Preparation of Nanocrystalline CeO\textsubscript{2} by nanocasting with mesoporous silica

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Abstract. Nanocasting is one of the methods that can be used to prepare nanostructured materials. The mesoporous silica with \textit{Ia3d} structure was used as template for the nanocrystalline CeO\textsubscript{2} synthesis. The as synthesized CeO\textsubscript{2} powder was characterized with XRD and TEM. The crystal size was determined to be about 8.3 nm, a little smaller than that of the pore size of the mesoporous silica used.

1. Introduction

Nanostructured materials, a new branch of materials research, are attracting a great deal of attention because of their potential applications in the areas such as electronics, optics, catalysis, ceramics, magnetic data storage and nanocomposites. The unique properties and the improved performances of nanomaterials can be determined by their sizes, surface structures and inter-particle interactions [1]. The development of synthetic strategies to obtain nanocrystals has progressed impressively in the last decade. Nanocasting is one of the methods that could be used to obtain nanostructured materials. In this case, the nanocrystals are formed in the confined space of a host material. The host can be soft, for instance micelles formed by the self assembly of diblock copolymers [2] or hard, for instance anodic alumina membranes [3], single-wall carbon nanotubes [4], crystalline microporous or mesoporous solids. Among the variety of potential hard hosts, mesoporous silicas, have several advantages: their uniform mesopore dimensions that can be adjusted; several channel structures (ranging from layers to 3D) are available; after crystallization of the nanostructures, the silica template can be removed by acidic or basic chemical treatments.

Basically, the nanocasting route comprises three steps: Infiltration of the porosity of the template with a solution containing the precursors of the synthesized material; Heat treatment under a controlled atmosphere of the impregnated template to convert the infiltrated precursor into the synthesized material and the third to remove the template framework, by dissolution or by oxidation at high temperatures. Due to the fact that the synthesis takes place in a confined nanospace, the sintering of the particles is restricted and the preparation of high surface area materials (nanostructures or nanoparticles) is achieved [5].

Crystalline CeO\textsubscript{2} materials are often desired for potential applications, e.g. with respect to their catalytic [6], gas sensing [7, 8], or ion conducting properties [9]. In this paper, nanocrystalline CeO\textsubscript{2} was synthesized by nanocasting with mesoporous silica as template.
2. Experimental
The mesoporous silica used as template in this experiment was synthesized by Ting Yu, the Ph.D student from DY Zhao’s group at Fudan University, China. The synthesis route of the mesoporous silica is referred to the publication [10], just the sodium dodecyl sulfate (SDS) was replaced by FC80. Impregnation experiment was performed by dissolving 1.5 g of mesoporous silica in 8 g ethanol, then 0.5 g Ce(NO\(_3\))\(_3\)•6H\(_2\)O was added to this solution and stirred for 2 h. The resultant mixture was dried at 40°C and calcined at 300°C for 3 h. 8 g ethanol was added to the dried powder again and stirred, then 0.3 g Ce(NO\(_3\))\(_3\)•6H\(_2\)O was added to the solution. The resultant mixture was dried at 40°C and calcined at 550°C for 5 h. The obtained CeO\(_2\)–silica composite powder from above procedure was washed in 20 ml of 2 mol/L NaOH solution in order to dissolve the mesoporous silica wall.

The CeO\(_2\) powder was performed the XRD analysis with D/Max 2550 diffract meter. The sample for TEM observation is prepared with the powder dissolving in ethanol and then dried on a holy carbon film grid. The TEM work is done in the Tecnai G\(^2\) 20 ST TEM with 200 kV accelerating voltage.

3. Results and discussions
The TEM observation of mesoporous silica is shown in Figure 1. The unit cell of the mesoporous silica was determined to be about 21 nm, with Ia\(^3\)d structure and the pore size is about 9 nm. The image in Fig. 1 is obtained along the [111] direction of the mesoporous silica structure. It can be clearly seen that the mesoporous silica used in this experiment is well ordered. The CeO\(_2\) powder was synthesized by taking this mesoporous silica as template with the route described in the experimental section.

![Figure 1. The image of Ia\(^3\)d mesoporous silica taken along [111] direction](image)

The XRD pattern of the obtained CeO\(_2\) powder is shown in Figure 2. From the peaks presented in the figure, one can certain that the CeO\(_2\) powder synthesized with nanocasting method has Fluorite structure with the space group Fm-3m and the lattice parameter \(a = 5.4104\) Å. From the broaden peaks in the figure, we can measure that the half width for the (111) peak is about 0.948°. In Debye-Scherrer equation \(d\) is the average grain size, \(K\) is set to be 0.89 for normal, \(\lambda\) is the wavelength of X ray (1.54184 Å), \(\beta\) is the half width of the diffraction peak and \(\theta\) is the Bragg diffraction angle.

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d = \frac{K \times \lambda}{\beta \cos \theta}
\]

From this equation, the calculated grain size for the synthesized CeO\(_2\) powder is about 8.3 nm, which is a little smaller than the pore size of mesoporous silica.
Figure 2. The XRD pattern of the synthesized CeO₂ powder.

The TEM image of the synthesized CeO₂ powder is shown in Figure 3. From the image, we can see that the powder size is about 9 nm, similar to that calculated by the Debye-Scherrer equation from the XRD result. The particles are mostly with unique size and quite well separated. It could be concluded that nanocasting is a very powerful and useful way for synthesis of nano particles. Also the nano particles from nanocasting could be separated and with very narrow particle sizes distribution.

Figure 3. The TEM image of synthesized CeO₂ powder.

4. Conclusions
By controlling the synthesis condition, nanocrystalline CeO₂ powder with unique particle size can be obtained. By XRD and TEM analysis, the particle size of CeO₂ powder obtained from the nanocasting by using the ordered mesoporous silica as template is a little smaller than that pore size of the mesoporous silica. It was testified that the synthesis of CeO₂ powder is confined to the nanospace of mesoporous silica. So nanocasting is very powerful and useful method that can be used to prepare nanostructured materials, especially nanomaterials, which is difficult obtained by other synthetic method.
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