Facile synthesis of three-dimensionally ordered macroporous LaFeO₃-supported gold nanoparticle catalysts with high catalytic activity and stability for soot combustion

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A strategy for the facile synthesis of three-dimensionally ordered macroporous (3DOM) LaFeO₃-supported gold nanoparticle catalysts is reported, namely in situ colloidal crystal template (CCT) method. The synthetic process involving in three steps are listed in detail, for example, the synthesis of monodisperse polymethyl methacrylate (PMMA) microspheres accompanied by polyelectrolyte brushes ([=NH₃]⁺·Cl⁻, PEBs), the preparation and assembling of CCT with spherical Au/PMMA compound, and the formation of 3DOM LaFeO₃-supported gold catalysts via calcination to remove the CCT. All the catalysts have well-defined 3DOM structures, and gold nanoparticles are uniformly dispersed on the inner wall of 3DOM LaFeO₃ support. 3DOM structure can improve the contact efficiency between soot particle and catalyst, and the strong metal (Au)-oxides (LaFeO₃) interaction provides the active sites for activation of O₂. 3DOM Auₓ/LaFeO₃ catalysts obtained by in situ CCT method show high catalytic activity and stability for diesel soot oxidation. It suggests that 3DOM Auₓ/LaFeO₃ catalysts are excellent systems for catalytic oxidation of solid soot particle, and the design concept and facile synthesis method of 3DOM oxide-supported Au nanoparticle catalysts can be extended to other metal/oxide compositions.

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1. Introduction

Soot particles emitted from diesel engines is a main source of urban ambient PM10 and PM2.5 (mass concentrations of particulate matter-PM <10 μm and <2.5 μm aerodynamic diameter, respectively) which can cause acute human health and environmental problems [1,2]. This calls for efficient treatment systems for the exhaust gas from diesel engines [3,4]. The combination of traps and oxidation catalysts in the continuously regenerating particulate trap (CRT) appears to be one efficient after-treatment technique for diesel engines [5,6]. The key challenge is to find effective catalysts for soot combustion that operates at low temperatures [7–11]. The catalytic combustion of diesel soot is a typical reaction of heterogeneous catalysis containing solid particle as reactant. Noble metals, [12] transition metal oxides, [13] alkaline metal oxides, [14,15] perovskite-like type oxides [16,17] and Ce-based oxides [18] have exhibited good catalytic performance for diesel soot combustion. Especially, perovskite-like type oxides (ABO₃) are one of the key components in auto-exhaust treatment catalysts due to a variable valence of B-site ions and thermal stability. The catalytic oxidation of soot particles takes place at the three-phase boundary among a solid catalyst, a solid reactant (soot) and gaseous reactants (O₂, NO) [11,19]. The catalytic performance for soot combustion is affected by two factors: the contact between soot particles and the catalyst, and the intrinsic activity of the catalyst. For the conventional catalysts having smaller pore sizes (<10 nm) than soot particles (20 nm–1 μm), it is difficult for the soot particles to enter the inner pores of these catalysts which may have high surface area. Thus, the catalytic activity for soot combustion may be restricted by the poor soot/catalyst contact and/or limited active sites. One way to increase the contact between solid reactant and catalyst is through fabricating macroporous nanostructure materials.

Three-dimensionally ordered macroporous (3DOM) materials have become a focus research topic due to their potential applications, such as catalysts, photonic crystals, chemical sensors and absorbers [20–22]. Because of their periodic features with uniform big pore size (>50 nm), 3DOM materials would enhance the catalytic activity by providing more reaction active sites on accessibly macroporous wall surfaces, and by permitting high flow-through capability within a low-density structure. We have found that
3DOM oxides show better catalytic performances for diesel soot oxidation compared with disordered macroporous and nanoparticle samples [23,24]. And soot particles can enter the inner pores of 3DOM catalyst with the help of the reactant gas flow during the rising temperature observed by TEM images of 3DOM catalyst after undergone the TPO reaction, although the soot particles are sphere particles with the average particle diameter of 25 nm in TEM image of soot agglomerates [25]. However, the catalytic performances of 3DOM oxides are limited by their intrinsic activity, i.e., the catalytic combustion of soot over perovskite-type oxides requires a higher temperature (ca. 350–450 °C) than that of exhaust gas from a diesel engine (150–400 °C) [5–18]. It is generally known that the addition of metal (active site) to oxides can modify the intrinsic catalytic properties of themselves due to the establishment of an interaction between metal and support, which can enhance the redox properties of the modified materials [26].

Since the pioneering studies by Haruta [27] and Hutchings [28], supported gold catalysts have become one of the most extensively research issues in the field of heterogeneous catalysis. In our group’s previous works [29,30], 3DOM oxides (LaFeO3 and Ce1-xZrO2)-supported gold catalysts which combine the two advantages of good contact between soot and catalyst by 3DOM supports and the efficient active sites for activation of O2 by Au nanoparticles, exhibited super catalytic performance for soot oxidation. Unfortunately, the stabilities of supported Au-based catalyts are poor. We found that this is a result of the sintering of supported Au nanoparticles in processing of catalyzing soot oxidation which leads to the increasing in Au nanoparticle sizes, and the suitable size of supported Au nanoparticles is important for catalytic oxidation of soot particles, the increasing size of Au nanoparticle can lead to deactivation of Au-based catalysts [30]. And assembly of multifunctional nanostructure materials with ordered macroporous and high dispersed Au nanoparticles is still a great challenge because of the poor control over these parameters in the fabrication of much elaborate nanocrystals [31].

Motivated by the above considerations, we present a novel route to the facile synthesis of 3DOM LaFeO3-supported Au nanoparticles (NPs) with high thermal stability via in situ colloidal crystal template (CCT) method [32]. The structural characteristics of pre-synthesized materials in the synthesis process are investigated and elaborated by the typical transmission electron microscope (TEM) and scanning electron microscope (SEM). In this explorative work, 3DOM AuNPs/LaFeO3 catalysts exhibit good catalytic performances and high catalytic stability for soot combustion. Thus, the multifunctional nanostructure catalyst of 3DOM LaFeO3 perovskite-type oxide-supported gold nanoparticles is an excellent system for catalytic reactions or surface chemical processes that occur at the interfaces of reactant and catalyst.

2. Experimental

2.1. Preparation of catalyst

3DOM LaFeO3-supported Au nanoparticle catalysts were prepared by in situ CCT method which was just developed in our lab [32], As shown in Scheme 1, the in situ CCT method involves in three processes as following: (1) Non-crosslinked, monodispersed poly-methyl methacrylate (PMMA) microspheres accompanied with polyelectrolyte brushes ([=NH4]+·Cl−, PEBs) were synthesized using a modified emulsifier-free emulsion polymerization technique. (2) The Au nanocrystals deposited on the surface of PMMA microsphere were obtained by GBMR method. (3) The spherical Au/PMMA compounds were used to assemble into the colloidal crystal template (CCT). And then the inorganic precursor solution containing La and Fe ions were added to the CCT and permeated the voids between the close-packed spheres. Finally, 3DOM perovskite-type oxide LaFeO3-supported gold nanoparticle catalysts were obtained by calcinations to remove the CCT. The processes of in situ CCT method are presented in detail as follows.

2.1.1. Synthesis of spherical PMMA accompanied with polyelectrolyte brushes

Non-crosslinked, monodispersed PMMA microspheres accompanied with PEBs ([=NH4]+·Cl−) were synthesized via a modified emulsifier-free emulsion polymerization technique using water-oil biphase double initiators [32]. The PEBs ([=NH4]+·Cl−) came from the initiators of 2,2’-azobisis (2-methylpropionamide) dihydrochloride (AIBA), and the preparation principles are showed in Scheme 2. All water in the forthcoming synthetic steps were distilled and deionized, and their resistivity is more than 12 MΩ cm. And the refined monomers were obtained by reduced pressure distillation. The mixture of acetone (50 ml) and water (150 ml) were poured into a four-necked and round-bottomed flask (1000 ml). When the mixture was heated to 70 °C by a hot water bath, the refined monomers were also added into it. A Teflon stirring paddle attached to the flask was driven by an electric motor after N2 was bubbled for 2 h in order to deaerate the air. In a separate polyethylene bottle, 0.31 g of AIBA (water phase initiator) and 0.18 g of azodisobutyronitrile (AIBN, oil phase initiator) were added into the water (150 ml). When the solution was heated to 70 °C, it was added to the flask. Under the constant stirring rate (380 rpm) and the protection of nitrogen, the mixture was kept at 70 °C for 2 h. After the reaction was finished, the reaction system was naturally cooled to room temperature, and the homogeneous latex were filtrated using filter paper (pore sizes, ~1 µm) to remove any agglomerates. Finally, the PMMA microspheres accompanied with PEBs ([=NH4]+·Cl−) were obtained.

2.1.2. Synthesis of PMMA-supported Au nanoparticles compounds

The PMMA-supported Au NPs compounds were synthesized by GBMR method using NaBH4 as reduction agent, which was similar to the literature [29,30,33]. The schematic of the preparation method is presented in Scheme 3. The typical preparative procedures are described as follows: The 250 ml of PMMA latex (average size of 350 nm, solid content ~10 wt%) was placed in a precursor tank, then the HAuCl4 solution was poured slowly into the microspheres latex under stirring conditions. The surface PEBs ([=NH4]+·Cl−) of PMMA microspheres can interact with the anions of [AuCl4]−. The number of PEBs was determined by adding the amount of AIBA in the preparation microspheres solution. The mixture solution was driven to form a cycling flow between the membrane reactor and the beaker I by a peristaltic pump at ~360 ml min−1 flow rate. The redundant solution (NaBH4) (50 ml) was injected into the membrane reactor with two ceramic membrane tubes (Φ 3 mm × 160 mm) by a constant flow pump at flow rate of 1 ml min−1. Meanwhile, the hydrogen gas was also injected with two other membrane tubes. The metal precursor solution flowed in the glass tube reactor and outside the ceramic tubes. The NaBH4 solution was infiltrated into the glass tube reactor through the abundant holes (d = 40 mm) on the wall of the ceramic tubes, where the reduction of metal ions occurred immediately when the two solutions met. The molar ratio of [AuCl4]− to NaBH4 was about 1:5. The [AuCl4]− ions adsorbed on the surface of PMMA microspheres were reduced to Au NPs by NaBH4. The color of the mixture changed from faint yellow to wine red. The hydrogen bubbling-assisted stirring operation (10 ml min−1) was developed to vigorously stir the solution. The synthesis process was not stopped until complete consumption of the NaBH4 solution. The Au NPs were obtained and stabilized on the surface of PMMA microspheres, and they are generically named as Au/PMMA compounds. Finally, Au/PMMA compounds were centrifuged to form CCT at 3000 rpm for 10 h. The clear liquid was decanted, and the solid block
was dried at room temperature. Finally, the highly ordered CCT was obtained.

2.1.3. Synthesis of 3DOM LaFeO₃-supported Au NPs catalysts

A series of 3DOM perovskite-type composite oxide LaFeO₃-supported Au NP catalysts were prepared by CCT method using ethylene glycol (EG)-methanol solution of various metal nitrates (La(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O) as precursors. The stoichiometric amount of mixed metal nitrates were dissolved with 15 ml of EG in a 100 ml beaker at room temperature, and the produced EG solution was poured into a 50 ml volumetric flask. Methanol (6 ml) and EG were added to achieve the desired concentration of methanol (the final concentration of methanol was ~12 vol%). Then the inorganic precursors were added to the CCT and permeated the voids between the close-packed spheres, and condensed into a hard inorganic framework upon drying. Excessive
liquid was removed from the impregnated microspheres template via suction filtration with a Buchner funnel connected to vacuum. The infiltrated template was dried in a desiccator using anhydrous calcium chloride at room temperature overnight. The dried sample mixed with quartz sand (10–15 mesh) was baked to remove the CCT in a tube furnace from room temperature to 600 °C at the rate of 1 °C min⁻¹ in air, and kept the temperature at 600 °C for 5 h. Finally, 3DOM LaFeO₃-supported gold catalysts were obtained. The catalysts will be generically named as 3DOM Auₓ/LaFeO₃, where n is the weight percent of gold in the catalyst and its value was determined by inductive coupled plasma atomic emission spectrometry (ICP-AES).

2.2. Catalyst characterization

The scanning electron microscope (SEM) observations were carried out on a FEI Quanta 200F instruments using accelerating voltage of 5 kV.

The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained on a JEOL JEM 2010 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV.

Mercury intrusion porosimetry (MIP) experiments were carried out on a Micromeritics AutoPore IV 9500 apparatus in the pressure range of 0–30,000 psia.

The Brunauer–Emmett–Teller (BET) method was used to measure the specific surface areas of the samples by the N₂ isotherms using a Micromeritics ASAP 2010 analyzer.

The actual contents of Au in catalysts were determined by inductive coupled plasma atomic emission spectrometry (ICP-AES) (PE, OPTIMA 5300DV).

X-ray diffraction (XRD) patterns were measured on a powder X-ray diffractometer (Shimadzu XRD 6000) using Cu Kα (λ = 0.15406 nm) radiation with a Nickel filter operating at 40 kV and 10 mA in the 2θ range of 20–80°.

FT-IR spectra were obtained in the wavenumber range of 4000 and 400 cm⁻¹ by a FTS-3000 spectrophotometer manufactured by American Digilab Company. The sample wafer was prepared as a KBr pellet with the weight ratio of sample to KBr, 1:100.

Temperature-programmed reduction with H₂ (H₂–TPR) measurements were performed in a conventional flow apparatus. One hundred milligram sample was pretreated in an air atmosphere at 200 °C for 1 h and subsequently cooled to 100 °C. Then 10% H₂/Ar flow (40 ml min⁻¹) was passed over the catalyst bed while the temperature was ramped up from 30 to 900 °C at a heating rate of 10 °C min⁻¹. The hydrogen consumption signal was monitored by a thermal conductivity detector (TCD).

2.3. Evaluation of catalytic activity for soot combustion

The catalytic activities of the prepared samples were tested with a temperature-programmed oxidation (TPO) reaction on a fixed bed tubular quartz system (dₜ = 6 mm). The model soot was Printex-U (diameter 25 nm, purchased from Degussa). The catalyst (100 mg) and soot (10 mg) were mixed at a mass ratio of 10:1 with a spatula in order to reproduce the loose contact mode. The reaction temperature varied during each TPO run from 200 to 600 °C at a rising rate of 2 °C min⁻¹. Reactant gases (50 ml min⁻¹) contain 5% O₂ and 0.2% NO balanced with Ar in the presence of NO, or 5% O₂ balanced with Ar in the absence of NO. Reactant gases were passed through a mixture of the catalyst and soot at a flow rate of 50 ml min⁻¹. The outlet gas compositions was analyzed with an on-line gas chromatograph by using FID. The catalytic activity was evaluated by the values of T₁₀, T₅₀, and T₉₀, which were defined as the temperatures at 10%, 50%, and 90% of soot conversion, respectively, were oxidized during the TPO procedure. The selectivity to CO₂ formation (SCO₂) was defined as that the CO₂ outlet concentration (SCO₂) divided by the sum of the CO₂ and CO outlet concentration, i.e., \( \text{SCO}_2 = \frac{\text{SCO}_2}{\text{SCO}_2 + \text{C}_2\text{O}_2} \). \( \text{SCO}_2 \) was denoted as SCO₂ at the maximum temperature corresponding to the soot-burnt rate was the highest. In all TPO experiments, the reaction was not finished until the soot was completely burnt off.

3. Results and discussions

3.1. Characterizations of the spherical PMMA-supported Au NPs compounds

Fig. 1 exhibits the typical SEM and TEM images of spherical PMMA as carrier for gold nanoparticles synthesized via membrane-diffused reduction method with the NaBH₄ solution as reduction agent. As shown in Fig. 1a, it can be seen that the average size of the monodispersed PMMA microspheres is about 350 nm. The PMMA microspheres are uniform and spherical without any aggregation. As shown in Fig. 1b and c, well-defined metallic nanoparticles have been obtained for two different ratios of [Au] to [PMMA] (0.1 and 0.2 wt%) used herein. The average size of the nearly monodispersed Au NPs on the surface of PMMA is 3.0 nm and the particles size distribution of Au NPs is narrow.

3.2. Characterizations of 3DOM Auₓ/LaFeO₃ catalysts

Fig. 2(a) shows the typical SEM images of three-dimensional ordered CCT assembled using 350 nm spherical Au/PMMA compounds via centrifugation method. It is observed that the spheres complexes are highly uniform with narrow size distribution, and are closely packed into a highly ordered three-dimensional arrangement with long range order both parallel and perpendicular to the substrate in a large area. A face-centered-cubic (fcc) array of spheres with facets corresponding to the (1 1 1) sets of planes can be clearly observed from the image. It indicates that the supported Au particles do not interrupt the assembling of the colloidal crystals template. These well-arranged three-dimensional CCT containing Au particles could be available hard templates for the creation of 3DOM Auₓ/LaFeO₃ materials.

Fig. 2(b–d) displays the SEM images of 3DOM Auₓ/LaFeO₃ catalysts synthesized by using in situ CCT method. The images reveal the formation of Auₓ/LaFeO₃ catalyst with well-defined 3DOM structures. The macropores are connected with each other by the small windows. Their pore sizes estimated from the SEM image are about 200–250 nm, which corresponds to shrinkage of 25–35% compared with the initial size of PMMA microspheres. This shrinkage is caused by melting of the microspheres and sintering of the produced perovskite-type compound. Nevertheless, the uniform pore structure of catalyst is not destroyed with the large shrinkage. The wall thickness of catalysts is 35–45 nm. Three small windows in the bottom of macropore could be seen, which indicates the face-centered cubic (fcc) structure of 3DOM materials. From the above investigation, it is demonstrated that by using Au/PMMA colloidal crystal arrays as template, 3DOM Auₓ/LaFeO₃ material can be successfully fabricated.

Fig. 3 exhibits the typical TEM images of the 3DOM Au₁.25/LaFeO₃ catalyst. The 3DOM structures with overlapped pores can be clearly observed by TEM image. The Au nanoparticles are well distributed on 3DOM LaFeO₃ supports. The interconnected networks of 3DOM Au₁.25/LaFeO₃ are obvious, and slightly larger Au nanoparticles supported on inner wall of the 3DOM LaFeO₃ are also observed. The magnification of Au particles in the inset image of Fig. 3 shows that the hemispherical gold particle locates on the surface of LaFeO₃ carrier and the contact angle is about 90°. It is evident that the roughness is originated from the contact between...
the Au nanoparticles and the LaFeO₃ support, indicating a strong metal–support interaction. The HRTEM image exhibits that supported Au particles are crystallized and exposed fcc (111) plane. The Au particle size is in the range of 5–15 nm and the average size is 10 nm by statistical analyses of Au particles in TEM images. In addition, the formation and phase structures of 3DOM LaFeO₃ and Auₙ/LaFeO₃ catalysts are further confirmed by XRD (Figure S1) and FT-IR (Figure S2) spectra.

The presence of macropores in 3DOM Auₙ/LaFeO₃ catalysts was assessed by means of mercury intrusion porosimetry. Fig. 4 displays the differential curves of pore size distribution of concretes. The diameter corresponding to the peak value of different curve is regarded as the most probable pore diameter, whose size occupies the largest proportion of pores compared with other pore diameters. The smaller the most probable pore diameter, the finer the pore structure. It can be seen from Fig. 4 that the macropores (those in the 50–200 nm range) in this sample are very regular, and after supporting gold nanoparticles, the most probable pore diameters (95 nm) of concretes do not obviously change, which is similar to the open windows interconnected macropores in SEM images. The total specific pore volumes and most probable pore diameters of various concretes are analyzed and compared, and the results are given in Table 1. As shown in Table 1, the total pore volume of the materials determined by N₂ physisorption (~0.06 ml g⁻¹) is less than 3% of the total pore volume (~2.3 ml g⁻¹) determined by mercury porosimetry, indicating main contribution of macropores to the total porosity in these materials. The average pore diameter of 3DOM materials is about ~250 nm, which is agreement with the results of SEM images. The porosity of 3DOM materials is beyond 90%, indicating that the solid reactants can easily diffuse into the materials. Therefore, 3DOM LaFeO₃ perovskite-type oxide materials will be hereafter considered as one of the widest pore support.

3.3. Catalytic activity for the soot combustion

The catalytic activities of 3DOM LaFeO₃ and Auₙ/LaFeO₃ catalysts for diesel soot combustion were evaluated by TPO method and the results are listed in Table 2 and Fig. 5(A). For comparison, the TPO results of bare soot (i.e., without catalyst) and the catalytic combustion of soot over particle LaFeO₃ are also included. The results indicate that all the catalysts can promote soot combustion, comparing with bare soot combustion whose Tₜ₅₀ and S°C₀₂ are 585 °C and 55.0%, respectively. And 3DOM LaFeO₃ catalyst has higher catalytic activity than the corresponding particle catalyst. Moreover, the main product of soot combustion is CO₂ and the selectivity to CO₂ is about 92% for 3DOM LaFeO₃ catalyst. Thus, it can be concluded that the macroporous structure is superior for diesel soot combustion to the particle catalysts. Furthermore, as shown in Table 2, a series of 3DOM Auₙ/LaFeO₃ catalysts exhibit good catalytic activity for soot oxidation under the loose contact condition between soot and catalysts in the presence of NO. The catalytic activity increases with increasing of Au content. It indicates that supported-Au nanoparticles can further enhance the activity of catalysts. Among these catalysts, 3DOM Au₁.₂₅/LaFeO₃ catalyst shows the highest catalytic activity, i.e., T₁₀, T₅₀, and T₉₀ are 312, 387, 415 °C, respectively. The combustion temperature is decreased by 170, 198 and 231 °C comparing with bare soot combustion, respectively. And the S°C₀₂ of 3DOM Auₙ/LaFeO₃ catalysts for soot combustion are higher than 98% in the presence of NO gas.

In the after-treatment techniques for diesel engines, NOₓ is used as an efficient mobile oxidizing agent that accesses the soot and
Fig. 2. SEM images of CCT and 3DOM Au\textsubscript{x}/LaFeO\textsubscript{3} catalysts. (a) CCT; (b) Au0.46/LaFeO\textsubscript{3}; (c) Au0.75/LaFeO\textsubscript{3}; (d) Au1.25/LaFeO\textsubscript{3}.

Table 1
Porosities, average diameters, pores volume and pore areas of 3DOM LaFeO\textsubscript{3}, Au0.75/LaFeO\textsubscript{3} and Au1.25/LaFeO\textsubscript{3} catalysts.

<table>
<thead>
<tr>
<th>Catalyst (3DOM)</th>
<th>(V_p^a) (m\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(A_p^b) (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>(V_{Hg}^c) (m\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(D_p^d) (nm)</th>
<th>% Porosity\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO\textsubscript{3}</td>
<td>0.06</td>
<td>37.6</td>
<td>2.5</td>
<td>262</td>
<td>91</td>
</tr>
<tr>
<td>Au0.75/LaFeO\textsubscript{3}</td>
<td>0.06</td>
<td>38.3</td>
<td>2.3</td>
<td>245</td>
<td>90</td>
</tr>
<tr>
<td>Au1.25/LaFeO\textsubscript{3}</td>
<td>0.07</td>
<td>36.9</td>
<td>2.4</td>
<td>256</td>
<td>91</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Pore volume for pores determined by BET method.
\textsuperscript{b} Total pore area determined by Hg porosimetry.
\textsuperscript{c} Total pore volume for pores.
\textsuperscript{d} The median pores diameter (4V/A).
\textsuperscript{e} Determined by Hg porosimetry.

Table 2
The BET surface areas, Au actual contents and their catalytic performances of Au\textsubscript{x}/LaFeO\textsubscript{3} catalysts for soot combustion under loose contact condition between catalyst and soot in the presence and absence of NO.

<table>
<thead>
<tr>
<th>Catalysts (3DOM)</th>
<th>S\textsubscript{BET} (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Au (wt%)\textsuperscript{f}</th>
<th>(T_{10}^g) (\degree C)</th>
<th>(T_{50}^g) (\degree C)</th>
<th>(T_{90}^g) (\degree C)</th>
<th>(S_{m}^{CO_2}^g) (%)</th>
<th>(T_{10}^g) (\degree C)</th>
<th>(T_{50}^g) (\degree C)</th>
<th>(T_{90}^g) (\degree C)</th>
<th>(S_{m}^{CO_2}^g) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot (without catalyst)</td>
<td>100</td>
<td>–</td>
<td>482</td>
<td>585</td>
<td>646</td>
<td>55.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LaFeO\textsubscript{3} (particles)</td>
<td>21</td>
<td>0</td>
<td>378</td>
<td>491</td>
<td>517</td>
<td>80.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LaFeO\textsubscript{3}</td>
<td>30</td>
<td>0</td>
<td>347</td>
<td>419</td>
<td>455</td>
<td>92.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Au0.46/LaFeO\textsubscript{3}</td>
<td>27</td>
<td>0.46</td>
<td>344</td>
<td>403</td>
<td>438</td>
<td>98.5</td>
<td>366</td>
<td>475</td>
<td>516</td>
<td>90.6</td>
</tr>
<tr>
<td>Au0.75/LaFeO\textsubscript{3}</td>
<td>28</td>
<td>0.75</td>
<td>327</td>
<td>396</td>
<td>427</td>
<td>99.1</td>
<td>341</td>
<td>463</td>
<td>498</td>
<td>97.2</td>
</tr>
<tr>
<td>Au1.25/LaFeO\textsubscript{3}-first</td>
<td>25</td>
<td>1.25</td>
<td>312</td>
<td>387</td>
<td>415</td>
<td>99.4</td>
<td>320</td>
<td>446</td>
<td>480</td>
<td>99.0</td>
</tr>
<tr>
<td>Au1.25/LaFeO\textsubscript{3}-2nd</td>
<td>–</td>
<td>–</td>
<td>310</td>
<td>385</td>
<td>416</td>
<td>99.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Au1.25/LaFeO\textsubscript{3}-3rd</td>
<td>–</td>
<td>–</td>
<td>311</td>
<td>382</td>
<td>415</td>
<td>99.4</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{f} Determined by ICP-AES.
\textsuperscript{g} Reaction gas: 5% O\textsubscript{2} and 0.2% NO in Ar, 50 ml min\textsuperscript{-1}.
\textsuperscript{h} Reaction gas: 5% O\textsubscript{2} in Ar, 50 ml min\textsuperscript{-1}.
causes light-off of soot in an appropriate temperature range. This mechanism subtly changes solid (soot)–solid (catalyst) contact into solid (soot)–gas (NO2)–solid (catalyst) contact [3,4]. Therefore, the catalytic performance of general catalysts for soot combustion is strongly dependent on the presence of NOx in the reactant gas. However, technical developments of diesel engines strive to suppress raw NOx emissions, which call for a good catalytic system in the absence of NOx. As shown in Table 2, the catalytic activities of 3DOM Au0.75/LaFeO3 catalysts are still very high in the absence of NOx which is strongly related to the structures of catalysts and the amount of active oxygen amount. For example, compared with the results in the presence of NO gas, the increased values of T50, T90, and T90 over 3DOM Au1.25/LaFeO3 catalyst in the absence of NO gas are only 8, 59 and 65 °C, respectively. Therefore, 3DOM structure of supported Au-based catalyst is a solution for weakening the NOx constrain on the catalytic activity for soot combustion. In addition, 3DOM Au0.75/LaFeO3 catalysts still showed the high catalytic selectivity of CO2 production for soot oxidation in the absence of NO gas. It is easy to understand that supported-Au nanoparticles can activate the gas molecule such as O2 and promote CO oxidation [34]. In our previous works [19,25], it is found that the reaction pathways of soot combustion can be divided into two parts: One is that active oxygen species directly oxidize soot particles; the other one is that NO2 acts as intermediate to catalyze soot oxidation. In this manuscript, it is not denied the role of NO for catalyzing soot combustion, but Au nanoparticles supported on 3DOM LaFeO3 carrier can enhance the adsorption and activation for O2, which is favorable for enhancing the catalytic performance of soot combustion by whatever direct or indirect pathways. The active oxygen species over 3DOM oxides–supported Au catalysts may be derived from the two approaches (or “generator”): one is direct activation of oxygen on the surface of gold nanoparticles. The other is derived from the synergistic effect of metal (Au)–support (oxides) during which the induced support may give rise to serving as a reservoir for oxygen in the reaction oxidation [25]. The abundant active oxygen species of 3DOM oxides–supported Au catalysts can not only improve the NO oxidation to NO2, but also can further promote the CO oxidation to CO2.

It is generally known that the catalytic stability of supported Au-based catalysts for oxidation reaction is poor [28,29]. The catalytic stability of typical 3DOM Au1.25/LaFeO3 catalyst was further examined by the TPO tests for three cycles and the results are shown in Table 2 and Fig. 5(B). As shown in Fig. 5(B), the CO2 concentration profiles of 3DOM Au1.25/LaFeO3 catalyst have no dramatic changes in the three cycles of TPO measurements, indicating that 3DOM Au1.25/LaFeO3 catalyst maintains its high catalytic activity under the condition of loose contact between catalysts and soot particles. For example, the numerical values of T50 during the three cycle tests are 385 ± 3 °C (Table 2). The result indicates that 3DOM Au0.75/LaFeO3 catalysts obtained by in situ CCT method have good catalytic stability for soot oxidation. The improving stability of 3DOM Au0.75/LaFeO3 catalysts may be attributed to the role of the strong interaction between oxides and Au nanoparticles via the calcination at the high temperature (600 °C) for 5 h.

3.4. The result of H2–TPR

Generally speaking, the catalytic performance of materials for oxidation reaction is closely related to the redox property. H2–TPR results can reflect the redox property of metal oxide catalyst. In this work, the reduction peak temperature (T_red) is taken as a measure of the reducibility of the catalyst system. The lower T_red is, the stronger the redox property is. Since in practical application, the rate of soot oxidation at low temperature is more important than that at high temperature, we especially focus on the lowest T_red of H2–TPR. Fig. 6 exhibits the H2–TPR results of 3DOM LaFeO3 and Au0.75/LaFeO3 catalysts. For the H2–TPR profile of 3DOM LaFeO3 perovskite-type oxide, two obvious peaks around 432 and 527 °C are presented, the first peak centered at 432 °C can be attributed to the reduction of surface adsorption oxygen and surface Fe3+ to Fe2+, and the second peak can be ascribed to the reduction of

![Fig. 3. TEM and HRTEM images of 3DOM Au1.25/LaFeO3 catalyst. The inset shows an enlarged Au nanoparticle whose lattice fringes correspond to the fcc(1 1 1) plane determined by Fast Fourier Transform (FFT) image.](image-url)

![Fig. 4. Pore size distribution of 3DOM LaFeO3 and Au0.75/LaFeO3 catalysts.](image-url)
surface Fe$^{2+}$ to Fe$^{0}$ (metallic iron) [35]. There is no reduction peak for the profile of pure 3DOM LaFeO$_3$ at the low temperature (~300°C). After introduction of supported Au nanoparticles, a peak of H$_2$ consumption centered at 286°C appears in the profile of 3DOM Au$_{0.46}$/LaFeO$_3$ catalyst. This peak can be attributed to the reduction of the chemisorption’s oxygen species on highly dispersed Au nanoparticles or the interface between Au particles and supports [25]. With increasing of the Au loading amounts, the peak becomes stronger and the peak temperature shifts to lower temperature, and the lowest $T_{red}$ shifts from 286 to 206°C. The reduction peaks of 3DOM Au$_n$/LaFeO$_3$ catalysts during 300–700°C shift to the lower temperature in comparison with those of 3DOM LaFeO$_3$ perovskite-type oxide. For example, for 3DOM Au$_{1.25}$/LaFeO$_3$ catalyst, the reduction peak centered at 432°C shifts to 391°C, and the reduction peak centered at 527°C shifts to 481°C. It is noted that two reduction peaks are too much overlap to form one new reduction peak, indicating that the subsurface lattice oxygen of support may migrate to the surface and become active oxygen species. It is probably attributed to the strong metal (Au)–support (LaFeO$_3$) interaction. However, in principle, the results of H$_2$–TPR reflect to the oxidizing ability of catalyst for H$_2$, which is not directly relevant for soot oxidation. It is generally related to the ability of the Au-based catalysts for H$_2$ activation and oxidation. It is known that the metallic Au exhibits stronger ability for H$_2$ dissociation than Au ions, showing more obvious hydrogen spillover effect [36]. Based on the analyzing results of H$_2$–TPR, we found that the redox ability of 3DOM Au$_n$/LaFeO$_3$ catalysts is much better than that of pure 3DOM LaFeO$_3$ catalyst. Among these catalysts, 3DOM Au$_{1.25}$/LaFeO$_3$ catalyst displays the best redox property, which is consistent with that of the best catalytic performance for soot combustion.

In summary, based on the above results and discussion, it can be known that 3DOM Au$_n$/LaFeO$_3$ catalysts can be successful synthesized by in situ CCT method just developed in our lab. 3DOM Au$_n$/LaFeO$_3$ catalysts have well defined three-dimensionally ordered macroporous structures and connect with each other through the small windows. The Au nanoparticles are well distributed on inner wall of 3DOM LaFeO$_3$ supports. 3DOM LaFeO$_3$ is the better candidate catalyst for diesel soot combustion than particle LaFeO$_3$. A possible reason is considered for the increasing of the available active surface, and thus for the enhancement of the catalytic activities for diesel soot combustion. The macropore structure of the catalyst permits model diesel soot to enter their inner pores, and the uniform macroporous network allows soot particles easy mass transfer and less diffusional resistance, resulting in the highly efficient contact between soot and catalysts. Therefore, the 3DOM catalysts can enhance the catalytic activity for diesel soot combustion. And gold nanoparticles supported on 3DOM LaFeO$_3$ further enhance the catalytic activity. Among these catalysts, the 3DOM Au$_{1.25}$/LaFeO$_3$ catalyst gives the highest catalytic activity. The results of H$_2$–TPR show that the more the supported-Au amount, the lower the $T_{red}$ temperature, indicating that supported-Au nanoparticles can improve the redox ability of 3DOM Au$_n$/LaFeO$_3$ catalysts, which is in good agreement with their excellent catalytic performances.

4. Conclusions

3DOM LaFeO$_3$-supported gold nanoparticle catalysts synthesized by in situ CCT method have well-defined three-dimensionally ordered macroporous structures, and the macropores are connected with each other through small windows. Gold nanoparticles with average size of 10 nm are well-distributed on inner pore wall of 3DOM LaFeO$_3$ supports. The macropore structure of the catalysts is favorable for improving the contact between model soot particles and catalysts, and gold nanoparticles supported on 3DOM LaFeO$_3$ carrier can enhance the redox ability of catalysts. 3DOM Au$_n$/LaFeO$_3$ catalysts exhibit high catalytic activity and stability for soot oxidation under the loose contact condition between soot and catalysts. Among these catalysts, 3DOM Au$_{1.25}$/LaFeO$_3$ catalyst exhibits the highest catalytic activity for soot combustion, whose $T_{10}$, $T_{30}$, $T_{50}$ and $S_{286}$ are 312, 387, 415°C and 99.4%, respectively. The facile synthesis method of 3DOM oxides-supported Au

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**Fig. 5.** The CO$_2$ concentration profiles of 3DOM Au$_n$/LaFeO$_3$ catalysts (A) and 3DOM Au$_{1.25}$/LaFeO$_3$ catalyst used in three cycles (B) for soot oxidation.

**Fig. 6.** The H$_2$–TPR profiles of 3DOM LaFeO$_3$ and Au$_n$/LaFeO$_3$ catalysts. (1) LaFeO$_3$; (2) Au$_{0.46}$/LaFeO$_3$; (3) Au$_{0.75}$/LaFeO$_3$; (4) Au$_{1.25}$/LaFeO$_3$. 
nanoparticle catalysts can potentially be extended to other active metal nanoparticle and to other oxide supports. The design and fabrication of ordered nanostructure catalysts could be widely applied in various heterogeneous oxides-metals catalytic systems and could illustrate a promising and efficient way to design active sites for nanocatalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2014.07.023.

References

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