Chem. Mater. **2005,** *17,* 3546−3551

Facile Procedure To Prepare Three-Dimensionally Ordered Macroporous (3DOM) Perovskite-type Mixed Metal Oxides by Colloidal Crystal Templating Method

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Received March 11, 2005. Revised Manuscript Received April 26, 2005

A new facile procedure to prepare three-dimensionally ordered macroporous (3DOM) materials of perovskite-type $La_{1-x}Sr_xFeO_3$ ($x = 0-0.4$) mixed metal oxides by using colloidal crystal templating method is presented. This method can ensure the desired metal ratio throughout the preparation procedure, and the desired single-phase materials can successfully be prepared. Mixed metal nitrates were dissolved in ethylene glycol−methanol mixed solvent and penetrated into the colloidal crystal template of polystyrene spheres. During the calcination process, the mixed metal nitrates react with ethylene glycol and converted to mixed metal glyoxylates in voids of colloidal crystals before the polymer sphere bursts. After removing the sphere template and converting the mixed metal glyoxylates to the mixed metal oxides, the 3DOM materials of the perovskite-type $La_{1-x}Sr_xFeO_3$ ($x = 0-0.4$) mixed metal oxides were obtained, which was characterized on the basis of thermogravimetric−differential thermal analysis, X-ray diffraction, chemical analysis, scanning electron microscopy, and nitrogen adsorption−desorption technique. Furthermore, the advantage of the 3DOM perovskite-type materials for combustion of nanosize carbon, which is a model of particulate matter exhausted from diesel engines, was demonstrated.

Introduction

Particulate matter (PM) emitted from diesel engines is a precursor of photochemical smog and a probable human carcinogen. Especially dangerous for human health are particles less than 2.5 μm in size.[1] Development of catalysts, which decompose such macrosize particles, has attracted enormous attention.[2]

Perovskite-type mixed metal oxides ABO_3, where A and B represent 12-coordinated and 6-coordinated metals, respectively, are possible candidates as catalysts for combustion of PM, because of their thermochemical stability and tunable catalytic activity.[3] Generally, the A position is occupied by lanthanide metals (La, Sm, etc.) and/or alkaline earth metals (Sr, Ca, Ba, etc.), and the B position is chosen from transition metals (Fe, Co, Mn, Cr, Cu, V, etc.) and noble metals. The oxidation activity of the perovskite catalysts can be comparable to that of the noble metal catalysts under a suitable condition.[4]

Recently, much attention has been attracted to three-dimensional ordered macroporous (3DOM) materials with pores sized in the sub-micrometer range,[5] because of their applications in catalysis, photonic crystal, and separation. To date, almost all of the 3DOM metal oxides (oxides of Si, Ti, Zr, Al, Sb, W, Fe, and mixtures of some of these) have been synthesized by alkoxide-based sol−gel processes: (i) a colloidal crystal template is prepared by ordering monodisperse spheres [e.g., polystyrene, poly(methyl methacrylate), or silica] into a close-packed array; (ii) interstices in the colloidal crystal are then filled with liquid metal alkoxides, either neat or in solution, which is solidified in situ sol−gel transformation, resulting in an intermediate composite structure; and (iii) an ordered foam is produced after removing the template by calcinations or extraction. The ordered foam ("inverse opals") structures synthesized using this method consist of a skeleton surrounding uniform close-packed macropores. The macropores are interconnected

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10.1021/cm050551u CCC: $30.25

through windows that form as a result of the contact between the template spheres prior to infiltration of the precursor solution. This macroporous network allows easy mass transport of large materials as PM through the structure and less diffusional resistance to active site, which is an attractive feature for catalysis.

The alkoxide-based sol−gel method, however, becomes difficult for the formation of three-dimensionally ordered macroporous (3DOM) perovskite-type mixed metal oxides, because of the difficulty and high cost of obtaining metal alkoxide precursors of transition metals and lanthanide metals. Commercially available common salts of these metals are usually not suitable for starting materials, because of their melting feature. These salts melt at a temperature where the templates decompose, and therefore destroy the 3DOM structure, except a special case.[6,7] Solidification of the transition and lanthanide metals before the template polymer bursts are necessary.

An elegant method producing the 3DOM materials of the transition metal oxides was reported by Stein et al.[8] They infiltered metal salts (acetate or nitrate) into the void of the colloidal crystals and solidified as oxalate salts by reacting the incorporated metal salts with oxalic acid in the voids. The metal oxalate could be converted to metal oxides without melting, which seems to be a key point in successfully producing 3DOM metallic oxides (MgO, Cr_2O_3, Mn_2O_3, Fe_2O_3, Co_3O_4, NiO, and ZnO) materials. In other cases, solidification by reacting with base like ammonia[9] or ethylenediaminetetraacetic acid (EDTA)[10] was reported.

These methods are, however, not suitable for preparation of 3DOM materials of mixed metal oxide. Each metal has different reactivity with oxalic acid or base, and the produced oxalate salts or metal hydroxides have different solubility in the reacting media, which produce mixed metal oxide with undesired metal ratio.[9a,11] Synthetic procedures, which ensures chemical homogeneity of the product, must be needed.

A solution to this problem is to synthesize a well-defined mixed metal precursor, which could be infiltrated into the polymer template and converted to the mixed metal oxide without melting. This ensures the desired metal ratio throughout the preparation procedure, and subsequent calcination results in formation of a single-phase material with the desired stoichiometry. A sol−gel route seems to be the most promising way, and several mixed metal alkoxide precursors have been used to fabricate 3DOM mixed metal oxide.[12−14]

As for 3DOM perovskite-type mixed oxides, only two kinds of methods have been reported to date. It is reported that $Sm_{0.5}Sr_{0.5}CoO_3$ could be prepared from their mixed nitrate salts and surprisingly that their 3DOM structure did not decompose by melting under the presented condition.[6,7] Very recently, Hur et al. prepared 3DOM $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$-type perovskite compounds from their mixed metal alkoxide precursor, which was synthesized by reacting their acetate salts with 2-methoxyethanol repeatly.[14]

In this paper, we describe a facile one-pot procedure to prepare 3DOM perovskite-type mixed metal oxide, $La_{1-x}Sr_xFeO_3$ ($x = 0-0.4$), which does not need any alkoxide precursor preparation. Our strategy is to use an ethylene glycol (EG) solution of metal nitrate salts, which converts to a mixed metal glyoxylate salt by an in-situ nitrate oxidation at low temperature before the template bursts. Further calcination converts the glyoxylate salt to mixed metal oxide and removes the polymer template, resulting in the desired 3DOM perovskite-type materials.

Experimental Section

Materials. All chemicals were reagent grade and used as supplied. Suspension (pH 8) of 35 wt % monodisperse polystyrene (PS) spheres with a diameter of 161 ± 10 nm was purchased from Mitsui-Chemicals Inc. Nanoamand, which is nanoscale diamond (diameter < 10 nm) colloid dispersed in ethanol (8.23 wt %), was purchased from NanoCarbon Research Institute Ltd.

Characterizations. Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer (Rigaku, RINT Ultima+) using Cu Kα radiation. The diffraction line widths were obtained after the subtraction of the instrumental width determined by the line width of silicon powder, and crystallite sizes were calculated by the Scherrer equation. Images of scanning electron microscopy (SEM) were obtained with a JSM-6300 or JSM-6500F (JEOL) using accelerating voltages of 5 kV. Samples for SEM were dusted on an adhesive conductive carbon paper attached on a brass mount and were coated with platinum before examination. FT-IR spectra were recorded by the KBr method with a Perkin-Elmer Paragon 1000 Fourier transform infrared spectrometer with 2 cm^{-1} resolution. Thermogravimetric−differential thermal analysis (TG-DTA) measurements were performed with a TG-8120 (Rigaku) thermogravimetric analyzer. Nitrogen adsorption measurements were performed on a Autosorb 3 (YUASA IONICS) sorption analyzer. Prior to the sorption measurements, the samples were degassed under vacuum at 573 K for 3 h. Surface areas were calculated by the Brunauer−Emmet−Teller (BET) method. Elemental analyses were performed by the Center for Instrumental Analysis at Hokkaido University.

Synthesis of 3DOM Perovskite Mixed Metal Oxides. PS spheres (161 ± 10 nm) were packed into colloidal crystals by centrifugation (2000 rpm, 740 G) of 10.0 g of colloidal suspension

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in a 50 mL centrifugation tube for 48 h. The PS template was annealed at 393 K for 5 min before being soaked in the EG−methanol solution of mixed metal nitrates.

The desired amount of mixed metal nitrates ($LaNO_3 \cdot 6H_2O$: $Sr(NO_3)_2$:$Fe(NO_3)_3 \cdot 9H_2O$ = $(1 - x)$:x:1, where $x = 0-0.5$) was dissolved with ca. 5 mL of EG by stirring in a 100 mL beaker at room temperature for 2 h, and the produced EG solution was poured into a 25 mL volumetric flask. Methanol (40 vol %) and EG were added in amounts necessary to achieve the desired concentration. Then, ca. 1.0 g of the PS colloidal crystals were soaked in the produced dark brown solution for 5 h. Excess solution was removed from the impregnated PS template by filtration. The obtained sample was allowed to dry in air at room temperature overnight. A 0.5 g amount of the dried sample was mixed with 2.5 g of quartz sands (10−15 mesh) and calcined in a tube furnace with an air flow (50 $mL \cdot min^{-1}$). The temperature was raised at a rate of 1 $K \cdot min^{-1}$ to 873 K and held for 5 h.

Synthesis of Nonporous Perovskite Mixed Metal Oxides. The EG−methanol (40 vol %) solution of the mixed metal nitrate (total metal concentration, 1 M) was heated in a muffle oven at a rate of 1 K/min to 873 K. A 0.5 g amount of the produced solid was calcined in a tube furnace with an air flow (50 $mL \cdot min^{-1}$). The temperature was raised at a rate of 1 $K \cdot min^{-1}$ to 873 K and held for 5 h.

Catalytic Tests. Catalytic activity of the prepared materials was tested in a TG-DTA apparatus. A 20 mg amount of the prepared materials was soaked in 25 μL of the carbon particle colloidal solution diluted with 625 μL of ethanol and ultrasonicated for 5 min. The solution was dried at 373 K for 1 h and the obtained 1:10 by weight mixture (10 mg) of carbon and catalyst was heated in a TG-DTA apparatus under air flow (30 $mL \cdot min^{-1}$). The TG-DTA scan was also performed on an α-alumina/carbon mixture, so as to estimate the combustion feature of the carbon particle.

Results and Discussion

EG Solution Containing Mixed Metal Nitrates. To obtain 3DOM perovskite-type mixed metal oxide by the colloidal crystal templating method, several requirements should be satisfied. First, starting metal salts should be transferred to a solid-state material before the polymer template decomposes. Second, the homogeneous distribution of metal ions should be kept at the solidification process. Third, the solid materials should be converted to the desired mixed metal oxide without melting. To satisfy these requirements, we have focused on an efficient method of obtaining heterometallic complexes coordinated by glyoxylate ($[C_2H_2O_4]^{2-}$) as a ligand reported by Stefanescu et al.[15] This method consists of low-temperature oxidation (<373 K) of EG to the glyoxylate dianion in aqueous solution by nitrate of certain metals (Cr, Cu, Zn, Ni, Fe). The metal glyoxylates convert to their metal oxide at relatively low temperature (up to 673 K).

Because this method has never been applied for the preparation of any perovskite-type mixed oxides, thermochemical transformations of the EG solution containing starting metal nitrates were followed by TG-DTA analysis. Stefanescu et al. produced the glyoxylate salt in an aqueous solution, but we used EG solution, because aqueous solution usually has difficulty in being infiltrated into hydrophobic PS template. TG-DTA curves of a EG solution containing $Fe(NO_3)_3$ and $La(NO_3)_3$ (1 M each) is represented in Figure 1a. Weight of the EG solution containing $Fe(NO_3)_3$ and $La(NO_3)_3$ started decreasing with increasing temperature. The weight loss up to ca. 503 K corresponds to the removal of NO produced by nitrate oxidation of EG and evaporation of the remaining EG. As shown in Figure S1a (Supporting Information), the weight of EG endothermally decreased from ca. 373 to 469 K under the same condition. We also heated the solution in an oil bath and observed brown gas evolution (the color of NO) at 353−373 K. Between ca. 503 and ca. 603 K, the TG curve made a plateau. The weight loss until 563 K was ca. 73%, indicating the presence of a desired LaFe-glyoxylate.[16] The weight decrease continued up to ca. 823 K with a total weight loss of 85%, indicating the presence of $LaFeO_3$.[16] The production of $LaFeO_3$ was also confirmed by XRD measurement of a solid material obtained by a calcination at 873 K.[17] The solidification temperature is below the oxidative degradation temperature of PS exothermically observed from 473 to 693 K (Figure S1b, Supporting Information), indicating this method is applicable for preparation of 3DOM $LaFeO_3$ mixed metal oxide.

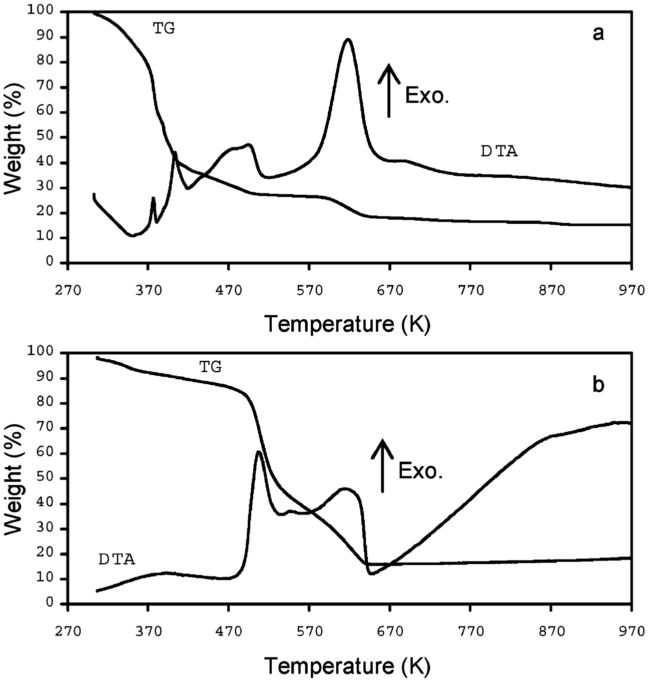

Figure 1. TG-DTA curves of (a) EG solution of $Fe(NO_3)_3$ and $La(NO_3)_3$ (total metal concentration, 2 M) at a heating rate of 10 $K \cdot min^{-1}$ and (b) PS filled with EG−methanol (40 vol %) mixed solution of $Fe(NO_3)_3$ and $La(NO_3)_3$ (total metal concentration, 2 M) at a heating rate of 1 $K \cdot min^{-1}$. Air flow rate was 30 $mL \cdot min^{-1}$.

Preparation of 3DOM $LaFeO_3$ Mixed Metal Oxide. $Fe(NO_3)_3$ and $La(NO_3)_3$ (1.0 M each) were dissolved in EG−methanol(40 vol %) solvent and penetrated into the PS template. Infiltration of the prepared solution took place

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(16) A density of EG solution containing $Fe(NO_3)_3$ and $La(NO_3)_3$ (1 M each) was ca. 1.57 $g \cdot cm^3$. The presence of $LaFe(C_2H_2O_4)_3$ and $LaFeO_3$ corresponds to weight loss of 70 and 85%, respectively.

(17) The crystal structure of $LaFeO_3$ was confirmed with reference to JCPDS data bank (37-1493).

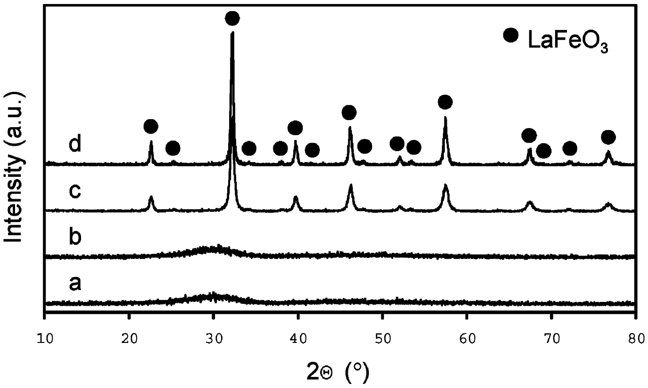

Figure 2. XRD patterns of solid materials prepared at different calcination temperatures of EG−methanol (40 vol %) mixed solution of $Fe(NO_3)_3$ and $La(NO_3)_3$ (total metal concentration, 2 M) infiltrated into PS temperature: (a) 673, (b) 773, (c) 873, and (d) 973 K. The calcination rate was 1 K·min^{-1}, and the calcination temperature was kept for 5 h. Markers are located according to the JCPDS 37-1493 $LaFeO_3$ card.

slowly (ca. 5 h) compared to other alcohol solutions (2−3 min) reported by others,[5] because of its higher viscosity. After the infiltration, the weight of PS increased ca. 64%, indicating almost all the void in the PS was filled by the EG−methanol solution.[18]

To determine an optimal calcination temperature, TG-DTA of the infiltrated PS was measured under air flow condition and shown in Figure 1b. Up to a temperature of ca. 473 K, ca. 14% of weight loss was observed, which corresponded to the evaporation of the methanol, the produced NO, and the remaining EG. The weight loss between ca. 473 and ca. 643 K corresponded to the decomposition of PS and $LaFe(C_2H_2O_4)_3$. Therefore, minimum calcination temperature was decided to be 673 K.

In the calcination process, the temperature was raised at a rate of 1 K·min^{-1} to given calcination temperatures and kept for 5 h under air flow (50 mL·min^{-1}). Figure 2 shows powder XRD patterns of the products calcined at 673, 773, 873, and 973 K. Calcination temperature more than 873 K was necessary to produce the desired $LaFeO_3$ mixed metal oxide (Figure 2c). Any byproducts as lanthanum carbonate derivatives or iron oxide derivatives could not be observed, indicating that homogeneous distribution of metal ions could be kept using this procedure. The product calcined up to 773 K of final calcination temperature was an amorphous compound (Figure 2b).

Figure 3 shows SEM images of the products calcined at 773, 873, and 973 K. Up to 873 K, the 3DOM structure was observed but the 3DOM structure collapsed at 973 K. The desired 3DOM perovskite-type $LaFeO_3$ mixed metal oxide was successfully obtained at a calcination temperature of 873 K. Well-ordered air spheres and interconnected walls created an "inverse-opal" structure in three dimensions. Although the structure is sometimes partially obscured by fragments and fractures on the surface, the next layer is visible in the SEM image (Figure 3d).

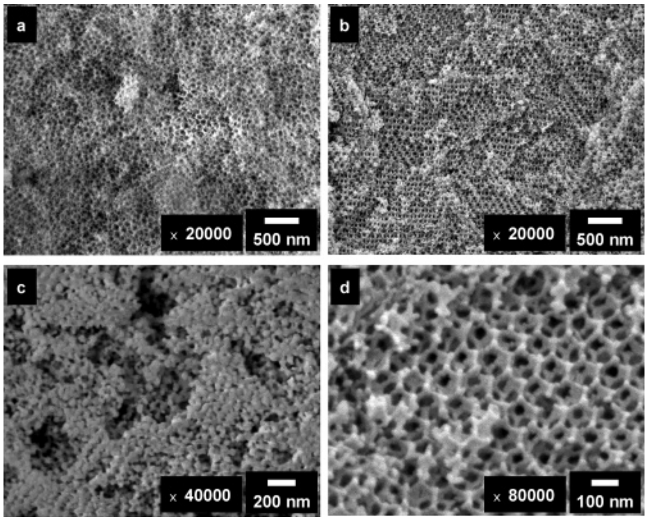

Figure 3. SEM images of solid materials obtained at different calcination temperatures of PS infiltrated by EG−methanol (40 vol %) mixed solution of $Fe(NO_3)_3$ and $La(NO_3)_3$ (total metal concentration, 2 M): (a) 773, (b) 873, (c) 973 K, and (d) high magnification of b. The calcination rate was 1 K·min^{-1}, and the calcination temperature were kept for 5 h.

Addition of methanol to EG solution was important for fabricating the desired 3DOM material. Using EG solution containing metal nitrates without methanol, 3DOM structure could only be partially produced (ca. 60−70% of particles had the 3DOM structure and others had no porous structure by SEM images). Addition of methanol increased the fraction of particles having the 3DOM structure (ca. 80−90%). Above the glass transition temperature of the PS (ca. 363−378 K), the PS sphere fuses, the void between the PS becomes smaller, and finally the air void disappears. Around this temperature, the mixed metal glyoxylate present in EG solution (boiling point of EG is 469 K) was squeezed out from the PS template. Further calcination of the precursor solution outside of the PS template did not produce the 3DOM structure.

Methanol could be easily removed from the infiltrated PS,[9a] because of its low boiling point (338 K). The removal of methanol of the infiltrated solution will make a space in the template void, and the amount of the precursor solution, which was squeezed out from the template, decreased. Therefore, the fraction of the 3DOM structure increased by using the EG−methanol mixed solvent.

Methanol had another effect. Adding methanol decreased the viscosity of the nitrate solution and increased the penetration rate from ca. 10 h without methanol to ca. 5 h with 40 vol % methanol.

Effect of the mixed metal nitrate concentration (0.5, 1.0, and 2.0 M total metal concentration) in the EG−methanol solution was examined. Higher concentrations of 1.0 M (Figure 4a) and 2.0 M (Figure 3b) were suitable to produce the desired 3DOM $LaFeO_3$ mixed metal oxide. At this concentration was the 3DOM structure stable up to the calcination temperature of 873 K. At a concentration of 0.5 M was observed the 3DOM structure, when the sample was calcined at 773 K. Calcinaton at more than 873 K collapsed the 3DOM structure. At lower concentration, the solid wall

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[18] A 1 g amount of PS sphere colloidal crystal has ca. 0.33 mL of void (density of PS is 1.04 g·cm^3 and void in face-centered cubic structure is ca. 26 vol %), if all spheres are packed in face-centered cubic (fcc) structure. Theoretical weight of the EG−methanol (40 vol %) solution containing $Fe(NO_3)_3$ and $La(NO_3)_3$ (1 M each; density is ca. 1.46 g·cm^3) in the void is 0.48 g (48 wt % increase). The excess of the obtained value over the theoretic value (64% instead of 48%) is caused by both imperfection of fcc structure and extra solution on the surface.

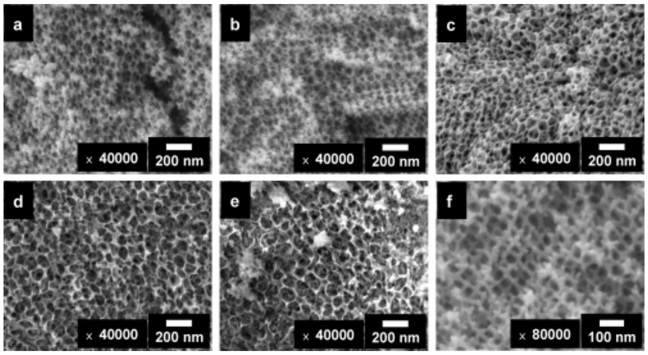

Figure 4. SEM images of solid materials obtained by calcination (873 K) of EG-methanol (40 vol %) solution of mixed metal nitrate ($LaNO_3$:$Sr(NO_3)_2$:$Fe(NO_3)_3$ = (1 − x):x:1, where x = 0.1−0.5; total metal concentration was 1.0 M): (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$, and (f) high magnification of b. The calcination rate was 1 $K\cdot min^{-1}$, and the calcination temperature were kept for 5 h.

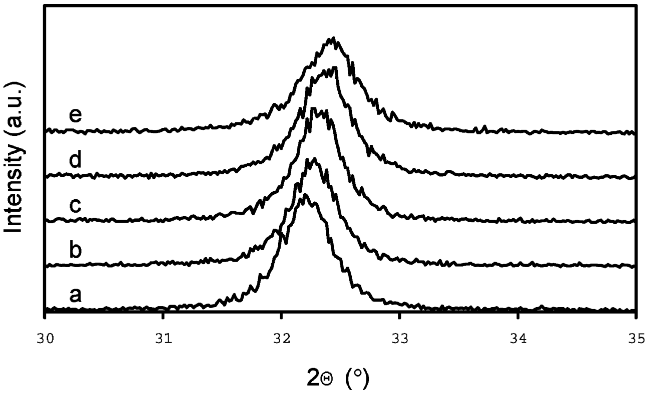

Figure 5. XRD patterns (2θ = 30−35° extended) of solid materials obtained by a calcination (873 K) of EG−methanol (40 vol %) solution of mixed metal nitrate ($LaNO_3$:$Sr(NO_3)_2$:$Fe(NO_3)_3$ = (1 − x):x:1, where x = 0−0.4; total metal concentration was 1.0 M): (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, and (e) $x = 0.4$. The calcination rate was 1 $K\cdot min^{-1}$, and the calcination temperature were kept for 5 h.

did not have enough strength to support itself and tended to collapse easily as reported by others.[8]

Preparation of 3DOM $La_{1-x}Sr_xFeO_3$ (x = 0.1−0.4) Mixed Metal Oxide. The desired amount of mixed metal nitrate ($LaNO_3$:$Sr(NO_3)_2$:$Fe(NO_3)_3$ = (1−x):x:1, where x = 0−0.4; total metal concentration was 1.0 M) was dissolved in EG−methanol solution. The prepared solution was penetrated into the PS template and calcined at 873 K for 5 h. Their SEM images and powder XRD patterns are presented in Figures 4, S2 (Supporting Information), and 5, respectively. Peaks corresponding to $SrCO_3$ (JCPDS 05-0418) were observed in the case of $x = 0.5$ (Figure S2f, Supporting Information). Between $x = 0$ and 0.4, any byproducts as lanthanum carbonate derivatives, strontium carbonate derivatives, or iron oxide derivatives could not be observed (Figure S2a−e, Supporting Information). Furthermore, peaks shifted to higher angle by increasing the amount of strontium, indicating that the added strontium metal was incorporated into perovskite structure under the applied calcination condition up to $x = 0.4$ (Figure 5).[19]

Macroporous structures were observed in the $La_{1-x}Sr_xFeO_3$ (x = 0.1−0.4) perovskite materials (Figure 4). By increasing the amount of strontium, however, the solid skeleton started to warp. We suppose that these changes were caused by different decomposition behavior of the PS template (different evolution rate of CO and CO_2) by changing its Sr contents. It is known that the partial substitution of lanthanum metal by the strontium metal changes an oxidation activity.

Characterization of 3DOM $La_{1-x}Sr_xFeO_3$ (x = 0−0.4) Mixed Metal Oxide. Structural parameters of the produced 3DOM $La_{1-x}Sr_xFeO_3$ (x = 0−0.4) perovskite materials were summarized in Table 1. For comparison, nonporous $La_{1-x}Sr_xFeO_3$ (x = 0−0.4) perovskite materials were prepared in the absence of PS colloidal crystal template, and their structural parameters were also listed in parentheses. The mixed metal nitrate in the EG−methanol mixed solvent was heated to 473 K (heating rate, 1 $K\cdot min^{-1}$), and produced solid materials were calcined at 873 K (heating rate, 1 $K\cdot min^{-1}$) and kept for 5 h.

Carbon (0 wt %) and hydrogen (0.30 wt %) were detected by elemental analysis of the material obtained at 873 K, while carbon (1.33 wt %) and hydrogen (0.33 wt %) remained in the solid obtained at 773 K (Table 2). The calcination temperature of 873 K was needed to remove the PS template completely. Sulfur was detected in the 3DOM $LaFeO_3$ material. We believe that this sulfur was present in the PS template, because this PS was synthesized by using $K_2S_2O_8$ as a polymerization initiator. Existence of peaks appeared around 1000 cm^{-1} in the IR spectrum of the 3DOM $LaFeO_3$ material, suggesting that the sulfur exits in the 3DOM perovskite material as sulfate (Figure S3, Supporting Information).

Pore sizes estimated from the SEM images were 72−94 nm, which corresponds to shrinkage of 45−58% with respect to the initial size of PS. This shrinkage was caused by melting of the PS spheres and sintering of the produced perovskite compound. High BET surface area of the material (entry 1) obtained at calcination of 773 K was due to the amorphous nature of the product and the remaining carbon. Increasing of the calcination temperature increased the crystallite sizes and decreased the BET surface areas. Wall thickness estimated from the SEM images was 16−22 nm, which was similar to the crystallite size (15.9−18.7 nm). The walls seem to be composed of linearly fused grains of the produced perovskite compound. If the crystallite size was in excess of the wall thickness by an increase in the calcination temperature, the 3DOM structure collapsed (entry 3 and Figure 3c). The nonporous materials prepared without template have similar crystallite size (14.3−19.7 nm) and smaller surface areas (27.3−30.1 $m^2\cdot g^{-1}$) compared to porous materials (35.7−44.9 $m^2\cdot g^{-1}$). By using the PS template, the surface areas could be increased by ca. 7−17 $m^2\cdot g^{-1}$, but the reason is not yet clear.

It is reported that fabrication of 3DOM materials using bigger spheres are suitable.[20] Furthermore, PMMA (poly(methyl metacrylate)) are suitable sphere as templates,[11,20] because the PMMA has better wettability with polar solvents such as alcohols and better combustion behavior than the

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(19) In the JCPDS data bank search, incorporation of strontium in the $La_{1-x}Sr_xFeO_3$ structure reduces unit cell parameters (peaks shift to higher angle).

(20) Sasahara, K.; Hyodo, T.; Shimizu, Y.; Egashira, M. *J. Eur. Ceram. Soc.* **2004**, *24*, 1961−1967.

Table 1. Summary of the Synthesis Conditions and Physicochemical Properties

entry	sample	total metal concn (M)	calcination temp (K)	crystallite size[a,b] (nm)	BET surf area ($m^2 \cdot g^{-1}$)	pore size[c] (nm)	wall thickness[c] (nm)
1	$LaFeO_3$	2	773	ND	60.7	87 ± 11	13 ± 2
2	$LaFeO_3$	2	873	15.9	49.0	94 ± 8	20 ± 3
3	$LaFeO_3$	2	973	25.8	24.1	ND	ND
4	$LaFeO_3$	1	873	18.7 (18.8)[d]	44.9 (28.0)[d]	94 ± 12	22 ± 5
5	$La_{0.9}Sr_{0.1}FeO_3$	1	873	18.0 (18.8)[d]	41.6 (27.3)[d]	72 ± 9	17 ± 9
6	$La_{0.8}Sr_{0.2}FeO_3$	1	873	18.0 (19.7)[d]	37.4 (28.6)[d]	79 ± 10	22 ± 2
7	$La_{0.7}Sr_{0.3}FeO_3$	1	873	17.2 (15.9)[d]	35.7 (28.9)[d]	89 ± 13	16 ± 2
8	$La_{0.6}Sr_{0.4}FeO_3$	1	873	18.8 (14.3)[d]	39.0 (30.1)[d]	93 ± 15	16 ± 3

[a] Crystallite sizes were calculated by Scherrer's equation from XRD data. [b] ND = not determined. [c] Pore size and wall thickness were estimated from SEM images. [d] Values in parentheses were ones obtained from nonporous materials.

Table 2. Elemental Analysis of the Produced Material

sample	C (wt %)	H (wt %)	N (wt %)	S (wt %)
porous $LaFeO_3$ calcined at 500 °C [a]	1.33	0.33	0	0.52
porous $LaFeO_3$ calcined at 600 °C [b]	0	0.3	0	1.09
nonporous $LaFeO_3$ calcined at 600 °C [c]	0	0.26	0	0

[a] Sample at entry 1. [b] Sample at entry 4. [c] Sample at entry 4 in parentheses in Table 1.

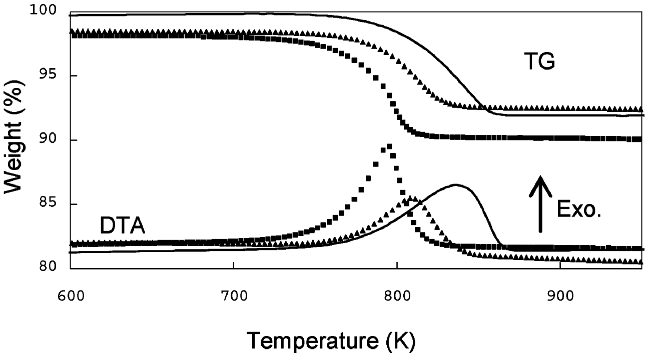

Figure 6. TG-DTA curves of (a) 3DOM $LaFeO_3$ (entry 4 in Table 1) mixed with carbon (solid square), (b) nonporous $LaFeO_3$ (entry 4 in parentheses in Table 1) mixed with carbon (solid triangle), and (c) α-alumina mixed with carbon (solid line). The heating rate was 10 $K \cdot min^{-1}$, and the air flow was 30 $mL \cdot min^{-1}$.

PS. The PS spheres smaller than 200 nm are one of the smallest spheres, and fabrication using these spheres seems to be a difficult matter. In our case, the 3DOM $La_{1-x}Sr_xFeO_3$ ($x = 0-0.4$) perovskite materials were successfully prepared by using 161 ± 10 nm PS spheres, which demonstrate the facility of this procedure.

Catalytic Activity. Catalytic activity of the 3DOM perovskite-type mixed metal oxide for carbon particle combustion was tested using the TG-DTA apparatus. Nanosize carbon particle (diameter < 10 nm) colloid in ethanol solution was mixed with the mixed metal oxide, and the ethanol was evaporated by drying at 373 K.

TG-DTA curves of carbon particles in the presence of the 3DOM $LaFeO_3$ or nonporous $LaFeO_3$ or without the $LaFeO_3$ at a heating rate of 10 $K \cdot min^{-1}$ under air flow (30 $mL \cdot min^{-1}$) are depicted in Figure 6. Weight-loss of carbon particles started at ca. 773 K, and T_{50} (a temperature where half of the carbon was burned) without the perovskite-type catalyst was 829 K (Figure 6a). In both cases where the $LaFeO_3$ was present with carbon particles, the weight decrease was observed up to ca. 573 K, which was most probably due to the evaporation of H_2O adsorbed on the surface of the $LaFeO_3$ material. In the presence of the nonporous $LaFeO_3$ material shifted the T_{50} to 807 K (Figure 6b), indicating that the nonporous $LaFeO_3$ material prepared by our method has catalytic activity similar to a $LaFeO_3$ catalyst prepared by the combustion method reported by Fino et al.[3i] Furthermore, T_{50} decreased to 791 K in the presence of the 3DOM $LaFeO_3$ material (Figure 6c). This result demonstrated an advantage of the 3DOM structure over the commonly prepared catalyst for combustion of carbon particles.

The nonporous $LaFeO_3$ material prepared by our method is an agglomerate of nanosized (<20 nm, corresponding to crystallite size calculated by XRD) particles (Figure S4, Supporting Information), similar to the $LaFeO_3$ material prepared by Fino et al.[3i] Bigger pores (ca. 90 nm diameter) in the 3DOM $LaFeO_3$ material compared to the nonporous $LaFeO_3$ material intensify the contact conditions between the catalyst and the carbon particles, and combustion activity of the carbon particle can be increased.

Conclusion

We have presented a facile procedure to produce 3DOM perovskite-type $La_{1-x}Sr_xFeO_3$ mixed metal oxide, which does not need any presynthesis of alkoxide precursors. Further applications of this procedure to fabricate other 3DOM mixed metal oxides are under investigation. Furthermore, we could demonstrate that the 3DOM perovskite-type materials have higher catalytic activity for combustion of nanosized carbon, which is a model of PM exhausted from diesel engines. Catalytic activity of the perovskite-type mixed oxides is tunable by changing the metal components, and pore size can be controlled by changing the size of the polymer templates. Further attempts to fabricate a better PM combustion system are also under way.

Supporting Information Available: TG-DTA curves of EG and PS (Figure S1), XRD 3DOM $La_{1-x}Sr_xFeO_3$ ($x = 0-0.4$) perovskite material (Figure S2), IR of 3DOM $LaFeO_3$ and nonporous $LaFeO_3$ perovskite materials (Figure S3), and TEM image of nonporous $LaFeO_3$ perovskite material (Figure S4) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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