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° 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 consumptions, 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 kgₘ₉⁻¹ s⁻¹ and 0.71 mmolH₂ kgₙ₁⁻¹ s⁻¹) when compared to state-of-the-art photocatalytic approaches (~0.07 mmolCO kgₘCat⁻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 Fe₃O₄ 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 standpoint. 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.
RESULTS

Rationale for redox material selection

Performance of the redox material is critical to the hybrid solar-redox scheme. Desirable properties for the redox materials include high syngas yield and productivity, excellent CO₂ conversion and CO productivity, and good redox stability. Ideal redox materials should also be affordable, environmentally benign, and attrition-resistant. Among the various metal oxides investigated to date, iron–oxide–containing materials are the most promising ones because of their low cost, abundance, and low toxicity (16, 17, 30–36). However, pure iron oxides are not suitable for the proposed redox reactions from a thermodynamics viewpoint.

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 (MeOₓ/MeOₓ₋₁) with a high equilibrium oxygen pressure (Pₒ₂) can lead to overoxidation of syngas (Eqs. 3 and 4) and low CO₂ conversion (Eq. 7). In contrast, redox pairs with a low Pₒ₂ will result in low methane conversion (Eq. 2). CO₂ splitting, on the other hand, is monotonically favored at lower Pₒ₂. The relationship among equilibrium Pₒ₂, 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 Pₒ₂ 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 (O²⁻). Thus, equilibrium Pₒ₂ of Sr–Fe mixed oxides can be tailored by adjusting Sr/Fe ratios (Fig. 2). For example, spinel-type SrFeₓO₄ exhibits lower Pₒ₂ than FeO. Further increases in Sr/Fe ratios leads to the formation of perovskite oxides such as Brownmillerite-type SrₓFe₂O₅ and Ruddlesden-Popper (R-P)–phase SrₓFeₓOₓ₃₋₁₋₅ with n = 2, both having notably lower Pₒ₂ than FeO (Fig. 2). Among the three Sr–Fe mixed oxides investigated, SrFeO₄, 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 SrₓFeₓO₄ and SrₓFeₓO₆ can be effective for methane POX and CO₂ splitting, with SrₓFeₓO₄ offering improved redox properties for the hybrid solar-redox scheme.

Redox performance of SrₓFeₓO₄–₅

As-prepared SrₓFeₓO₄–₅ (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). SrₓFeₓO₇–₅ is also superior to CeO₂-modified FeₓO₃ 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 SrₓFeₓO₄–₅ (tetragonal I4/mmm), whose oxygen stoichiometry decreases to about 6 in an inert atmosphere at 900°C. Metallic iron, iron carbides, FeₓO₄, 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 SrₓFeₓO₄ 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 (Ca\(_{0.5}\)Mn\(_{0.5}\)O) phase.

**Sr\(_3\)Fe\(_2\)O\(_7\)−\((\text{SF7-CM NCs})\)**

Formation of Sr\(_3\)Fe\(_2\)O\(_7\)−\((\text{SF7-CM NCs})\) is revealed by electron microscopy (figs. S5 and S6), and reducibility of the sample is characterized by hydrogen temperature-programmed reduction (H\(_2\)-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 CO\(_2\)-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 cm\(^3\) g\(_{\text{SF7-CM}}\)\(^{-1}\) hour\(^{-1}\). Specifically, syngas productivity decreased from 4.42 to 4.28 mol kg\(_{\text{SF7-CM}}\)\(^{-1}\), whereas CO productivity decreased from 4.28 to 4.28 mol kg\(_{\text{SF7-CM}}\)\(^{-1}\) hour\(^{-1}\). The peak CO production rate in this open-loop thermochemical scheme was one order of magnitude higher than that in conventional solar-thermal CO\(_2\) 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 CO\(_2\) depends on factors like the flow rate of feed, amount of redox materials, and inlet concentration of CO\(_2\). As shown in Fig. 4B, CO\(_2\) flow rate leveled off after 180 s. In the first 3 min, the average CO production rate was 8.23 mmol kg\(_{\text{SF7-CM}}\)\(^{-1}\) hour\(^{-1}\), significantly higher than that (<3 mmol kg\(_{\text{oxide}}\) hour\(^{-1}\) in a recently reported methane-assisted thermochemical scheme (33).

One key issue with thermochemical CO\(_2\)-splitting studies conducted to date is the incomplete CO\(_2\) conversion (<90%). For SF\(_7\)-CM NCs, near-complete CO\(_2\) conversion was achieved during the early stage of the reaction (fig. S11). However, the average CO\(_2\) conversion in the first 3 min was only 32.3% in the 30th cycle (Fig. 4B). To improve...
CO₂ conversion, we attempted to shorten the duration of the CO₂-splitting step. As shown in Fig. 4B, CO₂ conversion was above 98%, and the average CO production rate was 13.8 mmol kg⁻¹ SF₃-CM⁻¹ s⁻¹ for a shorter feeding period. Such a short regeneration period was adequate to replenish over 80% of the active lattice oxygen of the reduced NCs. To the best of our knowledge, such a high CO₂ conversion has yet to be reported for thermochemical CO₂ splitting. These findings clearly demonstrate that this NC outperforms the other redox materials for thermochemical CO₂ splitting.

**SrFeO₃₋₈-CaO NCs**

To further verify the role of the dispersing medium, we prepared another NC with SrFeO₃₋₈ as the active phase and CaO dispersing medium. SrFeO₃ has the highest oxygen capacity among the R-P type perovskite family (Srₙ₋₁Feₙ₋₁O₃₋₈, n = ∞) while still having desirable redox properties (Fig. 2). XRD and Rietveld refinement do not indicate significant Ca substitution of Sr in SrFeO₃₋₈ 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 CO₂ splitting (Figs. S14 and S15). Apart from the faster redox kinetics, the redox stability of SrFeO₃₋₈-CaO NCs (SF₃-C NCs) was also excellent at 900°C. After the first two cycles, syngas (H₂/CO = 2) productivity and selectivity (eq. S3) maintained at around 5.8 mol kg⁻¹ SF₃-C⁻¹ and 96%, respectively, in the methane POX step (fig. S16). Meanwhile, CO productivity in the CO₂-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 CO₂ 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 CO₂ conversions were high compared to complete reduction/oxidation cycles but with slightly lowered syngas and CO productivity. The redox stability of SF₃-C NCs that underwent partial reduction and oxidation at 980°C with a WHSV of 12,000 cm³ g⁻¹ SF₃-C⁻¹ hour⁻¹ is shown in Fig. 5. In the methane POX step, syngas (H₂/CO = 2.13) productivity maintained at around 4.63 mol kg⁻¹ SF₃-C⁻¹ after 13 cycles with insignificant CO₂ production (<0.08 mol kg⁻¹ 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 CO₂-splitting step, CO₂ conversion was 98%, the average CO production rate was 9.13 mmol kg⁻¹ SF₃-C⁻¹, and CO productivity was 2.17 mol kg⁻¹ SF₃-C⁻¹ in the last 17 cycles. A further increase in syngas yield can be realized by tuning the redox window of SF₃-C NCs. Over partially reoxidized SF₃-C NCs, methane conversion of 90% was achieved with 89% syngas selectivity (table S2) at 980°C with a WHSV of 2045 cm³ g⁻¹ SF₃-C⁻¹ hour⁻¹. Moreover, CO₂ conversion was nearly 100% in the CO₂-splitting step before methane POX (fig. S19).

**DISCUSSION**

The hybrid solar-redox scheme offers various attractive options for CO₂ utilization and liquid fuel/chemical production. Here, acetic acid production was investigated as an example. Direct conversion of methane and CO₂ 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 CO₂. This is followed by methanol synthesis (CO + 2H₂ ⇌ CH₃OH) and subsequent carbonylation of methanol (CH₃OH + CO ⇌ CH₃COOH). Methane is not an ideal feedstock for acetic acid synthesis via the conventional syngas route because the CO/H₂ 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−δ demonstrated extraordinary methane POx and CO2-splitting activity at 900°C. However, it deactivated over redox cycles. Dispersing Sr3Fe2O7−δ in a Ca0.5Mn0.5O matrix significantly enhanced the redox stability of the R-P-structured Sr3Fe2O7−δ. Further investigation of the perovskite-structured SrFeO3−δ compositing with CaO indicated that the inert CaO phase not only enhanced the redox kinetics but also improved its redox stability at 900°C 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 kgSF3-C−1 s−1, and CO productivity was 2.17 mol kgSF3-C−1. The former is 6.8 times higher than state-of-the-art solar-thermal CO2-splitting schemes (1.35 mmol kggoxide−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 kggoxide−1). For partially reoxidized SF3-C NCs, methane conversion reached 90% with 89% syngas selectivity at 980°C with a WHSV of 2045 cm3 gSF3-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 SF3-C NCs [18 weight % (wt %) SF3-C], 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 resulted 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 ultrasonicating...
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 300 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$_2$·$\delta$), 0.70 g of Sr(NO3)$_2$·6H$_2$O, 0.90 g of iron nitrate [Fe(NO3)$_2$·9H$_2$O], 4.57 g of Ca(NO3)$_2$·4H$_2$O, and 11.97 g of C$_6$H$_8$O$_7$ 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 C$_2$H$_6$O$_2$ 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.

For the synthesis of Sr$_3$Fe$_2$O$_7$ and SrFeO$_3$·$\delta$, these two redox materials were prepared by the Pechini method as described above. The molar ratio of Sr/Fe in the precursor solutions was 3:2 and 1:1 for Sr$_3$Fe$_2$O$_7$·$\delta$ and SrFeO$_3$·$\delta$, respectively. The molar ratio of C$_2$H$_6$O$_2$/C$_6$H$_8$O$_7$/total cations was 3.75:2.5:1 in the gel. The calcination temperature was 1200°C.

**Material characterization**

The oxygen stoichiometry of as-prepared redox materials was determined by H$_2$-TPR, which was carried out on a TA Instruments thermogravimetric analyzer (SDT Q600). About 50 mg of the sample was loaded into an alumina crucible. Before measurements, the as-prepared sample was treated at 900°C for 1 hour in 20 volume percent (volume %) O$_2$/80 volume % Ar (74.4 μmol s$^{-1}$). After treatment, the sample was cooled down and subsequently heated up to 100°C and then kept at this temperature for 30 min in 10 volume % H$_2$/90 volume % Ar (74.4 μmol s$^{-1}$). Then, it was heated up to 1150°C at a ramping rate of 10°C min$^{-1}$. To obtain O$_2$- or CO$_2$-regenerated sample, the sample was first reduced in 10% CH$_4$/90% Ar (74.4 μmol s$^{-1}$) and then oxidized in 10% O$_2$ (or CO$_2$)/90% Ar (74.4 μmol s$^{-1}$) at 900°C, followed by cooling down to room temperature. The oxygen stoichiometry of redox materials under inert conditions was estimated from the amount of lattice oxygen released from the as-prepared sample (after 20% O$_2$ pretreatment) at a temperature range of ~25° to 900°C in Ar. Around 580 mg of the sample was loaded to a U-type quartz tube (Ø = 15 mm) and then kept at this temperature for 1.5 hours in nitrogen. Finally, the sample was cooled down to room temperature in nitrogen.

**Reactor setup and redox experiments**

The redox performance was evaluated in a microreactor (U-type quartz tube; Ø = 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 specific surface area was calculated by using the Brunauer-Emmett-Teller method in the relative pressure range from 3 × 10$^{-6}$ to 0.2.

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 N Cs 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 part of the last oxidized sample in 10 volume % CH4/90 volume % Ar (74.4 μmol s−1) at 900°C for 15 min.

**SUPPLEMENTARY MATERIALS**

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

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