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Solar thermochemical splitting of CO_2 into separate streams of CO and O_2 with high selectivity, stability, conversion, and efficiency

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SUPPLEMENTARY INFORMATION

Figure S1 shows the nominal solar reactor temperature, total pressure, and specific O_2 and CO evolution rates during three CO_2-splitting redox cycles, with the reduction step conducted under varying p_{total} (Fig. S1a) or $\dot{V}_{Ar}$ (Fig. S1b) applied during the reduction step. Figure S2 shows the absolute O_2/CO evolution, energy required for vacuum pumping (Q_{pump}) and inert gas separation (Q_{inert}), and $\eta_{solar\text{-}to\text{-}fuel}$ as a function of p_{total} (Fig. S2a) or $\dot{V}_{Ar}$ (Fig. S2b) applied during the reduction step. Figure S3 shows the nominal solar reactor temperature, total pressure, and specific O_2 and CO evolution rates for a CO_2-splitting cycle with ambient air purging (no pre-treatment) during the reduction step.

Stability – The experimental setup for multiple cycling is schematically shown in Figure S4. The furnace (VHT-E48, Ulvac-Riko) consists of four electric heating elements surrounded by gold-coated refrigerated mirrors to direct IR radiation towards the centerline. A 1.6 g RPC sample was placed inside a 24 mm-outer diameter, 1.5 mm-thickness, 500 mm-length quartz tube. Temperature was measured using a B-type thermocouple. Argon (99.996% purity) and synthetic air flow rates were regulated with electronic mass flow controllers (Bronkhorst, EL-FLOW). Steam flow rate

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was controlled by a liquid flow meter (Bronkhorst, Liqui-Flow) connected to an evaporator (Bronkhorst, Controlled Evaporator Mixer, T = 175 °C). Oxygen evolution during reduction was analyzed with a calibrated mass spectrometer (GSD 320, Pfeiffer Vacuum). To initiate the redox cycle, the RPC sample was heated to the reduction temperature $T_{\text{reduction}}$ = 1500 °C at a heating rate 600°C min^{-1} while flowing Ar at a rate $\dot{V}_{\text{Ar}}$ = 0.3 L min^{-1}. Reduction was continued isothermally at $T_{\text{reduction}}$ for 3.5 min. The sample was then cooled to $T_{\text{oxidation}}$ = 600 °C at a cooling rate 600 °C min^{-1}. Oxidation was performed isothermally at $T_{\text{oxidation}}$ for 5 min. with a mixture of steam and Ar at flow rates of 0.15 and 0.3 L min^{-1}, respectively. To ensure full oxidation, the sample was subsequently oxidized for additional 0.5 min with a mixture of synthetic air and Ar at flow rates of 0.15 and 0.15 L min^{-1}, respectively. The cycle was then repeated. For these experimental conditions, δ_{red} - δ_{ox} = 0.031. Figure S5 shows the specific yield of O_2 as a function of the cycle number for 500 consecutive redox cycles. Figure S6 presents scanning electron micrographs (SEM) of the strut's porosity of the RPC sample before and after the 500 consecutive redox cycles of Fig. S7.

Energy efficiency – The solar-to-fuel energy efficiency $\eta_{\text{solar-to-fuel}}$ is defined as:

$$\eta_{\text{solar-to-fuel}} = \frac{Q_{\text{fuel}}}{Q_{\text{input}}} = \frac{Q_{\text{fuel}}}{Q_{\text{solar}} + Q_{\text{pump}} + Q_{\text{inert}}} \tag{1}$$

Q_{fuel} is the energy content in the fuel (CO) produced, given by:

$$Q_{\text{fuel}} = \Delta H_{\text{fuel}} \int r_{\text{fuel}} dt \tag{S2}$$

where ΔH_{fuel} is the molar heating value of CO produced (ΔH_{fuel} = 283 kJ/mol) and $\int r_{\text{fuel}} dt$ is the measured molar rate of CO produced integrated over the duration of the oxidation step. Q_{solar} is the total solar energy input integrated over the duration of the reduction step:

$$Q_{\text{solar}} = \int P_{\text{solar}}\, dt \tag{S3}$$

where P_{solar} is the measured radiative power input through the solar reactor's aperture, accounting for the measured 93.2% total transmittance of the quartz window[1]. Q_{pump} and Q_{inert} are the energy penalties associated with vacuum pumping and inert gas consumption during the reduction step. Q_{pump} is calculated as the thermodynamic minimum pumping work divided by the product of two efficiencies, namely the heat-to-work efficiency $\eta_{\text{heat-to-work}}$ (assumed 0.4) and the vacuum pump efficiency η_{pump}, according to:

$$Q_{\text{pump}} = \frac{1}{\eta_{\text{heat-to-work}} \cdot \eta_{\text{pump}}} \int \dot{n}(t) \cdot R \cdot T \cdot \ln\left(\frac{p_{\text{atmospheric}}}{p_{\text{reactor}}(t)} \right) dt \tag{S4}$$

where $\dot{n}$(t) is the sum of the measured molar flow rates of Ar gas injected and O_2 released by ceria during the reduction step. The pump efficiency for a multi-stage industrial arrangement is given by:

$$\eta_{\text{pump}} = 0.07 \cdot \log\left(\frac{p_{\text{total}}}{p_{\text{atmospheric}}} \right) + 0.4 \tag{S5}$$

where p_{total} is the measured total pressure inside the cavity. Note that $\eta_{\text{solar-to-fuel}}$ is weakly depended on η_{pump} because $Q_{\text{solar}} >> Q_{\text{pump}}$ at the moderate vacuum pressure levels applied during reduction in the range 10-1000 mbar. The energy required for inert gas separation is given by:

$$Q_{\text{inert}} = \frac{1}{\eta_{\text{heat-to-work}}} E_{\text{inert}} \int r_{\text{inert}}\, dt \tag{S6}$$

where r_{inert} is the measured Ar gas flow rate during reduction and E_{inert} is the work required for inert gas separation, assumed 20 kJ per mole[2]. Re-radiation losses were calculated according to:

$$Q_{\text{rerad}} = \int_0^t \varepsilon_{\text{apparent}} A_{\text{aperture}} \sigma T(t)^4\, dt \tag{S7}$$

where σ is the Stefan-Boltzmann constant, T(t) is the measured nominal reactor temperature, $A_{aperture}$ is the aperture area, and $\varepsilon_{apparent}$ is the apparent emissivity of the cavity, assumed unity based on Monte Carlo ray tracing simulations. The energy required for the reduction of ceria was calculated using the measured amount of oxygen evolved and the enthalpy change of 475 kJ per mole of atomic oxygen[4,5]. For the sensible heating of ceria, a heat capacity of 83 J mol^{-1} K^{-1} was used[9]. Convection losses were calculated using Nusselt correlations for natural convection with the measured metallic shell temperatures[6,7].

Nomenclature

$A_{aperture}$ = aperture surface area
E_{inert} = energy required for inert gas separation
P_{solar} = solar radiative power input
p = pressure
r_{fuel} = molar rate of fuel (CO) production
r_{inert} = inert gas flow rate
$T_{reduction}$ = maximum temperature during the reduction step
$T_{oxidation,start}$ = temperature at the beginning of the oxidation step
$T_{oxidation,end}$ = temperature at the end of the oxidation step
R = universal gas constant
$\varepsilon_{apparent}$ = apparent emissivity of cavity
σ = Stefan-Boltzmann constant
t = time duration
δ = nonstoichiometry
ΔH_{fuel} = heating value of the fuel
$\eta_{heat\text{-}to\text{-}work}$ = heat-to-work efficiency
η_{pump} = vacuum pump efficiency
$\eta_{solar\text{-}to\text{-}fuel}$ = solar-to-fuel energy efficiency
$\dot{V}$ = volumetric flow rate

Q_{inert} = heat equivalent of work required for inert gas separation

Q_{input} = total thermal energy input ($Q_{input} = Q_{solar} + Q_{inert} + Q_{pump}$)

Q_{pump} = heat equivalent of work required for vacuum pumping

Q_{rerad} = re-radition losses through the cavity aperture

Q_{solar} = solar radiative energy input

Q_{fuel} = heating value of fuel produced

Abbreviations

CPC compound parabolic concentrator

CSP concentrated solar power

DNI direct normal solar irradiation

L standard liters (at 273.15 K and 1 atm)

RPC reticulated porous ceramic

SEM scanning electron micrograph

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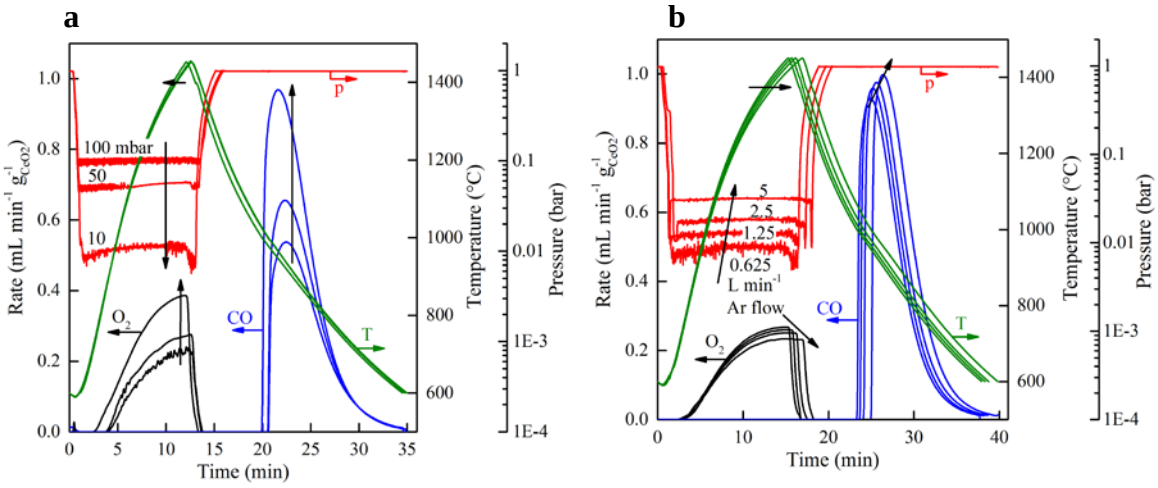

Figure S1. CO_2-splitting cycles for various pressures and purge gas flow rates. Nominal solar reactor temperature, total pressure, and specific O_2 and CO evolution rates during CO_2-splitting redox cycles, with the reduction step conducted under: a, varying p_{total}, and b, varying $\dot{V}_{Ar}$. Black arrows indicate the trends for increasing $\dot{V}_{Ar}$ (a) and decreasing p_{total} (b). Experimental conditions during reduction for cycles of Fig. S1a: P_{solar} = 3.5 kW, $T_{reduction}$ = 1450 °C, $\dot{V}_{Ar}$ = 0.625 L min^{-1}, and p_{total} = 10, 50, and 100 mbar. Experimental conditions during reduction for cycles of Fig. S1b: P_{solar} = 2.9 kW, $T_{reduction}$ = 1450 °C, p_{total} = 10-20 mbar, and $\dot{V}_{Ar}$ = 0.625, 1.25, 2.5 and 5 L min^{-1}. Experimental conditions during oxidation for cycles of Figs. S1a and S1b: P_{solar} = 0 kW, $T_{oxidation,start}$ = 1000 °C, $\dot{V}_{CO2}$ = 7 L min^{-1}, and p_{total} = 1 bar.

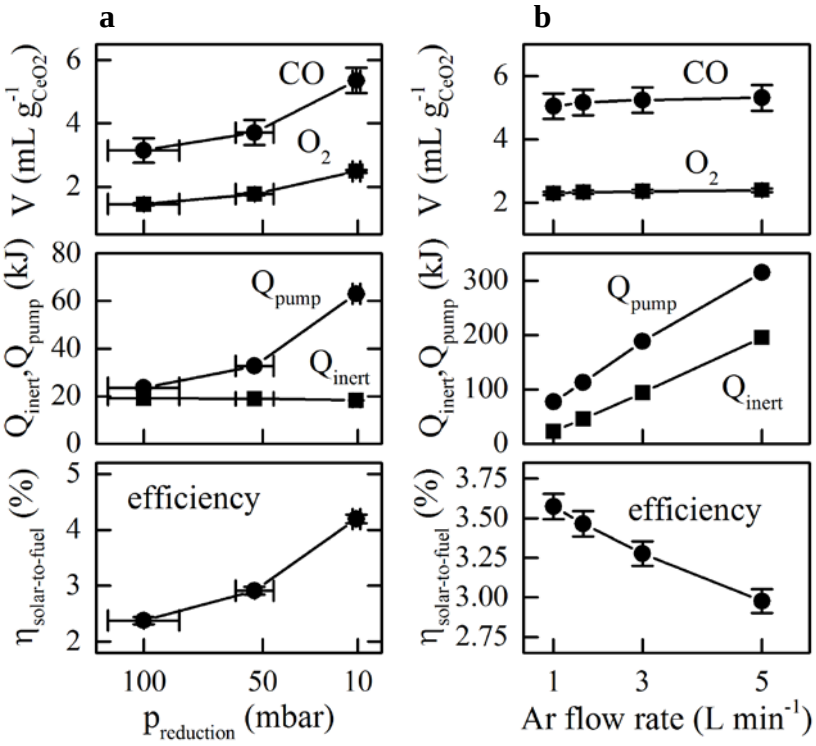

Figure S2. Performance indicators for various pressures and purge gas flow rates. Absolute O_2/CO evolution, energy required for inert gas separation and vacuum pumping, and solar-to-fuel energy efficiency as a function of: a, the total pressure applied during the reduction step; and b, the Ar gas flow rate applied during the reduction step. Experimental conditions during reduction for S2a: P_{solar} = 3.5 kW, $T_{reduction}$ = 1450 °C, $\dot{V}_{Ar}$ = 0.625 L min^{-1} at p_{total} = 10, 50, and 100 mbar. Experimental conditions during reduction for S2b: P_{solar} = 2.9 kW, $T_{reduction}$ = 1450 °C, and $\dot{V}_{Ar}$ = 0.625, 1.25, 2.5, and 5 L/min at p_{total} = 10 mbar. Experimental conditions during oxidation for S2a and S2b: P_{solar} = 0 kW, $T_{oxidation,start}$ = 1000 °C, $T_{oxidation,end}$ = 600 °C, and $\dot{V}_{CO2}$ = 7 L min^{-1} at p_{total} = 1 bar.

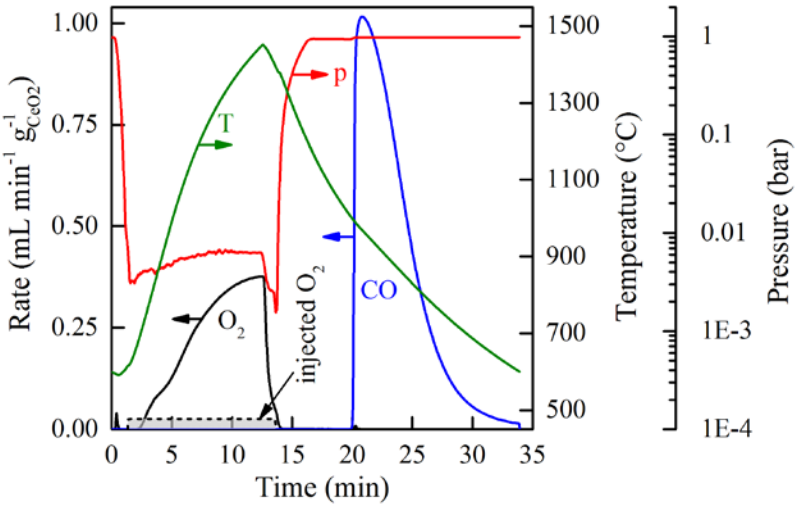

Figure S3. CO_2-splitting cycle without inert gas. Nominal solar reactor temperature, total pressure, and specific O_2 and CO evolution rates for a CO_2-splitting cycle with ambient air purging during the reduction step. The dashed line indicates the rate of O_2 injected with the air. Experimental conditions during reduction: P_{solar} = 3.5 kW, $T_{reduction}$ = 1450 °C, p_{total} = 10mbar, and $\dot{V}_{air}$ = 0.2 L min^{-1}. Experimental conditions during oxidation: P_{solar} = 0 kW, $T_{oxidation,start}$ = 1000 °C, p_{total} = 1 bar, and $\dot{V}_{CO2}$ = 7 L min^{-1}.

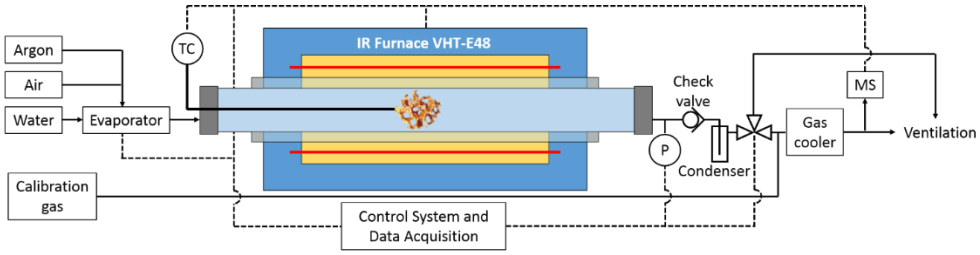

Figure S4. Schematic of the experimental setup for multiple cycling. The RPC sample is placed in a quartz tube enclosed by an IR furnace. Temperature is measured with a type-B thermocouple. Purge and oxidant gases are delivered with electronic mass flow controllers. Excess steam is condensed in a glass condenser and product gases are cooled in a gas cooler. The oxygen evolved during reduction is analyzed by a calibrated mass spectrometer.

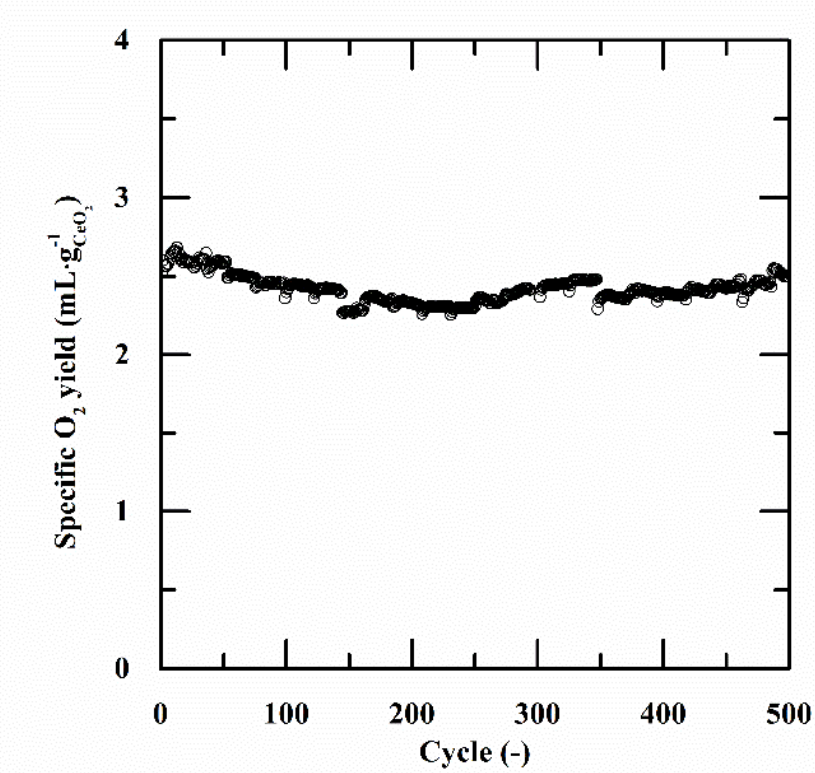

Figure S5. Material stability. Specific yield of O_2 for 500 consecutive redox cycles (δ_{red} - δ_{ox} = 0.031). Experimental conditions: heating/cooling rate 600 °C min^{-1}; reduction at $T_{reduction}$ = 1500 °C for 3.5 min with $\dot{V}_{Ar}$ = 0.3 L min^{-1}; oxidation at $T_{oxidation}$ = 600 °C for 5 min with $\dot{V}_{H2O}$ = 0.15 L min^{-1} and $\dot{V}_{Ar}$ = 0.3 L min^{-1} and for 0.5 min with $\dot{V}_{air}$ = 0.15 L min^{-1} and $\dot{V}_{Ar}$ = 0.15 L min^{-1}.

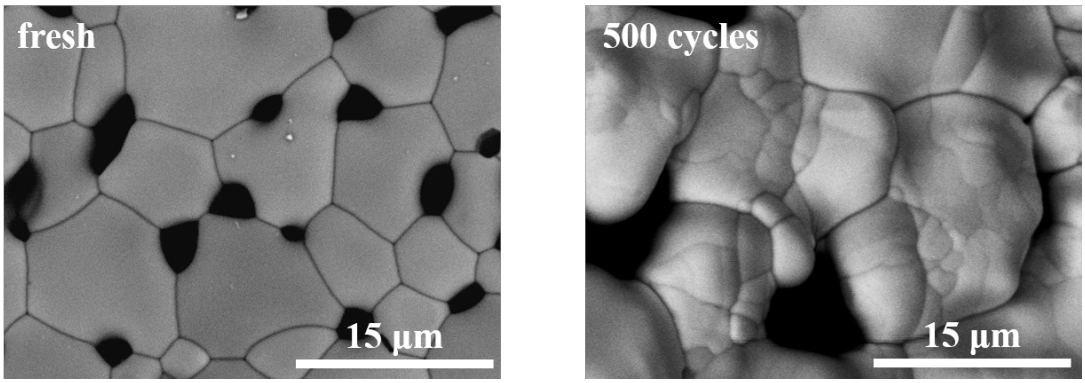

Figure S6. SEM of the RPC sample showing the strut's porosity before and after 500 consecutive redox cycles of Fig. S5.