Electronic Supplementary Information

First demonstration of direct hydrocarbon fuel production from water and carbon dioxide by solar-driven thermochemical cycles using rhodium-ceria

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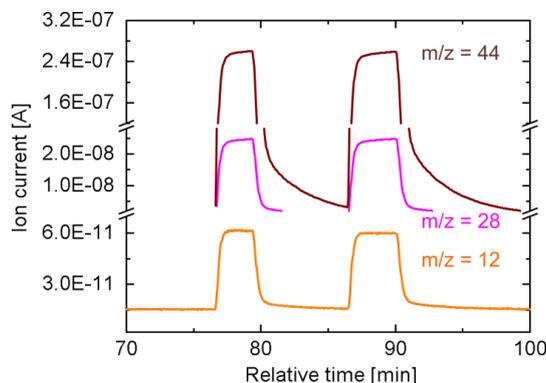

Fig. S1 Ion current at m/z = 44 (CO_2^+), 28 (CO^+) and 12 (C^+) when carbon dioxide is introduced to the reactor at room temperature (no reaction, i.e. CO_2 splitting, occurring). Due to fragmentation of CO_2 to CO^+ and C^+ during ionization, the signals of m/z = 28 and m/z = 12 exhibit a step increase in the same manner as the signal of m/z = 44.
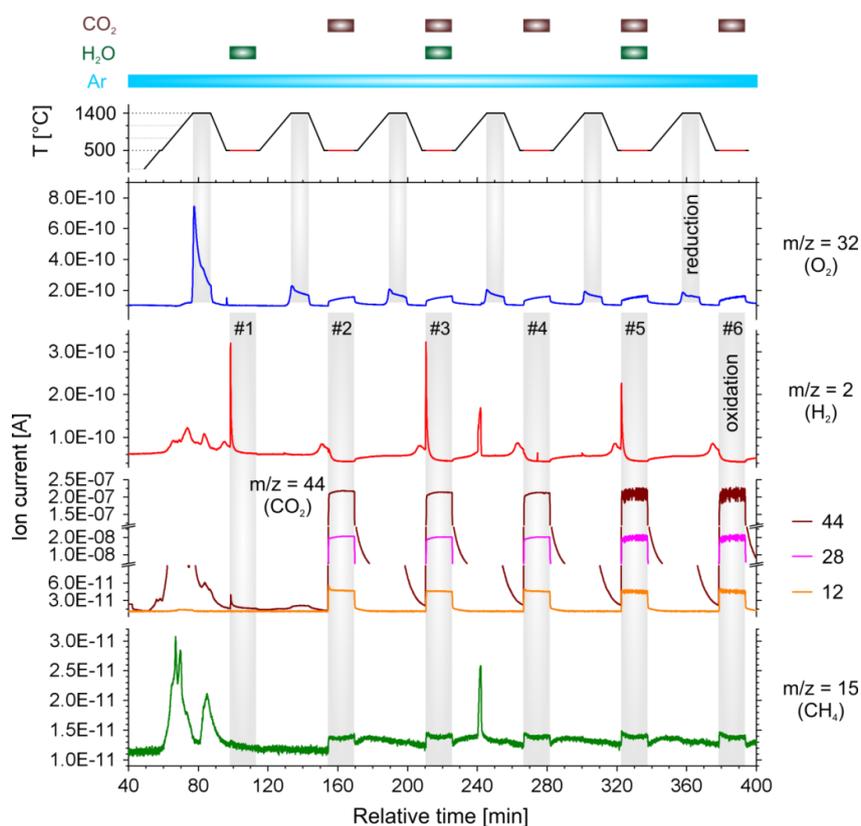

Fig. S2 Six thermochemical cycles using 10 mol% nickel-doped ceria (~90 mg) with thermal reduction in argon at 1400 °C and reoxidation by either water or carbon dioxide, or both, at 500 °C. Oxygen evolution profiles shows little reduction after the very first cycle. A very poor redox capacity of nickel-doped ceria in the thermochemical cycles is observed. Methane is not produced when water and carbon dioxide are used simultaneously as the oxidants (cycle #3 and #5). However, after the third reoxidation at about 240 min and 1200 °C (sample being cheated in argon), hydrogen and methane peaks are observed. This could potentially come from the release of surface hydroxyl groups at the ceria surface and carbon groups at the nickel surface formed during the third reoxidation step. However this was not observed again after the 5th reoxidation step. Note that the regions marked with grey areas indicated the isothermal segments of reduction and oxidation steps (1400 °C and 500 °C)
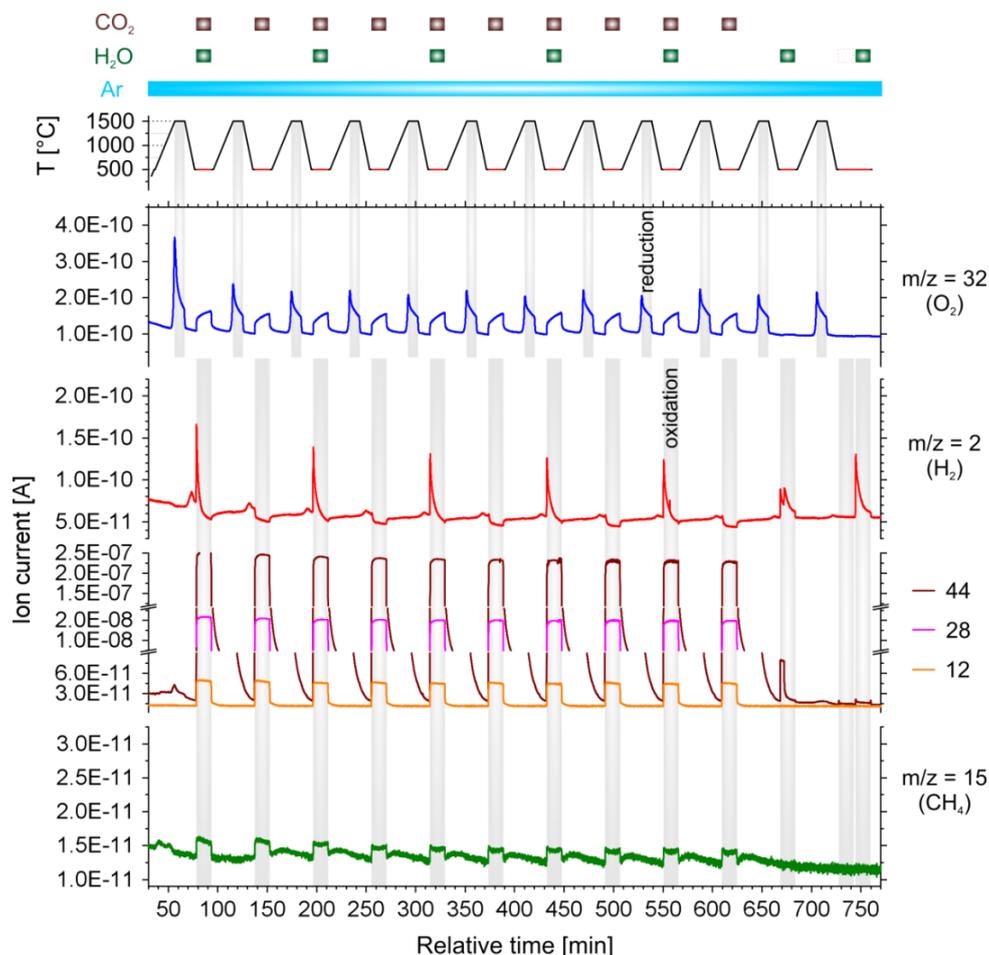
Fig. S3. Eleven thermochemical cycles using 10 mol% nickel-doped ceria (~40 mg) with thermal reduction in argon at 1500 °C and reoxidation by either water or carbon dioxide, or both, at 500 °C. Oxygen evolution profiles also show little reduction after the first cycle. Again, no methane is produced when water and carbon dioxide are used simultaneously as the oxidants (cycle #1, #3, #5, #7 and #9). The materials used for this experiment firstly underwent 6 cycles at 1400|500 °C (results presented in Fig. S2).
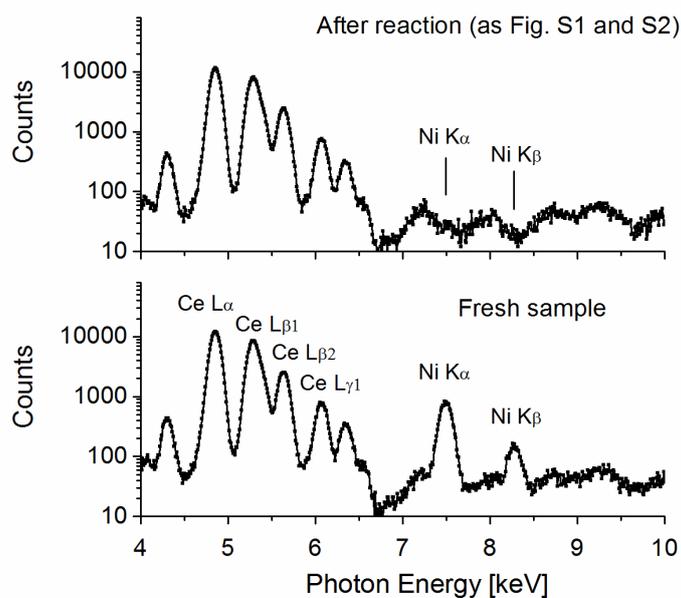

Fig. S4 XRF results showing complete loss of nickel from nickel-doped ceria after 6 cycles at 1400|500 °C (Fig. S2) and the additional 11 cycles at 1500|500 °C (Fig. S3).
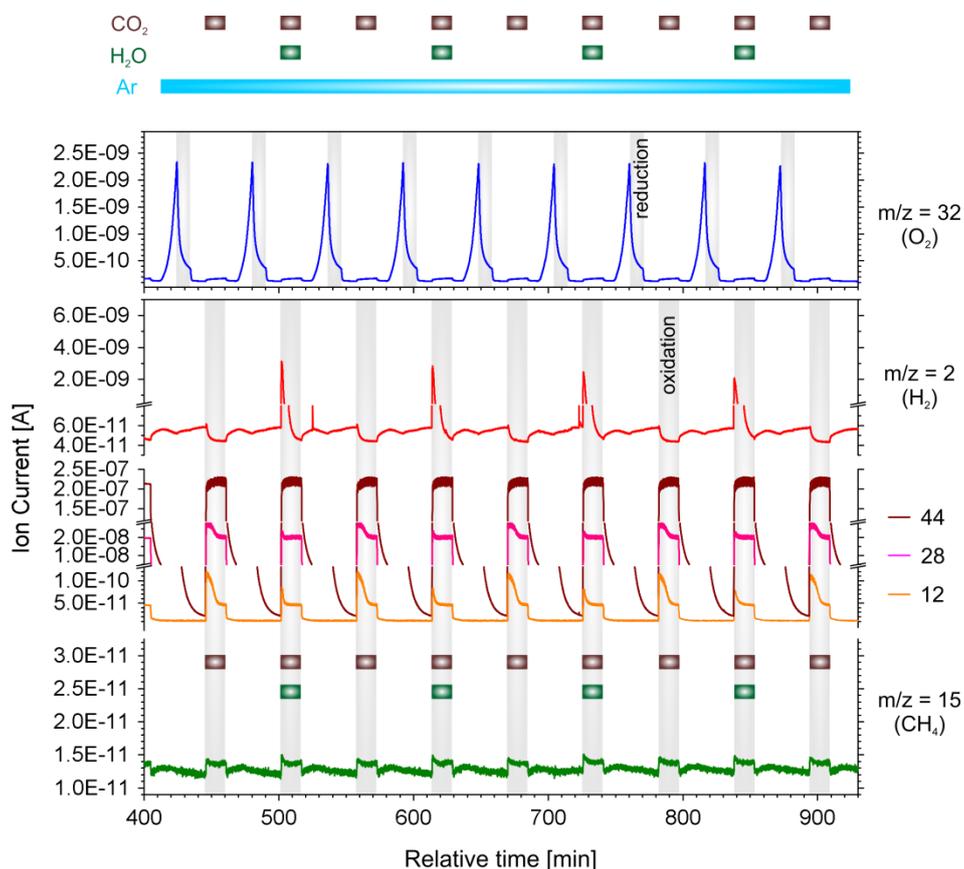
Fig. S5 Nine thermochemical cycles using pure ceria (~158 mg) with thermal reduction in argon at 1400 °C and reoxidation either by only carbon dioxide or by carbon dioxide and water, at 500 °C. Oxygen evolution profiles also show stable amounts of oxygen released. Essentially no methane is produced when water and carbon dioxide are used simultaneously as oxidants (even numbered cycles). Note that this experiment with pure ceria was carried out using the same alumina tube reactor after the experiments with rhodium-ceria (Fig. 4 and Fig. 8) and nickel-ceria samples (Fig. S2 and Fig. S3). The arguably very slight increase of methane signal when both oxidants are used compared to when only carbon dioxide is used, even if it is valid, could be due to the deposition of sublimated nickel (Fig. S4) at downstream of the reactor during the nickel-ceria experiments. Nevertheless, essentially no methane is produced with pure ceria as reactive medium.
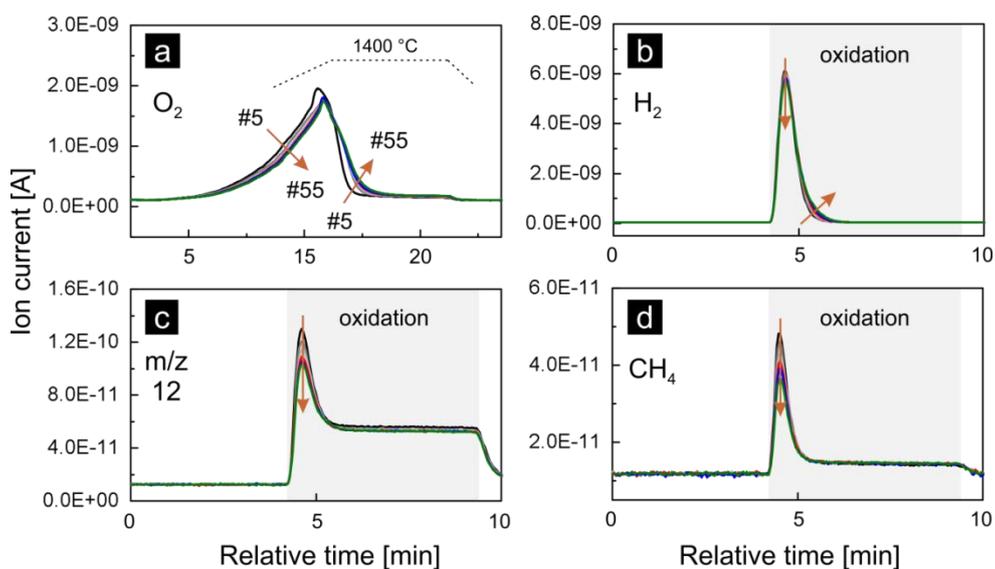

Fig. S6 Comparison between cycles #5, #15, #25, #35, #45 and #55 during the long-term testing of rhodium-doped ceria at 1400|500 °C (results presented in Fig. 6): evolution of signals (a) oxygen, (b) hydrogen, (c) m/z = 12 indicative of carbon monoxide, and (d) methane.
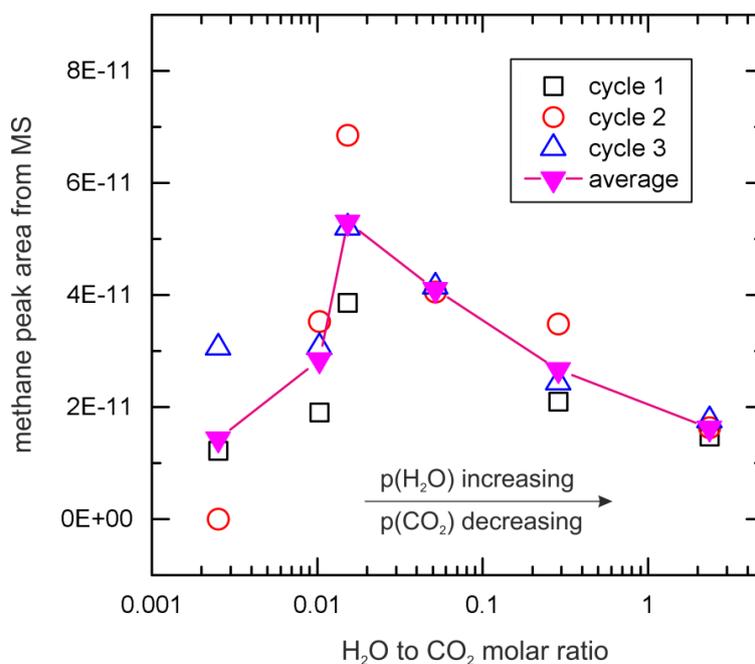
Fig. S7 Relative amounts of methane produced (peak area under methane MS signal) over three consecutive thermochemical cycles using rhodium-doped ceria as the starting material, with reoxidation carried out at various molar ratios of water to carbon dioxide. The very first data point of the whole series of experiment (cycle 1 at molar ratio 5.17E-02) was excluded as the background of methane was not yet stabilized. For the second to forth ratios (counting from left), the water partial pressures were kept same or very close. Experimental details are described in the following.

Experimental details for Fig. S7

Approximately 400 mg of fresh rhodium-doped ceria sample were used in the form of loose powder for each experiment at a given molar ratio. These experiments were carried out using a TGA (thermogravimetric analysis) reactor (Netzsch TA409) as the main setup used in the paper was not any more accessible. The sample was placed inside an alumina crucible supported by an alumina rod, which houses a thermocouple and is atop the balance. The total flow rate was set to 100 Nml min^{-1}. The reduction was carried out at 1450 °C in argon and oxidation at 500 °C. The partial pressures of carbon dioxide and water, listed in the following table, were adjusted by changing the flow rate of carbon dioxide, the flow rate of argon passing through a bubbler (with controlled temperatures at 10 °C, 18 °C or 22 °C), and the flow rate of the balancing argon. Three cycles were measured for each fresh sample at a given molar ratio. For the second to forth ratios (highlighted in the table), the water partial pressures were kept same or very close.

p_H2O/p_CO2 [-]	p_CO2 [mbar]	p_H2O [mbar]
2.53E-03	800	2.056
1.03E-02	600	6.17
1.53E-02	400	6.1
5.17E-02	143	7.4
2.88E-01	50	14.4
2.35	10	23.5

Rough estimation of the amount of methane produced

Compared to the amount of CO produced when CO_2 is the sole oxidant, much lower amount of CO is produced when H_2O is present as an oxidant in addition to CO_2 (judging from the magnitude of "overshoot" of m/z=28 and 12 in Fig. 5). The H_2/O_2 molar ratio is about 1.86 (Table 1). If we neglect the amount of CO is produced in the effluent gases (as water is present as

oxidant), and assume a stoichiometric H_2/O_2 molar ratio of 2.0 with H_2O splitting, estimation of CH_4 produced can be based on the following two equations

$$2\ H_2O \rightarrow 2\ H_2 + O_2 \qquad\qquad 1\ O_2\ \text{release, 2 } H_2\ \text{release}$$
$$2\ H_2O + CO_2 \rightarrow CH_4 + 2O_2 \qquad\qquad 1\ O_2\ \text{release, 0.5 } CH_4\ \text{release}$$

The missing 0.14 units of H_2 per unit O_2 (2 minus 1.86) is thus translated to 0.14/4 = 0.035 units of CH_4. Thus the ratio of CH_4 and H_2 is estimated as 0.035 to 1.86. With about 135 µmol g^{-1} of H_2 produced per cycle, one could thus estimate production of methane at 2.5 µmol g^{-1}. Assuming 2 min of reoxidation (Fig. 4), "2.5 µmol g^{-1}" methane corresponds to 40 ppm level (averaged over 2 min) of CH_4 after taking into account of the flow rate (106.2 Nml min^{-1}) and sample mass (~150 mg).

$$\text{p\_CH4 (average)} = [2.5\ \text{µmol } g^{-1} \times 0.15\ g \times 22.4\ \text{L mol}^{-1} / (2\ \text{min} \times 106.2\ \text{ml min}^{-1})] \times 1\ 000000\ \text{ppm}$$
$$= 39.6\ \text{ppm}$$