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Three-dimensionally ordered macroporous perovskite materials for environmental applications

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ABSTRACT

Three-dimensionally ordered macroporous (3DOM) perovskite materials have attracted the interest from researchers worldwide due to their unique macroporous structure, flexible composition, tailorable physicochemical property, high stability and biocompatibility. In particular, they were widely used in environmental field, such as photocatalysis, catalytic combustion, catalytic oxidation and sensors. In this review, the recent progresses in the synthesis of 3DOM perovskite materials and their environmental applications are summarized. The advantages and the promoting mechanisms of 3DOM perovskite materials for different applications are discussed in detail. Subsequently, the challenges and perspectives on the topic are proposed.

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1. Introduction

In recent years, three-dimensionally ordered macroporous (3DOM) materials, also known as inverse opal materials, have been widely studied by researchers worldwide [1–4]. The 3DOM materials possess general features of macroporous material, such as large surface area, high porosity, large pore volume and excellent mass transfer ability. Besides, the materials also own some distinctive characteristics including periodic pore structure, uniform and controllable pore size, as well as

the unique optical properties as a kind of photonic crystal derived from their three-dimensional long-range ordered structure [5]. In addition, 3DOM materials with mesoporous walls can be obtained by simply adding surfactants in the fabrication process. The incorporation of mesopores provides more reactive sites for molecules and imparts size-selectivity to the hierarchical porous materials [6].

Perovskite is an abundant compound widely distributed on the earth. The general formula of perovskite is ABO₃ (e.g. CaTiO₃), where the A-site cations are usually rare-earth or alkali-

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line-earth elements, the B-site cations are transition metals and O is oxygen. Other perovskite-type materials consist of double perovskite [7] ($A_2BB'O_6$, e.g. Sr_2FeMoO_6), perovskite-like [8] (A_2BO_4 , e.g. La_2CuO_4), antiperovskite [9] (AXM_3 , e.g. $CuNNi_3$), post-perovskite [10] (ABO_3 , e.g. $MgSiO_3$) and pre-perovskite [11] (ABO_3 , e.g. $PbTiO_3$). Its low cost, excellent redox property, improved ion mobility, high stability, low toxicity and good biocompatibility make perovskite possible to be broadly used. Through partial or complete substitution of the A-/B-site cations, the physicochemical properties of perovskite materials can be adjusted, giving the perovskite controllable properties and making it a potential research focus.

Recently, because of their tailorable structural and physicochemical properties, ongoing progresses and systematic studies of 3DOM perovskite materials have been reported for numerous applications, such as photocatalysis, soot combustion, catalytic oxidation of volatile organic compounds (VOCs), emission reduction and utilization of greenhouse gases, and sensors for gases or liquids.

Herein, an up to date review focused on the advances of 3DOM perovskite materials for environmental applications is expected urgently due to the rapid development of this field. Although some excellent reviews have been published about perovskite materials [12–16], only certain applications are involved and 3DOM morphology is not mentioned. In the feature article written by Arandiyana et al. [17], the use of porous perovskite and spinel oxides as advanced catalysts for energy conversion applications and various heterogeneous reactions were reviewed, but not focused on the environmental applications. As the consequence, we think it is necessary to write a new review concentrating on 3DOM perovskite materials for environmental applications. In the first part of the review, the general fabrication approach of 3DOM perovskite materials will be provided. Afterwards, we intend to introduce recent progresses of the materials in environmental applications. Lastly, we provide conclusions and the authors' views of future prospects are presented.

2. Fabrication of 3DOM perovskite materials

3DOM materials are usually prepared by an etching method, biological template method or colloidal crystal template method. Among these methods, the first two, which require special instruments, strict conditions and complex operations, are difficult for most laboratories. The colloidal crystal template (CCT) method is simple, low-cost and suitable for applications in most

laboratories. As the result, it is the most commonly used method for fabricating 3DOM materials [18]. Generally, the preparation of 3DOM materials by CCT method includes the following four steps [19,20]: (1) Synthesis of monodisperse colloidal microspheres; (2) Assembly of monodisperse colloidal microspheres into opal-structured CCT by appropriate methods; (3) Filling and solidifying the voids between the microspheres by appropriate precursor; (4) Calcination to form the skeleton and removing the template. In order to fabricate 3DOM materials with mesoporous walls, the surfactant-assisted method is used, in which surfactants are added into the precursor solution. Conventional surfactants include Pluronic P-123, Pluronic F-127, polyethylene glycol (PEG400), L-lysine, dimethoxytetraethylene glycol (DMOTEG), and cetyltrimethylammonium bromide (CTAB). Scheme 1 shows the schematic diagram of 3DOM materials prepared by CCT method.

Colloidal microspheres used as templates should be chemically stable and easily wetted by the precursor solution. Usually, polystyrene (PS), polymethyl methacrylate (PMMA) and SiO_2 colloidal microspheres are selected to fabricate the CCT by self-assembly [21]. The pore size of the 3DOM material can be controlled by adjusting the average particle sizes of the colloidal microspheres. The polymer microspheres can be prepared by soap-free emulsion polymerization method [22,23], and the SiO_2 microspheres can be synthesized by Stöber method [24,25]. Although the SiO_2 CCT is high-temperature resistance, it can only be removed by the highly corrosive hydrofluoric acid solution, which limits its application. By contrast, the polymer CCT can be easily removed by calcination, making the polymer microspheres more commonly used in fabricating CCT [26,27].

The self-assembly process of the CCT is a critical step in the preparation of 3DOM materials because the order of CCT directly affects the final 3DOM structures. Several methods of assembling monodisperse colloidal microspheres into three-dimensionally ordered CCT have emerged, such as centrifugation, gravity deposition [28,29], accelerated deposition [30], vertical deposition, electrophoretic deposition [31], and self-assembly under confinement [32,33]. Among them, centrifugation is considered as the priority option to assemble CCT, because it is a fast, low-cost and facile method. Moreover, the obtained CCT is highly-ordered.

After the assembly of the colloidal template, choosing reasonable precursors is another critical step of the preparation of 3DOM materials [34]. Specifically, for the preparation of 3DOM perovskite materials, more than one metal cations will be used.

Scheme 1. The preparation process of 3DOM materials by colloidal crystal template method.

Consequently, the composition and physicochemical properties of precursor solutions, such as pH and viscosity, are more important. The precursor should be able to (1) fill the voids between the microspheres sufficiently, (2) convert into the desired materials through appropriate reaction, (3) should not interfere with the skeleton structure during the CCT removal process and (4) solidify before the glass transition temperature (T_g) of the polymer sphere template [35]. Various materials can be used as precursors, including metal alkoxides, inorganic salts, dispersed nano-microcrystalline particles, and other organic compounds.

A typical synthesis process of 3DOM perovskite materials is illustrated by the fabrication of 3DOM LaMnO_3 [36–38]. Firstly, the uniform ordered PMMA CCT was prepared by the centrifugation. From the scanning electron microscope (SEM) image of PMMA CCT as described in Fig. 1(a), the average diameter of the PMMA microspheres was about 218 nm. Then, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$ were dissolved in methanol with L-tryptophan acting as the chelating agent to the obtained precursor solution. After impregnation, filtration and drying, the sample was first heated under a nitrogen atmosphere to solidify the 3DOM structure by carbonization and then calcined in air to form LaMnO_3 and remove the CCT. As shown in Fig. 1(b), the 3DOM LaMnO_3 sample with an average pore diameter of about 160 nm was obtained, which showed shrinkage of ~27% compared with the PMMA microspheres. If the PEG400 was added in the precursor solution as the surfactant, the 3DOM LaMnO_3 obtained (Fig. 1(c)–(d)) can be found with 3DOM structures which are well maintained and the diameters of the mesopores were about 3–16 nm. The result showed that the addition of surfactants played an important role in the formation of mesopores on the 3DOM skeleton.

3. Environmental applications of 3DOM perovskite materials

Fig. 1. (a) SEM image of CCT fabricated by PMMA microspheres with an average diameter of ca. 218 nm. Reprinted from [36]. Copyright (2016) American Chemical Society. (b) SEM image of 3DOM LaMnO_3 . Reprinted from [37] with permission from Elsevier. (c–d) TEM images of 3DOM LaMnO_3 with mesopores. Reprinted from [38] with permission from Elsevier.

3.1. Photocatalysis

As a kind of photonic crystals, the three-dimensionally ordered spatial lattice structures of 3DOM materials denote obvious photonic band gap effect [39] and the slow photon effect [40,41]. The incident light with certain wavelengths will be hindered from propagating through the 3DOM materials along a specific crystal direction results in the stop-band reflection, also called photonic band gap [42]. If the photons propagate at the lower (blue edge), or higher (red edge) wavelength edge of the photonic band gap, their group velocity decreases. This phenomenon is called the slow photon effect and is the result of increased interaction between photons and the 3DOM material [43]. When the blue or red edge overlap with the absorption band of these 3DOM semiconductors, the slow photon effect occurs, causing the light utilization efficiency of photocatalyst increases greatly [44,45]. Perovskite materials have shown great potential as efficient photocatalysts due to the unique crystal structures and electronic properties [15]. The band gap and the band edge potential are tunable to utilize visible light and satisfy specific photocatalytic reactions. Moreover, the lattice distortion in perovskite can be used to depress the recombination of photogenerated charge carriers.

Sun et al. [46] synthesized a typical double perovskite 3DOM Bi_2WO_6 with SiO_2 CCT and its catalytic activity was evaluated by the decomposition of phenol and aqueous ammonia under a 500 W Xe lamp. The total organic carbon (TOC) analysis of the phenol solution showed that only 15% of phenol remained after 60 min irradiation and the Nessler's reagent colorimetric method indicated that 87% of the ammonia was degraded in 120 min. The 3DOM Bi_2WO_6 exhibited much higher photocatalytic activity than that of the Bi_2WO_6 samples prepared by the hydrothermal and the solid-state method. This was attributed to the slow photon effect of 3DOM structure, which can increase the light-harvesting efficiency. Additionally, the highly ordered structure can facilitate the migration of the contaminants.

Ha et al. [47] employed double perovskite 3DOM $\text{LaSrCoFeO}_{6-\delta}$ as the photocatalyst for the reduction of CO_2 to CH_4 in the presence of H_2O vapor by the thermal and photo-thermal reaction. Due to the composition of double perovskite, the material was self-doped, the heterostructures and the oxygen vacancies were self-formed. Consequently, the absorbance ranges of these double perovskite materials were broadened to the visible light region and the recombination of photogenerated electrons and hole pairs were suppressed. Under 350 °C and visible light irradiation, the yield of CH_4 from CO_2 and H_2O reached 557.88 $\mu\text{mol} \cdot \text{g}^{-1}$ over 3DOM $\text{LaSrCoFeO}_{6-\delta}$ in 8 h, which was 60% higher than that of the catalyst without 3DOM morphology, and performed 5 times better than under thermal-only conditions. The solar-to-methane (STM) energy conversion efficiency was 1.933% for 3DOM $\text{LaSrCoFeO}_{6-\delta}$ in the photothermal mode. The selectivity and durability of the 3DOM $\text{LaSrCoFeO}_{6-\delta}$ were good as well, showing that double perovskites with 3DOM morphology are promising catalysts for the photothermal reduction of CO_2 to hydrocarbon fuels.

Although the slow photon effect is regarded as the key fac-

tor of the improved light harvesting efficiency of these 3DOM photocatalysts, the direct experimental evidence should be provided through controlled experiments by tuning the stop-band of the 3DOM materials [48] or irradiation by monochromatic light [49]. Recently, our group fabricated a series of 3DOM-SrTiO₃ materials with different pore sizes for the generation of H₂ by water splitting [50] and demonstrated the slow photon effect of 3DOM photocatalyst in powder suspension photocatalytic water splitting system. As described in Fig. 2(a), the as-synthesized 3DOM-SrTiO₃ catalysts exhibited notably enhanced H₂ evolution rate compared with SS-SrTiO₃ (SrTiO₃ prepared by solid state method) and Disorder-SrTiO₃ (SrTiO₃ with disordered macropores), indicating the promoting effect of 3DOM morphology. In order to further investigate the slow photon effect of 3DOM-SrTiO₃, the monochromatic experiments were carried out as depicted in Fig. 2(b). With the short-wavelength pass filters, the samples represented different activities under the irradiation of light with different wavelengths. When the wavelength of incident light was overlapped with the edges of stop-band of 3DOM materials, the light harvesting efficiency and photocatalytic performance would increase significantly. The results of monochromatic experiments provided the direct experimental evidence of the slow photon effect of 3DOM-SrTiO₃.

Based on pristine 3DOM-SrTiO₃, the ternary composite photocatalysts, including CdS/Au/3DOM-SrTiO₃ [51], 3DOM-SrTiO₃/Ag/Ag₃PO₄ [52], and Pt/CdS/3DOM-SrTiO₃ [53] were fabricated by our group. Notably enhanced photocatalytic performance was obtained under visible or UV-Vis light irradiation for the photodegradation of organic contaminants and

water splitting for H₂ evolution. The reduced rates of electron-hole pairs recombination, increased surface plasmon resonance (SPR) effect of noble metal nanoparticles and enhanced light harvesting efficiency by slow photon effect present in the system are all attributed to the increased photocatalytic activity. For example, the ternary CdS/Au/3DOM-SrTiO₃ composite photocatalysts exhibited excellent efficiency of H₂ evolution (up to 5.46 mmol/(g·h)) from water splitting under visible light irradiation, as depicted in Fig. 2(c). The mechanism of these systems with remarkable apparent quantum efficiency (42.2% at 420 nm) is illustrated in Fig. 2(d). Additionally, the 3DOM structure and the crystallinity of the photocatalyst were well maintained under continuous stirring and after successive recycles, suggesting the sufficient durability of these ternary composite materials under photocatalytic conditions.

To summarize, the results above demonstrated that 3DOM perovskite materials have broad prospects in photocatalysis. However, until now, only a limited number of 3DOM perovskite materials were synthesized and applied in the photocatalysis field. Considering of the tremendous application potential of perovskite materials in the photocatalysis and photovoltaic fields, the fabrication of new kinds of 3DOM perovskite photocatalysts are highly desirable. In spite of this, additional research into the promoting mechanism of slow photon effect, as well as the influence of surface microstructure and surface property of 3DOM perovskites are still required.

3.2. Soot combustion

As a form of solid contaminants, soot particles emitted from

Fig. 2. (a) The efficiencies of H₂ evolution over 3DOM-SrTiO₃, Disorder-SrTiO₃, and SS-SrTiO₃. (b) H₂ evolution rate of 3DOM-SrTiO₃ with different pore diameters under certain wavelength light irradiation. Reprinted from [50] with permission from Elsevier. (c) The mechanism of CdS/Au/3DOM-SrTiO₃ catalyst under visible light irradiation. (d) The efficiencies of H₂ evolution over Pt-decorated CdS/Au/3DOM-SrTiO₃ and sole CdS/Au/3DOM-SrTiO₃. Reprinted from [51] with permission from Elsevier.

diesel engines, act as the main source of PM_{2.5} and PM₁₀ (particulate matter with diameter ≤ 2.5 or ≤ 10 μm) in urban ambient conditions [54], and have caused a series of environmental and health problems [55,56]. To solve the problem, catalytic combustion is an effective and economical method. The mechanism of soot oxidation is proposed by Liu et al [57]. Oxygen is adsorbed by the catalyst to generate O_2^- or O^- species, then reacts with soot to produce carbon oxides. The oxygen species can also react with NO in reactant gas to form nitrates or NO_2 . In the next step, nitrates are decomposed to N_2 or N_2O , and NO_2 reacts with soot particles which are not adjacent to the catalyst to form NO and N_2 according to Eq. (1) and Eq. (2).

Perovskite materials were considered as promising catalysts candidates for soot oxidation. This is because of their good redox property, high oxygen mobility and thermostability [58,59]. Moreover, in this specific form of heterogeneous catalysis, contact between the catalyst and the soot particles is a key factor. The diameter of soot particles ranges between 10 and 50 nm [60], which is larger than the pore size of mesoporous materials. It leads to the difficulties due to lack of contact between soot particles and active sites on the internal surface of catalysts. Using 3DOM materials which have macroporous structure (> 50 nm) can effectively increase the mass transfer efficiency and the number of available active sites [61–63]. Combining the benefits of the 3DOM structure and excellent reactive properties of perovskite materials could lead to promising catalytic performance. Table 1 lists the 3DOM perovskite catalysts applied in the soot combustion reaction, in which $T_{50\%}$ mean the temperatures at 50% of soot conversion. Elements La, Ce, Fe, Co and Mn used most frequently in the catalysts and all the catalysts were tested under loose contact conditions.

Sadakane et al. [26,64] studied the effect of 3DOM perovskite catalysts in the combustion of nanosized carbon (< 10

nm), which was considered a suitable model of soot. The T_{20} of 3DOM LaFeO_3 catalyst was 55 $^\circ\text{C}$ lower than that of non-porous LaFeO_3 and the catalytic combustion activity of 3DOM LaFeO_3 was enhanced through addition of more $\text{K}_2\text{S}_2\text{O}_8$, a polymerization initiator. It can be inferred that the residual K impurities may partly substitute A-site cations due to the increase of initiator, which decreased of the average pore diameter of 3DOM skeletons from 321 to 127 nm [78]. However, the carbon particles were still smaller than the macropores of the catalyst and the shrinkage of the pore size did not affect the combustion activity. Although carbon particles are different from soot particles, their research cast light on the study of soot oxidation.

Zhao's group carried out a series of experiments on the application of 3DOM perovskite materials in soot combustion. Starting with 3DOM LaFeO_3 [65], they found that compared with nanosized LaFeO_3 , 3DOM LaFeO_3 exhibited notably enhanced catalytic performance for soot combustion, which was attributed to the improved mass transfer of soot particles. Then, they attempted to dope the B-site of 3DOM LaFeO_3 material with Co [66] and found that with the increase of doping level of Co in 3DOM LaFeO_3 (from 0% to 50%), the activity of the as-prepared catalysts was enhanced. Moreover, the catalytic activity of the 3DOM catalyst can be further improved through grinding to decrease the particle sizes to 5–20 μm . This indicated the crucial role of mass transfer of soot particles in the reaction. Similarly, the B-site doping of 3DOM LaMnO_3 materials with Fe [69] as accomplished and the subsequent materials were used in soot combustion. The influence of macropores, with diameters 140–600 nm, on catalytic performance was studied and it was found that the 3DOM $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ catalysts with pore diameters above 400 nm possessed the highest catalytic activities for soot combustion.

Besides the doping in B-site of 3DOM perovskite materials, A-site doping is also an important method to tailor their catalytic performance. Zhao and coworkers [68] synthesized a

Table 1
Summary of 3DOM perovskite catalysts for soot combustion.

Catalyst	Soot/catalyst weight (mg/mg)	Reactant feed	Heat rate ($^\circ\text{C}/\text{min}$)	$T_{50\%}$ ($^\circ\text{C}$)	Ref.
3DOM LaFeO_3	0.909/9.09	Air, 30 mL/min	10	518	[26]
3DOM LaFeO_3	0.909/9.09	Air, 50 mL/min	—	195 ^a	[64]
3DOM LaFeO_3	10/100	0.2% NO, 5% O_2 , He balance, 50 mL/min	2	412	[65]
3DOM $\text{LaCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$	10/100	0.2% NO, 5% O_2 , Ar balance, 50 mL/min	2	397	[66]
0.04wt% Au/3DOM LaFeO_3 (3.0 nm)	10/100	0.2% NO, 5% O_2 , Ar balance, 50 mL/min	2	368 ^b	[67]
3DOM $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$	10/100	0.2% NO, 5% O_2 , Ar balance, 50 mL/min	2	378	[68]
3DOM $\text{LaMn}_{0.95}\text{Fe}_{0.05}\text{O}_3$	10/100	0.2% NO, 5% O_2 , Ar balance, 50 mL/min	2	392 ^b	[69]
1.25wt% Au/3DOM LaFeO_3	10/100	0.2% NO, 5% O_2 , Ar balance, 50 mL/min	2	387	[70]
3DOM $\text{LaCo}_3/\gamma\text{-Al}_2\text{O}_3/\text{cordierite}$	200/3000	0.2% NO, 5% O_2 , Ar balance, 50 mL/min	2	348.4	[71]
3DOM $\text{La}_{0.7}\text{Ce}_{0.3}\text{Fe}_{0.4}\text{Co}_{0.6}\text{O}_3$	20/180	0.05% NO, 5% O_2 , N_2 balance, 100 mL/min	2	410	[72]
KNO_3 /3DOM $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.6}\text{Fe}_{0.4}\text{O}_3$	20/180	20% O_2 , N_2 balance, 50 mL/min	2	379	[73]
Si doped 3DOM $\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$	20/180	0.05% NO, 5% O_2 , N_2 balance, 50 mL/min	2	396	[74]
K–Mn/3DOM $\text{La}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$	20/180	0.05% NO, 5% O_2 , N_2 balance	2	377	[75]
3DOM $\text{La}_{0.8}\text{Ce}_{0.2}\text{CrO}_3$	20/180	0.05% NO, 5% O_2 , N_2 balance, 50 mL/min	2	425	[76]
3DOM $\text{Sr}_{0.8}\text{K}_{0.2}\text{TiO}_3$	5/45	0.05% NO, 20% O_2 , N_2 balance, 100 mL/min	5	367	[77]

^a This datum is T_{20} , which means 20 wt% of the carbon particles are oxidized.

^b The data are T_m , which mean the temperatures by which the combustion rate of soot is maximum during the temperature-programmed oxidation procedure.

K-substituted catalysts, 3DOM $\text{La}_{1-x}\text{K}_x\text{CoO}_3$ ($x = 0-0.3$). Compared with non-doped 3DOM LaCoO_3 , the K-substituted catalyst exhibited better redox property and higher activity in soot combustion, comparable to a Pt catalyst. Usually, the B-site cations in perovskite-type oxide catalyst acted as the active center in soot combustion. Partial replacement of La^{3+} at A-site by K^+ ions with KNO_3 can increase the oxidation state of B-site cations or form the oxygen vacancies necessary to keep the electron neutrality of this material. As the consequence, the oxidizability of B-site cations was obviously increased and the mobility of lattice oxygen was accelerated. Besides, the substitution enriched the alkali metal cations on the surface of the catalyst and therefore created basic sites, which can adsorb nitrogen oxides and produce active surface oxygen species for soot combustion [79,80]. The addition of KNO_3 may facilitate the contact between soot and catalyst. By the reaction $2\text{KNO}_3 + \text{C} \rightarrow 2\text{KNO}_2 + \text{CO}_2$, KNO_3 also acted as the catalyst [81]. Moreover, K may modify the crystallographic orientation of the catalyst and promote the exposure of active facets [82]. All of these effects are all benefits to soot combustion. Similar results were reported also by Guan and coworkers in K doped 3DOM LaCoO_3 [74] and 3DOM SrTiO_3 [77] materials. They also studied the catalytic performance in soot combustion using A-site substituted Ce^{3+} 3DOM perovskite materials, including $\text{La}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ [75], $\text{La}_{1-x}\text{Ce}_x\text{CrO}_3$ [76], and the co-doping 3DOM perovskite materials in A-site and B-site, such as $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ [72] and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ [73]. In these reports, the partial substitution of La^{3+} by Ce^{3+} can hinder the increase of crystal size and prevent the 3DOM structure from being destroyed. In addition, as an appropriate oxygen storage carrier, Ce^{3+} improved the oxygen species concentration.

Recently, 3DOM LaCoO_3 was coated on monolith cordierite substrate using a dip-coating method by employing $\gamma\text{-Al}_2\text{O}_3$ as the washcoat [71]. The catalyst maintained both the 3DOM structure of the coating layer and the mechanical properties of the ceramic substrate. Coating the porous hollow $\gamma\text{-Al}_2\text{O}_3$ nanoparticles further increased the surface area of the catalyst, which resulted in an improved activity of the 3DOM $\text{LaCoO}_3/\gamma\text{-Al}_2\text{O}_3/\text{cordierite}$ catalyst for soot combustion. Furthermore, the durability of the composite material was also enhanced due to the thermal stability of $\gamma\text{-Al}_2\text{O}_3$. This work offered a new route for more efficient utilization of the 3DOM materials.

Although the non-noble metal catalysts were widely researched and promising catalytic performance was obtained for diesel soot combustion, it is still a huge challenge to get an ignition temperature (T_{ig}) less than 250 °C. Therefore, modification of noble metal nanoparticles, such as Au, on the inner surface of 3DOM perovskite materials was carried out to further decrease the T_{ig} . Zhao and coworkers [67] used a hydrogen gas-bubbling-assisted membrane reduction method to prepare the 3DOM Au/LaFeO_3 catalysts, as described in Fig. 3. Compared with 3DOM LaFeO_3 , the 0.04wt% $\text{Au}/3\text{DOM LaFeO}_3$ catalysts exhibited decreased T_{ig} (decrease from 347 to 228 °C). The role of Au nanoparticles in this situation was considered to be the adsorption and activation of oxygen. In another article published by Zhao's group [70], the enhanced activity of

$\text{Au}/3\text{DOM LaFeO}_3$ was further discussed. The active oxygen species of the catalysts can be derived from two approaches. One is direct activation of oxygen on the surface of Au nanoparticles, and the other is originated from the synergetic effect of $\text{Au}-3\text{DOM LaFeO}_3$ during which the induced support may serve as the reservoir for oxygen [83]. As the consequence, the oxidation was accelerated and a better performance was obtained. In addition, the increasing Au particle size would lead to a decrease of d-electron density, which was unfavorable for the adsorption and activation of oxygen. It indicated that the Au particle size was an important factor in the reaction.

3.3. VOCs oxidation

Mainly coming from industrial emission and traffic exhaust, VOCs, such as toluene and 1,2-dichloroethane, not only cause environmental pollution but also threaten human health [84,85]. Similar to soot combustion, perovskite materials exhibit a huge potential in the catalytic elimination of VOCs, due to their low oxidation temperature, high oxygen mobility, low cost and excellent thermal stability [13,86,87]. It has been reported that the dissociation of the weakest C–H bond is the rate-determining step in the oxidation of VOCs [88–90]. By doping other elements or changing the oxidation state of B-site cation, the surface oxygen vacancy is formed and the redox property of the catalyst is altered. As the result, the bond dissociation energy is decreased and the reaction is accelerated. Because of the interconnected pore architecture of 3DOM catalysts, high mass transfer performances were shown in recent research [91–93]. Furthermore, taking into account of the smaller molecular size of VOCs, surfactants are usually used as the mesoporous porogens merged with CCT to fabricate the 3DOM materials with mesoporous skeletons. Table 2 illustrates the catalytic performance of 3DOM perovskite catalysts and their experimental conditions for toluene oxidation, in which $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ represent the temperatures corresponding to toluene conversions of 10%, 50%, and 90%, respectively. In addition, the activation energies (E_a), specific reaction rates and turnover frequency (TOF) values of these reaction systems are also involved in Table 2.

It can be seen from Table 2 that the catalytic activities of the 3DOM perovskite materials are in the order of cobaltates > manganates > ferrites in toluene oxidation, which are con-

Fig. 3. (a) Preparation of Au nanoparticles on 3DOM LaFeO_3 carrier by gas-bubbling-assisted membrane reduction method. (b) The HRTEM image of 3DOM 0.04wt% Au/LaFeO_3 sample. The inset images are the enlarged Au particle whose lattice fringes correspond to the fcc (111) plane at 2.3 Å in the fast Fourier transform (FFT) image. Reprinted from [67] with permission from Wiley-VCH.

Table 2

Summary of 3DOM perovskite catalysts for toluene oxidation.

Catalyst	Weight (g)	Reactant feed	Space velocity (mL/(g·h))	Toluene conversion capacity			Specific reaction rate (μmol/(g _{cat} ·s))	TOF _{Au} (s ⁻¹)	E _a (kJ/mol)	Ref.
				T _{10%} (°C)	T _{50%} (°C)	T _{90%} (°C)				
3DOM LaMnO ₃	0.1–0.2	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	169	222	243	—	—	58	[38,94]
3DOM SrFeO _{3-δ}	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	—	292	340	—	—	—	[95,96]
3DOM La _{0.6} Sr _{0.4} FeO _{3-δ}	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	54	225	280	—	—	—	[97]
3wt%Co ₃ O ₄ /3DOM Eu _{0.6} Sr _{0.4} FeO ₃	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	213	251	269	—	—	75.2	[98]
3DOM La _{0.6} Sr _{0.4} Fe _{0.8} Bi _{0.2} O _{3-δ}	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	147	220	242	—	—	45.9	[99]
3DOM Eu _{0.6} Sr _{0.4} FeO ₃	0.05	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	233	278	305	0.0301 (240 °C)	—	81.1	[100]
3wt%CoO _x /3DOM Eu _{0.6} Sr _{0.4} FeO ₃	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	220	251	270	0.0473 (240 °C)	—	72.3	[101]
8wt%Co ₃ O ₄ /3DOM La _{0.6} Sr _{0.4} CoO ₃	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	158	210	227	—	—	43.3	[102]
4.9wt%Au/chain-like LaMnO ₃	0.05	0.1% toluene, 40% O ₂ , N ₂ balance, 16.7 mL/min	20000	138	201	226	—	2.80 × 10 ⁻³ (200 °C)	47	[103]
12wt%MnO _x /3DOM LaMnO ₃	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	152	193	215	0.0290 (160 °C)	—	61	[37]
7.63wt%Au/3DOM LaCoO ₃	0.1	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	136	188	202	—	1.04 × 10 ⁻³ (200 °C)	31.4	[104]
3DOM EuFeO ₃	0.1–0.2	0.1% toluene, 40% O ₂ , N ₂ balance, 33.3 mL/min	20000	254	312	347	—	—	82.0	[105]
5.92wt%Au/8wt%MnO _x /3DOM La _{0.6} Sr _{0.4} MnO ₃	0.05	0.1% toluene, 40% O ₂ , N ₂ balance, 16.7 mL/min	20000	160	205	220	—	—	52.8	[106]
1.67wt%Mn ₃ O ₄ -2wt%Au/3DOM La _{0.6} Sr _{0.4} CoO ₃	0.05	0.1% toluene, 40% O ₂ , N ₂ balance, 16.7 mL/min	20000	164	214	230	0.410 (230 °C)	3.90 × 10 ⁻³ (230 °C)	41.7	[107]
MnO ₂ /LaMnO ₃	0.05	0.2% toluene, 20% O ₂ , N ₂ balance, 100 mL/min	120000	—	263	279	—	—	57	[108]

sistent with the performances of bulk catalysts in the oxidation of NO and soot particulates [109–111]. However, the stabilities of the three salts under high temperature were in the opposite order [112]. Consequently, the manganates were widely researched in VOCs oxidation due to their moderate catalytic activity and stability.

Dai et al. [38,94] did lots of valuable works on this topic together with his research partners. In 2011, they synthesized 3DOM LaMnO₃ using PMMA CCT with the assistance of surfactants, such as PEG 400, P123 and L-lysine. The introduction of surfactants was favorable for the formation of mesoporous skeletons increased the surface area of 3DOM LaMnO₃. These mesoporous 3DOM materials achieved notably enhanced catalytic activity for the combustion of toluene. It can also be found from these papers that the catalyst with the larger BET surface area exhibited the higher catalytic activity for toluene combustion, indicating that the active sites were mainly located at the inner surface of 3DOM LaMnO₃ materials.

The oxidation of toluene usually occurs on the surface transition metal ion-sites (e.g. Mn cations) [113]. Therefore, the introduction of highly active manganese oxides promoted the exposure of Mn active sites and further improved the catalytic

activity for toluene oxidation. For instance, 3DOM LaMnO₃ supported MnO_x [37] was prepared via the *in situ* tryptophan-assisted PMMA-templating route which uniformly dispersed MnO_x nanoparticles on the surface of 3DOM LaMnO₃. For both toluene and methanol combustion reaction, the 12 wt% MnO_x/3DOM LaMnO₃ exhibited enhanced catalytic performance compared with 3DOM LaMnO₃ and 12 wt% MnO_x/bulk LaMnO₃. These results can be attributed to the strong interaction between MnO_x and 3DOM LaMnO₃, as well as the increased adsorbed oxygen concentration and low-temperature reducibility. The similar MnO₂/LaMnO₃ catalysts were also prepared by Si et al. [108] through a facile one-step method, in which 3DOM LaMnO₃ was immersed in diluted HNO₃ solution and the La cations were partially removed from perovskite structure, as shown in Fig. 4. After treatment with acid, the well-ordered structure of 3DOM LaMnO₃ became disordered, but multiple nanopores appeared and the surface area increased. The obtained catalyst exhibited improved activity compared with 3DOM LaMnO₃ for toluene combustion. This result indicates that the surface area and surface chemical properties of 3DOM perovskite catalysts are the crucial factors for toluene oxidation rather than the degree of

Fig. 4. (a) The synthesis of the $\text{MnO}_2/\text{LaMnO}_3$. The green structure is LaMnO_3 , and the yellow structure is MnO_2 . TEM images of 3DOM LaMnO_3 (b) and $\text{MnO}_2/\text{LaMnO}_3$ (c). Reprinted from [108]. Copyright (2016) American Chemical Society.

structural order of 3DOM skeletons.

Another example to support this viewpoint is the disassembled 3DOM LaMnO_3 as support for Au nanoparticles reported by Liu et al. [103]. Through a controlled calcination program, the 3DOM LaMnO_3 can be well dissociated into two-dimensionally chain-like building blocks as described in Fig. 5. Although the three-dimensionally ordered materials were reduced to the two-dimensionally ordered materials, the surface area of these chain-like materials might be slightly increased. After deposition of Au nanoparticles, the obtained 4.9 wt% Au/LaMnO_3 exhibited a high catalytic activity for the oxidation of CO and toluene. The higher surface area, better low-temperature reducibility and the strong metal-support interaction are attributed the enhanced catalytic performance.

Although ferrite perovskites have a slightly lower catalytic activity in toluene, 3DOM ferrite perovskites are still considered as the potential catalysts for practical application due to their good anti-poisoning capacity [114]. In the research on ferrite perovskites, the A-site cations can be either Sr [95,96], Eu [105], or a co-doping of La & Sr [97] or Eu & Sr [100]. The B-site cation Fe can also be partly substituted by Bi to produce catalyst 3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Bi}_{0.2}\text{O}_{3-\delta}$ [99]. To improve the activity of the catalyst, the CoO_x was used as co-catalyst and dispersed on the walls of 3DOM $\text{Eu}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ [98,101]. The ap-

propriate amounts of CoO_x brought higher surface oxygen vacancy density, which absorbed and activated oxygen. As the result, the catalytic performance was benefited. For example, the specific reaction rate for toluene oxidation at 240 °C increased from 0.0301 to 0.0473 $\mu\text{mol}/(\text{g}_{\text{cat}}\cdot\text{s})$ after decoration of 3 wt% of CoO_x on the surface of 3DOM $\text{Eu}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$.

Similar to Mn and Fe, the valence state variation of Co makes cobaltate perovskites suitable for catalytic oxidation of toluene. Dai and coworkers [102] investigated the catalytic performance of $\text{Co}_3\text{O}_4/3\text{DOM La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, $\text{Au}/3\text{DOM LaCoO}_3$ [104] and $\text{Mn}_3\text{O}_4\text{-Au}/3\text{DOM La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ [107] for toluene combustion. Using a co-catalyst of metal oxide or noble metal, the cobaltate perovskite catalysts exhibited high catalytic performances. The $T_{90\%}$ (202 °C) and the E_a (31.4 kJ/mol) for toluene oxidation were significantly lower than that of 3DOM manganate and ferrite perovskites catalysts [104].

In addition to the oxidation of toluene, 3DOM perovskites can also be applied in the catalytic elimination of other VOCs, such as 1,2-dichloroethane. Catalyzed by $\text{Co}_3\text{O}_4/3\text{DOM La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3$ with mesopores [115], the dehydrochlorination and chlorination were enhanced due to the intimate contact between the reactant molecules and the chemisorbed oxygen species on the surface. With the better transportation and diffusion properties, 10 wt% $\text{Co}_3\text{O}_4/3\text{DOM La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3$ with mesopores presented the lowest E_a (22.6 kJ/mol) and highest reaction rate ($2.29 \times 10^{-11} \text{ mol}/(\text{g}\cdot\text{s})$) for 1,2-dichloroethane oxidation. The high chlorine poisoning tolerance and selectivity were shown to be advantages of the catalyst. Although only a limited number of VOCs are selected as target contaminants in this research field, the 3DOM perovskite materials with mesopores have demonstrated their huge potential in the catalytic elimination of VOCs.

In this part, various 3DOM perovskite materials were employed in the oxidation of VOCs and good catalytic performances were achieved. The introduction of transition metal oxides on 3DOM perovskite materials can additionally increase the active sites. With high dispersion of noble metal Au on perovskite surface, the hydrocarbon is activated more easily and lower E_a can be attained. Especially, the disassembled materials

Fig. 5. (a) Schematic diagram of the preparation process of the chain-like LaMnO_3 and $x\text{Au}/\text{LaMnO}_3$ samples; TEM images of chain-like ordered macroporous LaMnO_3 (b) and 4.9 wt% $\text{Au}/\text{chain-like ordered macroporous LaMnO}_3$ (c). Reprinted from [103] with permission from Elsevier.

behaved good activities in the catalytic elimination of VOCs, suggesting that the surface area and surface chemical constitution of 3DOM perovskite catalysts are the crucial factors for VOCs oxidation.

3.4. Methane combustion

Apart from CO₂, unburned CH₄, the major component of natural gas, is regarded as a highly problematic greenhouse gas [116–118]. Complete combustion of CH₄ promoted by catalysts under a relatively low temperature could solve two problems at once by reducing emissions and making full use of energy from natural gas [119]. According to the Mars and van Krevelen mechanism (MvK mechanism) [120], the reaction pathway of methane combustion over perovskite catalysts is divided into three steps [121]: (1) gas phase CH₄ adsorbs on the A-site of perovskite oxides; (2) adsorbed CH₄ is attacked by surface lattice oxygen to form CH₃, then continuously oxidized to form adsorbed CO₂ and H₂O, accompanied by the generation of oxygen vacancies; (3) adsorbed CO₂ and H₂O desorb from the surface of catalysts to produce molecule CO₂ and H₂O, and the oxygen vacancies are refilled with surface adsorbed oxygen. The cleavage of the first C–H bond is considered as the rate-determining step for the catalytic combustion of methane [122]. The excellent ion mobility, redox property and thermal stability also make perovskite a good candidate for suitable catalysts [123]. The reactivity of lattice oxygen of perovskite oxides plays a crucial factor in methane combustion. In particular, partly substituting B-site cations with other elements can modify the redox properties to specifically enhance their catalytic activity [124]. As one kind of hierarchical porous structure, 3DOM structure can reduce the flow resistance and promote the contact between catalyst and reaction gases in the methane combustion [125,126]. The appropriate pore diameters, large surface area, abundant active sites and good mass

transfer property of 3DOM structure are also favorable for the reaction [127,128]. Considering this, 3DOM perovskite materials are promising catalysts or catalyst supports in the methane combustion. The 3DOM perovskite catalysts used for methane combustion are listed in Table 3. The temperatures of $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ for methane conversion, specific reaction rates, TOF values, and E_a of these catalytic systems are also involved in Table 3.

Yuan et al. [129] reported that 3DOM La₂CuO₄, which belongs to the perovskite-like structure, was successfully synthesized in the presence of citric acid. It demonstrated the importance of incorporating an appropriate amount of citric acid in the preparation of 3DOM materials. The 3DOM La₂CuO₄ sample showed better low-temperature reducibility than the wormhole-like macroporous structured La₂CuO₄, which may be the reason for its higher catalytic activity in methane combustion.

It has been reported that the combustion of methane involves in the activation of C–H bonds by active oxygen species [130,131]. Therefore the defect structure, pore structure, and surface area of a catalyst were regarded as important factors for the development of an efficient catalyst [129]. Arandiyan et al. [132] fabricated high-quality 3DOM La_{0.6}Sr_{0.4}MnO₃ using nanovoids with appropriate amounts of DMOTEG and Pluronic P-123 assisted PMMA-templating route. In the reaction, $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ of 3DOM La_{0.6}Sr_{0.4}MnO₃ were lower by 125, 106 and 88 °C than those of bulk La_{0.6}Sr_{0.4}MnO₃. The higher adsorbed oxygen species concentration, resulting from the higher concentration of surface oxygen vacancies, acted as a crucial component in the promoting of catalytic activity. In addition, the thermal stability of 3DOM La_{0.6}Sr_{0.4}MnO₃ was very good, with the 3DOM structure maintaining perfectly after being aged at 800 °C. The 3DOM La_{1-x}Ce_xCoO₃ with nanovoids were also synthesized through the similar method using CTAB and Pluronic P-123 as the surfactant [133].

Table 3
Summary of 3DOM perovskite catalysts for methane combustion.

Catalyst	Weight (g)	Reactant feed	Space velocity (mL/(g·h))	Methane conversion capacity			Specific reaction rate (μmol/(g _{cat} ·s))	TOF _{Noble Metal} (s ⁻¹)	E_a (kJ/mol)	Ref.
				$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)				
3DOM La ₂ CuO ₄	0.05	2% CH ₄ , 20% O ₂ , N ₂ balance, 41.6 mL/min	50000	—	560	672	ca. 11.1 (672 °C)	—	—	[129]
1.18wt%Pd/3DOM La _{0.6} Sr _{0.4} MnO ₃	0.05	0.5% CH ₄ , 20% O ₂ , N ₂ balance, 33.3 mL/min	40000	405	489	583	0.09 (350 °C)	—	—	[134]
3DOM La _{0.6} Sr _{0.4} MnO ₃	0.02	2% CH ₄ , 20% O ₂ , N ₂ balance, 41.6 mL/min	30000	437	566	661	0.0143 (300 °C)	—	56.6	[132]
3.63wt%Ag/3DOM La _{0.6} Sr _{0.4} MnO ₃	0.02	2% CH ₄ , 20% O ₂ , N ₂ balance, 41.6 mL/min	30000	361	454	524	0.000351 (300 °C)	1.86 × 10 ⁻⁵ (300 °C)	37.5	[135,136]
3DOM LaMn _{0.97} Pd _{0.03} O ₃	0.05	1% CH ₄ , 17% O ₂ , He balance, 30 mL/min	32000	325	412	504	0.0252 ^a	—	51.5	[137]
3DOM-m La _{0.7} Ce _{0.3} CoO ₃	0.02	2% CH ₄ , 20% O ₂ , N ₂ balance, 41.6 mL/min	30000	381	479	555	—	—	53	[133]
3.0wt%Au-Pd/3DOM La _{0.6} Sr _{0.4} MnO ₃	0.02	5% CH ₄ , 30% O ₂ , N ₂ balance, 42.8 mL/min	50000	280	331	354	3.52 (270 °C)	1.60 × 10 ⁻² (270 °C)	46.3	[36]
3D-hm La _{0.6} Sr _{0.4} MnO ₃	0.05	5% CH ₄ , 30% O ₂ , N ₂ balance, 42.8 mL/min	50000	310	360	438	11.2 (350 °C)	—	67.3	[138]

^a The unit of the datum is [μmol_{CH₄}/(m²_{cat}·s)].

To further improve on the catalytic activity, different kinds of noble metal nanoparticles, such as Pd [134], Ag [135,136] and Au-Pd alloy [36], were loaded on 3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ with mesopores. After loading noble metals on 3DOM perovskites, the conversion temperature of methane and the E_a obviously decrease as shown in Table 3. Among these catalysts, the bi-metallic 3.0 wt% Au-Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ [36] performed the best, giving $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ of 280, 331, and 354 °C, respectively. The $\text{TOF}_{\text{Au-Pd}}$ ($1.60 \times 10^{-2} \text{ s}^{-1}$ at 270 °C) was higher than other catalyst as well. Importantly, according to *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra as depicted in Fig. 6(a), CH_3^- species (1300 cm^{-1}) emerged at 200 °C over Au-Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ while at 300 °C over Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. Moreover, almost all the methane (1300 and 3014 cm^{-1}) was converted to CO_2 (2330 and 2360 cm^{-1}) at 550 °C for Au-Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, indicating the enhanced low-temperature conversion ability of adding Au. In the detailed discussion of the mechanism in the reaction as described in Fig. 6(b), it was found that the presence of Au in the bimetallic catalyst modified the electronic distribution on the surface of the catalyst and changed the reaction pathway. In addition, Au weakened the bonding strength of important chemical intermediates and the Pd atoms, resulting in the intensification of the adsorbed oxygen species on the surface of the catalyst. In summary, contact between the metals and the support, as well as oxidized noble metal species on the surface were responsible for the

enhanced activity.

Changing exposed crystal facet is another effective strategy to accelerate the reaction rate. On the basis of 3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, the 3D hexapod mesostructured (3D-hm) $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ was prepared by Amal et al. [138] using ultrasonic method to cleave the weak connection points within the 3DOM framework as shown in Fig. 6(c). Both experimental results and density functional theory (DFT) calculations proved that, compared to the (110) facet of 3DOM catalyst, the newly exposed (001) facet of 3D-hm catalyst required lower energy to break the C–H bond of CH_4 . The catalytic performance was highly efficient, the specific reaction rate was $11.2 \mu\text{mol}/(\text{g}_{\text{cat}}\cdot\text{s})$ at 350 °C. It proved the feasibility of using structural disassembly method to synthesize nanostructure with specified crystal facet exposed. This method is expected to be used not only in catalytic combustion but also in other fields.

In conclusion, almost all the 3DOM perovskite materials in this part are doped or partly substituted in B-sites to attain more surface adsorbed oxygen. It has been reported that the asymmetric and unsaturated coordination environment of lattice oxygen in oxide materials can significantly enhance the reactivity of lattice oxygen in redox reactions and obtain more efficient active sites in methane combustion [139]. Moreover, the decoration of noble metals on the surface of 3DOM perovskites can accelerate the fracture of the first C–H bond in CH_4 and decrease the conversion temperature of methane and the E_a . However, the durability of 3DOM materials under practical

Fig. 6. (a) *In situ* DRIFT spectra of methane oxidation over Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (marked as Pd/3DOM LSMO) and Au-Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (marked as AuPd/3DOM LSMO). (b) Proposed steps in the oxidation of methane over Au-Pd/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. Reprinted from [36]. Copyright (2016) American Chemical Society. (c) Schematic illustration of the synthesis process of 3D-hm $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. Reprinted from [138] with permission from Nature.

application conditions is still an issue.

3.5. Carbon dioxide methanation

Apart from the applications mentioned aforesaid, 3DOM perovskite materials can be used in CO₂ methanation reaction, which is the initial step of CO₂ hydrogenation for the acquisition of value-added chemicals and is regarded as a potential strategy to solve the CO₂-relevant environmental problems [140].

Arandiyani et al. [141] fabricated Rh-Ni alloys on 3DOM LaAlO₃ with voids of c.a. 30–40 nm by *in situ* exsolution of Ni from 3DOM LaAl_{0.92}Ni_{0.08}O₃ and followed by the *in situ* growth of Rh-Ni nanoalloys on both external and internal surfaces of 3DOM perovskite. In the CO₂ methanation reaction, compared with the conventional catalyst Rh/3DOM LaNi_{0.08}Al_{0.92}O₃, the Rh-Ni/3DOM LaAlO₃ catalyst showed a 52% higher turnover frequency. The hierarchically porous structure of the 3DOM perovskite support provided a high dispersion of bimetallic Rh-Ni nanoparticles. The richness of basic sites and the surface adsorbed oxygen species are important to the adsorption of CO₂, which is the key factor in the CO₂ methanation process as well. This work provided a promising catalyst design pathway for preparing highly dispersed bimetallic catalysts on perovskites as well as a good reference for the conversion and utilization of CO₂ using 3DOM perovskite materials.

3.6. Sensors

Sensors, which can detect and monitor toxic, hazardous or combustible gases or liquids, play crucial roles in safety supervision and environmental protection. In bulk materials, sensing reaction occurs only near the surface, and the inner part is inactive. However, with the large surface area as well as the uniform and ordered macropores [142–144], the target gas or liquid can diffuse into both the surface and the inner regions of 3DOM materials, which is beneficial for its utilization as sensing materials [145]. In addition, perovskites can express high responses and are stable at high temperatures, which are suitable for gas or liquid sensors [146,147].

Qin et al. synthesized 3DOM LaFeO₃ [145] and 3DOM La_{1-x}Mg_xFeO₃ [148] and used them as the gas sensors for methanol. As a p-type semiconductor, the conductivity of the materials depended on the presence of holes. When the sensor was exposed to air, electrons from the conduction band would be trapped by O₂ adsorbed on the surface of the sample due to the strong electronegativity of oxygen and produced adsorbed oxygen. Therefore, the concentration of the holes increased and the electric resistance decreased. During oxygen absorption on the surface of the semiconductors, Eq. (3) may occur. While

reducing methanol gas was introduced, Eq (4) occurred.

After the gas sensor was exposed to a methanol gas environment, a large number of electrons were released. As the consequence, the concentration of holes in the system decreased and the electrical resistance of the sensor increased. By monitoring the electric resistance, the methanol concentration was obtained. The responses of materials to methanol were donated by R_g/R_a , where R_g and R_a represented the resistance of sensor in air and methanol, respectively. The response time represented the time that the variation in electrical resistance to reach 90% of the equilibrium value after injecting methanol, and the recovery time indicated the time that the sensor returned to 90% above the original resistance in air. With the large surface area and the uniform macropores of the 3DOM structure, more surface-active sites were exposed for both oxygen adsorption and surface reactions, resulting in enhanced gas sensing property of the materials. Moreover, in contrast with ethanol or acetone, the samples exhibited good selectivity to methanol. In 3DOM La_{1-x}Mg_xFeO₃ material, to reconstruct the charge neutrality, oxygen vacancies were formed which acted as the centers of the positive charges [149]. The electrons around oxygen vacancies can be excited to the conduction band easily. Consequently, the sensing performance of the Mg²⁺ doped sample for methanol gas was better than the pristine sample, as described in Table 4.

Apart from methanol sensing, 3DOM perovskite can also work as H₂O₂ sensor as shown with 3DOM SmCoO₃, which was fabricated by He et al. [150]. In the chronoamperometric test at 0.35 V (the oxidation peak potential measured by cyclic voltammetry), the electrode with 3DOM SmCoO₃ displayed the fastest response (4 s) to the change of H₂O₂ concentration. This mechanism can be explained by the valence state variation of Co, as shown in Fig. 7(a). In the first step, Co³⁺ was oxidized to Co⁴⁺ by releasing H⁺, which reacted with OH⁻ to form water. In the second step, Co⁴⁺ was reduced to Co³⁺ by obtaining H⁺, and OH⁻ was generated. Fig. 7(b) illustrates the overall processes, including diffusion, adsorption, electrooxidation and desorption steps. The 3DOM sample performed better for H₂O₂ electrooxidation, with higher sensitivity, higher selectivity, lower limit of detection and noise, as well as wider linear ranges. This should be ascribed to the larger surface area of the 3DOM materials, enabling faster electron transfer kinetics and diffusion rate.

4. Conclusions and perspectives

The unique structures and the versatile features of 3DOM

Table 4

The responses of 3DOM LaFeO₃ and 3DOM La_{0.95}Mg_{0.05}FeO₃ as methanol sensors.

Material	Gas concentration/ Optimal temperature	Temperature range (°C)	Response (R_g/R_a)	Response time/Recovery time (s/s)	Ref.
3DOM LaFeO ₃	0.01%/190 °C	150–300	96	25/23	[145]
3DOM La _{0.95} Mg _{0.05} FeO ₃		150–280	146.5	17.7/25.4	[148]

Fig. 7. (a) Electrooxidation mechanism of the reaction; (b) Reaction processes on the electrode. Reprinted from [150] with permission from Elsevier.

perovskites have attracted the interest of many scientists and made these materials widely applied in environmental fields. After years of exploration, many kinds of 3DOM perovskite materials were synthesized by CCT method. Under the assistance of surfactants, 3DOM perovskite materials with mesoporous skeletons can be successfully synthesized. Moreover, the disassembling of 3DOM materials can also fabricate novel nanostructures, such as chain-like and hexapod-like nanostructures. For different application fields, some common strategies of 3DOM perovskites exist, such as tailoring the cations in A/B-sites and surface modification, which has been widely employed and systematically investigated. Fortunately, ca. 90% elements in the periodic table can be involved in perovskite materials and are waiting to be tested. As the consequence, theoretical prediction by DFT and high throughput material genome were developed to guide people for designing better materials rationally. However, the research focus should be very different for various reaction systems.

In photocatalysis, the slow photon effect of 3DOM structure can improve light utilization efficiency. Thus, for promoting photocatalytic activity, the order of the 3DOM structure and the location of the slow photon regions should be the crucial factors. For soot combustion reaction, due to the large size of soot particles, contact between soot particles and active sites is the

key factor of soot combustion. Therefore, the average pore diameter of the macropores, especially the window size of the 3DOM materials plays a more important role compared to other reaction systems. For the combustion of VOCs and methane, the surface area of the 3DOM materials plays a crucial role because of the relatively smaller size of the target molecules. In this situation, 3DOM materials with mesoporous skeletons become the preferred choice.

To date however, no report suggests 3DOM perovskite materials have been used in practical applications. With complicated fabrication and unsatisfactory stability to blame. Therefore, the facile method for large-scale preparation of 3DOM materials should be further investigated. In addition, the crystal nucleation and the growth mechanism in the formation of skeletons of different 3DOM perovskite materials are still far from clear. It is important for researchers to focus on the fabrication of new kinds of 3DOM perovskites and the modification of surface structures and properties of these materials. In conclusion, there is still a long way to go in order to make 3DOM perovskite materials available for practical utilization and efforts should be made in order to create and study highly active 3DOM perovskite materials.

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Graphical Abstract

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Three-dimensionally ordered macroporous perovskite materials for environmental applications

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The applications of three-dimensionally ordered macroporous perovskite materials in environmental fields are summarized, including photocatalysis, soot combustion, oxidation of volatile organic compounds, carbon dioxide methanation and sensors for gas or liquid. The materials present a good performance owing to the properties, such as slow photon effect, strong mass transfer ability, high surface area and adjustable composition.

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三维有序大孔钙钛矿材料在环境领域的应用

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摘要: 近年来, 三维有序大孔(3DOM)材料吸引了世界各国研究者的广泛关注. 除了表面积大、孔隙率高、孔体积大、传质性能好等大孔材料的普遍特性, 3DOM材料的孔结构分布均匀, 且具有规律的周期性, 其大孔尺寸也可在制备过程中自由调控. 在制备过程中, 通过加入适当的表面活性剂, 可以得到骨架上具有介孔的3DOM材料. 这使3DOM材料具有了多级孔结构, 为其提供了更多的反应活性位点和对反应物的尺寸选择性. 此外, 作为一种三维光子晶体, 3DOM材料还具有光子禁带、慢光效应等独特的光学性质.

钙钛矿是一类广泛分布于地球上且储量丰富的化合物, 具有成本低廉、氧化还原性能好、离子迁移率高、稳定性高、毒性较低、生物相容性好等优点. 并且通过部分或完全取代钙钛矿材料中位于A位或B位的阳离子, 可以有效调控其物理化学性质, 使其在环境领域中表现出巨大的应用潜力. 3DOM钙钛矿材料结合了3DOM结构和钙钛矿材料各自的优点, 逐渐成为环境领域中的热门材料. 已被广泛应用于光催化分解水产氢或降解污染物、碳烟催化燃烧、挥发性有机化合物(VOCs)催化氧化、温室气体减排和利用、传感器等多种环境应用领域.

本文综述了近年来3DOM钙钛矿材料的一般合成方法, 并列出了3DOM钙钛矿材料在环境领域的应用和研究进展, 详细讨论了其在不同反应体系中的独特优势和反应机理. 除了3DOM钙钛矿材料灵活的组成及可调变的物理化学性质对于其催化性能的提升具有显著的作用. 此外, 在光催化中, 3DOM材料独特的慢光效应, 使半导体材料的光吸收范围与光子禁带边重叠时, 可以显著提高半导体材料的光吸收效率, 进而有效提高催化剂的光催化活性. 因此, 3DOM材料的结构有序性和光子禁带调控是3DOM钙钛矿材料在光催化领域应用中的关键因素. 对于碳烟催化燃烧, 由于碳烟颗粒尺寸较大, 碳烟颗粒与催化活性位点的接触成为影响催化活性的关键因素. 因此, 3DOM钙钛矿材料的大孔孔径, 特别是其孔与孔之间的窗口尺寸对于其催化性能起着重要的作用. 而对于VOCs催化氧化、CH₄催化燃烧、CO₂甲烷化、传感器等应用领域, 3DOM钙钛矿材料比表面积的提升以及多级孔道结构的构建对催化活性的促进作用更为显著. 最后, 本文提出了该研究领域所面临的挑战, 并对未来的发展进行了展望.

关键词: 三维有序大孔材料; 钙钛矿; 环境应用; 光催化; 催化氧化; CO₂甲烷化; 传感器

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