

Fabrication of three-dimensionally ordered macroporous gadolinia-doped ceria films

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In this paper, three-dimensionally ordered macroporous (3-DOM) gadolinia-doped ceria (CGO) thin films were prepared by an aqueous organic gel method through the interstitial spaces between polystyrene spheres assembled on glass substrates. The concentration of CGO precursor, the pH value and infiltration times had important effects on the formation of the ordered porous structure. The morphologies of the porous CGO films were characterized by scanning electron microscopy (SEM). Phase development of PS–CGO composites with increasing calcination temperature, and the interactions between PS templates and the CGO precursor were investigated by Fourier transform infrared spectroscopy (FT-IR). X-Ray diffraction (XRD) spectra indicated the thin film calcined at 600 °C had a cubic structure and the CGO phase was formed directly by thermal decomposition of the precursor gel. The chemical composition of the porous CGO films was also studied by X-ray photoelectron spectroscopy (XPS).

Introduction

Porous ceria doped with rare earth oxides such as Gd₂O₃ has attracted great attention for oxygen sensors,¹ electrocatalysts² and NO_x adsorbents.³ In these applications, the high diffusivity of reactants and products in the porous structure are important to improve device performance. Three-dimensionally ordered macroporous (3-DOM) materials have attracted extensive interest as a means of obtaining much higher porosity. Moreover, macroporous materials can also present unique physical and chemical properties, leading to several potential applications such as electrochemical sensors, catalysis, separation, adsorbents, materials for solid oxide fuel cells (SOFC) and optoelectronics.^{4,5}

A typical procedure for preparing 3-DOM materials by the colloidal crystal template method includes three steps, namely, the self-assembly of the template, infiltration of the desired precursor and removal of the template. Over the past decade, various methods have been applied to introduce the precursors inside the templates. These are rf magnetron sputtering,⁶ chemical vapor deposition,^{7,8} nano-particle infiltration,^{9,10} electro-chemical deposition,^{11–15} chemical precipitation¹⁶ and sol–gel processes.⁴ Among these, the sol–gel process based upon hydrolysis–condensation of alkoxides has been successfully applied to the synthesis of 3-DOM materials. So far, nano-structured macroporous oxides of Si, Ti, Zr, Al, Fe, W, Sn and Sb have all been obtained by sol–gel processes.^{4,16–18} However, the major disadvantage of the alkoxide-based sol–gel process is that the alkoxide precursor solution is extremely sensitive to moisture and has to be processed under a strictly dry atmosphere. It becomes more difficult to fill the

voids if the hydrolysis and condensation rates are too rapid. Moreover, the high cost and difficulty of obtaining some commercial metal alkoxides, such as those of rare earths, hinder research progress in the fabrication of these important materials with 3-DOM structures.

For this reason, several other methods have been developed to prepare the precursors. For example, Yan and co-workers reported a general method for the preparation of macroporous transition metal oxides;¹⁵ Zhang *et al.* presented a novel sol–gel method for the preparation of well-ordered rare-earth oxides, including Eu₂O₃, Nd₂O₃ and Sm₂O₃.¹⁹

In this work, we propose the synthesis of 3-DOM gadolinia-doped ceria (CGO) materials by using an aqueous organic gel method, which has been intensively used for the preparation of polycation oxide ceramic powders or thin films.^{20–22} This method is based on chelating or complexing between metal cations and polyfunctional carboxylic acids such as citric acid, EDTA, *etc.* The source of cations can be diverse. The chelation process occurs during the mixing of cations and polyfunctional carboxylic acid in an aqueous solution to form soluble metal carboxylate complexes which can form the desired compound after firing at elevated temperatures. This method has the advantages of using common reagents, low cost, homogeneous mixing at molecule-level, good stoichiometric control, low processing temperature, use of an aqueous based processing system and no need for a special atmosphere. Despite these advantages, to the best of our knowledge there are no papers that describe the preparation of CGO 3-DOM materials by using an aqueous organic gel method. There is only one paper that describes rf magnetron sputtering of a CGO macroporous film.⁶ Here CGO 3-DOM thin films have been prepared for the first time by an aqueous organic gel method. Aqueous precursors were introduced into the spaces between the templating sphere array and an optimized procedure for the formation of CGO thin films by using aqueous organic gel method was proposed.

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Experimental section

Materials

The starting materials used were styrene (C_8H_8 , 99.99%), potassium persulfate ($K_2S_2O_8$, 99.99%), Gd_2O_3 , $Ce(NO_3)_3 \cdot 6H_2O$, nitric acid, citric acid and ammonia solution.

Preparation of macroporous CGO

Monodisperse PS spheres with an average diameter of 220 nm and 250 nm and relative standard deviation smaller than 4% (on the diameter) were obtained by using an emulsifier-free emulsion polymerization technique.²³

Microslides (10×60 mm) were used as substrates for polystyrene (PS) template growth. The substrates were washed sequentially with acetone, methanol and deionised water. Polystyrene thin film colloidal crystals were grown by using a controlled vertical drying method, which has been previously reported.²⁴ A typical process was that the glass substrates were placed into cylindrical vessels and PS latex with a concentration of 0.1% was added. The vessels were then placed into a temperature stable incubator at 55 °C until the growth was complete, after which well ordered multi-layer PS thin films can be formed on the substrate surface and displayed bright iridescence due to Bragg diffraction.

The CGO precursor solutions were prepared according to the formula $Ce_{0.8}Gd_{0.2}O_{2-\delta}$. First, a stoichiometric amount of Gd_2O_3 was dissolved in nitric acid solution and cerium nitrate was dissolved in deionised water separately. Then these two solutions were mixed together, followed by addition of citric acid in the molar ratio of citric acid : metal cations = 1.5 : 1. The pH was then raised to 8 by the addition of ammonia solution. The clear precursor solution was then evaporated at 80 °C to obtain a viscous sol. The clear transparent CGO precursor, which had high stability and no precipitation for several months after preparation, can be used to infiltrate into the voids of the templates. The concentration of the precursor solutions was varied by dilution with water and ethanol, ranging from 0.1 mol L⁻¹ to 1.0 mol L⁻¹.

The dip-drawing method was used to fill the CGO precursor on the PS templates. When the templates entered the precursor sol, the sol could permeate the spaces of close-packed PS array templates by capillary force. The process of infilling the films was repeated two times to ensure filling will occur through all the layers of the template film. The composites were subsequently dried for 6 h, and heated in air up to 600 °C for 4 h at a heating rate of 1 °C min⁻¹ to remove the PS templates and obtain porous structure of CGO thin films.

Characterization

The phase composition of the CGO thin films was analyzed by using X-ray diffraction (XRD) on a Phillips X Pert diffractometer equipped with $Cu_{K\alpha}$ radiation in the range of $2\theta = 10\text{--}80^\circ$. An FT-IR spectrometer (Nicolet FT520) was used for studying the coordinated structure of the CGO-PS composites. The samples, mixed with 99 wt% KBr, were pressed into pellets for the FT-IR examination in the frequency range 350–4500 cm⁻¹. Morphological investigation was performed using a Hitachi S-4800 scanning electron microscope operating

at 20 kV. The samples were sputter-coated with gold before examination. X-Ray photoelectron spectroscopy (XPS) analyses of the samples were performed on a Perkin-Elmer PHI 5000C XPS system with a AlK_{α} source. All the binding energies were referenced to the C 1s peak at 284.6 eV of surface adventitious carbon.

Results and discussion

Morphology of porous CGO films

In contrast to the sol-gel method, one of the biggest advantages of the proposed method is the ability to work in aqueous solutions by using common reagents instead of metal alkoxides. Thus, the method allows one to adjust the concentration of the precursor by adding or evaporating water and to obtain a stable precursor solution without using a special atmosphere.

The structures of the final 3-DOM materials obtained are strongly dependent on the precursor concentration and infiltration times. Fig. 1 shows the influence of the precursor concentration on the morphology of 3-DOM CGO films. At high concentration (1.0 mol L⁻¹), as shown in Fig. 1(a), there is a CGO film covering the top of the spheres due to the high viscosity and poor permeation, although the ordering of the underlying spheres appears to have been maintained. After calcination, the 3-DOM structure collapses due to incomplete infiltration (Fig. 1(b)), and the film loses the pore organization and is constituted only of CGO particles.

If the concentration is slightly lower (0.7 mol L⁻¹), the result is that the wall thickness of the 3-DOM structure increases due to the high solid content of CGO in the precursor (Fig. 2(a)). On the contrary, lower concentration of the precursor

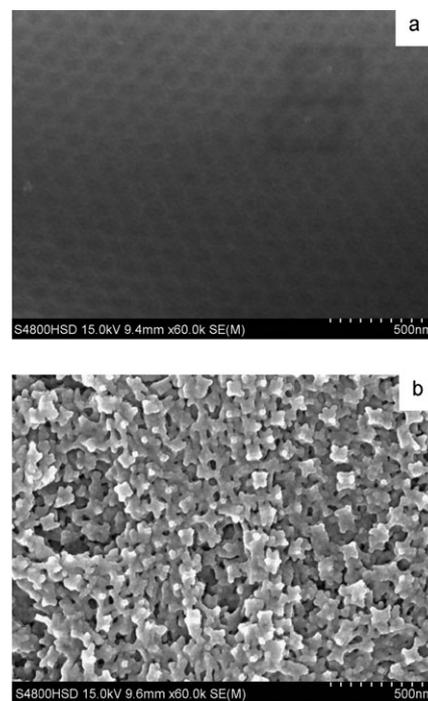


Fig. 1 SEM micrographs showing (a) the PS template film after infiltration with CGO precursor (1.0 mol L⁻¹) but before spheres removal and (b) CGO film losing pore organization.

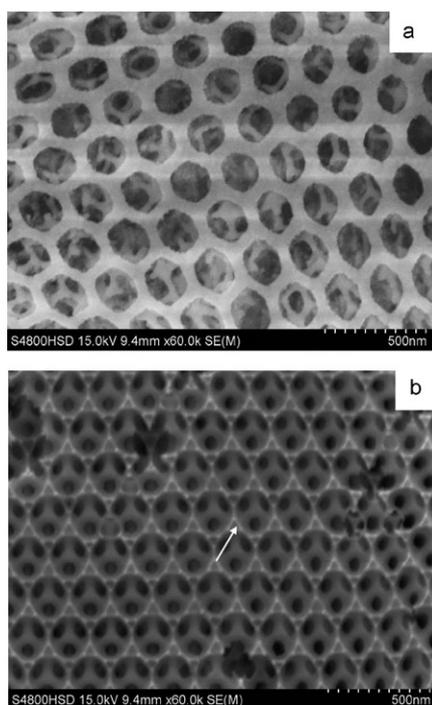


Fig. 2 SEM micrographs showing the surfaces of 3-DOM CGO thin films infiltrated with different CGO precursors (a) 0.7 mol L^{-1} and (b) 0.2 mol L^{-1} . The white arrow shows the void between air spheres.

(0.2 mol L^{-1}) has better permeation but a tendency to destroy the order level of the template due to the action of lower viscosity. The wall of the 3-DOM CGO film is very thin and easily disrupted due to the low strength, which results from the low CGO solid content in the precursor after calcination. Fig. 2(b) shows a 3-DOM CGO film with voids surrounded by a thin CGO wall. Moreover, voids between air spheres can be observed (marked with a white arrow), which result from insufficient CGO solid phase completely filling the interstices in the close packed structure. Similar voids have been observed by previous workers using a different infiltration method.⁴

Infiltration time also plays a key role in the formation of ordered porous CGO films. In the experiment, the templates are infiltrated twice to ensure that the voids in the template are sufficiently filled. It is found that when the templates are dipped more than three times, although the filling of the CGO precursor occurs through all the layers of the template to the substrate, the voids are overfilled slightly, which results in a decrease in the void diameter and an increase in the wall thickness (Fig. 3).

If the template is infilled 4 or 5 times, large pieces of the thin film are observed to delaminate from the substrate. After four dip cycles, approximately 50% of the film area has been lost. A monolayered macroporous structure is observed on the glass substrate as shown in Fig. 4. This two dimensional array of CGO indicates that delamination occurs and only a monolayer of PS spheres remained on the substrate due to dipping too many times.

Experimentally, it is found that $0.3\text{--}0.5 \text{ mol L}^{-1}$ CGO and 2–3 dips of the template film result in the best quality and coverage of the 3-DOM CGO films. Further infiltrations will

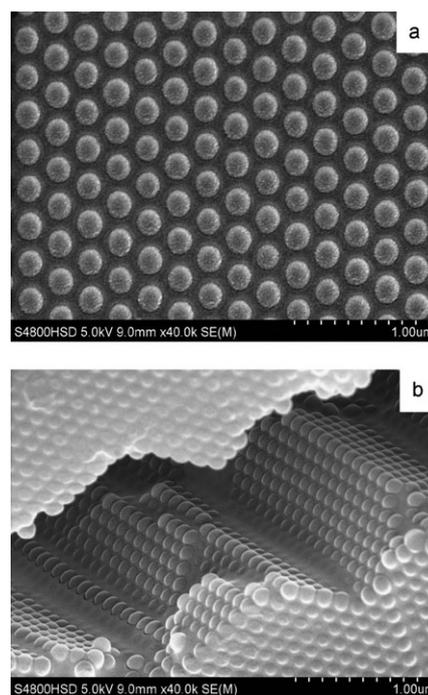


Fig. 3 SEM micrographs of the PS-CGO composites after infiltration three times with CGO precursor (0.3 mol L^{-1}). (a) Surface of the composite with PS spheres surrounded by CGO precursor showing slight overfilling and (b) template with cracks showing the voids have been infilled properly, while cracks have not been infilled.

lead to a reduction in the integrity of the films. Fig. 5 is the top-view image of the PS template infiltrated twice with the CGO precursor (0.3 mol L^{-1}), showing that the ordering of the spheres has been maintained. After calcination, the hexagonal packing of the latex spheres is replicated in the pore arrangement of CGO and the periodicity of the porous network has been preserved (Fig. 5(b)). The microstructure properties of 3-DOM materials are also affected by the heating rate. Cracks will be formed at a higher heating rate ($5 \text{ }^\circ\text{C min}^{-1}$) during the removal of polystyrene, if excessive bubbling results from the gas production.

The center to center distance between the air spheres is $210 \pm 10 \text{ nm}$, which is about 16% smaller than that of the original PS (250 nm). Usually shrinkage around 17–35% is

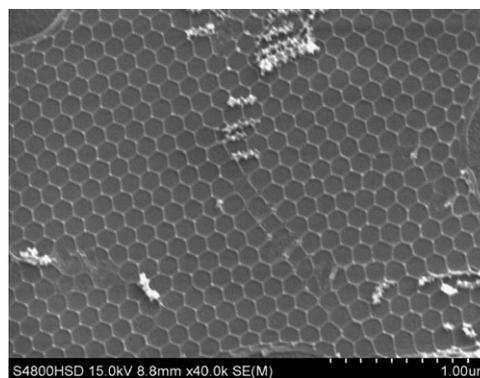


Fig. 4 SEM micrograph showing two dimensionally ordered macroporous CGO.

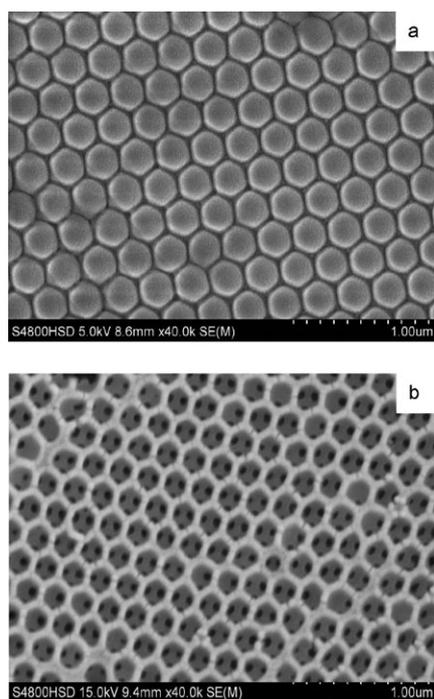


Fig. 5 SEM micrographs showing (a) the surface of the PS and CGO composite and (b) the surface of 3-DOM CGO film formed under the optimum conditions.

reported in the literature,^{19–21} which indicates that the special conditions in our experiments lead to a smaller shrinkage.

Effect of pH value

The pH value should affect the degree of chelation between the cation and the associated carboxylate acid ion. In aqueous solution, citric acid can remain as the compound H_3Y or dissociate increasing numbers of protons to form the species H_2Y^- , HY^{2-} , or Y^{3-} with the proportions of these species varying with pH values.²⁵ Since the anions, H_2Y^- , HY^{2-} , or Y^{3-} are the ligand species in complex formation, the complexation between cations and citric acid is affected markedly by the pH value. With increasing of the pH value, more citric acid is ionized and more carboxylate groups can be available to chelate the metallic ions in the solution at higher pH conditions.

To facilitate the formation of a stable CGO precursor solution, ammonia is used in this work as an easily removed pH modifier to obtain higher pH values. Further, ammonium nitrate will be produced by reaction of the ammonia with the NO_3^- groups from the cerium nitrate and nitric acid as water is removed. This compound greatly accelerates the decomposition of the gel precursors on heating and produces strongly exothermic reactions, which can result in disruption and deformation of ordered macroporous structure. Fig. 6 shows the morphology of a CGO film prepared with a precursor of pH = 10. Moreover, the average diameter of the voids is about 120 ± 10 nm, corresponding to a shrinkage of around 45%. It is indicated that different synthetic conditions can result in differences in shrinkage.

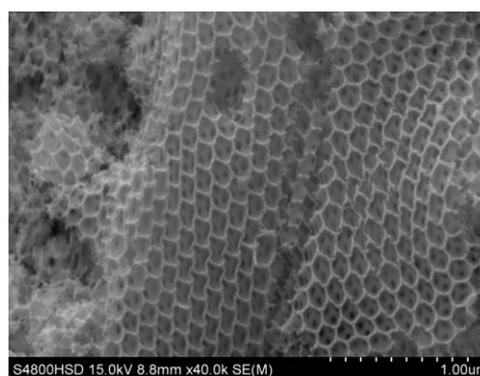


Fig. 6 SEM micrograph of 3-DOM CGO film showing disruption and deformation of the ordered macroporous structure (prepared at pH = 10).

Consequently, the addition of excess of ammonia is generally deleterious and to be avoided in the synthesis of 3-DOM CGO films by using the aqueous organic gel route. The optimum pH value for the formation of clear homogeneous precursor gel is 8.

Subsequent chemical conversion

In order to investigate the phase development of the PS–CGO composite with increasing calcination temperature and the interactions between PS templates and the CGO precursor, PS latex was centrifuged at 3000 rpm for 12 h and allowed to air-dry to form PS templates, which were then soaked in the CGO precursor solution for 12 h. Excess solution was then removed by vacuum filtration and the composites were dried at 60 °C for 4 h and calcined at 200–600 °C for 4 h, respectively. The samples obtained were characterized by FT-IR.

Fig. 7 shows the FT-IR spectra of PS–CGO composite and the samples calcined at different temperatures. For the spectrum of the PS–CGO composite (Fig. 7(a)), the band at 3412 cm^{-1} is attributed to the O–H stretching modes in water. The $\nu(C=O)$ stretching band at 1730 cm^{-1} of pure citric acid is absent. Instead, two characteristic bands appear at 1583 and 1382 cm^{-1} corresponding to the symmetric and asymmetric COO^- stretching vibrations in carboxylate group ($\nu_{as}(COO^-)$, $\nu_s(COO^-)$), which would indicate the coordination of the citric acid to metal cations. The carboxylate group may bind to a metal cation in either a monodentate, bidentate, or bridging fashion. From the wavenumber separation, Δ , between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, the coordination type can be interpreted.²⁶ As $\Delta \approx 201\text{ cm}^{-1}$, it indicates that a monodentate complex forms between Ce^{3+} and the COO^- group of citric acid. The characteristic bands of polystyrene at 3082, 3059, 3024, 756 and 695 cm^{-1} are still found.

In the spectrum of the composite calcined at 200 °C (Fig. 7(b)), small characteristic bands of polystyrene at 2920 and 2848 cm^{-1} still remain, indicating that PS is not completely removed at this temperature. At 400 °C (Fig. 7(c)), the absorption bands at 1583 and 1382 cm^{-1} related to a COO^- stretching mode remain in the spectrum of the sample, but the intensity of the stretching is reduced. This demonstrates that at this temperature a partial decomposition of the organic

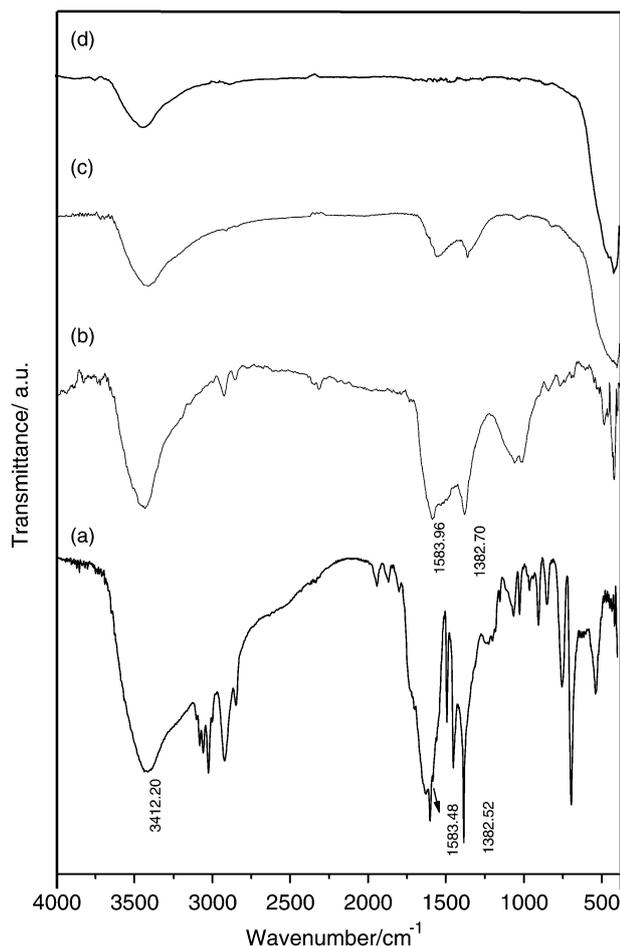


Fig. 7 FT-IR spectra of PS and CGO composites (a) 60 °C, (b) 200 °C, (c) 400 °C and (d) 600 °C.

components is occurring. Vibrations at about 430 cm^{-1} associated with metal oxygen stretching are observed, which indicates the presence of the CGO phase. Vibration bands relative to PS disappear, evidencing the complete removal of the organic template by this process. On further heating to 600 °C (Fig. 7(d)), the absorption peaks of the organic compounds disappear and the band of the Ce–O stretching vibration between 700 and 400 cm^{-1} becomes prominent.

Fig. 8 shows the X-ray diffraction (XRD) patterns of the macroporous samples calcined in air at 400, 600 and 700 °C. All the peak positions of the sample are in excellent agreement with those of authentic cubic CGO, indicating that the CGO phase is formed without passing through any intermediate phases due to chemical homogeneity in the amorphous precursors. Crystallization occurs at 400 °C and as the temperature is increased to 700 °C, the intensity of the diffraction peaks is strengthened, but the overall shape of the pattern remains almost unchanged.

The samples calcined were investigated by XPS. In Fig. 9, the X-ray photoelectron spectroscopy survey spectrum of the 3-DOM CGO thin film is shown. According to this, the sample contains only Ce, O and Gd as well as a small amount of carbon. The existence of a C1s peak is mainly caused by CO_2 , which is absorbed by the surface of the sample. High-resolu-

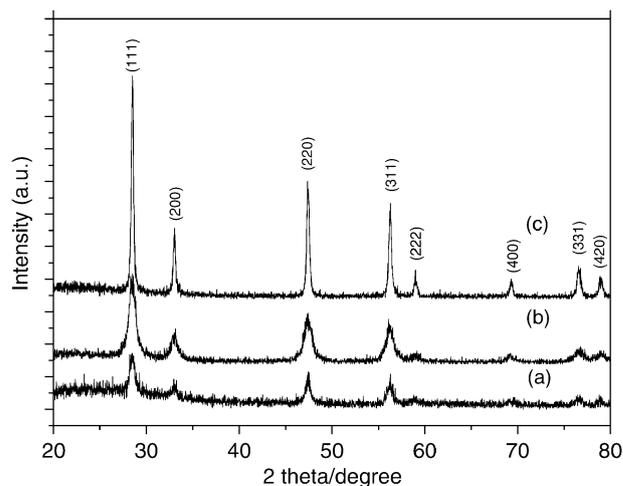


Fig. 8 X-Ray diffractograms of CGO nano-crystals prepared by the organic gel method at (a) 400 °C, (b) 600 °C, (c) 700 °C for 4 h in ambient air.

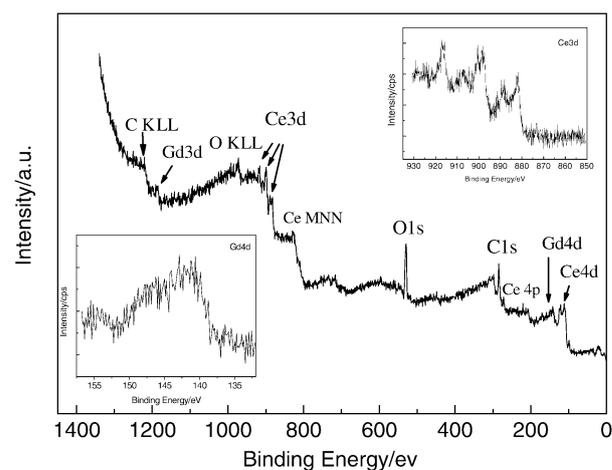


Fig. 9 Survey X-ray photoelectron spectrum of the 3-DOM CGO film. The left inset is the higher resolution spectrum of Gd 4d. The right inset is the higher resolution spectrum of Ce 3d.

tion spectra of Ce 3d and Gd 4d are shown in the insets of Fig. 9. The six-line spectrum of Ce 3d is characteristic of the Ce(IV) core level with the Ce($3d_{5/2}$) and Ce($3d_{3/2}$) peaks at 882.0 eV and 900.6 eV, respectively, which indicate that the 3-DOM CGO contains Ce(IV) only. For the core level of Gd in the CGO, it shows the $4d_{5/2}$ and $4d_{3/2}$ peaks at 141.8 and 146.6 eV, respectively. The line shape and peak positions are in agreement with earlier published data, confirming that the sample contains Gd(III).²⁷ The oxygen 1s signal can be resolved into two peaks, where the main peak at a binding energy of 529.4 eV refers to the lattice oxygen of the gadolinia-doped ceria and a smaller one at 531.7 eV can be ascribed to adsorbed oxygen.

Conclusions

We have demonstrated a promising route to prepare well-ordered macroporous gadolinia-doped ceria. The method reported here is simple, inexpensive and effective. It makes

use of common reagents and does not require a special atmosphere. This method can be extended to produce other macroporous rare earth oxides, which are difficult to prepare using the sol-gel method due to the lack of some commercial metal alkoxides.

The concentration and pH value of the CGO precursor, the infiltration times and heating rate affect the structure of the macroporous films. XRD and FT-IR have been used to investigate the phase development and crystallinity of the CGO films. The results have confirmed that the desirable cubic phase is formed after calcination at 600 °C. The oxidation level of CGO is verified by XPS and the binding energies are in agreement with earlier published data on Ce(IV) and Gd(III). Further investigations on the physical and chemical properties of 3-DOM materials are in progress.

Acknowledgements

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