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A simple method to controlled synthesis of CeO_2 hollow microspheres

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CeO_2 hollow microspheres have been synthesized by hydrothermal decomposition reaction of $Ce(NO_3)_3$ on the surfaces of silica microspheres. The shell thickness of CeO_2 hollow microspheres can be controlled from 20 to 50 nm by adjusting the concentration of $Ce(NO_3)_3$ in the reaction solution. The high UV absorption of CeO_2 hollow microspheres indicates that this material is suitable as a UV-blocking material.

Keywords: Oxides; Nanostructures; Crystal growth; Electron microscopy; Optical properties

Cerium oxide is an important compound that has been used in many areas including high-storage capacitor devices, buffer layers for conductors, fuel cells, polishing materials, UV blocks and optical devices [1–13]. In addition, cerium dioxide has been widely used in automotive catalysts [6,14–19] due to its unique characteristic of facile Ce^{IV} and Ce^{III} switching. Stimulated by both their promising applications and their fantastic properties, much attention has been directed to the controlled synthesis of CeO_2 nanostructured materials. Over the past few years, a remarkable process has been developed for the synthesis of ceria with different morphologies and sizes due to its size/shape-dependent properties. For example, Chen et al. reported that novel single-crystalline-like CeO_2 hollow nanocubes were synthesized through a solvothermal method using peroxyacetic acid (PAA) as the oxidant in the absence of any templates. It was found that the prepared CeO_2 hollow nanocubes exhibited a higher catalytic activity toward CO oxidation [20]. Gao et al. synthesized composite hollow microspheres of CeO_2–ZrO_2 by using anionic PSA latex particles as template and then calcining the PSA core particles at 600 °C [21]. Zhang et al. reported that novel single/multiwall hollow CeO_2 microspheres were synthesized by self-assemblage through hydrothermal method without any surfactant [22]. Furthermore, novel slight yellow CeO_2 single/multiwall hollow microspheres were synthesized by the hydrothermal method without any surfactant. The catalytic activity and the recycling performance of the sample on CO oxidation were tested and the T-100% (the temperature at which there is 100% conversion of CO) was 230 °C in the first run and decreased by 270 and 205 °C compared with that of bulk CeO_2 and CeO_2 nanocrystal, respectively [23].

In recent years, a large effort has been directed toward to the fabrication of uniform hollow particles with nanometer- to micrometer-scale dimensions that consist of either organic or inorganic cores coated with shells of different chemical composition [24–29]. These hollow particles often exhibit properties that are substantially different from common particles, and have been applied in many fields, including capsule agents for drug delivery, catalysis, coatings, composite materials, and protecting sensitive agents such as enzymes and proteins [30–35]. Template synthesis is a commonly used tool in the preparation of porous materials. Previous investigations have demonstrated that polymeric particles and inorganic cores can be coated with layers of various materials, including silica, yttrium basic carbonate, and zirconium hydrous oxide, either by controlled surface precipitation reactions on the core particles or by direct surface reactions [36–40].

Up to now, ceria hollow spheres were rarely reported. Here, we report a simple method to controlled synthesis of CeO_2 hollow spheres by the decomposition reaction of $Ce(NO_3)_3$ using silica spheres as templates.

The uniform silica spheres were synthesized using the Stöber method [41]. In a typical synthesis of CeO_2 hollow microspheres, different concentrations of $Ce(NO_3)_3 \cdot 6H_2O$ (0.050, 0.075, 0.100 and 0.125 M) were dissolved

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in 40 ml deionized water containing 0.1 g silica sol particles and the resulting mixture was treated by ultrasound for 30 min to form homogeneous suspension (Kunshan, KQ-50E, 40 kHz, controlled temperature range from 0 to 80 °C). The obtained homogeneous suspension was transferred to a Teflon-line stainless steel autoclave, which was sealed and maintained at 200 °C for 24 h, and then air-cooled to room temperature. The resulting yellow precipitate was collected, washed with distilled water, and dried in air at room temperature. The yellow precipitate was treated with 0.5 M NaOH solution to remove the silica sol. The crystal structures of the resulting products were characterized by X-ray powder diffraction (XRD, D/MAX-500 X-ray powder diffractometer with Cu K_α radiation, $\lambda = 1.5418$ Å at 40 kV and 70 mA). The morphologies, sizes, optical performance and surface area of the resulting products were determined by field-emission scanning electron microscopy (FE-SEM, JSM 6700F), transmission electron microscopy (TEM, JEM-2000EX), a UV–vis spectrophotometer (Cary 500), and BET surface area analysis was determined using Micromeritics Tristar-3000 analyzer, respectively.

XRD analysis was carried out to investigate the phases of the as-synthesized products. A typical XRD pattern of the as-synthesized products is shown in Figure 1. All of the diffraction peaks in Figure 1 can be exactly indexed to the face-centered CeO_2 with lattice constants $a = 5.410$ Å, which are in good agreement with the literature values (JCPDS 34-0394).

Figure 2 shows SEM image of CeO_2 hollow spheres synthesized at the concentrations of 0.075 M $Ce(NO_3)_3$. The SEM photograph reveals that the as-synthesized products consist of uniform monodisperse spheres. Furthermore, it is clear that CeO_2 hollow spheres are composed of CeO_2 nanoparticles. Several individual broken hollow microspheres are present in the products as indicated by arrows in Figure 2, indicating that CeO_2 spheres possess hollow structures. The shell thickness of CeO_2 hollow spheres is 35 nm.

Figure 3 shows TEM images of CeO_2 hollow microspheres synthesized with different concentrations of $Ce(NO_3)_3$. The strong contrast between the core and edge indicates that CeO_2 microspheres are hollow. The shell thickness of CeO_2 hollow microspheres can be controlled by adjusting the concentrations of $Ce(NO_3)_3$ in the reaction solution. As the concentrations of $Ce(NO_3)_3$ are 0.050, 0.075, 0.100 and 0.125 M, the shell thickness are 20, 35, 45 and 50 nm, the diameters of

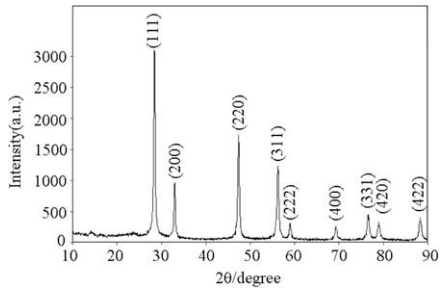

Figure 1. XRD patterns of as-synthesized CeO_2 hollow spheres.

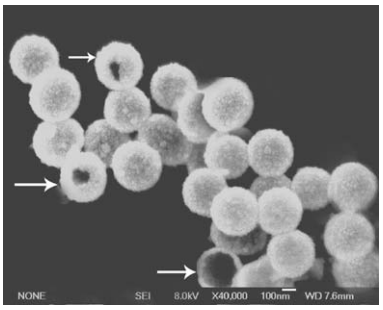

Figure 2. SEM image of as-synthesized CeO_2 hollow spheres synthesized at a concentration of 0.075 M $Ce(NO_3)_3$.

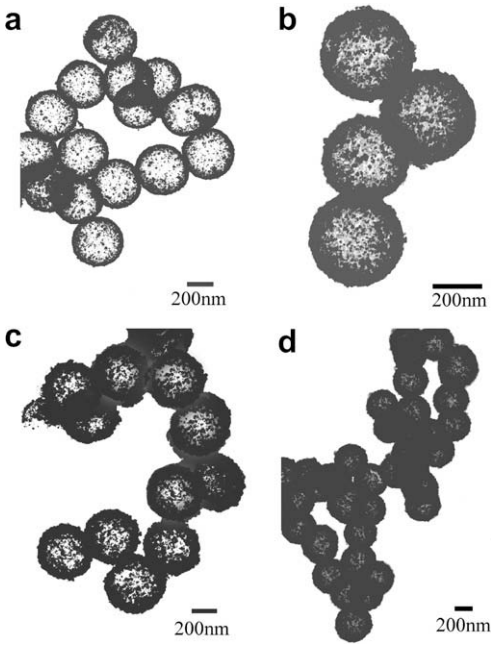

Figure 3. TEM images of as-synthesized CeO_2 hollow microspheres: the thickness of shell is (a) 20 nm, (b) 35 nm, (c) 45 nm and (d) 50 nm.

CeO_2 hollow microspheres are about 400, 430, 450 and 460 nm, respectively. The inner diameters of CeO_2 hollow microspheres are similar to that of silica microspheres. The BET surface area of CeO_2 hollow microspheres are 43.3, 35.4, 31.8 and 29.1 $m^2\,g^{-1}$, respectively.

Scheme 1 shows the overall procedure used to synthesize CeO_2 hollow microspheres. Before hydrothermal treating of the reaction solution, silica microspheres are dispersed in $Ce(NO_3)_3$ solution by ultrasonic vibration, a liquid–solid heterogeneous system is formed before nucleation of the CeO_2 nuclei. In such a system, the presence of ultrasound can enhance the reactions. The effects of interparticle collisions, microjets and shockwaves can drive high-speed jets of liquid to impinge upon the SiO_2 particles surface where they create a localized erosion to produce a newly exposed and highly active surface. Meanwhile, the ultrasound improves mass transport, and causes SiO_2 particles fragmentation which substantially increases the surface activity of the SiO_2 particles which have a large number of dangling bonds, defects or traps on their surface.