



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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ABSTRACT

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 with polyelectrolyte brushes ([=NH₂)⁺·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 Au_n/LaFeO₃ catalysts obtained by in situ CCT method show high catalytic activity and stability for diesel soot oxidation. It suggests that 3DOM Au_n/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 PM_{2.5} (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 performances 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 absorbents [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

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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 Ce_{1-x}Zr_xO₂)-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 catalysts 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 in 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 Au_n/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 ([=NH₂)⁺.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 ([=NH₂)⁺.Cl⁻) were synthesized via a modified emulsifier-free emulsion polymerization technique using water-oil biphasic double initiators [32]. The PEBs ([=NH₂)⁺.Cl⁻) came from the initiators of 2,2'-azobis (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 azodiisobutyronitrile (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 ([=NH₂)⁺.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 ([=NH₂)⁺.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 reductant 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. Meantime, 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 nm) 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

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