Electronic Supplementary Information

Si Photocathode with Ag-Supported Dendritic Cu Catalyst for CO₂ Reduction

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Materials and Methods

Chemicals and Materials. All materials were used as received unless otherwise specified. Cesium carbonate (Cs₂CO₃, ACS ≥99.995%) was purchased from Sigma-Aldrich. N-type <100> silicon wafers (300 µm thick, and 1-5 ohm-cm resistivity) were purchased from Silicon Valley Microelectronics Inc. (SVM). Carbon dioxide (CO₂, 99.995%), nitrogen (N₂, 99.999%), helium (He, 99.999%), and hydrogen (H₂, 99.999%) were purchased from Praxair. Electrolyte solutions were prepared with 18.2 MΩ deionized water from a Millipore system. CsHCO₃ electrolyte solutions (0.1- 0.5 M) were prepared by vigorously bubbling (0.05 – 0.25 M) Cs₂CO₃ solutions with CO₂ gas for a few minutes to achieve the desired pH. Copper sulfate (CuSO₄, ACS ≥99.99%), hexamethylenetetramine (C₆H₁₂N₄, ACS ≥99.0%), ethanolamine (NH₂OH, ACS ≥98%), 2-Methoxyethanol (CH₃OCH₂CH₂OH, ≥99%), hydrogen peroxide solution (H₂O₂, 30 wt.%), oxalic acid (C₂H₂O₄, anhydrous, ≥99.0%), sulfuric acid (H₂SO₄, ≥99.0%), and potassium carbonate (K₂CO₃, ACS ≥99.995%, trace metal basis) were purchased from Sigma-Aldrich. Zinc acetate (ZnC4₄h₆O₄, anhydrous, ≥99.98%, metal basis) and iridium chloride (IrCl₄, ≥99.95%, metal basis) were purchased from Sigma-Aldrich. Zinc acetate (ZnC4₄h₆O₄, anhydrous, ≥99.98%, metal basis) and iridium chloride (IrCl₄, ≥99.95%, metal basis) were purchased from Sigma-Aldrich.

Photocathode Preparation. n-type silicon wafers ($\rho = 1-5$ Ω-cm, thickness 300±25 µm) were textured by a solution of 1 wt% sodium hydroxide, 1 wt% sodium metasilicate and 6 wt% isopropanol at 80 °C for 30 min. Silicon wafers were cleaned by RCA 1 and RCA 2 solutions followed by oxygen plasma for 6 min. These n-type silicon wafers were transferred into ion implantation chamber for n⁺ (phosphorus) and p⁺ (boron) doping. A two-step method was used for the n⁺ and p⁺ implants. Phosphorus ions with energies of 50 keV and 30 keV and corresponding doses of $2x10^{14}$ and $1x10^{14}$ cm⁻² were used to form the n⁺ layer. Boron ions with energies of 35 keV and 25 keV and a dose of $2x10^{14}$ cm⁻² were implanted to form the p⁺ layer. The implanted wafers were annealed at 950 °C for 30 sec in a rapid thermal annealing (RTA) furnace and were subsequently etched by using HF. The calculated peak dopant concentration near the surface was 1.3×10^{19} cm⁻³ for the n⁺ side and 1.5×10^{19} cm⁻³ for the p⁺ side and the depth of the buried n-n⁺ junction was ~300 nm and n-p⁺ junction was ~470 nm (Fig. S1).



Fig. S1. Calculated implantation profile for (a) phosphorus and (b) boron implantation into Si followed by annealing at 900 °C for 30 s.

The etched wafer was immediately transferred to the ALD chamber for TiO_2 deposition. A 10 nm layer of TiO_2 was deposited on n⁺ side of Si wafer by using titanium tetraisopropoxide (TTIP) as the precursor. After TiO_2 deposition, a 100 nm silver layer was deposited by electron beam evaporation. Aluminum fingers were deposited on the p⁺ side of Si wafer via electron beam evaporation to form back contacts.

The dendritic copper "nano cactus" structure was grown by electrodeposition. To provide current for the deposition, an independent electrical contact was made to the silver. A Teflon cell was used for electrodeposition, in which a region of the silicon photocathode isolated by an o-ring formed the working electrode and a Pt mesh was used as the counter electrode. The electrodeposition process was performed at a constant current of 400 mA for 10, 20 and 60 sec. The 10 sec deposition time was found to be optimal in terms of selectivity to the target products; this condition was used throughout the study. Longer electrodeposition times creates thicker nanostructures, which completely cover the underlying silver. After electrodeposition, the photocathode was washed in DI water and dried with a gentle nitrogen stream. Under high current density conditions, the competitive reaction of hydrogen evolution forms a bubble template, which defines the nanocactus morphology and controls the amount of copper at the surface. Finally, an ohmic contact was formed by affixing copper wire to the aluminum fingers at the backside of silicon photocathode using conducting epoxy. Si photocathodes with an Au-supported dendritic Cu catalyst were fabricated by above method except that a 100 nm layer of Au was used instead. As experimental controls, we synthesized dark cathodes using Ag and Au supporting metal layers

followed by Cu deposition on n-type Si following the same procedure but omitting the p⁺ back contact.

Photocathode regeneration. After 10 days of simulated diurnal cycling, a reduction in selectivity to CO₂R and an increase in HER was observed, Fig 4b. As discussed in the main text, this is attributed to the poisoning of the photocathode surface by deposition of metals from the counter electrode. For regenerate the original catalyst selectivity for CO₂R, we mechanically removed the poisoned Cu from the photocathode surface with a soft tissue, while not damaging the Ag layer below. Next, the photocathode sample was sonicated for 30 sec and dried by nitrogen. Then, the copper nanocactus structure was regrown by the previously described electrodeposition method using a constant current of 400 mA for 10 sec. Regenerated Si photocathode shows lower hydrogen selectivity and slightly higher CO selectivity than the as-prepared Si photocathode during the entire length of CO₂RR measurements, Fig. 4d.

Cu-supported dendritic Cu catalyst on planar Si. A Si wafer was etched with 5% HF solution to remove the oxide layer and transferred immediately to the electron beam deposition chamber. 10 nm Ti was deposited as an adhesion layer followed by 100 nm of Cu. The same electrodeposition process described above was used to create the dendritic copper "nano cactus" structure. After Cu electrodeposition, the cathode was washed in DI water and dried with a gentle nitrogen stream.

IrO₂ anode preparation. We prepared high surface area IrO₂ by following our previous recipe.¹ Briefly, titanium foil was sonicated for 15 min in acetone, isopropanol, and DI water. Then, the foil was sanded by increasing grades of sandpaper from 1200 to 2500 grit, degreased in 0.1 M HCl for 5 min to remove the undesired oxide layer, and finally rinsed in DI water for 45 min. The ZnO template was prepared by a two-step method. First, a seed layer of ZnO was deposited by spin coating and then ZnO nanorods were grown on seed layer coated foils via hydrothermal synthesis. For perform the hydrothermal synthesis, an aqueous solution of 30 mM zinc nitrate and 15 mM hexamethylenetetramine were added to a Teflon liner with an Ir foil and then heated at 95 °C for 6 hrs. Afterwards, the hydrothermally grown ZnO nanorod samples were rinsed with DI water and blow-dried with nitrogen.

The iridium oxide precursor solution was prepared in 4 steps: (i) 50 ml of 0.005 M iridium chloride aqueous solution (dark brown) was stirred for 30 min; (ii) 0.5 mL hydrogen peroxide (30 wt%) was added slowly and stirred for 15 min until the solution color turned from light brown to

yellowish; (iii) 250 mg oxalic acid was mixed in the solution while, over 15 minutes, the solution turned to a light yellowish color; (iv) potassium carbonate was slowly added to change the pH to ~10. We aged the solution for three days until the solution turned a purple or blueish color. Electrodeposition of IrO_2 was performed in a two-electrode configuration, with Ir foil used as the working electrode, and Pt wire as the counter electrode. A constant current scan at 5 mA for 30 min was performed. After electrodeposition, the samples were soaked for 10 min in 0.01 M perchloric acid to etch the ZnO layer. Finally, the iridium oxide (IrO_2) nanotube array was washed with DI water and blow dried with nitrogen.

Semi-transparent perovskite solar cell fabrication. Fluorine doped tin oxide (FTO) glass substrates (Tec15) were cleaned sequentially by ultrasonication in a decon soap solution, deionized water and ethanol, followed by UV ozone treatment for 15 min. Compact TiO₂ (cTiO₂) was spray deposited at 500 °C on a sintering hot plate, using titanium diisopropoxide bis (acetylacetonate) (Sigma-Aldrich, 75 wt % in isopropanol) mixed with isopropanol (Sigma-Aldrich, anhydrous) and acethylacetone (Sigma-Aldrich). The mesoporous TiO₂ (mp-TiO₂) layer was then spin-coated on the substrate at 5500 rpm for 30 s by using a solution with Dyesol 30NRD diluted in absolute ethanol (ratio 1:5.5 (w/w)). The substrate was then sintered at 500 °C for 15 min. To form the triple cation perovskite precursor solution, $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ (1.5 M), MABr (Dyesol), FAI (Dyesol), PbBr₂ (TCI), and PbI₂ (TCI) were dissolved in a mixture of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solvent with a ratio of 4:1 (v/v) at room temperature for 30 min first, followed by the addition of small amount of CsI precursor (dissolved in DMSO).

The perovskite solution was spin-coated on the mp TiO₂ substrate first at 1000 rpm for 10 s followed immediately by 6000 rpm for 17 s, with 0.1 mL of dichlorobenzene dripped onto the substrate at 13 s. The film was then annealed at 100 °C for 1 hour to obtain black and dense perovskite film. A solution of spiro-OMeTAD (70 mg/mL in chlorobenzene) with addition of 4-tert-butylpyridine, lithium bis(trifluoromethylsulfonyl)imide (520 mg/mL in acetonitrile (ACN)), and FK209 (17.2mg/50 mL of ACN) was spin-coated on top of the perovskite layer at 5000 rpm for 30s. Perovskite and hole transport material (HTM) preparations were done inside a glovebox. ~1 nm Ag was thermally evaporated as a buffer layer prior to electrode deposition. 200 nm thick Indium tin oxide (ITO) was used as transparent electrode, which was deposited using DC

sputtering at 25 W power for 1 hour. A low sputtering power was used to avoid damage to the perovskite absorber layer which occurs at higher powers.

CoPi electrode synthesis. A CoPi oxygen evolution catalyst was synthesized via a previously reported electrodeposition method on fluorine doped tin oxide (FTO) coated glass substrate.² In brief, FTO coated glass substrates were cleaned in decon solution, IPA, DI water and blow dried with N₂ stream. Electrodeposition was performed by using FTO as a working electrode, Ag/AgCl and Pt foil as reference and counter electrodes respectively at -1.1 V vs Ag/AgCl for 30 min in 0.1 M KPi (pH 7) and 5 mM cobalt nitrate hexahydrate Sigma-Aldrich (99.999%).

Testing of photocathodes. A Biologic VSP-300 potentiostat with electrochemical impedance package was used throughout this study. A photo of the back-illumination PEEK cell is shown in Fig. S2. In this cell design no epoxy or other material besides PEEK, the O-rings, the membrane, and the electrodes is in contact with the electrolyte. IrO_2 and Ag/AgCl were used as counter and reference electrodes, respectively. A manual IR compensation has been made to compensate the series resistance within the PEEK cell before each CO₂ RR measurement, as described below. A typical linear scan voltammetry measurement is performed in a three-electrode configuration over a potential range from 0.5 V to - 2.0 V vs. RHE in 0.1 M CsHCO₃ electrolyte (pH = 6.8) purged with CO₂ at 10 sccm. A N₂ gas flow was directed onto the electrochemical cell during light illumination measurements to prevent heating of the cell.



Fig. S2. Photographic image of the photoelectrochemical cell (top view). The illuminated sample area is 1 cm².

Photoelectrochemical cell and measurement of gas and liquid products. The PEEK cell used in this work has been described in detail previously.³ We cleaned the sandwich cell in aqua regia or nitric acid and DI water before every measurement, and each measurement was repeated several times. All the gaseous products were measured with an inline GC (SRI 8610C) and liquid samples were collected after GC measurements and fed to the high-performance liquid chromatograph (HPLC) for liquid products analysis; see below for quantification protocol. The full list of detected products, along with the groupings used in the main text, is shown in Table S1.

Table S1. CO₂ RR products observed in this study. The first column shows all the products observed. The other columns are the grouping used in the main text to describe the product distribution.

CO ₂ RR Products				
All observed products	HCs+Oxygenates	C ₂₊ products	Liquids	C ₂₊ liquids
Hydrogen	Methane	Ethylene	Formate	Acetate
Carbon Monoxide	Ethylene	Ethane	Acetate	Acetaldehyde
Methane	Ethane	Acetate	Acetaldehyde	Propionaldehyde
Ethylene	Formate	Acetaldehyde	Propionaldehyde	Allyl Alcohol
Ethane	Acetate	Propionaldehyde	Allyl Alcohol	Ethanol
Formate	Acetaldehyde	Allyl Alcohol	Ethanol	Propanol
Acetate	Propionaldehyde	Ethanol	Propanol	Hydroxyacetone
Acetaldehyde	Allyl Alcohol	Propanol	Hydroxyacetone	Ethylene Glycol
Propionaldehyde	Ethanol	Hydroxyacetone	Ethylene Glycol	Glyoxal
Allyl Alcohol	Propanol	Ethylene Glycol	Glyoxal	Glycolaldehyde
Ethanol	Hydroxyacetone	Glyoxal	Glycolaldehyde	
Propanol	Ethylene Glycol	Glycolaldehyde		
Hydroxyacetone	Glyoxal			
Ethylene Glycol	Glycolaldehyde			
Glyoxal				
Glycolaldehyde				

Photoelectrochemical cell optimization in two-electrode mode for tandem configuration. Two electrode measurements were made to determine optimal conditions for coupling to solar cells. These were performed as described above but without the reference electrode. The overall cell potential was varied from -2.0 to -3.0 V and the electrolyte concentration was also varied, 0.1 M to 0.5 M CsHCO₃ electrolyte (pH = 6.8 - 7.2).

IR compensation and measurement of cell resistance. Electrolyte resistance causes a voltage drop between the working and reference electrode.

According to Ohm's law:

V=I×R_s

This solution resistance is usually referred to uncompensated resistance (R_s). Electrolyte solution resistance depends on a number of factors including the type of electrolyte (pH), the electrochemical cell geometry, and the electrode size. R_s can vary between experiments, so it has to be corrected in each experiment for consistency.

We measured the electrochemical impedance of the cell to evaluate Rs. The contributions of Rs can easily be calculated at high frequency because the impedance from other components of the electrochemical cells are negligible at high frequency. EIS was performed from 1 MHz to 100 Hz to obtain the correct frequency in determining Rs (10 kHz). The VSP-300 potentiostat's IR compensation function only compensates 85% of Rs, thus the remaining 15% of Rs was corrected manually. Final voltage calculation after 100% IR compensation is as below:

V100% IR_s (RHE)= V85% IR (RHE) + 15% average R_s (Ohms) \times average I (amps)

An example measurement the electrochemical impedance of planar and textured Si photocathode under dark and 1 sun simulated illumination at -0.4 V vs RHE is provided here. We used the equivalent circuit in Fig. S3 to fit the EIS data and calculate the interfacial resistance and capacitance values. Si photocathodes show a high resistance under dark, and low under illumination which is expected, Fig. S4 (a). The reactor resistivity (series resistance) is same (~46.2 Ω) under dark and illumination but the surface charge transfer R_{ct,trap} is very low as compared to the dark analysis. The R_{ct,trap} value is only 5.6 Ω for textured Si photocathode, whereas planar Si shows a R_{ct,trap} value of 31 Ω under 1 sun illumination.



Fig. S3. RC equivalent circuit for electrochemical impedance analysis.



Fig. S4. Nyquist plots of planar and textured silicon photocathodes at -0.4 V vs RHE under dark and illumination.

Analysis of gaseous products. Four gas phase CO_2R products (CO, CH₄, C_2H_4 , and C_2H_6) and also H₂ were detected and quantified with gas chromatography. The CO₂ was continuously flowing through the PEC cell; a portion of the exiting gas is directed into the sampling loops of the gas chromatograph. Two channels were used. Channel 1 comprises a 6' Heysep-D and a 6' Molsieve 13x column, a 1 ml sampling loop, Ar carrier gas and H₂ for flame ignition. This channel is

equipped with a flame ionization (FID) detector and a methanizer for CO to CH₄ conversion. Channel 1 has the ability to detect the CO, CH₄, C_2H_4 and C_2H_6 . Channel 2 has a 6' Heysep-D column, a 2 ml sampling loop, and N₂ carrier gas. This is equipped with a TCD detector for H2 detection. An example of raw GC data for textured Si at -1 V vs RHE is shown in Fig. S5. The concentration of the individual gases in the exit stream was quantified based on a 4 point calibration of the GC using a standard containing H₂, CO, CH₄, C₂H₄, and C₂H₆ diluted as appropriate with Ar. The GC software integration feature was used.



Fig. S5. Raw GC data, top trace is from channel 1 (FID) and bottom trace is from channel 2 (TCD). Peaks are labeled.

The Faradaic efficiency of the CO₂ reduction gaseous products is calculated as below;

$$FE(\%) = \frac{F \times n_e \times x \times F_r}{I}$$

where *F* is the Faraday constant (96485 C mol⁻¹), n_e is the number of the electrons required for a particular CO₂ reduction product, *x* is the mole fraction of the gaseous product obtained from the GC, F_{CO2} is the molar flow rate of CO₂ through the cell, and *I* is the average current during the run. The number of electrons required are 2, 8, 12, and 14 for CO, CH₄, C₂H₄, and C₂H₆

respectively. We show an example of an FE calculation of the gaseous products for the data shown in Fig. S5.

Table S2. Si photocathode J-V and CO₂R products concentration from GC (textured Si illuminated with AM 1.5 at -1 V vs RHE with 10 sccm CO₂ flow).

Voltage	Current	Mole	Mole fraction	Mole fraction	Mole
		fraction. of	of Hydrogen	of CO	fraction of
		Ethylene			Methane
-1. 0 V	27.7 mA	1310 ppm	3279 ppm	220 ppm	235 ppm

$$F_{CO2} = \frac{10 \ cm^3/min \times}{22.4 \ liter/mol} = 7.43 \times 10^{-6} \ mol \ sec^{-1}$$

$$FE_{C2H4}(\%) = \frac{96485 \text{ C mol}^{-1} \times 1310 \times 10^{-6} \times 12 \times 7.43 \times 10^{-6} \text{ mol sec}^{-1}}{27.7 \times 10^{-3} \text{ C sec}^{-1}} \times 100 = 40.7\%$$

$$FE_{H2}(\%) = \frac{96485 \text{ C mol}^{-1} \times 3279 \times 10^{-6} \times 2 \times 7.43 \times 10^{-6} \text{ mol sec}^{-1}}{27.7 \times 10^{-3} \text{ C sec}^{-1}} \times 100 = 16.9\%$$

$$FE_{C0}(\%) = \frac{96485 \text{ C mol}^{-1} \times 220 \times 10^{-6} \times 2 \times 7.43 \times 10^{-6} \text{ mol sec}^{-1}}{27.7 \times 10^{-3} \text{ C sec}^{-1}} \times 100 = 1.1\%$$

$$FE_{CH4}(\%) = \frac{96485 \text{ C mol}^{-1} \times 235 \times 10^{-6} \times 6 \times 7.43 \times 10^{-6} \text{ mol sec}^{-1}}{27.7 \times 10^{-3} \text{ C sec}^{-1}} \times 100 = 3.6\%$$

Analysis of liquid products. Liquid products were detected by HPLC (UltiMate 3000, Thermo Scientific) at the end of the run (70 min) by extracting the electrolyte from both the anode and cathode chamber. Analysis of both chambers is required as negatively charged species evolved at the cathode, such as formate and acetate, can cross the anion conducting membrane and accumulate in the anode chamber. The liquid-phase products contained in a 10 μ L aliquot were separated using a series of two Aminex HPX 87-H columns (Bio-Rad Inc.) and a 1 mM sulfuric acid eluent (99.999% Sigma Aldrich). The column oven was maintained at 60°C for the duration of the analysis. The signal response of the refractive index detector (RID) was calibrated by analyzing standard solutions of each product at a concentration of 1, 10, and 50 mM. An example chromatogram is shown in Fig. S6.



Fig. S6. Raw HPLC data from textured Si at -1 V vs RHE under 1 sun AM1.5 illumination. Peaks are labeled. The Faradaic efficiency of the CO₂ reduction liquid products is calculated as below;

$$FE(\%) = \frac{F \times n_e \times y \times V_e}{Q_t}$$

where *F* is the Faraday constant, n_e is the number of the electrons required for a particular CO₂ reduction product, *y* is the concentration (mol liter⁻¹) of the liquid product, *V_e* is the electrolyte volume (L) and *Q_t* is the total charge passed through during the CO₂R, which is 116.34 C in this example.

$$FE_{ethanol} = \frac{96485 \frac{C}{mol} \times 12 \times 6.98 \times 10^{-3} \frac{mol}{L} \times 1.8 \times 10^{-3} L}{116.34 C} \times 100 = 12.5\%$$

$$FE_{formate} = \frac{96485 \frac{C}{mol} \times 2 \times 10.57 \times 10^{-3} \frac{mol}{L} \times 1.8 \times 10^{-3} L}{116.34 C} \times 100 = 3.2\%$$

The FEs for the other liquid products are calculated similarly and are summarized along with the gas phase FEs in Table S2. In this example, the sum of the FEs is 99.4%.

Products	Faradaic Efficiency (%)
H ₂	16.9
СО	1.1
CH ₄	3.6
C ₂ H ₄	40.7
Formate	3.2
Ethanol	12.5
Propanol	8.5
Other C ₂ -C ₃ oxygenates	12.9
Sum	99.4

Table S3. The sum of FEs from above example calculation.

Reported Si based photocathodes

Table S4. Summary of reported Si photocathodes for CO_2RR . Studies used an aqueous electrolyte purged with CO_2 and front illumination with simulated AM1.5G unless otherwise noted.

Device structure/ catalyst	Electrolyte and illumination	Faradaic efficiency	Product distribution	Ref.
p-type Si-H/ Re(bipy- But)(CO)₃Cl	0.1 M TBAH 95 mW cm ⁻²	97±3% @ -1.4 V vs Ag/AgCl	СО	4
p-type Si nanowire/ [Ni(bpy)₂]	0.1 M TBAB, 0.5 mM [Ni(bpy) ³⁻ (BF ₄) ²] 100 mW cm ⁻²	64% @ -0.3 V vs Ag/Agl/I ⁻	Carboxylic Acid	5
p-type Si-H Nanowire/ [Mn(bpy or dmbpy) (CO) ₃ (CH ₃ CN)](PF ₆)	CH₃CN + 0.1 M Bu₄NClO₄ 20 mW cm⁻²	Not Provided	CO	6
p-type Si / Nanoporous Au	0.2 M KHCO ₃ 100 mW cm ⁻²	90% @ -0.59 V vs. RHE	СО	7
p-type Si/Cu nanoparticles	0.1 M KHCO ₃ 100 mW cm ⁻²	~5% at -1.4 V vs SCE	C_2H_4	8
p-type Si nanowire/ Sn Nanoparticles	1M KHCO ₃ 100 mW cm ⁻²	40% single cell, 88% in H cell	HCOOH	9
p-type Si/ Cu p-type Si/ Ag p-type Si/ Au	0.1 M KHCO_3 100 mW cm ⁻²	~55% for all C-C products @ -1.75 V vs SCE @ p-Si/Cu 50.9% for CO @ -1.05 V vs SCE @ p-Si/Ag 62.2% for CO @ -1.05 V vs SCE @ p-Si/Au	CH ₄ , C ₂ H ₄ , CO, HCOOH	10
p-type Si/ Graphene quantum sheet	0.1 M TBAH in acetonitrile 100 mW cm ⁻²	95% @ - 1.9 V vs Ag/AgCl	СО	11
p-type Si NW/Au₃Cu nanoparticles	0.1 M KHCO_3 100 mW cm ⁻² 18 hrs stability	80% @ -0.2 V vs RHE	CO	12
2 triple junction a-Si/ WSe ₂	EMIM-BF ₄	24% @ -0.164 V	со	13
n-type Si/ CuAg n-type Si/ CuAu	0.1M CsHCO ₃ 100 mW cm ⁻² 20 days stability	~70% Hydrocarbons and oxygenates	C₂H₄, C₂H₅OH, C₃H ₈ OH	This work

Supplemental SEM-EDX, XRD, and XPS data



Fig. S7. (a) Surface view SEM image of textured Si photocathode with Ag-supported dendritic Cu catalyst. (b) Cross-section EDX elemental mapping of textured Si photocathode with Ag-supported dendritic Cu catalyst. (c) Surface view SEM image of textured Si photocathode with Au-supported dendritic Cu catalyst. (d) EDX elemental mapping of Si photocathode integrated with Au-supported dendritic Cu catalyst. (e) Cross-section SEM image of textured Si photocathode with Au-supported dendritic Cu catalyst. (f) Cross-section EDX elemental mapping of textured Si photocathode with Au-supported dendritic Cu catalyst. (f) Cross-section EDX elemental mapping of textured Si photocathode with Au-supported dendritic Cu catalyst.



Fig. S8. (a) Surface view SEM image of planar Si photocathode with Au-supported dendritic Cu catalyst. (b) EDX elemental mapping of planar Si photocathode with Au-supported dendritic Cu catalyst. (c) Surface view SEM image of planar Si photocathode with Ag-supported dendritic Cu catalyst. (d) EDX elemental mapping of Si planar photocathode integrated with Ag-supported dendritic Cu catalyst.

The XRD patterns of the planar and textured Si photocathode integrated with dendritic catalysts can be indexed to the characteristic diffraction peaks of Cu (JCPDS no. 04-003-2953), Ag (JCPDS no. 04-089-3722) and Au (JSPDS no. 04-003-1953) (Fig. S9). The dominant reflection is related to the (111) crystal lattice in the case of Ag0 and Cu0, while in the case of Cu0 (111) and (200) both are present with the dominance of the (111) crystal lattice.



Fig. S9. (a) XRD pattern of Ag-supported dendritic Cu catalysts on planar (P Si) and textured Si (T Si) photocathode at two different deposition times. Note the relative increase of the Cu feature at the longer deposition time. (b) XRD pattern of Au-supported dendritic Cu catalyst on planar (P Si) and textured Si (T Si).

X-ray photoelectron spectroscopy (XPS) was conducted to analyze the surface composition of Ag supported dendritic Cu catalysts. All spectra were acquired using monochromatized Al Ka radiation. The energy scale was calibrated by setting the observed C 1s binding energy to 284.8 eV. XPS results of Si photocathode are shown in Table S5. High-resolution spectra of the characteristic lines (Cu 2p, Ag 3d, and Cu 3p) are shown in Fig. S10. A strong peak of Cu 2p at 932.6 eV can be assigned to the Cu⁰ or the Cu¹⁺ state, while the shoulder appeared at 934.8 eV and the presence of the characteristic "shake up" satellite structure is typical for Cu²⁺ state.¹⁴ Silver was detected in the metallic state with a low apparent atomic concentration (~1 at%) (Table S5), especially in areas which appeared to have lower coverages of Cu. It may be the case the Ag fraction of the catalyst in contact with the electrolyte is underestimated in the XPS measurement due to scattering of photoelectrons emitted by the Ag by the nanostructured Cu above it.



Fig. S10. High-resolution XPS spectra of the characteristic peaks: (a) Cu 2p; (b) Ag 3d; and (c) Cu 3p.



Supplemental photoelectrochemical data

Fig. S11. Double layer capacitance analysis of Ag-supported dendritic Cu on textured Si. (a) Capacitance current versus applied potential curve with various scan rates in $0.05 \text{ M K}_2\text{CO}_3$. (b) Capacitance current versus scan rate graph. The slope of this graph gives the double-layer capacitance and the ratio of this value to the flat copper or silver on planar Si gives the roughness factor. Double-layer capacitances and relative roughness factors for all catalysts are shown in Table S7.

Factor

15.74

Samples	Capacitance (µF)	Roughness
Cu on planar Si	42	1
Ag on planar Si	45	1.07
Ag-supported dendritic Cu on planar Si	302	7.19

Table S5. Double-layer capacitances and roughness factors.

Ag-supported dendritic Cu on textured Si

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Fig. S12. Photocurrent-potential curves of planar (green) and textured (blue) Si photocathodes with Au-supported dendritic Cu catalyst in 0.1 M CsHCO₃ under dark and simulated 1 sun (AM 1.5G, 100 mW cm⁻²) illumination.



Fig. S13. (a) Faradaic efficiency of planar Si photocathode with Au-supported dendritic Cu catalyst. and (b) Faradaic efficiency of textured Si photocathode with Au-supported dendritic Cu catalyst in 0.1 M CsHCO₃, pH 6.8 and under 1 sun illumination.

Estimation of photovoltage

The equivalent circuit for the photocathode device is a PV cell linked in series with the electrocatalyst.¹⁵ Thus, the photovoltage contributed by the PV portion of the photocathode can be estimated by comparing the JV curves of the electrocatalyst by itself to that of the illuminated device. In the current density range which is available from the PV element, that is up to the short circuit current of the device, the applied voltage for the illuminated device will be shifted anodically by the corresponding PV voltage. Thus here we can extract the PV parameters of the Si device by comparing J-V data from n⁺Si/TiO₂/CuAg (dark) with the photo response of the p⁺/n-Si/n⁺/TiO₂/CuAg photocathode using an analysis we have employed before for a similar constructed photoanode used for water oxidation.¹⁶ We used the following equation for the PV model,

$$J = J_{sc} - J_0 \cdot exp\left[\frac{q(V+JR_s)}{nkT}\right] - \frac{V+JR_s}{R_{sh}}$$

where *J* is the measured current density, J_0 is the reverse saturation current, J_{SC} is the short circuit current, *V* is the voltage across the PV junction, *n* is the ideality factor, *T* is temperature, and *q* is the fundamental charge. R_s and R_{sh} are the series and shunt specific resistances, respectively. In an ideal solar cell, R_s is zero and R_{sh} is infinite. Figure S14 shows the results of this analysis with the following: n = 1, $R_s = 0.1 \ \Omega$ -cm², $R_{sh} = 50 \ M\Omega$ -cm², and $J_{SC} = 28.4 \ mA \ cm^{-2}$. The upper fit uses $J_0 = 0.5 \times 10^{-10} \ mA \ cm^{-2}$ ($V_{oc} = 640 \ mV$) and the lower fit uses $J_0 = 1.45 \times 10^{-8} \ mA \ cm^{-2}$ ($V_{oc} = 550 \ mV$).



Fig. S14. Photocurrent-potential curves of a planar Si photocathode with Ag-supported dendritic Cu catalyst in 0.1 M CsHCO₃ under dark conditions (black points) and simulated 1 Sun (AM 1.5G, 100 mW cm⁻²) illumination conditions (red points). The J-V data under 1 Sun illumination was fit with a convolved model in the high (green line) and low (blue line) current density ranges. The region between the upper and lower fit is shaded in aqua.

Comparison of light and dark product distributions

The CO₂ RR product distribution produced by the dark cathode and the photocathode change with applied voltage. Our aim is to compare the FE of individual products at the same current density from both the dark cathode and the photocathode to estimate the photovoltage generated by photocathode. We assume at this point that the voltage between the metal and the solution is the same, with the difference in the applied potential corresponding to the photovoltage. To obtain a similar current density, a dark cathode was examined at a potential of -1.1 V vs RHE for CO₂RR, while a planar Si photocathode was investigated at -0.55 V vs RHE. Under these conditions, both electrodes produce -7.7 mA cm⁻² with a similar distribution of products, Fig. S15. The applied voltage difference is the photovoltage generated by photocathode, which is ca. 550 mV in this case.



Fig. S15. (a) CO_2 RR products distribution of Si photocathode at -0.6 V vs RHE under 1 Sun illumination. (b) CO_2 RR products distribution of dark cathode at -1.1 V vs RHE in the dark. In both cases the current density is -7.7 mA cm⁻². An integrated Ag-supported dendritic Cu catalyst was used for both of these experiments.

Photocathode stability and regeneration process

As shown in Fig. 4a, over 10 days of simulated diurnal testing, the current density was fairly stable in time but a reduction in selectivity for CO_2R was observed. SEM analysis revealed no obvious changes in photocathode morphology after 10 days of operation (Figs. S17a and b). However, XPS analysis of the photocathode surface revealed the presence of Ir contamination (Fig. S18c), which is the main cause of the decrease in CO_2R selectivity. When the IrO₂ counter electrode was replaced with Pt, we found that the photocathode poisoning happened faster, with Pt being observed at the cathode after only 2 days (Fig. S19c).

To address the issue of contamination from the counter electrode, we developed a catalyst regeneration scheme, which consists of removal of poisoned copper and redepositing fresh dendritic Cu on the photocathode (see Materials and Methods section above for photocathode regeneration process). There are some changes in surface morphology after regeneration (Figs. S17c and S21), as the redeposited Cu appears to preferentially nucleate on the dendrites as opposed to on the underlying Ag. As a result, more Ag is visible in the SEM image and a larger fraction of Ag compared to Cu is observed in XPS (Figs. S20, S21 and Table S6).

			Surface conc. (at.%)		
Elements / component	Binding energy (eV)	Chemical states	Ir contam	Pt contam	Regen.
Cu 2p	932.6	Cu(I) (Cu ₂ O)	22.3	48.8	34.4
	934.8	Cu(II) (CuO; Cu(OH) ₂)	5.4	3.3	4.2
O 1s	530.5	Cu ₂ O, C=O	14.5	18.0	18.7
	531.6	Hydroxides	23.2	9.8	18.3
C 1s	284.8	C-C	12.1	9.5	14.3
	286.2	C-0	10.5	4.0	4.3
	289.1	C-C=O, O-C=O, O=C-OH	3.6	4.3	5.2
Ag 3d	368.3	Ag^0	0.5	0.7	0.7
Cu 3p	75.2				
Ir 4f	62.4	IrO ₂	1.7		
Pt 4f	71.5	Pt^{0}		1.7	

Table S6. XPS surface composition of (1) Ir contaminated photocathode, (2) Pt-contaminated photocathode, and regenerated photocathode. The Pt contaminated sample was evaluated after 2 days of operation; the Ir contamination photocathode was evaluated after 10 days of operation.



Fig. S16. Current traces from simulated diurnal cycling of silicon photocathode in 0.1 M CsHCO₃ electrolyte solution at -0.4 V vs RHE and under simulated 1 Sun condition. The electrolyte was changed after each measurement (a) Ten days stability photocurrent of Si photocathode before regeneration. (b) Ten days stability photocurrent of Si photocathode after regeneration. Textured Si with an integrated Ag-supported Cu catalyst was used for these experiments.



Fig. S17. SEM image of textured Si photocathode with integrated Ag-supported Cu catalyst. (a) As prepared sample. (b) After 10 days stability measurements and (c) Regenerated photocathode.



Fig. S18. High-resolution XPS spectra of the Ir-contaminated photocathode with the characteristic peaks: (a) Cu 2p; (b) Ag 3d; and (c) Cu 3p with Ir 4f contamination.



Fig. S19. High-resolution XPS spectra of the Pt-contaminated photocathode with the characteristic peaks: (a) Cu 2p; (b) Ag 3d; and (c) Cu 3p with Pt 4f contamination.



Fig. S20. High-resolution XPS spectra of regenerated photocathode with the characteristic peaks: (a) Cu 2p; (b) Ag 3d; and (c) Cu 3p. Note the absence of features due to Ir, which were observed in Fig. S18.



Fig. S21. (a) SEM image and (b) EDX elemental mapping of regenerated Si photocathode with regrowth of dendritic Cu catalyst.

Calculation of solar to chemical product conversion efficiency

The solar-to-chemical (STC) conversion efficiency is calculated on the basis of all products generated during solar-powered catalysis, as, in principle, all could be converted back to CO_2 utilizing their free energy. The STC efficiency can be calculated from the FEs of individual product with knowledge of their standard thermodynamic potential, the operating current of the cell, and the input solar power.

$$\eta_{STC_i = \sum \frac{I_{op} \times E_i^o \times FE_i}{P_{in}}}$$

where, I_{op} is operating current, E_i^o is the thermodynamic potential of the respective product, FE_i is the Faradaic efficiency of individual product and P_{in} is input power. For example, the STC efficiency of a solar converter, which produced only CO, would be:

$$\eta_{\text{STC,CO}} = \frac{I_{\text{op}} \times 1.33 \times FE}{100 \times Area}$$

A compilation of the thermodynamic potentials for all CO₂RR products observed in this work can be found in our previous work.¹

Supplemental photovoltaic data

Self-powered CO₂ reduction device. Two perovskite solar cells masked to an area of 0.5 cm^2 each were connected in series with a Si photocathode of 1 cm^2 active area. In this configuration, we use the aperture area of the perovskite solar cells and the photocathodes, both 1 cm^2 , to define the active area. A short-circuited perovskite solar cell masked to 1 cm^2 was used to simulate the light filtering conditions for Si photocathode as shown in Fig S22. The total open circuit voltage is 2.80 V: 2.15 V from the series connected perovskite solar cells and 0.65 V from Si photocathode. Based on our two-electrode stability measurements, this is sufficient to drive CO₂ conversion into hydrocarbons and oxygenates (Fig. S24).



Fig. S22. Top view of self-powered device. The effective aperture area is 1 cm^2 . A short-circuited solar cell with an active area of 1 cm^2 placed in front of Si photocathode to filter the light. Two-perovskite solar cell with 0.5 cm² area each were connected in series with the Si photocathode.



Fig. S23. J-V curve of a single semitransparent perovskite solar cell under dark and simulated 1 Sun (AM 1.5G, 100 mW cm⁻²) illumination conditions. Cell area was 0.5 cm⁻².



Fig. S24. Current density vs time curve of a textured silicon photocathode with integrated Ag-supported dendritic catalyst. The durability test was performed with a 0.1 M CsHCO_3 electrolyte solution and in 2-electrode mode at 3 V total cell voltage and under simulated 1 Sun illumination.

Devices	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF	η (%)
Single semitransparent perovskite PV	14.5	1.06	55	8.4
2 series connected PV	5.8	2.15	56	7.1

Table S7. J-V parameters of semitransparent perovskite solar cells.

CoPi counter electrode

A CoPi anode was evaluated as a possible alternative to IrO₂ as the water oxidation anode. We performed a linear scan voltammetry measurement of CoPi in CO₂ saturated 0.1 M CsHCO₃

solution and compared the performance with IrO_2 electrode (Fig. S25); CoPi requires a higher overpotential at all relevant current densities. To assess the stability of the CoPi anode, we performed CO₂ reduction by using Ag-supported dendritic Cu as a dark cathode and CoPi as a counter electrode at -1 V vs RHE in CO₂ saturated 0.1 M CsHCO₃ solution for 12 hrs. Initially, the total cell voltage was 5.2 V, much higher than for IrO₂ under same conditions (4.1 V), and it increased to 5.4 V with time, which we attribute to partial delamination of CoPi from the FTO coated glass substrate. Interestingly, we did not observe significant changes in the product distribution during the course of electrolysis (Fig. S26). Thus, CoPi shows promise as an alternative to IrO₂ as the anode, provided the overpotential can be reduced and issues with delamination can be addressed.



Fig. S25. Current-potential curves of CoPi and IrO₂ nanotubes in CO₂ saturated 0.1 M CsHCO₃.



Fig. S26. (a) Stability curve of Ag-supported dendritic Cu working electrode and CoPi counter electrode in 0.1 M CsHCO₃ for 12 hr under constant CO₂ purging at 10 sccm at -1 V vs RHE. (b) CO₂ R product distribution.

CO₂ concentration in catholyte.

We analyzed the CO₂ concentration before and after the measurement by reading the pH values in cathode chamber. We have previously shown that pH can be used to measure the CO₂ concentration and thus reveal gas to liquid mass transfer limitations during electrolysis; Fig. S27 shows the expected relationship between pH and CO₂ concentration (expressed in terms of the equivalent pressure in the gas phase) at room temperature.³ We performed constant current electrolysis to determine if dissolved CO₂ was depleted in the cell during a run, using a flow of N₂ to maintain constant cell temperature. At the beginning of the run, the pH was 6.68, corresponding to a supersaturated condition. After 2 hours of operation at constant current densities typical of the range used in this study, the pH was observed to rise: pH 6.74 for 10 mA cm⁻² and pH 6.89 for 20 mA cm⁻². The pH values correspond to slightly supersaturated and slightly undersaturated CO₂ concentrations, cf. Fig S27. We conclude that gas to liquid mass transfer effects do not affect the operation of the electrolysis cell under the conditions employed in this study.



Fig. S27. Calculated equilibrium pH for 0.1 M MHCO₃ aqueous buffer solution as a function of CO_2 pressure. See ref. 3 for details on the calculation.

Comparison of Cu- and Ag-supported dendritic Cu catalysts on planar Si

Our motivation for using a high surface area catalyst structure comprising a CO-producing metal (Ag or Au) and Cu stems from our prior observations that the CO intermediate can increase selectivity to oxygenates over hydrocarbons and that Ag-supported dendritic Cu catalysts achieve superior CO₂R selectivity over a wide range of potentials compared to Cu-only catalysts of similar morphology.^{1,17} To elucidate the role of the Ag support in the configuration used in the present work, we compared Cu- and Ag-supported catalysts of similar morphology (Fig. S28) deposited on n⁺-planar Si forming dark cathodes. The two cathode were compared by operating them at -1.0 V vs RHE in 0.1 M CsHCO₃ electrolyte with a 5 sccm constant CO₂ purge. Compared to the Cu-supported dendritic Cu, the Ag-supported dendritic Cu on planar Si cathode has superior selectivity to CO₂R overall (i.e. FE for H₂ is 27% vs. 38% for the Cu on planar Si catalyst) and the selectivity to C₂/C₃ oxygenates is larger, as expected (Fig. S29).



Fig. S28. (a) Plan view SEM images of (a) Cu-supported dendritic Cu and(b) Ag-supported dendritic Cu, both deposited on planar Si.



Fig. S29. CO_2 RR products distribution produced by Cu-supported dendritic Cu (left) and Ag-supported dendritic Cu (right). Experiments were performed in the dark at -1.0 V vs RHE in 0.1 M CsHCO₃ electrolyte with a 5 sccm constant CO_2 purge.

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