

Synthesis of thermally stable mesoporous cerium oxide with nanocrystalline frameworks using mesoporous silica templates†

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Highly ordered mesoporous cerium oxides, composed of nanocrystalline pore walls and exhibiting high thermal stability even at 973 K, were synthesized using mesoporous silica templates with hexagonal $p6mm$ and cubic $Ia3d$ symmetries.

Cerium oxide is particularly interesting because of its catalytic activity and the ability to store and release oxygen depending on the redox environment. It is widely used as a promoter in three-way catalysts for the elimination of toxic auto-exhaust gases. Other large-scale applications include its uses as catalyst for fluid catalytic cracking in refineries and dehydrogenation of ethylbenzene to styrene. The catalytic performance in many of these applications can be improved by the preparation of thermally stable mesoporous CeO_2 with a uniform pore structure. To date, several attempts have been made to synthesize cerium oxides with uniform mesopores. However, reports on the synthesis of highly ordered thermally stable mesoporous CeO_2 with nanocrystalline walls are scanty.^{1,2}

Here we report the synthesis of highly ordered mesoporous cerium oxide of different structures using silica templates. Our synthesis procedure involves the incorporation of CeO_2 precursors into a mesoporous silica template, their conversion to cerium oxide, and the removal of the silica template. Mesoporous cerium oxides synthesized following this procedure exhibit ordered mesostructures with high similarities to the hexagonal $p6mm$ and cubic $Ia3d$ symmetries of the silica templates. Further, the template-free mesoporous materials are composed of nanocrystalline CeO_2 frameworks and exhibit remarkable stability in air at temperatures as high as 973 K.

The hexagonal SBA-15 silica template with $p6mm$ symmetry was prepared in aqueous solution using Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, MW = 5800, Aldrich) and sodium silicate solution ($\text{Si}/\text{Na} = 1.5$), following the recently-developed synthesis procedure using low HCl concentrations to facilitate the thermodynamic phase control.³ After calcination at 823 K, the SBA-15 silica exhibited a narrow distribution of pore diameters centered at 7.5 nm (determined by the BJH method using the adsorption branch of the N_2 isotherm). The extra-large mesoporous cubic $Ia3d$ silica was also prepared in aqueous solution at a similar HCl concentration using Pluronic P123 and sodium silicate, along with butanol as an auxiliary phase-controlling agent.⁴ The $Ia3d$ silica exhibited well-resolved X-ray powder diffraction (XRD) peaks, which were very similar to those for high-quality MCM-48 silica samples except for its comparatively very large lattice spacing ($a = 22.9$ nm after calcination at 823 K). The average mesopore diameter of the cubic $Ia3d$ silica was 9.5 nm.

The calcined cubic $Ia3d$ and hexagonal silicas were used to prepare mesostructured cerium oxides. In a typical synthesis, 2.0 g of cerium trichloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, 99%, Aldrich) was

dissolved in 1.0 g of distilled water. This solution was incorporated into 0.5 g of pure siliceous cubic $Ia3d$ template using the incipient wetness impregnation technique. After drying in an oven at 373 K, the cerium precursor/silica composite was contacted with ammonia vapor at 298 K in order to convert the cerium precursor to the metal hydroxides. Calcination of the composite at 973 K gave cerium oxide inside the silica template. The process (incorporation–neutralization–calcination) was repeated two more times with aqueous solutions of 1.5 g $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (in the second phase) and 1.0 g $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (in the third phase) to prepare crystalline cerium oxide nanorods inside the silica template. The silica template was then removed from the cerium oxide–silica composite by treating several times with dilute (1–2 M) NaOH solution.

Energy dispersive X-ray analysis (EDX) at different places of the samples confirmed almost complete removal of the silica template from the washed cerium oxide samples (see ESI†). The cerium oxide product obtained from the cubic $Ia3d$ mesoporous silica template exhibits XRD peaks characteristic of the same space group as for the silica template (Fig. 1). The transmission electron microscopic (TEM) analyses, as shown in Fig. 2, also indicate that the cerium oxide exhibits a high similarity to the cubic $Ia3d$ symmetry over a long range (ESI†).⁵ Highly ordered two-dimensional hexagonal cerium oxide was also prepared using SBA-15 as the template as confirmed by the XRD pattern and TEM images (Fig. 2 and ESI†). The nanocrystalline nature of the CeO_2 samples was confirmed by TEM (ESI†). The wide-angle X-ray reflections ($2\theta = 20$ – 80°) of the mesoporous CeO_2 samples are quite broad and low in intensity as compared to the

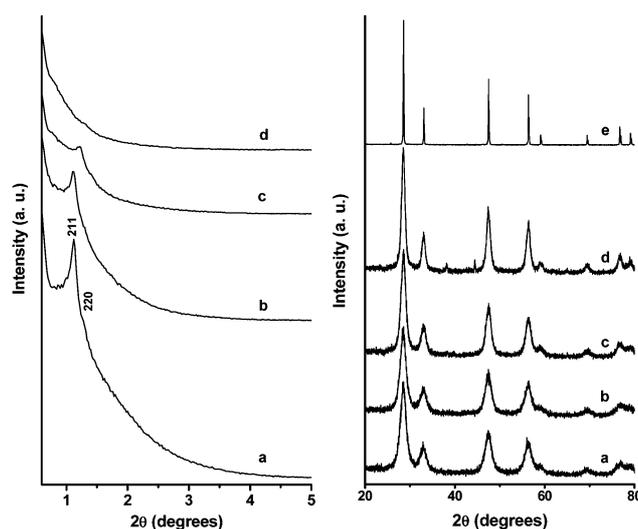


Fig. 1 Powder XRD patterns in low and wide-angle regions of the CeO_2 sample synthesized with cubic $Ia3d$ silica template: a) obtained after the removal of its template, and after subsequent calcination at b) 773 K, c) 973 K, and d) 1073 K. The same sample was repeatedly calcined for 4 h at each temperature after reaching the temperature at heating rate of $1.5^\circ \text{min}^{-1}$. Curve 'e' represents XRD peaks of commercial CeO_2 . The XRD patterns were obtained using $\text{CuK}\alpha$ X-ray source on Rigaku D/MAX-III operated at 2.0 kW.

† Electronic supplementary information (ESI) available: EDX profile of cerium oxide samples (Figure 1), XRD patterns for hexagonal CeO_2 (Figure 2), additional TEM images (Figure 3), and N_2 adsorption–desorption isotherm at 77 K for hexagonal CeO_2 and pore size distribution calculated using the BJH method (Figure 4). See <http://www.rsc.org/suppdata/cc/b3/b305524h/>

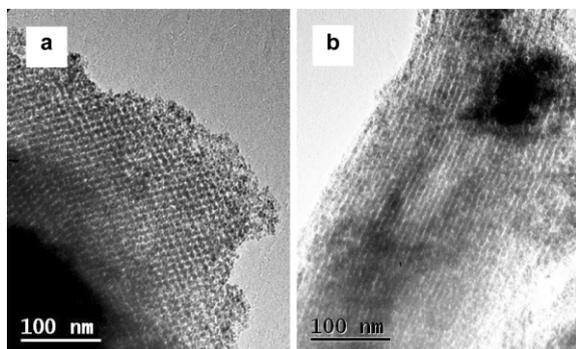


Fig. 2 TEM images of the template-free CeO_2 samples: a) synthesized with cubic $Ia3d$ silica template, and b) 2D hexagonal $p6mm$ template. The image in 'a' shows a high similarity with images taken along the [110] direction of cubic $Ia3d$ mesoporous carbons,⁵ and the image in 'b' corresponds to the [100] direction of the $p6mm$ structure. The images were taken from thin edges of particles supported on porous carbon grid, using a Philips F20 Tecnai instrument, operated at 160 kV.

bulk CeO_2 (cubic fluorite type) phase, signifying that the mesoporous walls of the present mesoporous CeO_2 samples are composed of nanocrystalline CeO_2 frameworks (Fig. 1) as was also observed by TEM. N_2 adsorption–desorption isotherms and the corresponding pore size distribution curve (inset) of $Ia3d$ CeO_2 sample are shown in Fig. 3 (see ESI† for N_2 isotherm and pore size distribution of hexagonal cerium oxide). The pore-size distribution is narrow and centered at ~ 3.5 nm. The BET surface area, and total pore volume of $Ia3d$ CeO_2 ($198 \text{ m}^2\text{g}^{-1}$, $0.24 \text{ cm}^3\text{g}^{-1}$), are in good agreement as reported in the literature.

The thermal stability of the template-free mesoporous CeO_2 samples has been investigated by XRD and BET surface area measurements, after calcination at different temperatures. Although the BET surface area of CeO_2 decreased by $\sim 40\%$ on heating from 273 to 973 K, the samples still show a well-defined diffraction peak in the small-angle region and nanocrystalline order in the wide-angle XRD (Fig. 1). The N_2 adsorption isotherm still shows the adsorption jump at $P/P_0 \approx 0.5$ – 0.7 , characteristic of capillary condensation in the mesopore. Therefore, it can be concluded that the thermal treatment does not lead to a collapse of the mesostructure as also evidenced by the well-resolved TEM images.

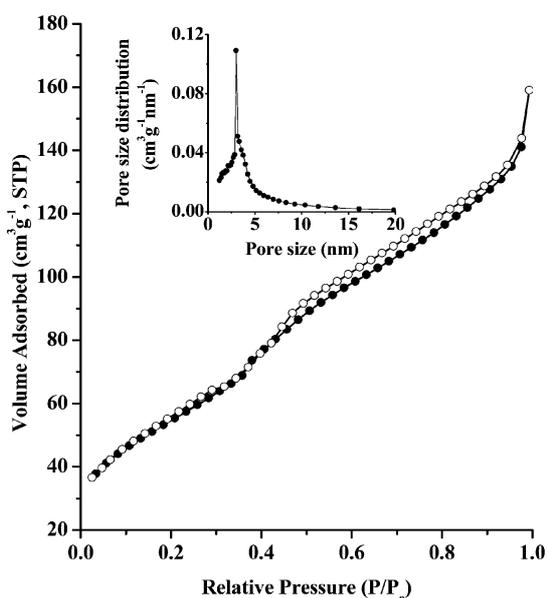


Fig. 3 N_2 adsorption–desorption isotherm at 77 K for the CeO_2 sample synthesized with cubic $Ia3d$ silica template (Quantachrome Autosorb-1MP) and pore size distribution (inset) calculated with the adsorption branch using the BJH method.

Mesoporous cerium oxides can also be synthesized via the direct supramolecular templating approach using surfactants, similar to the syntheses of mesoporous silicas.^{6–13} However, the as-synthesized cerium oxides do not possess fully-condensed framework structures. Extensive sintering of the pore walls is therefore accompanied by severe condensation of the surface hydroxyl group upon calcination to remove the surfactants. In contrast to loss of the mesostructural integrity after calcination at high temperatures above 773 K, the present synthesis strategy using the rigid silica templates has the advantage of achieving sufficiently high degrees of the M–O–M (M = metal) cross-linking before the template removal. The silica template is generally removable from the composite by treating with dilute HF and/or NaOH solution. Therefore, mesoporous metal oxides that are not soluble, or affected by either dilute HF or NaOH can be prepared conveniently by the nanofabrication method. It is remarkable that recently there have been significant progresses in nanofabrication strategies using rigid mesoporous silica templates for the synthesis of mesoporous carbons, metals, metal oxides, and so on.^{14–18} These nanofabrication techniques provide new opportunities towards the synthesis of non-siliceous mesoporous metal oxides that are difficult to obtain through direct synthesis using surfactants. Mesoporous cerium oxide materials might receive much future attention to exploit their electronic, magnetic and catalytic properties.

In summary, we have synthesized very highly ordered mesoporous cerium oxides with uniform mesopore sizes. Strategically, this synthetic approach using a silica template is very significant to obtain cerium oxides of different structures and mixed oxides of various compositions. We have already confirmed that the synthetic approach can be extended for the synthesis of highly ordered nanocrystalline mesoporous SnO_2 and ZrO_2 .¹⁹ Ordered nanocrystalline mesostructured materials are expected to be very important for catalytic applications, since these metal oxides are well known as solid catalysts. Further investigations on these aspects are currently ongoing and will be reported in due course.

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