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Controlled synthesis of $Ce(OH)CO_3$ flowers by a hydrothermal method and their thermal conversion to CeO_2 flowers

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ABSTRACT

Highly uniform $Ce(OH)CO_3$ flowers were successfully prepared in large quantities using a facile hydrothermal approach from the reaction of $Ce(NH_4)(NO_3)_4$ with $CO(NH_2)_2$ at 160 °C in a water–N_2H_4 complex. The influences of the N_2H_4 content and temperature on flower formation were discussed. CeO_2 flowers were prepared by thermal conversion of $Ce(OH)CO_3$ flowers at 500 °C in air. Both $Ce(OH)CO_3$ and CeO_2 flowers were characterized by X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). The UV–vis adsorption spectrum of the CeO_2 flowers showed that the band gap energy (E_g) is 2.66 eV, which is lower than that of bulk ceria.

1. Introduction

As an important rare earth oxide and owing to its unique structure and low cost, CeO_2 has found considerable applications in solar-cell, optical devices, sensors, sunscreen materials, oxygen storage devices, electrical devices, catalysts, etc. (Corma, Atienzar, Garcia, & Chane-Ching, 2004; Hernández-Alonso et al., 2004; Huang et al., 2005; Imanaka, Masui, Hirai, & Adachi, 2003; Jiang, Zhang, Guo, Jin, & Tian, 2009; Liao et al., 2008; Tago, Tashiro, Hashimoto, Wakabayashi, & Kishida, 2003; Zhou, Zhao, Xu, & Yuan, 2007). Moreover CeO_2 can absorb UV light as well as small amount of visible light covering larger fraction of the solar spectrum than TiO_2. Therefore, CeO_2 is regarded as a suitable photocatalytic material for degradation of organic pollutants (Chen, Cao, & Jia, 2011; Ji, Zhang, Chen, & Anpo, 2008; Valente, Tzompantzi, & Prince, 2011).

Being different from conventional bulk ceria, nanoscale CeO_2-based materials exhibit some unique properties, such as the Raman-allowed modes shifting and broadening, lattice expansion, transition from boundary diffusion to lattice diffusion, blue shift in ultraviolet absorption spectra (Tsunekawa, Fukuda, & Kasuya, 2000; Weber, Hass, & McBride, 1994), and so on. Hence, the fabrication of nanocrystalline CeO_2 has been drawing much attention by the material scientists and chemists. So far, CeO_2 with various structures and morphologies have been synthesized successfully, such as mesoporous structures (Corma et al., 2004; Lyons, Ryan, & Morris, 2002; Srivastava, 2010), 1D nanotubes (Tang, Bando, Liu, & Golberg, 2005; Wu & Kawi, 2010), nanorods (Lin, Wu, & Chiang, 2010; D.S. Zhang et al., 2007; Zhou, Wang, Sun, Peng, & Li, 2005), and nanowires (Liao et al., 2008; Lu et al., 2010; Tang, Zhuo, et al., 2005; Wang & Li, 2003), 2D nanobelts (Li, Qu, & Tong, 2008), nanocubes (Qian, Zhu, Du, & Qian, 2009; Yang & Gao, 2006), and nanopolyhedra (Mai et al., 2005; Si, Zhang, You, & Yan, 2005), and so on (Li et al., 2011).

It is known that the morphology of materials has important effects on their properties. Recently, the preparation of three-dimensional (3D) micro/nano-composite with microscale morphology formed by assembly of nanoscale building blocks, is of great interest, because the hierarchical structure with cooperation of micro- and nanostructure would exhibit unique properties and novel functionalities (Liu & Zeng, 2004; Yan & Xue, 2005; L.S. Zhang et al., 2007; Zhu et al., 2008). Many efforts have been devoted to synthesizing 3D micro/nano-CeO_2 with various composites and morphologies based on different driving mechanisms. For example, Zhong et al. (2007) reported the preparation of 3D flowerlike ceria at 180 °C with TBAB as a surfactant and EG as a solvent. Three-dimensional flowerlike CeO_2 microspheres can also be synthesized in the glucose/acrylic acid or glucose/acrylamide synthesis system at 180 °C for 3 days (Li et al., 2010; L.S. Zhang et al., 2007). In this paper, we report a simple approach to synthesize 3D $Ce(OH)CO_3$

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flowers from aqueous solution containing $Ce(NH_4)(NO_3)_4$ and urea and their thermal conversion to polycrystalline CeO_2 flowers. This method does not need any template or seed, thus avoiding subsequent complicated workup for removing the template or seed.

2. Experimental

All the analytical chemicals were purchased from Shanghai Chemical Reagents Company and used without further purification. A typical experiment was as follows: 10 mL hydrazine hydrate (N_2H_4, 80 wt%) were added into 35 mL aqueous solution of 0.15 g $Ce(NH_4)(NO_3)_4$ under stirring. Then 0.3 g urea was added. The whole mixture was stirred for another 30 min to obtain a homogeneous solution and subsequently transferred into a 50 mL autoclave. Due to the highly toxic and potentially explosive nature of hydrazine, all operations were performed in a hood. Then the autoclave was maintained at 160 °C for 24 h and then allowed to cool to room temperature by cold water. The white-colored precipitate was centrifuged, washed with absolute alcohol and distilled water, and dried at 80 °C under vacuum. Finally, to obtain CeO_2 particles, the white precipitate was calcined at 500 °C for 6 h, accompanied by a color change from white to slight yellow.

X-ray powder diffraction (XRD) patterns were determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images were taken with a JEOL JSM6700F scanning electron microscope.

3. Results and discussion

Fig. 1 presents the typical XRD pattern of the as-prepared $Ce(OH)CO_3$ samples. All the peaks could be indexed to the hexagonal phase of cerium carbonate hydroxide (JCPDS Data File # 32-0189). The strong and sharp reflection peaks suggest that the as-prepared products are well crystallized. No impurity peaks are observed, indicating the high purity of the final products.

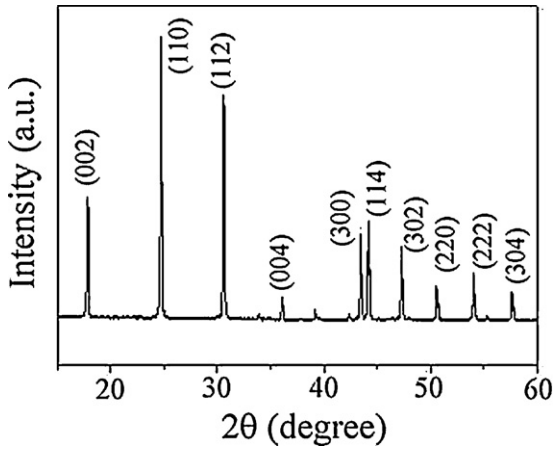

Fig. 1. XRD pattern of the $Ce(OH)CO_3$ precursor.

The micro-flowers were synthesized on a large scale and in high purity. Fig. 2 shows typical SEM images of $Ce(OH)CO_3$ flowers. The low-magnification image (Fig. 2(a)) shows that the product consists almost entirely of flower-like structures, indicating both high yield and good uniformity achieved with this approach. The magnified images (Fig. 2(b) and (c)) show that follower exhibited hierarchical and symmetric structure, comprising two layers epitaxially attached and fused together. Close examination indicated that each layer was made up of several folds radiating from the center (Fig. 2(d)). The as-prepared superstructures were very stable, and even long-time ultrasonication for 30 min could not break them into discrete platelets, suggesting that the flowers were

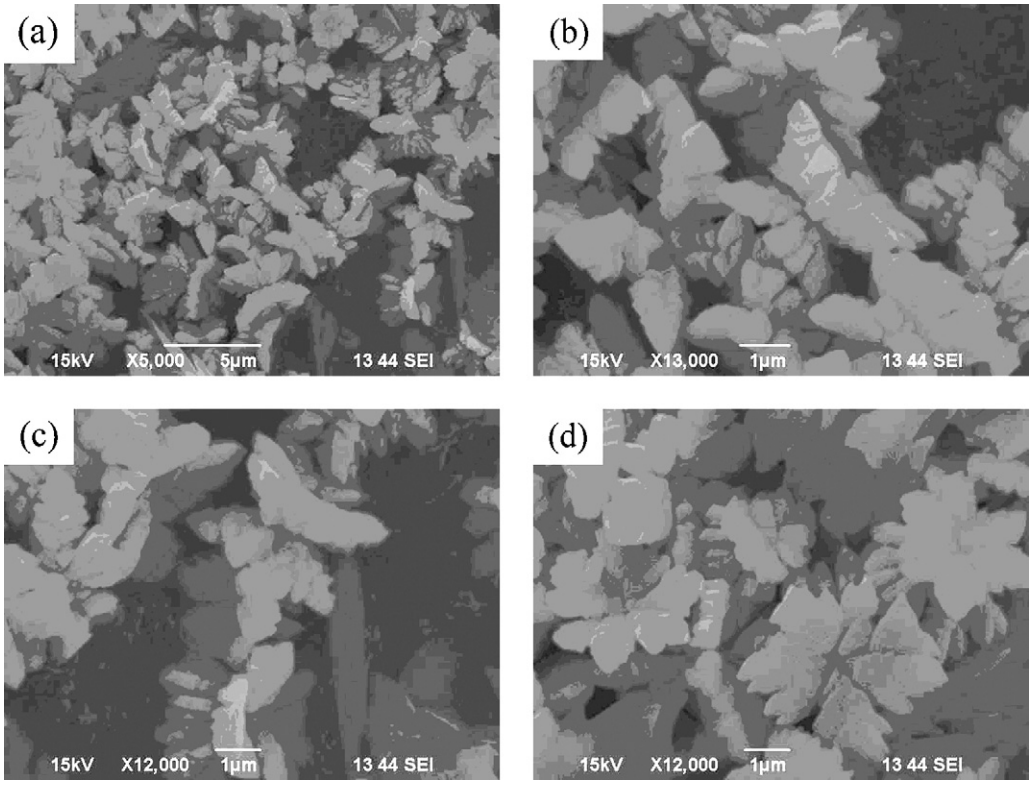

Fig. 2. SEM images of $Ce(OH)CO_3$ samples: (a) low magnification; (b–d) high magnification.