APPLIED SCIENCES AND ENGINEERING

Perovskite nanocomposites as effective CO₂-splitting agents in a cyclic redox scheme

Junshe Zhang,* Vasudev Haribal, Fanxing Li†

We report iron-containing mixed-oxide nanocomposites as highly effective redox materials for thermochemical CO₂ splitting and methane partial oxidation in a cyclic redox scheme, where methane was introduced as an oxygen “sink” to promote the reduction of the redox materials followed by reoxidation through CO₂ splitting. Up to 96% syngas selectivity in the methane partial oxidation step and close to complete conversion of CO₂ to CO in the CO₂-splitting step were achieved at 900°C to 980°C with good redox stability. The productivity and production rate of CO in the CO₂-splitting step were about seven times higher than those in state-of-the-art solar-thermal CO₂-splitting processes, which are carried out at significantly higher temperatures. The proposed approach can potentially be applied for acetic acid synthesis with up to 84% reduction in CO₂ emission when compared to state-of-the-art processes.

INTRODUCTION

As a clean and carbon-neutral energy source, solar energy has drawn increasing attention in recent years. To date, solar energy utilization has largely revolved around photovoltaic power generation (1–7). Although significant progress has been made in photovoltaics, electricity alone only accounts for less than 20% of the global delivered energy consumption, and the remaining energy is provided by solid, liquid, or gaseous fuels (8). Therefore, novel approaches that convert solar energy into fuels offer significant opportunities to reduce fossil fuel consumption in industrial and transportation sectors, thereby providing potentially effective means to mitigate anthropogenic CO₂ emissions.

Solar fuels can be produced from water and CO₂ by photocatalytic splitting under mild conditions (9–14). However, the efficiency and yields of existing photocatalytic processes are far from satisfactory due to the high thermodynamic and activation barriers of these reactions and challenges in band structure optimization for photocatalysts, electron-hole recombination, and photocatalyst stability (13). In addition, product separation for these processes can be problematic (14). As an alternative to photocatalytic processes, solar-thermal water/CO₂ splitting has shown excellent potential (15–21). For instance, solar-to-hydrogen efficiency can be as high as 18% for solar-thermal water splitting, whereas state-of-the-art photocatalytic processes have an energy conversion efficiency of less than 0.2% (22). Typical solar-thermal water/CO₂ splitting processes convert concentrated solar energy in a two-step, cyclic redox scheme: A redox material (usually a metal oxide) is first decomposed (or reduced) under an inert environment to (partially) release its lattice oxygen (MOₓ → MOₓ–δ + δ/2O₂) at elevated temperatures (>1200°C), and then the reduced metal oxide is reoxidized (or regenerated) by putting it in contact with water or CO₂ to replenish its lattice oxygen, producing hydrogen or carbon monoxide (MOₓ–δ + δH₂O/CO₂ → MOₓ + δH₂/CO). The resulting hydrogen (H₂) and/or carbon monoxide (CO) can be used as gaseous fuels or converted into liquid fuels or chemicals (23, 24). Such a two-step redox scheme eliminates the need for gas separation and has demonstrated notably higher CO/H₂ production rates (1.35 mmolCO mg⁻¹ oxide⁻¹ s⁻¹ and 0.71 mmolH₂ kg⁻¹ oxide⁻¹ s⁻¹) when compared to state-of-the-art photocatalytic approaches [-0.07 mmolCO kg⁻¹ cat⁻¹ s⁻¹ (21, 25)]. The challenge for solar-thermal processes resides in the high reaction temperatures for metal oxide decomposition. Reasonable decomposition rates are only achieved at temperatures above 1500°C for nonvolatile monometallic metal oxides (15, 21, 26, 27). Although recent studies on mixed metal oxides have led to notable decreases in the decomposition temperatures, most solar-thermal redox processes require an operating temperature above 1200°C (17, 26–30). In addition to the high reaction temperatures, water or CO₂ conversions in these schemes are far from satisfactory (typical below 10%), posing significant challenges for process heat integration and downstream product separations (31).

Introducing reducing agents can lower the decomposition (or reduction) temperature (32). In such an open-loop thermochemical approach, reducing agents such as carbonaceous fuels are used as oxygen “sinks” to facilitate lattice oxygen extraction from redox materials (15). Although significantly lower reduction temperatures (<800°C) have been demonstrated, steam or CO₂ conversion in the subsequent water- or CO₂-splitting step is still very low (33–35). To address this challenge, we proposed a hybrid solar-redox scheme for water splitting, wherein concentrated solar energy is used to drive the reduction reaction in the presence of methane (CH₄) that undergoes partial oxidation (POx) to produce Fischer-Tropsch (F-T) ready syngas. Using perovskite-supported Fe₂O₄ as the redox material, up to 77% steam-to-hydrogen conversion was achieved (16, 36). Although such a methane-assisted solar-thermal water-splitting scheme is applicable for CO₂ splitting, further increases in water/CO₂-splitting conversion is desirable from process efficiency and product separation standpoints. Another challenge is that iron oxide–based materials tend to overoxidize syngas products in the methane POx step, limiting the syngas selectivity to less than 70%. Herein, we report high-performance redox materials for CO₂ splitting using the aforementioned hybrid solar-redox concept. Perovskite nanocomposites (NCs) exhibit exceptional efficacy for both CO₂ splitting and methane POx: Over 98% CO₂-to-CO conversion was achieved in CO₂ splitting, and syngas selectivity reached 96% in methane POx. As a stand-alone process, methane-assisted CO₂ splitting offers an effective approach for both CO₂ utilization and F-T/methanol ready syngas production. As an example, the resulted syngas and CO products can be readily used for green acetic acid production (Fig. 1). Compared to conventional acetic acid synthesis, the proposed scheme has the potential to reduce fossil fuel consumption by 67% and produce 84% less CO₂ when compared to coal-based process.
iron oxides are not suitable for the proposed redox reactions from a
to the formation of perovskite oxides such as Brownmillerite-type Sr2Fe2O5
redox for syngas and CO coproduction, methanol synthesis from the syngas, and acetic acid production. 
Zhang, Haribal, Li,
and Ruddlesden-Popper (R-P)
Performance of the redox material is critical to the hybrid solar-redox
Rationale for redox material selection
RESULTS
Fig. 1. Hybrid solar-redox process and its application for green acetic acid production from methane and CO2. This process has three sections: hybrid solar-redox for syngas and CO coproduction, methanol synthesis from the syngas, and acetic acid production.

Table 1. Main reactions that occur in methane POx and CO2 splitting in the redox scheme.

<table>
<thead>
<tr>
<th>Reaction (Methane POx)</th>
<th>Reaction (CO2 splitting)</th>
</tr>
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<tbody>
<tr>
<td>( \text{MeO}<em>n \rightarrow \text{MeO}</em>{n-1} + \frac{1}{2}\text{O}_2 ) (1)</td>
<td>( \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2 ) (7)</td>
</tr>
<tr>
<td>( \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 ) (2)</td>
<td>( \text{MeO}_{n-1} + \frac{1}{2}\text{O}_2 \rightarrow \text{MeO}_n ) (8)</td>
</tr>
<tr>
<td>( \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 ) (3)</td>
<td>( \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2 + \text{CO}_2 ) (6)</td>
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A methane-assisted thermochemical CO2-splitting scheme can be
described by the reactions listed in Table 1. From a thermodynamic
standpoint, the redox material can be considered as an oxygen “source” in the methane POx step and an oxygen sink in the CO2-splitting step. Hence, a redox pair (\( \text{MeO}_n/\text{MeO}_{n-1} \)) with a high equilibrium oxygen pressure (\( P_{\text{O}_2} \)) can lead to overoxidation of syngas (Eqs. 3 and 4) and low CO2 conversion (Eq. 7). In contrast, redox pairs with a low \( P_{\text{O}_2} \) will result in low methane conversion (Eq. 2). CO2 splitting, on the other hand, is monotonically favored at lower \( P_{\text{O}_2} \). The relationship among equilibrium \( P_{\text{O}_2} \), syngas yield, and CO2 conversion, derived from minimizing Gibbs free energy of the reaction set (Eqs. 2 to 6), is illustrated in Fig. 2. As can be seen, equilibrium \( P_{\text{O}_2} \) of Fe/FeO redox pair, which is a commonly used redox material, is away from the ideal (high performance) region for the hybrid solar-redox scheme. This is confirmed by a number of studies that reported low syngas selectivity and limited CO2 conversions (16, 34–38). Thermodynamic analysis suggests that no first-row transition metal oxide has redox properties located in this region (39). Unlike monometallic oxides whose redox properties are fixed, mixed metal oxides offer potentially tunable thermodynamic properties. Using iron oxide (FeO) as an example, it can form mixed oxides with strontium oxide (SrO) at various Sr/Fe atomic ratios (40). Although SrO is not reducible, formation of Sr–Fe mixed oxides changes the coordination environments and electron density of oxygen anions (\( O_2^- \)). Thus, equilibrium \( P_{\text{O}_2} \) of Sr–Fe mixed oxides can be tailored by adjusting Sr/Fe ratios (Fig. 2). For example, spinel-type \( \text{Sr}_2\text{Fe}_2\text{O}_6 \) exhibits lower \( P_{\text{O}_2} \) than FeO. Further increases in Sr/Fe ratios leads to the formation of perovskite oxides such as Brownmillerite-type \( \text{Sr}_2\text{Fe}_2\text{O}_5 \) and Ruddlesden-Popper (R–P)–phase \( \text{Sr}_n\text{Fe}_{2n}\text{O}_{3n+1} \) with \( n = 2 \), both having notably lower \( P_{\text{O}_2} \) than FeO (Fig. 2). Among the three Sr–Fe mixed oxides investigated, \( \text{Sr}_2\text{Fe}_2\text{O}_6 \), with a marginally improved redox performance over FeO, is not an excellent redox material because of low equilibrium syngas yields (<90%) and CO2 conversions (<95%) at the temperature range of interest. To compare, both \( \text{Sr}_2\text{Fe}_4\text{O}_9 \) and \( \text{Sr}_2\text{Fe}_4\text{O}_9 \) can be effective for methane POx and CO2 splitting, with \( \text{Sr}_2\text{Fe}_4\text{O}_9 \) offering improved redox properties for the hybrid solar-redox scheme.

Redox performance of \( \text{Sr}_2\text{Fe}_4\text{O}_{n-\delta} \)
As-prepared \( \text{Sr}_2\text{Fe}_4\text{O}_{7-\delta} \) (SF7) exhibits excellent redox activity (figs. S1 and S2), but it deactivates continuously (fig. S3) at 900°C under a weight hourly space velocity (WHSV) of 60,000 cm3 gSF7−1 hour−1. Specifically, syngas productivity (eq. S1) dropped by 82% in the methane POx step, and CO productivity (eq. S2) decreased by 72% in the CO2-splitting step over 15 redox cycles. It is noted that even with significant deactivation, CO productivity in the 16th cycle (2.6 mol kgSF7−1) is still an order of magnitude higher than that in state-of-the-art solar-thermal CO2-splitting schemes [<0.3 mol kgoxide−1 for ceria and perovskites (21, 29, 41, 42)]. \( \text{Sr}_2\text{Fe}_4\text{O}_{7-\delta} \) is also superior to CeO2-modified FeO3 in a H2-assisted thermochemical CO2-splitting scheme, where CO productivity is about 1.1 mol kgoxide−1 (35). To shed light on the cause of deactivation, we acquired energy-dispersive x-ray spectroscopy (EDS) mapping and x-ray diffraction (XRD) patterns of as-prepared and spent samples (fig. S4). XRD measurements and thermogravimetric analysis suggest that the as-prepared sample has an R–P-phase \( \text{Sr}_2\text{Fe}_4\text{O}_{7-\delta} \) (tetragonal I4/mmm), whose oxygen stoichiometry decreases to about 6 in an inert atmosphere at 900°C. Metallic iron, iron carbides, FeO, and SrO were detected after the first reduction. It was found that CO2 can fully reoxidize metallic iron back to the R–P phase, but a significant portion of \( \text{Sr}_2\text{Fe}_4\text{O}_9 \) becomes unreducible in the 16th reduction (fig. S4). Elemental mappings indicate that significant phase segregation...
and sintering occurred in redox reactions (fig. S4); this may have caused the redox activity to decrease. To retard sintering and deactivation, the redox active-phase (SF7) was dispersed in an inert and earth-abundant calcium manganese oxide (Ca0.5Mn0.5O) phase.

Sr3Fe2O7−δ-Ca0.5Mn0.5O NCs

Formation of Sr3Fe2O7−δ-Ca0.5Mn0.5O NCs (SF7-CM NCs) is revealed by electron microscopy (figs. S5 and S6), and reducibility of the sample is characterized by hydrogen temperature-programmed reduction (H2-TPR) and in situ XRD (figs. S7 and S8). The redox stability of SF7-CM NCs is shown in Fig. 3. Both syngas productivity in the methane POx step and CO productivity in the CO2-splitting step decreased slightly in the first 21 cycles and then stabilized in the subsequent 9 cycles at 900°C at a WHSV of 24,000 cm3 gSF7-CM−1 hour−1. Specifically, syngas productivity decreased from 4.42 to 4.28 mol kgSF7-CM−1, whereas CO productivity varied from 1.74 to 1.53 mol kgSF7-CM−1 over the first 21 cycles. In the CO2-splitting step, CO productivity was significantly higher for SF7-CM NCs than for CeO2-Fe2O3 [1.1 mol kgoxide−1 (35)]. In the last 10 cycles, syngas selectivity was higher than 95% in the methane POx step. Moreover, the molar ratio of H2/CO remained around 1.96, and coke formation was negligible between 20 and 30 cycles. The excellent stability of the NCs is attributed to the confinement effect that involves dispersing an active phase in an inert medium. XRD measurements demonstrated that Ca0.5Mn0.5O acted as a dispersing medium (Fig. 3), which itself had no activity toward the redox reactions. In addition, elemental mappings demonstrate that all elements are uniformly distributed in as-prepared and spent samples (figs. S9 and S10).

Figure 4A shows typical gaseous product elution profiles in the methane POx step of the 30th cycle. After feeding CH4 to the NC bed, CO2 coeluted with CO and H2, but its elution profile was different from those of CO and H2. The peak production rates for CO2, CO, and H2 were 0.51, 4.14, and 8.03 mmol kgSF7-CM−1 s−1 at 16, 250, and 250 s, respectively. Such a pattern is typical for the redox-based methane POx (43). The gaseous compound elution profiles in the CO2-splitting step of the 30th cycle are presented in Fig. 4B. The breakthrough time of CO2, which is the time when CO2 flow rate at the outlet of a reactor reaches 2% of that at the inlet, was 35 s, and it coincided with the time at which the CO production rate maximized (22 mmol CO kgSF7-CM−1 s−1). The peak CO production rate in this open-loop thermochemical scheme was one order of magnitude higher than that in conventional solar-thermal CO2 splitting, which was carried out at temperatures 200°C higher than that in the former (21). It should be noted that the breakthrough curve of CO2 depends on factors like the flow rate of feed, amount of redox materials, and inlet concentration of CO2. As shown in Fig. 4B, CO2 flow rate leveled off after 180 s. In the first 3 min, the average CO production rate was 8.23 mmol kgSF7-CM−1 s−1, significantly higher than that (<3 mmol kgoxide−1 s−1) in a recently reported methane-assisted thermochemical scheme (33).

One key issue with thermochemical CO2-splitting studies conducted to date is the incomplete CO2 conversion (<90%). For SF7-CM NCs, near-complete CO2 conversion was achieved during the early stage of the reaction (fig. S11). However, the average CO2 conversion in the first 3 min was only 32.3% in the 30th cycle (Fig. 4B). To improve
To further verify the role of the dispersing medium, we prepared another NC with SrFeO$_3$ as the active phase and CaO dispersing medium. SrFeO$_3$ has the highest oxygen capacity among the R-P family (Sr$_{1−n}$Fe$_n$O$_3$, $n = \infty$) while still having desirable redox properties (Fig. 2). XRD and Rietveld refinement do not indicate significant Ca substitution of Sr in SrFeO$_3$-s phase in the NCs, and excess Sr atoms were incorporated into the crystal structure of CaO (Figs. S12 and S13). Redox testing indicated that the CaO phase significantly enhanced the redox kinetics, leading to more than 10-fold faster methane POx and CO$_2$ splitting (Figs. S14 and S15). Apart from the faster redox kinetics, the redox stability of SrFeO$_3$-CaO NCs (SF$_7$-CNCs) was also excellent at 900°C. After the first two cycles, syngas (H$_2$/CO ≈ 2) productivity and selectivity (eq. S3) maintained at around 5.8 mol kg$_{SF3-C}$$^{-1}$ and 96%, respectively, in the methane POx step (fig. S16). Meanwhile, CO productivity in the CO$_2$-splitting step decreased slightly over the first 10 cycles (less than 9%) and then remained unchanged between 10 and 16 cycles (fig. S16). The stability was further confirmed by XRD analysis, which demonstrated that the 1st and 16th reduced samples exhibited identical XRD patterns with iron reduced to its metallic form (fig. S17).

As demonstrated earlier, it is possible to achieve high CO$_2$ conversion by partially replenishing the active lattice oxygen. Meanwhile, high methane conversion can be reached with partially reoxidized NCs (for example, 90% reoxidation). For these POx/splitting cycles, both methane and CO$_2$ conversions were high compared to complete reduction/oxidation cycles but with slightly lowered syngas and CO productivity. The redox stability of SF$_7$-C NCs that underwent partial reduction and oxidation at 980°C with a WHSV of 12,000 cm$^3$ g$_{SF3-C}$$^{-1}$ hour$^{-1}$ is shown in Fig. 5. In the methane POx step, syngas (H$_2$/CO ≈ 2.13) productivity maintained at around 4.63 mol kg$_{SF3-C}$$^{-1}$ after 13 cycles with insignificant CO$_2$ production (<0.08 mol kg$_{SF3-C}$$^{-1}$). After the redox material stabilized, methane conversion reached 59%, and syngas selectivity was around 90% (fig. S18 and table S1). In the CO$_2$-splitting step, CO$_2$ conversion was 98%, the average CO production rate was 9.13 mmol kg$_{SF3-C}$$^{-1}$ hour$^{-1}$, and CO productivity was 2.17 mol kg$_{SF3-C}$$^{-1}$ in the last 17 cycles. A further increase in syngas yield can be realized by tuning the redox window of SF$_7$-C NCs. Over partially reoxidized SF$_7$-C NCs, methane conversion of 90% was achieved with 89% syngas selectivity (table S2) at 980°C with a WHSV of 2045 cm$^3$ g$_{SF3-C}$$^{-1}$ hour$^{-1}$. Moreover, CO$_2$ conversion was nearly 100% in the CO$_2$-splitting step before methane POx (fig. S19).

**DISCUSSION**

The hybrid solar-redox scheme offers various attractive options for CO$_2$ utilization and liquid fuel/chemical production. Here, acetic acid production was investigated as an example. Direct conversion of methane and CO$_2$ to acetic acid is thermodynamically unfavorable, albeit being atom-economic (44). State-of-the-art approach is the syngas route: Coal is first gasified to produce syngas, and then the syngas is cleaned and conditioned to remove excess CO and CO$_2$. This is followed by methanol synthesis (CO + 2H$_2$ $\leftrightarrow$ CH$_3$OH) and subsequent carbonylation of methanol (CH$_3$CHO + CO $\leftrightarrow$ CH$_3$COOH). Methane is not an ideal feedstock for acetic acid synthesis via the conventional syngas route because the CO/H$_2$ ratio is too low in methane-derived syngas. The solar-driven redox process, as shown in Fig. 1, produces a pure CO stream and a syngas stream with ideal compositions for methanol synthesis. Thus, the need for costly separation processes is eliminated.

The solar-driven redox process has three main sections (Fig. 1 and fig. S20): (i) the hybrid solar-redox section where syngas and CO are produced, (ii) the methanol synthesis section that converts syngas into methanol (45), and (iii) the acetic acid synthesis section in which methanol...
and CO are converted to acetic acid by the Cativa process (46). Using ASPEN Plus, the overall energy required for the process was calculated. This process was compared with a coal-based scheme (fig. S21) (47). For each metric ton of acetic acid produced, 20.4 GJthermal is required in the solar-driven process, whereas 37.8 GJthermal is needed in the coal-based process (Fig. 6). Regarding the productivity, the former produces 2.7 times as much acetic acid as the latter per gigajoule of feed fuel (Fig. 6).

Simulation results suggest that production of 1 metric ton of acetic acid results in 0.37 metric ton of CO₂ in the solar-driven process but 2.2 metric tons CO₂ in the coal-based approach.

We report iron-containing mixed metal oxides as effective CO₂-splitting and methane POx agents in a cyclic redox scheme. Unsupported Sr₃Fe₂O₇₋ₓ demonstrated extraordinary methane POx and CO₂-splitting activity at 900°C. However, it deactivated over redox cycles. Dispersing Sr₃Fe₂O₇₋ₓ in a Ca₀.₅Mn₀.₅O matrix significantly enhanced the redox stability of the R-P–structured Sr₃Fe₂O₇₋ₓ. Further investigation of the perovskite-structured SrFeO₃₋ₓ compositing with CaO indicated that the inert CaO phase not only enhanced the redox kinetics but also improved its redox stability at 900° to 980°C. At 980°C, the redox activity decreased slightly in the first 13 cycles and then remained unchanged in the last 17 cycles. In the last 17 cycles, the average CO production rate was 9.13 mmol kg⁻¹ SF₃-C⁻¹ s⁻¹, and CO productivity was 2.17 mol kg⁻¹ SF₃-C⁻¹. The former is 6.8 times higher than state-of-the-art solar-thermal CO₂-splitting schemes (1.35 mmol kg⁻¹ SF₃-C⁻¹ s⁻¹) carried out at significantly higher temperatures (above 1200°C), and the latter is sevenfold higher than that in solar-thermal schemes (<0.3 mol kg⁻¹ SF₃-C⁻¹). For partially reoxidized SF₃-C NCs, methane conversion reached 90% with 89% syngas selectivity at 980°C with a WHSV of 2045 cm³ g⁻¹ SF₃-C⁻¹ hour⁻¹. Moreover, CO₂-to-CO conversion maintained at near 100% in the CO₂-splitting step. The exceptionally high CO₂ utilization efficiency and high syngas yield make the redox materials and the hybrid solar-redox scheme potentially attractive. Process simulations indicate that the fossil energy consumption for acetic acid production can be reduced by 67% by the hybrid solar-redox process when compared to the state-of-the-art one while reducing CO₂ emission by as much as 84%.

**MATERIALS AND METHODS**

**Synthesis of the redox materials**

For the synthesis of SF₇-C NCs [18 weight % (wt %) SF₇], 0.83 g of strontium nitrate [Sr(NO₃)₂], 3.71 g of calcium nitrate [Ca(NO₃)₂·4H₂O], 4.94 g of manganese nitrate [Mn(NO₃)₂·4H₂O], and 18.90 g of citric acid (C₆H₈O₇) were dissolved in 80 ml of deionized (DI) water. The solution was then heated up to 40°C under agitation (600 rpm) on a hot plate, followed by maintaining at this temperature for 30 min. After that, 9.18 g of ethylene glycol (C₂H₆O₂) was added to the above solution. The result solution was subsequently heated up to 80°C and then kept at this temperature until a polymeric gel (ca. 25 cm³) was formed. Iron oxide dispersion was prepared by ultrasonicking...
0.50 g of nanoparticles in 51.5 g of 22.3 to 77.7 wt % ethylene glycol/water solution. The dispersion was then transferred to a 50-mL centrifuge tube, followed by centrifuging at 3500 rpm for 5 min. Around 30 ml of the upper part of the nanoparticle suspension was mixed with 20 ml of gel. The mixture was ultrasonicated for 15 min and then heated up to 80°C, followed by holding at this temperature for 2 days. Afterward, the gel was dried at 120°C overnight to evaporate the residual water. The dry precursor was put in a high-purity alumina crucible, which was then placed in a high-purity alumina ceramic tube that was mounted on an MTI furnace (GSL-1500X-50-UL), into which air continuously flew. The tube was heated up from room temperature to 1200°C for 30 min and then held at this temperature for 12 hours, followed by cooling down to 300°C for 300 min.

For the synthesis of SF3-C NCs (26 wt % SrFeO3-d0), 0.70 g of Sr(NO3)2, 0.90 g of iron nitrate [Fe(NO3)3·9H2O], 4.57 g of Ca(NO3)2·4H2O, and 11.97 g of C6H8O7 were dissolved into 80 ml of DI water. The solution was then heated up to 40°C under agitation (600 rpm), followed by maintaining at this temperature for 30 min. After that, 5.80 g of C2H4O2 was added. The resulted solution was further heated up to 80°C and then kept at this temperature until a polymer gel formed. Afterward, the gel was dried at 120°C overnight to evaporate the residual water. Finally, the dry precursor was calcined at 1200°C in air for 12 hours, as described before.

To examine the redox properties during the reduction of SF7-CM NC, we performed in situ crystallographic analyses of the sample on an Empyrean PANalytical XRD using a Cu Kα radiation operating at 45 kV and 40 mA, which is equipped with a disk-shaped high-temperature chamber. A sample pellet was placed on an aluminia sample holder (Ø = 15 mm) in the high-temperature chamber, and the sample was scanned at a 2θ range of 20° to 80° with a step size of 0.05°, using graphite monochromatic Cu Kα radiation (λ = 0.1542 nm) with a nickel filter and operating at 40 kV and 44 mA.

To determine the bulk composition of NC, samples were digested with hot concentrated nitric acid. The aliquots were filtered with a 0.45-μm filter (Whatman), and the metal concentrations were analyzed by using an inductively coupled plasma (ICP) optical emission spectrometry (PerkinElmer ICP Optical Emission Spectrometer model 8000).

N2 physisorption was performed at −196°C on a volumetric adsorption analyzer (Micromeritics ASAP 2020). Before the analysis, the sample was outgassed under vacuum at 300°C for 2 hours. The specific surface area was calculated by using the Brunauer-Emmett-Teller method in the relative pressure range from 3 × 10−6 to 0.2.

Reactor setup and redox experiments

The redox performance was evaluated in a microreactor (U-type quartz tube; Øin = 4 mm) that was vertically placed inside an electric furnace. The furnace was equipped with a K-type thermocouple whose tip touched the outside of the quartz tube at the location of the redox material. The gas flows were controlled by MCQ mass flow controllers (Alicat). The composition of the effluent stream was monitored by QMS.

In a typical experiment, 0.25 g of the redox material (250 to 425 μm) was loaded into the reactor, and quartz wool was packed on both ends of the oxide bed to keep the particles in place. The reactor was heated up to the targeted temperature in Ar (66.96 μmol s−1), and then these conditions were maintained for around 30 min to remove the residual air in the reaction system. After that, a CH4 stream (7.44 μmol s−1) was introduced to the Ar stream, and methane POx lasted for 15 min, followed by purging the reactor with Ar (66.96 mmol s−1) for 10 min. Next, a CO2 stream (7.44 μmol s−1) was introduced to the Ar stream, and CO2 splitting lasted for 10 min, followed by purging the reactor with Ar (66.96 μmol s−1) for 10 min. The above POx-splitting cycle was repeated 30 times. In the redox test with SF3-C NCs at 980°C, the amount of coke formed in the POX step was determined by in situ...
oxidizing the NCs in 10% O₂/90% Ar (37.2 μmol s⁻¹) at 900°C while measuring the CO₂ production with QMS.

The first reduced sample was recovered after the first methane POx step, and the last oxidized sample was collected after the redox experiment was completed. The last reduced sample was prepared by reducing the first oxidized sample in hydrogen.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/8/e1701184/DC1

Supplementary Text

fig. S1. Characterization of Sr₃Fe₂O₇–δ.
fig. S2. Redox kinetics on Sr₃Fe₂O₇–δ.
fig. S3. Redox stability of Sr₃Fe₂O₇–δ.
fig. S4. Characterization of as-prepared and spent Sr₃Fe₂O₇–δ under ambient conditions.
fig. S5. Characterization of as-prepared and spent (oxidized) SF₇-C NCs.
fig. S6. STEM image and EDS elemental mapping of as-prepared SF₇-C NCs.
fig. S7. H₂-TPR of SF₇-C NCs.
fig. S8. In situ XRD patterns of as-prepared SF₇-CM NCs during reduction in hydrogen.
fig. S9. STEM image and EDS elemental mapping of spent (reduced) SF₇-CM NCs after 20 cycles.
fig. S10. Redox kinetics on Sr₃Fe₂O₇–δ.
fig. S11. CO₂ splitting on SF₇-CM NC after methane POx.
fig. S13. Characterization of SF₇-C NCs.
fig. S14. Redox kinetics on SrFeO₃.
fig. S15. Redox kinetics on SF₇-C NCs.
fig. S16. Redox stability of SF₇-C NCs.
fig. S17. Characterization of as-prepared and spent SF₇-C NCs under ambient conditions.
fig. S18. Redox kinetics over SF₇-C NCs in a short redox period.
fig. S19. Redox kinetics on SF₇-C NCs.
fig. S20. Block diagram for the hybrid solar-redox (HSR)-AcOH.
fig. S22. Comparison in the overall energy demand and production of AcOH for CG and HSR processes.

**REFERENCES AND NOTES**


43. L. M. Neal, A. Shafiefarhood, F. Li, Dynamic methane partial oxidation using a Fe$_2$O$_3$@La$_{0.6}$Sr$_{0.4}$FeO$_{3-δ}$ core–shell redox material in the absence of gaseous oxygen. *ACS Catal.* **4**, 3560–3569 (2014).


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Perovskite nanocomposites as effective CO$_2$-splitting agents in a cyclic redox scheme

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