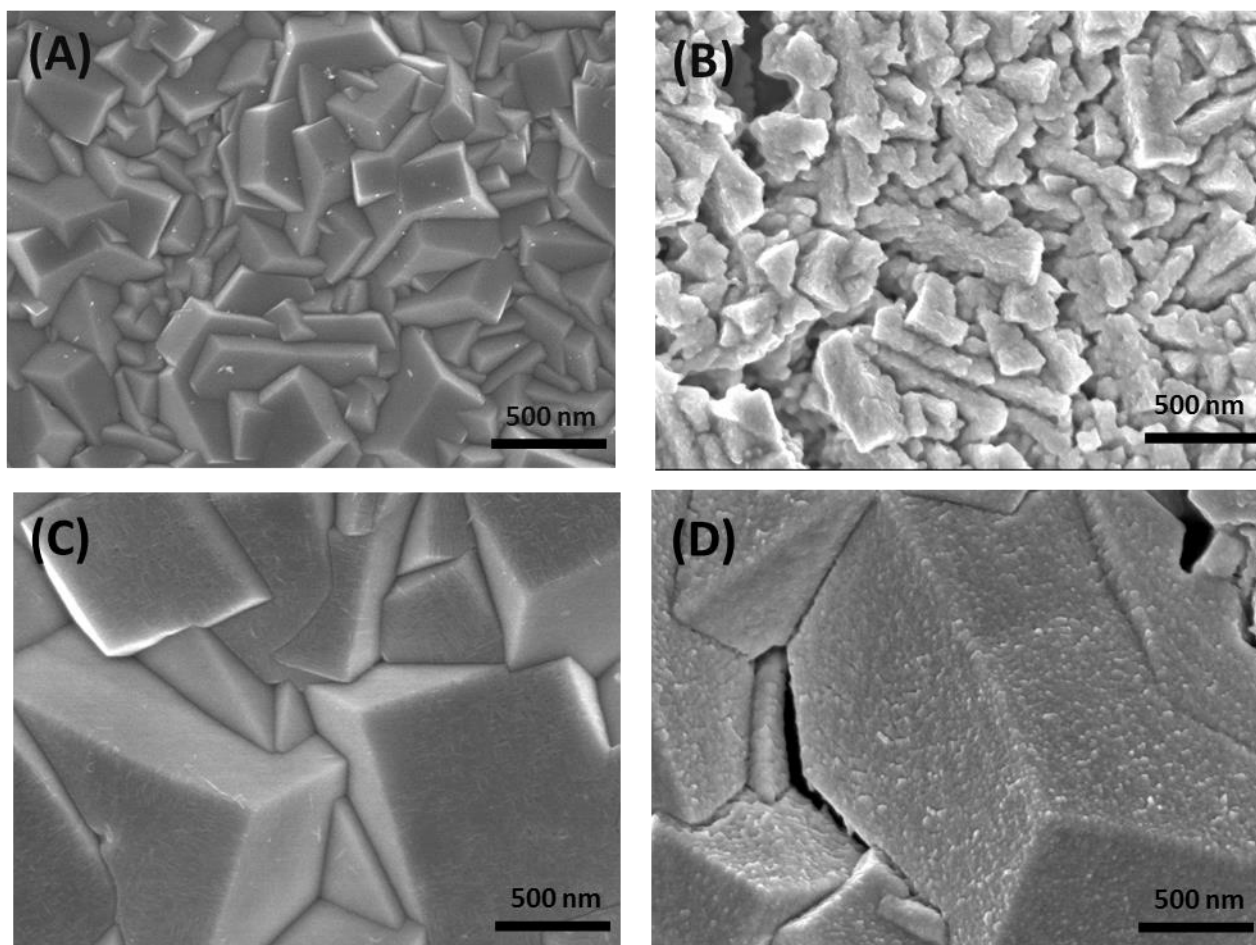


Figure S9. SEM images of Cu₂O coated electrodes. 0.9 μm thick film (A) before reduction and (B) after reduction; 6.4 μm thick film (C) before reduction and (D) after reduction.

Ex-situ SEM characterization was performed on a 1.7 μm Cu_2O film 1, 2 and 5 min after the start of CO_2 reduction at -0.99 V in 0.1 M KHCO_3 (Figure S10). The images show that cracks appear on these films early on during the CO_2 reduction process. These could be attributed to relief of strains caused by volume changes during the reduction of Cu_2O to metallic Cu.⁸

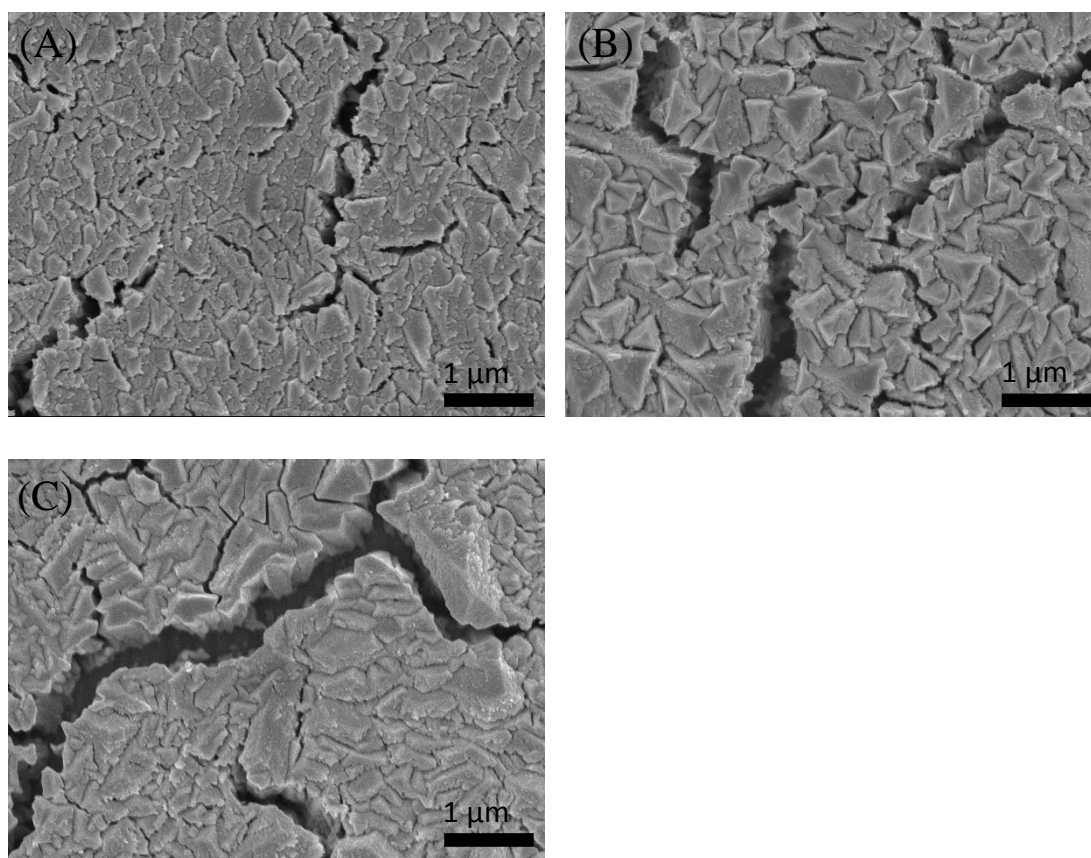


Figure S10. Time resolved ex-situ SEM micrographs of 1.7 μm Cu_2O film after (A) 1, (B) 2 and (C) 5 min of CO_2 reduction at -0.99 V vs. RHE in 0.1 M KHCO_3 .

S7. Partial current density of CO₂ reduction products

The average partial current densities (normalized to the electrochemically active surface area) of CH₄, C₂H₄, C₂H₅OH and H₂ were calculated and listed in Table S6.

Table S6. Partial current density for CH₄, C₂H₄, C₂H₅OH and H₂ on four catalysts at -0.99 V vs. RHE. N.D.: Not detected.

Catalyst	Partial current density (unit: mA/cm ²)			
	CH ₄	C ₂ H ₄	C ₂ H ₅ OH	H ₂
Electropolished Cu	-0.39	-0.61	N.D.	-1.80
0.2 μm film	-1.00	-2.95	-0.51	-2.74
1.7 μm film	-0.05	-2.43	-0.69	-2.21
3.6 μm film	-0.02	-2.39	-1.10	-2.41
8.8 μm film	-0.01	-0.59	-0.17	-1.71

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