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$\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ perovskites as efficient catalysts for two-step thermochemical water splitting in conjunction with exceptional hydrogen yields

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ABSTRACT

Solar-driven thermochemical water splitting represents one efficient route to the generation of H_2 as a clean and renewable fuel. Due to their outstanding catalytic abilities and promising solar fuel production capacities, perovskite-type redox catalysts have attracted significant attention in this regard. In the present study, the perovskite series $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ ($x, y = 0.2, 0.4, 0.6$, or 0.8) was fabricated using a modified Pechini method and comprehensively investigated to determine the applicability of these materials to solar H_2 production *via* two-step thermochemical water splitting. The thermochemical redox behaviors of these perovskites were optimized by doping at either the A (Ca) or B (Al) sites over a broad range of substitution values, from 0.2 to 0.8. Through this doping, a highly efficient perovskite ($\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$) was developed, which yielded a remarkable H_2 production rate of $429 \mu\text{mol/g}$ during two-step thermochemical H_2O splitting, going between 1400 and 1000°C . Moreover, the performance of the optimized perovskite was found to be eight times higher than that of the benchmark catalyst CeO_2 under the same experimental conditions. Furthermore, these perovskites also showed impressive catalytic stability during two-step thermochemical cycling tests. These newly developed $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ redox catalysts appear to have great potential for future practical applications in thermochemical solar fuel production.

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1. Introduction

Concerns regarding fossil fuel depletion and climate change have resulted in the development of alternative renewable and clean energy solutions, such as solar energy technologies. One viable means of converting concentrated solar power into clean energy sources such as hydrogen (H_2) is *via* thermochemical water splitting [1,2]. Compared with various other solar-based

H_2 generation methods, including photochemical and photoelectrochemical water splitting [3,4], the thermochemical water splitting route is capable of utilizing the entire solar spectrum and thereby results in higher solar energy conversion efficiency [5–7]. Since direct water thermolysis [8] requires very high temperatures ($>4000^\circ\text{C}$) that are not practical, thermochemical water splitting is typically divided into two separate steps utilizing a metal oxide as a redox catalyst. As shown in Fig. 1,

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the metal oxide (MO_x) is initially subjected to a high-temperature endothermic thermal reduction step to release part (or all) of its oxygen atoms, to generate oxygen-deficient $\text{MO}_{x-\delta}$ (Eq. (1)). Subsequently, through a low-temperature exothermic water splitting step, the oxygen-deficient $\text{MO}_{x-\delta}$ is re-oxidized to the original MO_x with the simultaneous production of H_2 (Eq. (2)).

Thermal reduction step:

Water splitting step:

Over the past several decades, numerous metal oxides have been assessed for this purpose, although only a few, such as ZnO [9–11], Fe_3O_4 [12–14], various ferrites [15–17], CeO_2 and doped CeO_2 [18–23], have been found to exhibit sufficient thermochemical water splitting activity. Among these, non-stoichiometric CeO_2 is generally recognized as the benchmark catalyst due to its favorable reaction kinetics and superior catalytic stability. However, the high processing temperatures required when using this material ($>1500^\circ\text{C}$) and its relatively low solar fuel production capacity limit the practical applications of CeO_2 in this field.

Perovskite-type metal oxides with the general formula ABO_3 have been widely studied in applications such as solid oxide fuel cells [24], electrocatalysts [25], and sensors [26]. Due to the unique structures of these compounds and their oxygen exchange properties, perovskite oxides may also have significant potential for thermochemical solar fuel production. Recently, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskites were investigated for the first time as thermochemical catalysts, and demonstrated promising oxygen exchange capacities and high theoretical energy conversion efficiencies [27–29]. McDaniel *et al.* [30,31] also reported an advanced perovskite system, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$, that exhibits fast water splitting kinetics and significant hydrogen yields. Furthermore, several other perovskites, including $\text{La}_{1-y}\text{Ca}_y\text{MnO}_3$ [32], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ [33], $\text{Y}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [34] and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-y}\text{Sc}_y\text{O}_3$ [35], have also been studied for thermochemical applications. However, none of these are ideal for

practical thermochemical applications due to challenges associated with their solar fuel production capacities and long-term catalytic stabilities. Considering the vast range of compositions possible with these compounds, the discovery of new and advanced perovskite-type redox catalysts for two-step thermochemical water splitting is of significant interest.

Recently, members of the $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ (LCMA) perovskite series were extensively studied for two-step thermochemical CO_2 splitting to produce CO , a similar process to thermochemical H_2O splitting [36,37]. Based on the outstanding oxygen exchange capacities and promising catalytic behavior observed during these previous trials, it is considered that LCMA perovskites may be applicable to two-step thermochemical water splitting to produce H_2 . However, until now, no such investigations have been performed. The present work represents the first-ever systematic investigation of LCMA perovskites as efficient catalysts for two-step thermochemical H_2O splitting, and demonstrates remarkable H_2 yields using these materials.

2. Experimental

2.1. Chemicals

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ceria, citric acid and ethylene glycol were all purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

2.2. Perovskites synthesis

All the LCMA perovskite oxides were synthesized using a modified Pechini method [38]. In a typical synthesis, the necessary metal nitrates were first dissolved in deionized (DI) water in the appropriate amounts. Citric acid was then added to the solution at a molar ratio of 1.5:1 with respect to the total metal cations, after which the mixture was heated to 70°C with stirring. After approximately 10 min, ethylene glycol was added to the solution at a molar ratio of 1:1 relative to the citric acid. The solution was then held at 90°C until a brownish gel was obtained, which was transferred to an electric oven and heated at 120°C for 12 h to obtain a resin. The resin was carefully collected and ground using a mortar and pestle. Finally, the resin was calcined in a tubular furnace (1300°C for 6 h) to remove any remaining organics or nitrates, to prepare the final perovskite sample.

2.3. Characterizations

X-ray diffraction (XRD) patterns of the perovskite samples were acquired with a Bruker D8 X-ray diffractometer operating at 40 kV with a current of 25 mA using $\text{Cu } K\alpha$ radiation. The XRD measurements were carried out over the 2θ range of 20° – 80° with a step size of 0.02° and a scanning rate of $2^\circ/\text{min}$. The results were compared with the standard Inorganic Crystal Structure Database (ICSD) to identify phases. The surface structures and particles sizes of the prepared perovskites were

Fig. 1. Schematic illustration of the two-step thermochemical water splitting process. In the first step, the metal oxide, MO_x , is thermally reduced to $\text{MO}_{x-\delta}$ via a high-temperature treatment to release O_2 . In the second step, the oxygen deficient $\text{MO}_{x-\delta}$ is re-oxidized by splitting H_2O to produce H_2 .

confirmed by scanning electron microscopy (SEM, JSM-7100) and transmission electron microscopy (TEM, Tecnai F20). Energy dispersive X-ray (EDX, JSM-7100) mapping was also used to characterize the surface morphologies and elemental distributions within the samples.

2.4. Thermochemical H₂O splitting tests

The two-step thermochemical H₂O splitting activity of each specimen was investigated using a laboratory-scale fixed-bed reactor. To facilitate effective testing, each freshly prepared perovskite sample (approximately 0.5 g) was made into a solid porous monolithic structure by mixing with a suitable quantity of isopropanol and heating at 1300 °C for 6 h in air [28,39]. The resulting redox sample was placed in the center of a tubular alumina reactor within a high temperature programmable electric furnace (MTI, KSL-1800X-S60). Ar (ultra-high purity; approximately 99.99%) was used as the carrier gas, with its flow rate determined by a mass flow controller (Alicat Scientific). Thermal reduction was carried out by heating the perovskite sample to 1400 °C and holding at that temperature for 1 h under an Ar flow of 200 sccm (with an oxygen partial pressure of approximately 20 ppm). The temperature was subsequently decreased to 1000 °C for H₂O splitting. Both the temperature increase and decrease rates were fixed at 10 °C/min. Water was introduced into the reaction chamber by a water pump (Easypump, BT100N) at a set rate, whereupon it vaporized and mixed with the Ar gas (such that the volume percentage of water vapor in the mixture was on the order of 40%). The H₂O splitting reaction was performed for 1 h to complete the re-oxidation process. During the thermal reduction and H₂O splitting process, the amounts of O₂ and H₂ produced were quantified using a mass spectrometer (MS, Omni Star GSD 320) that had been previously calibrated using O₂ and H₂ gas standards.

The re-oxidation yield (α) of each thermochemical H₂O splitting test trial was calculated as $\alpha = (n_{\text{H}_2}/2n_{\text{O}_2}) \times 100\%$, where n_{O_2} and n_{H_2} represent the total moles of O₂ and H₂ evolved during two-step thermochemical H₂O splitting.

3. Results and discussion

3.1. Structural characteristics

The XRD pattern of a typical as-synthesized LCMA perovskite (La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O₃ or LCMA-C0.4A0.4) is displayed in Fig. 2(a), with the remainder of the XRD results shown in Figs. 3 and 4. In keeping with results in the literature [36,40], the observed diffraction peaks indicate a typical orthorhombic perovskite structure (Pnma group) without impurity phases, demonstrating the successful preparation of perovskite structured oxides. During the high-temperature treatment, all the LCMA perovskites fabricated in this work were found to maintain a stable crystal structure without any phase changes. The surface morphologies of these perovskites were also observed by SEM. As shown in Fig. 2(b), the representative

Fig. 2. (a) XRD pattern, (b) SEM image, (c) TEM image, and (d) EDX elemental mapping of Ca, Mn and Al distributions for the LCMA-C0.4A0.4 perovskite. The inset in (c) shows a high magnification local TEM image.

Fig. 3. XRD patterns of La_{1-x}Ca_xMn_{0.6}Al_{0.4}O₃ perovskites with Ca doping levels of 0.2, 0.4, 0.6 and 0.8.

LCMA-C0.4A0.4 perovskite had a hierarchical porous structure composed of interconnected small particles. Similar surface microstructures were also observed for the other LCMA sam-

Fig. 4. XRD patterns of La_{0.6}Ca_{0.4}Mn_{1-y}Al_yO₃ perovskites with Al doping levels of 0.2, 0.4, 0.6 and 0.8.

ples having different doping levels. TEM was also performed to further confirm the structure and particle size of the LCMA-C0.4A0.4. In keeping with the SEM results, a porous surface structure was observed (Fig. 2(c)). The local high-resolution TEM image include as an inset in Fig. 2(c) shows that the particle size of the LCMA-C0.4A0.4 was less than 50 nm. EDX mapping was employed to determine the elemental distributions in the LCMA perovskites. As shown in Fig. 2(d), homogeneous distributions of the metal cations (Ca, Mn and Al) were evident in the LCMA-C0.4A0.4 sample. Based on these results, it is apparent that LCMA perovskites with different Ca and Al doping levels were successfully synthesized.

3.2. Thermochemical activity tests

The catalytic performance of a perovskite is strongly dependent on its composition. Thus, to optimize the catalytic behavior of these LCMA perovskites during the thermochemical H₂O splitting process, we systematically investigated the effects of both the A site dopant Ca and the B site dopant Al through varying their levels over a broad doping range.

3.2.1. Effect of the Ca doping level

We first examined the two-step thermochemical H₂O splitting performance of these materials while varying the Ca doping level from 0.2 to 0.8 at the A sites (samples LCMA-C0.2A0.4, LCMA-C0.4A0.4, LCMA-C0.6A0.4 and LCMA-C0.8A0.4). During

these trials, the Al level at the B sites was fixed at 0.4 based on previously reported results [30]. As shown in Fig. 5(a), different O₂ evolution profiles were obtained during the high temperature thermal reduction process ($T = 1400\text{ }^{\circ}\text{C}$). Clearly, increasing the Ca doping level improved the O₂ evolution performance of the LCMA perovskite. As an example, compared with LCMA-C0.2A0.4, LCMA-C0.8A0.4 exhibited a lower onset temperature for O₂ evolution and showed a significantly higher peak production rate. In these trials, the H₂O splitting reaction was carried out at a relatively low temperature of 1000 °C upon introducing the steam/Ar mixture to the reactor system. In contrast to the O₂ evolution rate, which increased in proportion to the increases in the Ca doping level, the specimens exhibited different H₂ production behaviors during the H₂O splitting process. Fig. 5(b) demonstrates that the H₂ production profiles of the LCMA perovskites were initially improved as the Ca doping level increased from 0.2 to 0.4. However, further increases above 0.6 resulted in reduced H₂ generation.

The different O₂ and H₂ evolution characteristics resulting from the thermal reduction and re-oxidation processes are evident from the final amounts summarized in Fig. 5(c). The O₂ evolution shows a linear increase as the Ca level increases. Thus, the maximum O₂ evolution (419 $\mu\text{mol/g}$) was achieved using LCMA-C0.8A0.4, which gave a value much higher than those obtained from the other LCMA perovskites (176, 231, and 280 $\mu\text{mol/g}$ for LCMA-C0.2A0.4, LCMA-C0.4A0.4 and LCMA-C0.6A0.4, respectively). These data demonstrate that

Fig. 5. (a) O₂ and (b) H₂ production curves, (c) final O₂ and H₂ production amounts, and (d) re-oxidation yields of LCMA perovskites with Ca doping levels from 0.2 to 0.8 in a two-step thermochemical H₂O splitting cycle carried out between 1400 and 1000 °C.

increasing the extent of Ca doping significantly promotes the O_2 evolution reaction during the thermal reduction process. In contrast, the H_2 production exhibits a different trend, with a parabolic shape. The LCMA-C0.4A0.4 showed the highest H_2 production rate (429 $\mu\text{mol/g}$) relative to those achieved with the LCMA-C0.2A0.4 (334 $\mu\text{mol/g}$), LCMA-C0.6A0.4 (364 $\mu\text{mol/g}$), and LCMA-C0.8A0.4 (260 $\mu\text{mol/g}$). To further clarify this anomalous behavior, the re-oxidation yields of LCMA perovskites were calculated based on the extent of O_2 recovered after the overall thermochemical H_2O splitting cycle. As shown in Fig. 5(d), at Ca doping levels less than 0.4, the O_2 evolved during the thermal reduction process could be almost fully recovered. However, the re-oxidation yields decreased rapidly above this concentration, such that only 30% of the O_2 was recovered in the case of LCMA-C0.8A0.4 after the thermochemical H_2O splitting. This result explains the poor water splitting reaction thermodynamics observed at doping levels of 0.6 and 0.8.

Based on the above results, it is evident that higher levels of A site Ca doping within the LCMA perovskites greatly promotes O_2 evolution. At the same time, elevated levels of Ca are also significantly detrimental to the reaction thermodynamics of the H_2O splitting process, leading to reduced levels of O_2 recovery and lower H_2 yields. Therefore, a Ca doping level of 0.4 was determined to be the most suitable.

3.2.2. Effect of the Al doping level

The extent of Al doping at the B sites in the LCMA may also have a pronounced effect on the thermochemical water splitting results. Therefore, after determining the optimal A site doping level, the thermochemical behaviors of LCMA perovskites with Al substitution at the B sites ranging from 0.2 to 0.8 (LCMA-C0.4A0.2, LCMA-C0.4A0.4, LCMA-C0.4A0.6 and LCMA-C0.4A0.8, respectively) were systematically investigated. As can be seen from the oxygen release curves presented in Fig. 6(a), in contrast to the data obtained when varying the Ca content of the A sites, the O_2 evolution of the perovskites is initially improved with increases in the Al doping content, up to a level of 0.4, and then starts to decrease. Similar H_2 production profiles (Fig. 6(b)) were found during the subsequent water splitting process. According to previous reports, specific Al doping levels at the B sites of perovskites can lower the thermal reduction enthalpy and thus improve the thermochemical performance [35,36]. However, in the case of LCMA perovskites, Mn is the only element with a variable valence, such that the transition between Mn^{3+} and Mn^{4+} is critical to the thermochemical catalytic process. Therefore, the proper tuning of the ratio between Al and Mn at the B sites of the LCMA is important. This can be seen by assessing the overall O_2 and H_2 production amounts. As shown in Fig. 6(c), both the O_2 and H_2 rates exhibited exactly the same production trend and LCMA-C0.4A0.4

Fig. 6. (a) O_2 and (b) H_2 production curves, (c) the overall O_2 and H_2 production amounts, and (d) re-oxidation yields of $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ perovskites with Al doping levels from 0.2 to 0.8 in a two-step thermochemical H_2O splitting cycle conducted between 1400 and 1000 $^{\circ}\text{C}$.

showed the best thermochemical performance (231 $\mu\text{mol/g O}_2$ and 429 $\mu\text{mol/g H}_2$), which was much higher than that shown by the other samples (201 and 374, 186 and 349, 126 and 239 $\mu\text{mol/g O}_2$ and H_2 for LCMA-C0.4A0.2, LCMA-C0.4A0.6 and LCMA-C0.4A0.8, respectively). Furthermore, all the specimens with varied Al doping levels gave high re-oxidation yields (Fig. 6(d)). These data demonstrate that the variation of Al at the B sites of LCMA perovskites has a slight effect on the water splitting reaction thermodynamics, and that most of the oxygen vacancies are recovered after the overall thermochemical process.

Based on these detailed investigations of the two-step thermochemical water splitting performances of LCMA perovskites while tuning both the Ca and Al doping levels at the A and B sites, LCMA-C0.4A0.4 was confirmed as the most suitable composition. This material exhibited remarkable thermochemical solar H_2 performance (429 $\mu\text{mol/g}$). A simple comparison test was carried out between our LCMA-C0.4A0.4 sample and

the current benchmark material CeO_2 under the same experimental conditions. The H_2 production of LCMA-C0.4A0.4 was found to be almost eight times higher than that achieved by the CeO_2 (56 $\mu\text{mol/g}$, Fig. 7). More importantly, the performance of the LCMA-C0.4A0.4 was also superior to that of other state-of-the-art perovskite-type redox catalysts, such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ [28] (397 $\mu\text{mol/g}$) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$ [30] (307 $\mu\text{mol/g}$).

3.3. Catalytic stability tests

Stability is another critical factor used to assess the long-term application of redox catalysts to thermochemical solar fuel production. Thus, multiple thermochemical H_2O splitting trials were performed with the same LCMA-C0.4A0.4 sample between 1400 and 1000 $^\circ\text{C}$. As shown in Fig. 8(a), steady O_2 and H_2 production rates were observed during five consecutive thermochemical cycles. This stability is also evident from the summarized O_2 and H_2 production amounts per cycle (Fig. 8(b)). Moreover, the molar ratio of H_2 to O_2 throughout these trials was reasonably to the theoretical value of 2:1, indicating that almost all the oxygen vacancies generated during the thermal reduction process were recovered during the re-oxidation. The XRD and SEM assessments also demonstrate

Fig. 7. (a) O_2 evolution and (b) H_2 production curves, and (c) summary of the results obtained with CeO_2 during two-step thermochemical H_2O splitting between 1400 and 1000 $^\circ\text{C}$.

Fig. 8. (a) Five consecutive O_2 and H_2 production profiles obtained from LCMA-C0.4A0.4 and (b) O_2 and H_2 yields and their corresponding ratios as functions of cycle number.

Fig. 9. (a) XRD pattern and (b) SEM image of LCMA-C0.4A0.4 after two-step thermochemical H₂O splitting cycling between 1400 and 1000 °C.

that no significant changes in the crystal structure or surface morphology (Fig. 9) took place during the thermochemical cycling. Thus, we can conclude that LCMA-C0.4A0.4 maintains its superior catalytic stability throughout thermochemical cycling and therefore has significant potential for practical applications in thermochemical solar fuel production.

4. Conclusions

A systematic investigation of $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ perovskites with regard to their thermochemical H₂O splitting performance was carried out at temperatures of 1400 and 1000 °C. To optimize the thermochemical redox behavior of these materials, the substitutions of both the A site dopant Ca and the B site dopant Al were varied over a broad range (from 0.2 to 0.8). $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$ was recognized as the optimal composition among the various perovskites, and generated a H₂ production rate (429 μmol/g) that was significantly higher (by

approximately eight times) than that of a CeO₂ catalysts under the same experimental conditions. This same material showed outstanding cyclic stability during replicate thermochemical H₂O splitting trials and thus is anticipated to have future long-term practical applications.

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Graphical Abstract

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$\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ perovskites as efficient catalysts for two-step thermochemical water splitting in conjunction with exceptional hydrogen yields

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Remarkable H₂ yields were obtained when using the $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{1-y}\text{Al}_y\text{O}_3$ perovskite series as efficient thermochemical water splitting catalysts following optimization of the A and B site doping levels.

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钙铝掺杂镧锰钙钛矿高效催化剂用于两步法热化学分解水取得出色产氢表现

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摘要: 太阳能热化学分解水是一种高效生产清洁和可再生氢能源的方法。由于出色的催化活性和太阳能燃料生产能力, 钙钛矿型的催化剂在热化学领域引起了强烈关注。我们采用改良的Pechini法合成了一系列钙铝掺杂的镧锰钙钛矿并系统考察了其在两步法热化学分解水中的产氢表现。为了优化热化学催化性能, 我们进行了镧锰钙钛矿A、B位上钙和铝的掺杂量(从0.2到0.8)的详细考察。通过调整掺杂比例, 得到了一种极其高效的钙钛矿催化剂 $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$ 。当两步法热化学分解水在1400和1000 °C之间, $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.4}\text{O}_3$ 取得了429 $\mu\text{mol/g}$ 的出色产氢表现, 比同等条件下基准催化剂氧化铈产氢结果高出8倍。与此同时, 钙铝掺杂镧锰钙钛矿在两步法热化学循环测试中展现出极其稳定的催化活性。因此, 这种新颖的钙铝掺杂镧锰钙钛矿具备巨大的潜质用于未来热化学太阳能燃料的实际生产。

关键词: 两步法热化学; 水分解; 太阳能燃料; 钙钛矿型氧化还原催化剂; 产氢

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