



Rapid communication

Facile synthesis of cubic fluorite nano-Ce_{1-x}Zr_xO₂ via hydrothermal crystallization method

Shaojie Feng*, Di Pan, Zhenghong Wang

School of Materials Science and Chemical Engineering, Anhui University of Architecture, Hefei 230022, PR China

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ABSTRACT

Nano-Ce_{1-x}Zr_xO₂ ($x = 0.15, 0.25, 0.5$) were synthesized via co-precipitation using NH₄OH as precipitant and hydrothermal crystallization. The XRD results confirmed that the cubic fluorite nano-Ce_{1-x}Zr_xO₂ can form in NH₄OH solution (pH > 10) at 150 °C for 12 h, and well crystallized 20–50 nm nano-Ce_{1-x}Zr_xO₂ were obtained at 200 °C for 22 h. The crystal growth of Ce_{1-x}Zr_xO₂ was suppressed under higher OH⁻ concentration and crystallite size decreased with increasing concentration of NH₄OH. Ce3d XP spectra showed that the main valence state of the cerium on Ce_{1-x}Zr_xO₂ surface is +4, and substituting Ce⁴⁺ with Zr⁴⁺ has no obvious influence on Ce³⁺/Ce⁴⁺ ratio.

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1. Introduction

Ceria is a very important material in many applications, such as used as a key component of the three-way catalysts (TWCs) in automotive exhausts [1] and as an oxygen-ion-conducting solid electrolytes material in solid-oxide fuel cells [2]. Specially, Zr-modified ceria solid solution has been paid more attention because of its higher oxygen storage capacity (OSC), superb redox properties and thermal stability at working condition [3,4]. In the past decades, a lot of efforts were focused on wet-chemical synthesis routes to obtain the well crystallized, narrow size distributed and weakly agglomerated the nano-CeO₂ particles, including co-precipitation [5,6], sol-gel method [7], microemulsion [8] and hydrothermal synthesis [9], etc.

However, the effect of oxidizer on valence state transformation of cerium from Ce (III) to Ce (IV) is an important issue for CeO₂ crystal growth while the soluble Ce (III) salt was selected as the starting material in wet-chemical synthesis routes. It was reported that the ultrafine particles of Mⁿ⁺-doped ceria could be prepared via co-precipitation method or hydrothermal synthesis using H₂O₂ as the oxidizer and NaOH or NH₄OH as the precipitant respectively, and the rod-like and spherical particles of ceria were formed depending on the solution pH during the oxidation reactions of Ce (III) to Ce (IV) [10,11]. On the other hand, some investigations showed that the Ce(OH)₃ was readily oxidized in the atmosphere at room temperature to form Ce(OH)₄, and nano-

CeO₂ can be synthesized by simple precipitation method without any additional oxidizer [12,13].

To date, hydrothermal crystallization synthesis of nano-Ce_{1-x}Zr_xO₂ from soluble Ce (III) salt with NH₄OH as precipitant alone is scarcely reported in literature. In the present work, the crystallization behavior of nano-Ce_{1-x}Zr_xO₂ at different temperatures, pH and crystallization time was investigated. Moreover, the valence state of the cerium on the surface of Ce_{1-x}Zr_xO₂ solid solution was discussed by X-ray photoelectron spectroscopy technique.

2. Experimental

Co-precipitation technique was applied to prepare a homogeneous mixture of Ce and Zr hydroxides. Stoichiometric amounts of Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·5H₂O were dissolved into deionized water, and then, NH₄OH was added dropwise into the solution with vigorous stirring until pH 10. The resulting suspension was deposited over night. The wet precipitates were separated by decantation, followed by washing with deionized water three times. Finally, the precipitates were dispersed into water; the pH of the solution was adjusted to 10 or 12 by NH₄OH, followed by transferring into a 60 mL Teflon-lined stainless steel autoclave. Hydrothermal crystallization was carried out at 150, 200 °C for 12, 22 h in electric oven, respectively. After cooling to room temperature naturally, the precipitates were collected, washed with deionized water and ethanol for several times, and dried at 100 °C for 2 h.

The as-synthesized materials were characterized by X-ray powder diffraction (Rigaku D/max-γA) using Cu Kα radiation. The size and morphology of the as-synthesized particles were characterized by transmission electron microscopy (JEM-2010, JEOL) technique.

* Corresponding author. Tel.: +86 0551 3828103; fax: +86 0551 3828106.

E-mail address: fengshaojie@aia.edu.cn (S. Feng).

The chemical composition and the surface properties of $Ce_{1-x}Zr_xO_2$ were examined by X-ray photoelectron spectroscopy (VGESCALAB MKII). All measurements were carried out at room temperature without any sample pretreatment. A Mg K α X-ray source (1253.6 eV) was used in this work. All the binding energies were calibrated to the C1s peaks at 284.6 eV.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of samples with three Ce/Zr ratio obtained under different hydrothermal conditions. It can be seen that the diffraction peaks of all samples are in accordance with the cubic fluorite phase c-CeO₂ (Fm3m space group), indicating that the $Ce_{1-x}Zr_xO_2$ solid solution has been synthesized at pH \geq 10 without additional H₂O₂ as oxidizer for Ce (III) to Ce (IV) transformation. In the co-precipitation experiment, the pH values of solution were controlled at 10, and the yellow floccule deposits were formed under vigorous stirring, confirming that the Ce³⁺ can be oxidized to Ce⁴⁺ by oxygen in the air during co-precipitation and ripeness [12]. Furthermore, it can be seen that the diffraction peaks of samples under pH 10 are higher and sharper than that of pH 12, suggesting crystal growth of $Ce_{1-x}Zr_xO_2$ is suppressed under higher hydroxyl group concentration and crystallite size decreased with increasing concentration of NH₄OH [14].

The effect of hydrothermal temperatures and time on the $Ce_{1-x}Zr_xO_2$ crystallization is illustrated synchronously in Fig. 1. It is obvious that higher hydrothermal temperatures and longer time favor the crystallization of $Ce_{1-x}Zr_xO_2$ particles at pH 10. After hydrothermal treatment at 200 °C for 22 h, the peaks of all samples corresponding to c-CeO₂ become stronger and sharper gradually, which means a better crystallization occurred. However, for Ce_{0.5}Zr_{0.5}O₂ samples, the weak peaks associated with ZrO₂ phase were observed in XRD patterns. The appearance of impurity suggests the formation of $Ce_{1-x}Zr_xO_2$ is more difficult with the increasing amount of zirconium in the mixture under these conditions.

The morphology of the well crystallized $Ce_{1-x}Zr_xO_2$ was characterized by transmission electron microscopy (TEM). Fig. 2 shows the TEM micrographs of the particles obtained at 200 °C and pH 10 for 22 h. It can be seen that cubic particles with a narrow size distribution of 20–50 nm were crystallized much fine for these three Ce/Zr ratio samples, and the Zr⁴⁺-doping has no evident effect on the morphology of $Ce_{1-x}Zr_xO_2$. This result is different from that of by co-precipitation method [10], in which, the shape of CeO₂ particle is depended on the solution pH during the oxidation reactions of Ce (III) to Ce (IV), rod-like particles can be formed at pH > 8 condition and spherical particles are formed at pH < 7.

Moreover, the composition and valence state of cerium on the surface of ceria-zirconia solid solutions can be analyzed by XPS. Fig. 3 displays the Ce3d XP spectra of $Ce_{1-x}Zr_xO_2$ samples with the photoemission peaks from Ce⁴⁺ labeled (i.e., u/v, u''/v', u'/v''). The Ce3d spectrum is complicated because of the multiple splitting of Ce3d spectrums of Ce³⁺ and Ce⁴⁺ ion and the hybridization of the O2p bands with ceria 4f levels [15]. In despite the difficulty in calculating the multiple structure of Ce³⁺ and Ce⁴⁺ ion quantitatively, three spectrums represent the typical peaks shape corresponding to the predominance of Ce (IV) oxidation state on the surface of $Ce_{1-x}Zr_xO_2$ samples [16]. And it also reveals that an increase of substituting Ce⁴⁺ with Zr⁴⁺ has no obvious influence on Ce³⁺/Ce⁴⁺ ratio but an evident decrease in the intensity of the Ce3d peaks due to reducing the content of Ce on the surface of $Ce_{1-x}Zr_xO_2$.

4. Conclusions

In summary, well crystallized 20–50 nm cubic fluorite nano- $Ce_{1-x}Zr_xO_2$ ($x = 0.15, 0.25, 0.5$) particles have been synthesized in

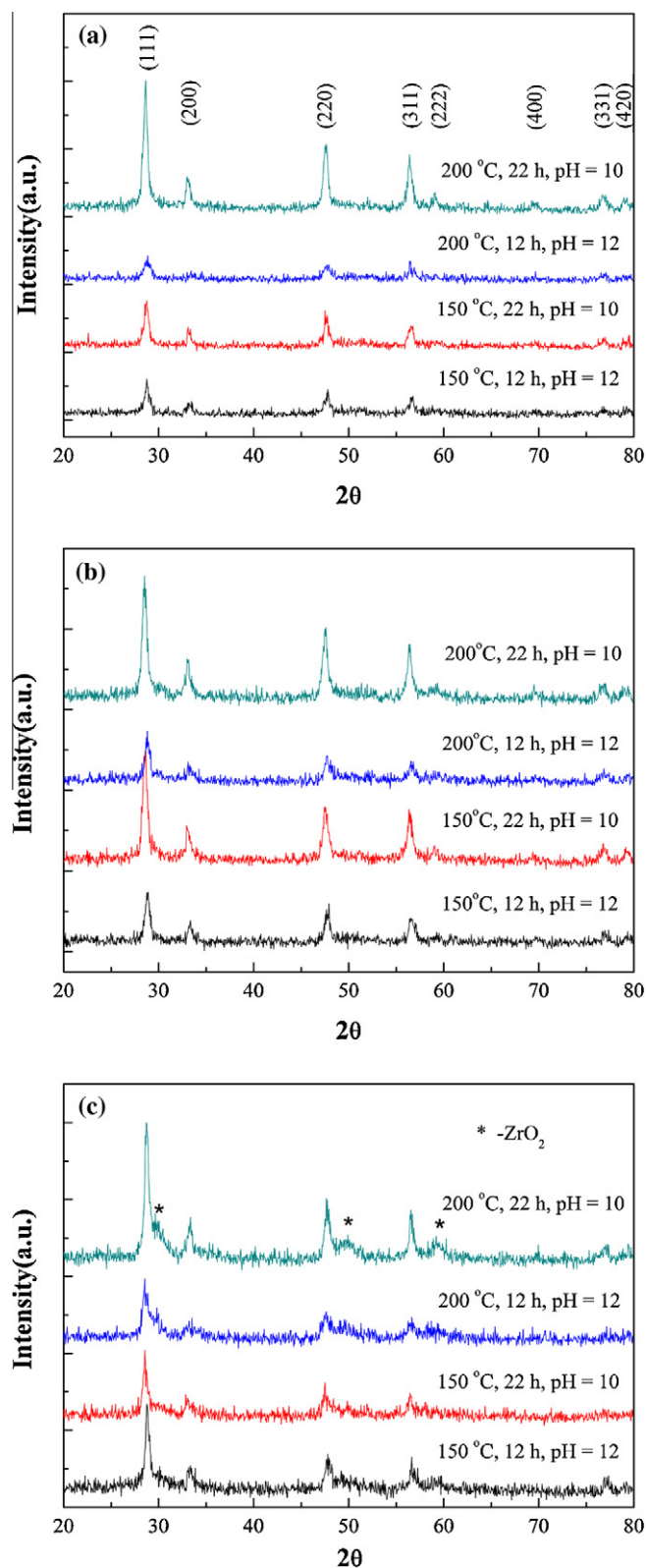


Fig. 1. XRD patterns of the $Ce_{1-x}Zr_xO_2$ particles obtained under different conditions (a) $x = 0.15$; (b) $x = 0.25$; (c) $x = 0.5$.

NH₄OH solution (pH 10) at 200 °C for 22 h by co-precipitation and hydrothermal crystallization. Crystal growth of $Ce_{1-x}Zr_xO_2$ is benefited from the higher temperature and long time but be suppressed under higher hydroxyl group concentration, in which the crystallite size decreased with increasing concentration of NH₄OH.

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