Supporting Information for:

**Prototype reactor for highly selective solar-driven CO₂ reduction to synthesis gas using nanosized earth-abundant catalysts and silicon photovoltaics**

_Félix Urbain*, Pengyi Tang¹,², Nina M. Carretero¹, Teresa Andreu¹,⁵, L. G. Gerling³, Cristobal Voz³, Jordi Arbiol²,⁴, and Joan Ramon Morante¹,⁵_

¹ IREC, Catalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 08930 Sant Adrià de Besòs, Barcelona, Catalonia, Spain

² Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology (BIST), Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain.

³ Electronic Engineering Department, Universitat Politècnica de Catalunya, Jordi Girona 1–3, 08034 Barcelona, Catalonia, Spain

⁴ ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, Spain

⁵ Departament of Electronics, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Catalonia, Spain

*Correspondence to: furbain@irec.cat

<table>
<thead>
<tr>
<th>Index</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Details</td>
<td>S2</td>
</tr>
<tr>
<td>Solar-to-Syngas Conversion Efficiency Calculation</td>
<td>S2</td>
</tr>
<tr>
<td>Figures</td>
<td>S3-S6</td>
</tr>
</tbody>
</table>
Experimental Details

1. Chemicals and Materials
Zinc sulfate pentahydrate (ZnSO$_4$.7H$_2$O, 99.995% trace metals basis) was purchased from Merck Millipore; copper and nickel foams (2.5 mm and 1.6 mm thick, respectively) were purchased from Recemat BV; potassium hydrogen carbonate (KHCO$_3$, ACS purity>99.7%) was purchased from Merck Millipore. The laminating acrylic tape (0.075 mm thick) was purchased from Thorlabs, Inc. Electrolyte solutions were prepared with deionized water (DI-H$_2$O, Ricca Chemical, ASTM Type I).

A bipolar membrane (fumasep FBM-type) was purchased from FuMA-Tech GmbH and kept in 1 M NaCl. The Nafion (N-117 membrane, 0.18 mm thick) was purchased from Alfa Aesar and kept in 0.5 M NaOH solution. A leak-free reference electrode (Ag/AgCl 3.4 M KCl) was purchased from Warner Instruments.

Solar-to-Syngas Conversion Efficiency Calculation
Considering an active electrode area of 10 cm$^2$ for CO$_2$RR and OER, respectively, the bias-free operation CO$_2$RR current of 5 mA/cm$^2$, which we measured (Fig. 5), corresponds to an electric charge of 50 mC, i.e. 31.2*10$^{16}$ electrons (assuming 1 s of interval duration). These charges are used produced H$_2$ and CO which both need 2 electrons to be formed. Over the course of the bias-free measurement, a faradaic efficiency of 76 % for the H$_2$ production and 16 % for the CO production was measured. Consequently, for the number of molecules we can derive that:

$$0.76 \times 31.2 \times 10^{16} / 2 = 11.86 \times 10^{16} \text{ molecules of H}_2$$

$$0.16 \times 31.2 \times 10^{16} / 2 = 2.49 \times 10^{16} \text{ molecules of CO were produced, which correspond to}$$

$$1.97 \times 10^{-7} \text{ moles of H}_2 \text{ and 4.15 } \times 10^{-8} \text{ moles of CO.}$$

Considering the respective molar masses, we obtain 0.394 µg of H$_2$ and 1.16 µg of CO.

Taking into account the higher heat value (HHV) and lower heat value (LHV) for H$_2$ and CO of 286 kJ/mol and 283.5 kJ/mol, respectively, the specific power of the produced products can be obtained as 143330 kW/kg for H$_2$ and 10125 kW/kg for CO.

Using these values allows to calculate the total bias-free power output of the device. $\eta_{STS}$ is given by

$$\eta_{STS} = \frac{0.394 \mu g \ H_2 \times 143330 \ kW/kg + 1.16 \mu g \ CO \times 10125 \ kW/kg}{\text{total integrated power input}}$$

where the input power (for 16 cm$^2$ illuminated solar cell area) is the incident light intensity (1600 mW). Thus, the solar-to-syngas efficiency of our device was 4.26 %.
Figures

**Fig. S1** Potential-time curves during electrodeposition of Zn on Cu-foams at –40 mA.

**Fig. S2** SEM images of a bare Cu foam (low magnification) and of the Zn catalyst coated Cu-foam after electrodeposition for 15, 30, and 60 minutes, respectively (low and high magnification).
**Fig. S3** Low magnification EELS chemical composition maps obtained from the red rectangled area on the ADF-STEM micrograph. Individual Zn (red), O (green), Cu (blue) maps and their composite.

**Fig. S4** Cyclic voltammetry (CV) curves of Cu-foam decorated cathodes measured in the filter-press cell with electrolyte flow (20 ml/min) and CO$_2$ (green curve) or Ar (purple curve) flow (20 ml/min). The electrolyte was 0.5 M KHCO$_3$ in both measurements, which were conducted at a scan rate of 10 mV/s. The black squares represent the average current density values from hour-long potentiostatic experiments carried out at different applied potentials (see Fig. 4(a)).
**Fig. S5** (a) SEM image of the Cu-Zn cathode after CO$_2$RR at -0.8 V$_{RHE}$ for one hour. (b) With high magnification. (c) XRD pattern of the bare Cu-foam, of the as-prepared Cu-Zn cathode, and of the Cu-Zn cathode after one hour electrolysis.
**Fig. S6** Faradaic efficiencies of CO and H\textsubscript{2} production from CO\textsubscript{2}RR at different potentials for a flat Zn foil cathode measured in 0.5 M KHCO\textsubscript{3}. The error bars are standard deviations obtained from 3 experimental repeats. All measurements were conducted at a CO\textsubscript{2} and electrolyte flow rate of 20 ml/min.

**Fig. S7** Left: Schematic drawing of the layer stack used for the deposition of Si heterojunction solar cells. Right: Linear sweep measurement of the Si/Ni foam photoanode in 1 M KOH solution under 100 mW/cm\textsuperscript{2} of simulated AM1.5 illumination. The inset illustrates the Si/Ni foam photoanode structure under illumination. Details on the fabrication of the Si heterojunction solar cells can be found in Supplementary Ref. 1.
Fig. S8 Photographs of the prototype reactor device under operation. (a) Prototype reactor device under continuous flow and illumination. Catholyte and anolyte flows are highlighted. (b) Complete set-up for the solar CO$_2$ conversion experiments comprising mass flow controller, solar light simulator, potentiostat, gas chromatograph, and the reactor device, shown in more detail in Fig. 1 and Fig. S8(a).

Fig. S9 Two-electrode current density-voltage characteristics with a Si heterojunction solar cell/Ni foam photoanode and a Zn catalyst coated Cu foam cathode in a bipolar membrane configuration using 1 M KOH as anolyte and 0.5 M KHCO$_3$ as catholyte solution. The measurements were conducted under simulated AM1.5 illumination at a scan rate of 10 mV/s before and after the bias-free stability testing. The illuminated area of the PV cells was 16 cm$^2$, while the active electrode/liquid areas of the cathode and anode were 10 cm$^2$. 
**Fig. S10** Operation of the prototype solar CO$_2$ conversion reactor (see Fig. 1) as a function of the operation time under an applied bias potential of 1.7 V. Left y-axis: Solar-driven CO$_2$RR current density (normalized to the area of the electrodes in contact with the electrolyte; 10 cm$^2$) as a function of the operational time using a photoanode based on two Si HIT cells and Ni foam catalyst and a Cu-Zn cathode in a biased two-electrode 0.5 M KHCO$_3$/BPM/1 M KOH configuration under simulated AM1.5G illumination. Right y-axis: Faradaic efficiencies of H$_2$ and CO production as a function of the operation time.

**Supplementary Reference:**