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Morphology-selective synthesis method of gear-like CeO_2 microstructures and their optical properties

Cheng Zhang [a], Fanming Meng [a,b,*], Leini Wang [a], Miao Zhang [a], Zongling Ding [a]

[a] Key Laboratory of Opto-electronic Information Acquisition and Manipulation, Ministry of Education, School of Physics and Materials Science, Anhui University, Hefei 230601, PR China

[b] Key laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, PR China

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ABSTRACT

Gear-like CeO_2 microstructures have been successfully synthesized by a CTAB (cetyltrimethyl ammonium bromide)-assisted hydrothermal method using $Ce(NO_3)_3 \cdot 6H_2O$ as the cerium source and ammonium hydrogen carbonate as the precipitator. X-ray diffraction (XRD) inferred that the synthesized CeO_2 microstructures exhibited a fluorite cubic structure. A scanning electron microscope (SEM) revealed that the CeO_2 microstructures have a gear-like microstructure. X-ray photoelectron spectroscopy (XPS) and the Raman spectroscopy reflected the existence of the oxygen vacancies and Ce^{3+} ions in the bowknot-like CeO_2 microstructures. The synthesized CeO_2 shows excellent room temperature optical properties, which is likely associated with Ce^{3+} ions and oxygen vacancies in the gear-like CeO_2 samples.

1. Introduction

Morphology-controlled synthesis of inorganic nanomaterials has been the focus of much research because of their unique morphology-dependent properties and their capability of self-assembly as building blocks [1]. Ceria (CeO_2), as one of the most important functional rare-earth oxides, has attracted more attention for its promising application in catalysts, fuel cells, oxygen sensors, mechanical polishing, ultraviolet blocks, and luminescent materials [2]. Therefore, nano-CeO_2 materials have attracted much attention recently. So far, various precipitants have been used to synthesize such shape-controlled nanomaterials. Lu et al. [3] obtained nanopolyhedra and square-like CeO_2 using $Ce(NO_3)_3 \cdot 6H_2O$ as the cerium resource and $N_2H_4 \cdot H_2O$ as a mineralizer. Meng et al. [4] synthesized CeO_2 nanopoles using $CeCl_3 \cdot 7H_2O$ as the cerium resource, NaOH as the mineralizer, and ethylenediamine as the complexant. Li et al. [5] synthesized CeO_2 nanosheets using $Ce(NO_3)_3 \cdot 6H_2O$ as the cerium resource, urea as both precipitator and carbon source. Sun et al. [6] synthesized flower-like CeO_2 microspheres using $Ce(NO_3)_3 \cdot 6H_2O$ as the cerium resource and $NH_3 \cdot H_2O$ as the mineralizer. Ammonium hydrogen carbonate could be hydrolyzed to produce ammonium and bicarbonate ions, but its involvement as a precipitant in preparing nanomaterials was seldom reported. In this paper, we report on the synthesis of gear-like CeO_2 microstructures using $Ce(NO_3)_3 \cdot 6H_2O$ as the cerium resource and ammonium hydrogen carbonate as the precipitator via a facile hydrothermal method.

2. Experimental

Material preparation: All the reagents were of analytical grade purity and used as received without further purification. The detailed synthetic process was as following: 4 mmol cetyltrimethyl ammonium bromide (CTAB) and 40 mmol NH_4HCO_3 were dissolved in 20 mL distilled water under vigorous stirring for 30 min. 8 mmol $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in 20 mL distilled water under vigorous stirring for 30 min,respectively. And then, 20 mL $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution were added to 20 mL CTAB and NH_4HCO_3 aqueous solution under continuous stirring for 30 min, forming a homogeneous solution. The mixed solution was transferred into a 50 ml Teflon-lined autoclave and heated at 180 °C for 12 h. After the autoclave was cooled to room temperature naturally, fresh precipitates were washed with distilled water and ethanol for three times, and then dried at 80 °C overnight. CeO_2 microstructures were obtained by calcinating at 400 °C for 5 h, accompanied by a color change from white to slight yellow.

* Corresponding author at: Key Laboratory of Opto-electronic Information Acquisition and Manipulation, Ministry of Education, School of Physics and Materials Science, Anhui University, Hefei 230601, PR China.Tel.: +86 551 63861257; fax: +86 551 63861992.
E-mail address: mrmeng@ahu.edu.cn (F. Meng).

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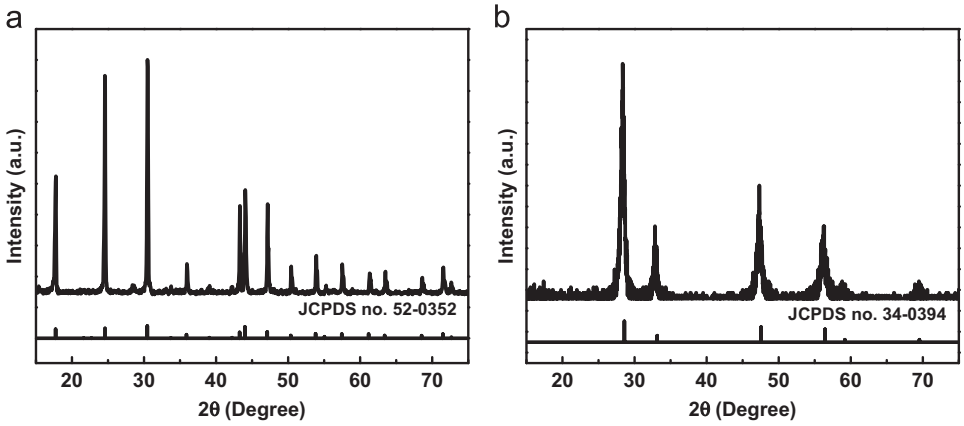

Fig. 1. The XRD patterns of the samples as-obtained (a) and calcined (b) at 400 °C for 5 h.

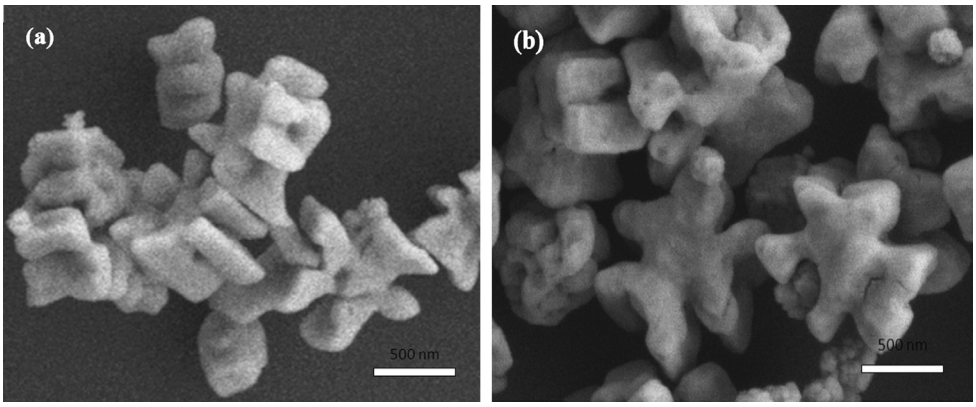

Fig. 2. SEM images of (a) gear-like $Ce(CO_3)OH$ obtained at 180 °C for 12 h and (b) CeO_2 obtained by calcining as-prepared gear-like $Ce(CO_3)OH$ at 400 °C for 5 h.

Characterization: The crystal phases of CeO_2 microstructures were analyzed by an X-ray diffractometer (XRD, XD-3) with Cu Kα radiation ($\lambda = 0.1506$ nm). The morphologies were characterized by a scanning electron microscope (SEM, S-4800). The chemical state was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 US Thermo Electron Co.). The Raman spectrum was recorded by a Raman spectrometer system (in Via-Reflex) using a laser with 532 nm excitation at room temperature. Photoluminescence (PL) spectra were obtained by a fluorescence spectrophotometer (HORIBA FluoroMax-4P, HORIBA Jobin Yvon) using an excitation light of 340 nm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples as-obtained (a) and calcined (b) at 400 °C for 5 h. All peaks of the pattern in Fig. 1a can be indexed to hexagonal $Ce(CO_3)OH$ (JCPDS no. 52-0352). And after annealing the precursors, the gear-like CeO_2 with pure face-centered cubic (JCPDS no. 34-0394) structure is obtained, as shown in Fig. 1b. The sharp peaks demonstrate that both the as-obtained and calcined materials show good crystallinity.

The morphologies of the $Ce(CO_3)OH$ and CeO_2 are shown in Fig. 2a and b, respectively. Fig. 2a shows the gear-like $Ce(CO_3)OH$ microstructures of 1 μm in diameter and 500 nm in length, and this microstructure is made up of nanosheets of 600 nm in length, 400 nm in width, and 50 nm in thickness. After being annealed, as shown in Fig.2b, the gear-like structure did not change on the overall appearance, but the morphology of nanosheets was destroyed and the surface was not so smooth than before. The variation can be attributed to the decomposition of the precursors which is shown by the following equation:

$$4Ce(CO_3)OH + O_2 \rightarrow 4CeO_2 + 4CO_2 + 2H_2O$$

Fig. 3 typically depicts the Ce 3d (a) and O 1s (b) X-ray photoelectron spectra (XPS) of CeO_2 microstructures. From Fig. 3a, it can be found that six Ce 3d BE peaks, at 916.35 eV, 906.96 eV, 900.50 eV, 897.98 eV, 888.45 eV, and 881.99 eV, respectively, were assigned to Ce $3d_{5/2}$ for Ce^{4+} state [7,8], indicating the main valences of cerium in the sample was +4. However, two weak peaks at 902.82 eV and 884.05 eV should be assigned to Ce $3d_{3/2}$ for Ce^{3+} state [9,10], indicating a small amount of Ce^{3+} ions existed in the samples. The typical satellite peaks of the "shape-down" type indicates that the as-prepared nanostructures contains both Ce^{4+} and Ce^{3+} ions oxidation states. As shown in Fig. 3b, the O1s spectra consist of two peaks at binding energy 531.57 and 529.33 eV, respectively. The peak at binding energy 531.57 eV can be attributed to lattice oxygen ions in Ce_2O_3, the peak at 529.33 eV originates from lattice oxygen ions in CeO_2 [7,10].

To better understand the defects in the gear-like CeO_2 microstructures, the Raman scattering was carried out and is shown in Fig. 4a. One strong Raman peak centered at about 464 cm^{-1} dominates the spectrum. This peak originates from the F2g Raman-active mode of CeO_2 cube structure [11], i.e. a symmetrical stretching mode of the Ce–8O vibrational unit [12], which is very sensitive to any disorder in the oxygen sub-lattice. As we know