



Synthesis and characterization of biomorphic CeO₂ obtained by using egg shell membrane as template

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Abstract

A new technology based on bio-templating approach was proposed in this paper. Egg-shell membrane (ESM) has been employed as a natural biotemplate. Fibrous oxide ceramics was prepared by wet impregnation of biological template with water solution of cerium nitrate. The template was derived from membranes of fresh chicken eggs. Repeated impregnation, pyrolysis and final calcination in the range of 600 to 1200 °C in air resulted in template burnout and consolidation of the oxide layers. At low temperatures, the obtained products had structure which corresponded to the negative replication of biological templates. Unique bio-morphic CeO₂ microstructures with interwoven networks were synthesized and characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD), whereas low-temperature nitrogen adsorption (BET) method was used in order to characterize porous properties.

Keywords: bio-templating, CeO₂, microstructure, SEM, XRD, BET

I. Introduction

Template synthesis is an effective way to control ceramic morphology, specific functional properties and structure [1–3]. One of the methods for preparing template ceramics is biological templating. Namely, the morphology of bioorganic materials is characterized by hierarchically ordered structure ranging from millimetre to nanometre scale. The use of natural biological materials as templates offers the possibility to manufacture novel hierarchical ceramic materials with unique and complex microstructure [4]. So far, several types of biological materials such as diatoms, bacteria, pollen, chitin, wood, cotton and egg-shell membrane (ESM) have been used as a template [5–7]. Until now, biomorphic ZrO₂ [8], ZnO, CoO₄, PdO [9], SiC [10] and Ce_xZr_{1-x}O₂ [11] have been synthesised. Bio-templates such as butterfly wing and egg-shell membrane (ESM) are especially attractive for synthesizing metal oxide ceramics because of strong metal-protein bonding. ESM is a cheap and easily available biomaterial with an interwoven fibrous structure. Unlike the ceramics synthe-

sized by other templates, the ESM-templated ceramics could tolerate high temperatures owing to the interwoven fibrous structure.

One of the most important interests is development of materials that are suitable for trapping radioactive waste. Among ceramic materials, ceria (CeO₂) has a high positional as a host material for radioactive isotopes storage [1–3,12]. Furthermore, ceria is very important as a model material for studying plutonia properties. Ceria and plutonia have quite similar physicochemical properties such as ionic size in octahedral and cubic coordination, melting point, standard enthalpy of formation and specific heat [4–6]. Therefore, the plutonium chemistry could be simulated using ceria instead of highly active PuO₂ [7]. CeO₂ can also make a stable solid solution with many di- and trivalent ions [13], which makes it suitable for transmute and host materials [14–16].

Since the key factor in the preparation of host materials is to tailor and control morphology, the aim of the present paper is to describe the technological approach for the synthesis of biomorphous ceria ceramics for possible application as a host material for radioactive isotope storage. According to the authors' knowledge,

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there is no report on the previous work on the synthesis of biomorphic ceria ceramics from ESM template.

II. Experimental

ESM were extracted from the fresh chicken eggs. The membranes were washed and immersed in 1 M water solution of $\text{Ce}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$ for seven days. After drying, the samples were pyrolysed at 600°C in argon, for 2 h. In order to eliminate the residual organic compounds and study crystallization process, the samples were subsequently calcinated at different temperatures (600 , 800 , 1000 and 1200°C) for 2 h, in air.

Ceria samples were characterized by recording their powder X-ray diffraction (XRD) patterns on a Siemens D500 X-ray diffractometer with $\text{Cu K}_{\alpha 1,2}$ radiation, at room temperature. Data were taken in the 20 – $80^\circ 2\theta$ range, with the step of 0.03° and scanning time of 5 s per step.

The scanning electron microscopy (SEM) observation was carried out on ceria samples using the JEOL 6300F microscope. For SEM analysis of biotemplated ceria samples, the electron microscope model FE-SEM Jeol JSM 6330F (Japan) was used. The samples were pre-coated with a several nanometers thick layer of gold before observation. For coating procedure, a device Fine Coat JFC - 1100 Ion Sputter, company JEOL was used. The images were recorded in SEI mode at a magnification of $\times 1000$ up to $\times 10000$, with the accelerating voltage of 30 kV. Energy-dispersive X-ray spectroscopy analysis was carried out at the invasive electron energy of 30 keV by means of QX 2000S device, a product of the company Oxford Microanalysis Group.

Adsorption and desorption isotherms of N_2 were

measured on the obtained powder at -196°C using the homemade gravimetric McBain method [17]. Mass changes of the sample due to adsorption or desorption of the gas was determined from the change in the length of the quartz spiral on which the sample was hanged. Changing of the length of spiral was read using cathetometer. Before the start of the measurement, samples were degassed at 120°C and kept at vacuum for 24 h. Achieved vacuum was measured using Pirani meter (measuring range 5.6×10^{-3} – 1×10^3 mbar, with a measurement error of 2% for pressure 10^{-2} mbar). The size range order mbar pressure measurement was performed mercury manometer.

III. Results and discussion

The XRD patterns of ceria samples obtained after thermal treatment in argon as well as calcination at different temperatures are presented in Fig. 1. All Bragg peaks with Miller indices were associated with the cubic lattice of pure CeO_2 (CeF_2 structural type), and was in good agreement with literature data (JCPDS No. 34-0394). Figure 1 reveals that CeO_2 can be formed after pyrolysis even at temperature as low as 600°C . Furthermore, secondary crystalline phases were not observed in pyrolysed sample indicating that residual carbon is in an amorphous form. Detailed study on the residual carbon had not been conducted since the subsequent calcination in air was supposed to completely remove carbon. Figure 1 also shows that calcination at different temperatures increases the intensity of characteristic CeO_2 peaks. This result is quite expected knowing that the increased temperature improves diffusivity leading to faster crystallization of CeO_2 . At calcinations tem-

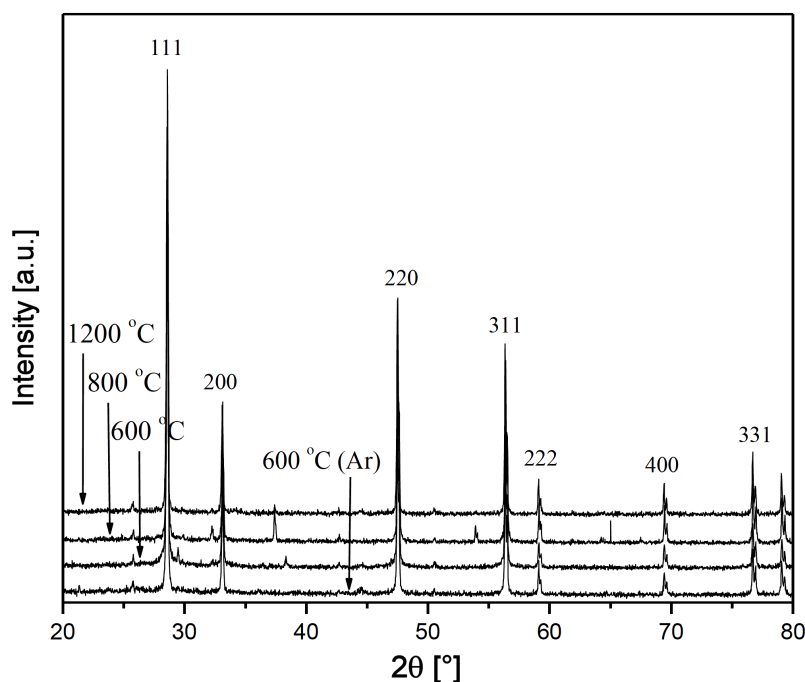


Figure 1. X-ray diffraction patterns of CeO_2 samples pyrolysed at 600°C in argon and samples subsequently calcinated at different temperatures

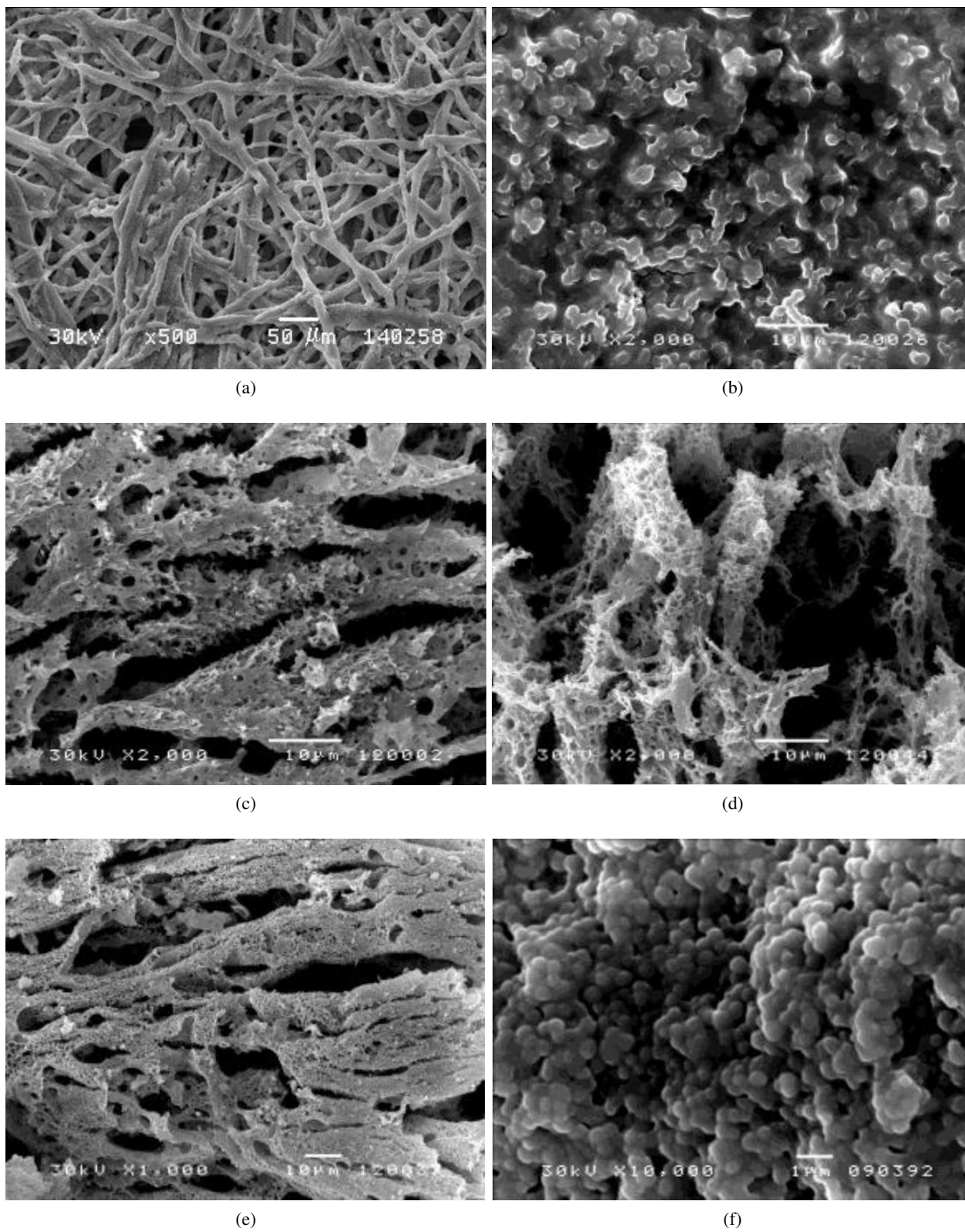


Figure 2. SEM images of CeO₂ samples: a) impregnated ESM, b) CeO₂ sample obtained at 600 °C in argon flow, c-f) CeO₂ samples obtained at 600, 800, 1000 and 1200 °C, in air, respectively

perature at 600 and 800 °C there is also a formation of some unknown secondary phase in small amount, because some additional peaks are observed. But it is important to emphasize that at higher temperature this phase disappears.

Figure 2 presents SEM images of the initial ESM template, as well as of the impregnated EMS samples pyrolysed at 600 °C and the finally calcinated samples at different temperatures.

The initial ESM possesses fibrous nano-porous structure composed of interlaced protein fibres, with diameter of $\sim 2 \mu\text{m}$, as it was shown in Fig. 2a. The impregnated EMS fibres with $\text{Ce}(\text{NO}_3)_3$ solution are represented at Fig. 2b. Although Fig. 2b cannot prove that the fibres are infiltrated with nitrate solution, the porous microstructure of sample pyrolysed at 600 °C in argon (Fig. 2c) clearly shows that nitrate solution was actually infiltrated into EMS fibers. Thermal decomposition of the fibre material during pyrolysis leaves pores that are surrounded by the infiltrated cerium nitrate which crystallizes as CeO_2 , which means that the interwoven fibrous structure was replicated, as shown in Fig. 2c. The sample calcinated at 600 °C is more porous than the sample pyrolysed in argon (Fig. 2c,d). The increased porosity is considered to be the result of oxidation and consequent removal of residual carbon that occurs during calcinations in air.

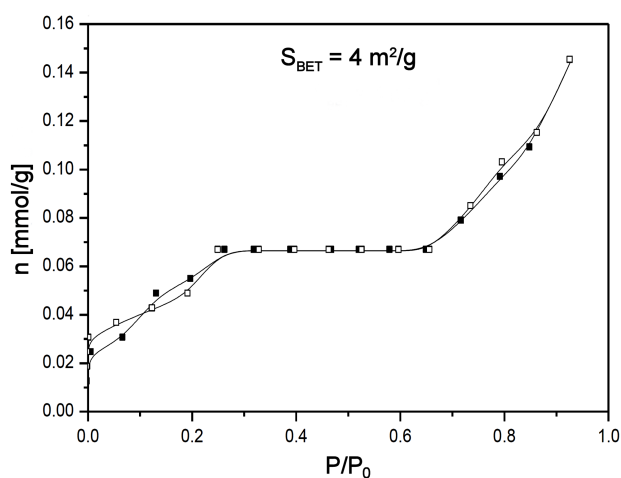


Figure 3. Nitrogen adsorption isotherm for CeO_2 sample calcinated at 600 °C (solid symbols – adsorption, open symbols – desorption)

As Fig. 2e shows, further increase in calcinations temperature to 800 °C does not change porosity in any significant way. It can be explained by the fact that temperature of 600 °C is sufficiently high for complete oxidation of carbon and further increase in temperature cannot introduce additional porosity. However, an increase of calcinations temperature to 1000 °C completely changes the morphology. Figure 2f reveals that microstructure of the sample calcinated at 1000 °C in air consists of spherical grains. It seems that temperature of 1000 °C is sufficiently high to promote sintering and cause considerable shrinkage which is followed by dis-

integration of fibrous network into porous lumps. After 2 hours long calcination the lumps transform into spherical grains of CeO_2 with maximum diameter of $4 \mu\text{m}$. Further increase in calcination temperature causes sintering of these, newly formed CeO_2 grains. Formation of neck between CeO_2 particles and elimination of porosity after calcination at 1200 °C can be clearly seen in Figure 2g. Although pore elimination, i.e., densification is evident, there is no considerable grain growth of CeO_2 as temperature is still much lower than 1500 °C, which is temperature required for fabrication of dense CeO_2 samples.

Nitrogen adsorption measurements on the pyrolysed and calcinated CeO_2 have showed that the obtained samples have low specific surface. Typical adsorption isotherm, for the CeO_2 sample calcinated at 600 °C, is presented at Fig. 3. The nitrogen adsorption isotherms of other samples are very similar and, for the clarity of presentation, did not show. According to the IUPAC classification [17] isotherms are of type II, which are frequently encountered when adsorption occurs on non-porous materials or materials with macropores or open voids. Specific surface areas calculated by BET equation, S_{BET} , for all samples, are below $5 \text{ m}^2/\text{g}$. Literature data about surface area of ESM [18] showed that S_{BET} is below $2 \text{ m}^2/\text{g}$. Since the obtained samples are replica of the ESM template, low specific surface is a consequence of the template structure. On the other side, our results about S_{BET} are not in agreement with some literature data where the authors reported $S_{\text{BET}} = 66 \text{ m}^2/\text{g}$ for $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ synthesized using the ESM as template [11].

IV. Conclusions

Biomorphic ceria was synthesized by infiltration of cerium nitrate hexahydrate in ESM template. Firstly, samples were dried out, then pyrolysed at 600 °C and at the end calcinated at 600–1200 °C. XRD of prepared samples revealed that CeO_2 can be formed after pyrolysis even at temperature as low as 600 °C. The calcination at different temperatures increases the intensity of characteristic CeO_2 peaks. No secondary crystalline phases were observed after pyrolysis. SEM analysis reveals porous bio-morphic CeO_2 microstructures with interwoven networks of obtained samples at low temperatures (600 and 800 °C). The increase of calcinations temperature to 1000 °C completely changes the morphology of the samples. The microstructure of the sample calcinated at 1000 °C in air consists of spherical grains, which means that temperature of 1000 °C is sufficiently high to promote sintering. Nitrogen adsorption measurements have shown that the samples are macroporous. Consequently, the specific surfaces of all samples are below $5 \text{ m}^2/\text{g}$. The obtained ceramics have a potential to serve as a host material for storage of radioactive isotopes. Specific surface area of the obtained material is not quite well developed, nevertheless material is porous and it has fibrous microstructure so it can

mechanically store other materials in the pores, which will be bounded to the walls of CeO_2 . Namely, relatively open fluorite type of crystal structure that CeO_2 has is capable of picking up radioactive trash (radioactive isotopes), which can even react with the wall of CeO_2 , resulting in formation of real solid solution.

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