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Tuning the phase composition and particle characteristics of partially stabilized yttria and ceria co-doped zirconia nanocrystals via a sol–gel process with sodium chloride as an additive

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Abstract

The aim of the current work was to prepare partially stabilized yttria and ceria co-doped zirconia nanocrystals (PS-YCZ-NCs) with a controlled phase state and morphology. PS-YCZ-NCs were prepared via the sol–gel method based on the direct reaction of metal nitrates with ethylene glycol in the presence of sodium chloride. The effect of the NaCl dosage on the particle morphology and phase state was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The addition of NaCl in the sol–gel process was determined to improve the formation of tetragonal zirconia at calcination temperatures of less than 600 °C and to induce a phase transformation from tetragonal to monoclinic at temperatures above 600 °C. Therefore, PS-YCZ-NCs with different tetragonal and monoclinic phase ratios can be prepared by changing the dosage of NaCl and the calcination temperature. In addition, the optimal synthesis conditions for PS-YCZ-NCs with pseudo-sphere morphology and a particle size ranging from 15 to 30 nm have been determined.

Keywords: ZrO_2; Powders: Chemical preparation; Sol–gel process; X-ray method

1. Introduction

Due to the unique physical and chemical properties of ZrO_2, this compound has an extremely wide range of applications in various fields and has attracted considerable attention for a long time [1]. The most important application areas for ZrO_2 include toughened ceramics [2,3], refractories [4], piezoelectrics [5], solid electrolytes [6], active component and/or supports in catalysis [7,8], and photonics [9]. The crystal structure of ZrO_2 has a substantial influence on its characteristics and applications. ZrO_2 can be used in many applications due to the potential for structural changes between monoclinic, tetragonal and cubic phases [10]. For example, monoclinic zirconia is important materials for catalysis [11] and adsorbed materials [12], while tetragonal zirconia are promising candidates for gas sensors [13], catalysis [14] and phase-transformation-toughened structural materials [15]. Cubic zirconia can be used in solid oxide fuel cells [16]. In some catalytic reactions, the unique property of mixed phase structures containing ZrO_2 is required to improve the catalytic rate. For example, Ag loaded on monoclinic and tetragonal phases that coexist (i.e., Al_2O_3-ZrO_2) can improve the oxidation rate of o-methylphenol [17].

Zirconia has three thermodynamically stable crystalline phases under atmospheric pressure as follows: monoclinic (up to 1170 °C), tetragonal (1170–2370 °C), and cubic (2370–2680 °C) [18]. Doping ZrO_2 with small quantities of different metal oxides has been reported to tune the phase structure and improve the application properties. According to the phase diagram of doped zirconium, the phase of zirconia can be stabilized as the tetragonal or cubic structure by doping with some oxides. Many metal oxides, such as Sc_2O_3 [19], Y_2O_3 [20], Er_2O_3 [21] and Al_2O_3 [22], can be used to tune the phase structure of zirconia. However, the

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crystalline structure and phase state can also be affected by the media [23–26], additive [1,20], calcination temperature [27], sintering atmosphere [28] and grain size [29,30] during the preparation process.

Another very important factor influencing the properties of zirconia is the particle characteristics, such as the particle size and morphology. Therefore, to obtain zirconia materials with the desired properties, it is crucial to understand the effects of tuning the particle characteristics and phase structure of materials during the preparation process. In our previous study, the introduction of sodium chloride (NaCl) to a modified sol-gel or combustion synthesis process was determined to significantly affect the particle size and the morphology of metal oxides, and a novel salt-assisted method was developed for the preparation of spherical nano-particles [26]. However, the effect of NaCl on the phase composition and particle characteristics of zirconia was not clear. In this study, a salt-assisted sol–gel method using NaCl as additive was designed to synthesize yttrium and cerium co-doped zirconia nanocrystals (PS-YCZ-NCs). The particle characteristics and phase structure of the as-synthesized products were investigated.

2. Experimental procedures

A mixture of metal nitrates (MMNs) solution containing 3 mol% yttrium nitrate, 1 mol % cerium nitrate and 96 mol % zirconium nitrate (all of the nitrates are hydrate nitrates with purities more than 99.5% and supplied by the Aladdin Reagent Company, Shanghai, China) was prepared by dissolving these nitrates in deionized water. Then, ethylene glycol (EG) was added to the solution with a molar ratio of EG to metal nitrates of approximately 0.86.

To study the influence of the NaCl dosage on the characterization of PS-YCZ-NCs, NaCl was added as an additive to the MMNs solution with a mass percentage of NaCl to all of the solid MMNs ranging from 0% to 30%. The obtained transparent solutions were refluxed for several hours to form sols at 130 °C. Then, the resulting sols were dried in an oven at a temperature of 110 °C for 12 h to produce solid gels. These gels are the precursors of PS-YCZ-NCs with NaCl remained. To investigate the influence of NaCl on the particle characterization during the calcination process, some of these solid gels were washed with deionized water to remove the NaCl, and the as-obtained material was the precursors for the PS-YCZ-NCs in the absence of NaCl. Next, these PS-YCZ-NCs precursors with and without NaCl were calcined in a Muffle furnace at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C for 3 h to yield the corresponding PS-YCZ-NCs. The PS-YCZ-NCs obtained by calcining the precursors without and with NaCl are respectively denoted as PS-YCZ-NCs-1 and PS-YCZ-NCs-2. In all the treatments of eliminating NaCl, the absence of NaCl was justified by 0.5 wt% $AgNO_3$ with no white precipitation being detected.

The electron microscopic study of PS-YCZ-NCs was performed with a scanning electron microscope (FEI Quanta 200F) under a pressure of $< 5.0 \times 10^{-3}$ Pa. The samples were coated with gold using a Polaron Sputter Coater. The test voltage was 20.00 kV. TEM images were examined using a transmission electron microscope (JEM-1011, JEOL, Japan) operating at 100 kV.

The crystalline phase composition of the as-prepared PS-YCZ-NCs was identified on a Focus D8 Powder X-ray Diffractometer (Bruker Company, Germany) with CuKα radiation ($\lambda = 1.5405$ Å). The samples were scanned at room temperature with a scanning rate of 0.04 $^{\circ} \cdot s^{-1}$. The phase composition of the PS-YCZ-NCs was calculated based on the area of all peaks of tetragonal ZrO_2 (01-081-1544) and monoclinic ZrO_2 (00–036-0420) using the EVA software available with the XRD equipment [31].

3. Results

3.1. The effects of NaCl dosage on the phase composition of PS-YCZ-NCs-1

Fig. 1 shows the XRD pattern and the corresponding percentage of tetragonal phase in PS-YCZ-NCs-1 obtained by calcining their precursors at 800 °C. The crystalline phases of all of the PS-YCZ-NCs samples include both tetragonal and monoclinic structures. In addition, the content of tetragonal phase decreased as the NaCl dosage increased, Therefore the amount of tetragonal phase in PS-YCZ-NCs-1 was dependent on the dosage of NaCl added in the sol–gel process. Without the addition of NaCl, the amount of the tetragonal phase in the prepared PS-YCZ-NCs-1 was as high as 93.5%, which indicates that the ceria and yttria doping in zirconia can stabilize the metastable tetragonal zirconia. With the addition of only 0.3% NaCl, the percentage of tetragonal phase sharply decreased from 93.5% to 80%. The percentage of tetragonal phase remains a constant at approximately 80% until the dosage of NaCl reaches 8%. Another sharp decrease in the percentage of tetragonal phase from 80% to 20% occurs when the NaCl dosage increased from 8% to 15%. With a further increase in the NaCl dosage from 15% to 30%, the percentage of tetragonal zirconia decreased gradually from 20.2% to 10.9%.

3.2. Effect of NaCl dosage on the crystallization of the solid gels

Fig. 2 shows the XRD patterns of the solid gels prepared with the addition of different dosages of NaCl. No obvious crystalline characterization was observed in the solid gel prepared without the addition of NaCl. However, some diffraction peaks representing crystalline zirconia appear in the solid gels synthesized with the addition of NaCl. This result indicates that the presence of NaCl during the sol–gel preparation process can promote the crystallization of zirconia.

3.3. Effect of NaCl dosage on the phase composition of PS-YCZ-NCs-2

Fig. 3 shows the XRD patterns of PS-YCZ-NCs-2 and the corresponding dependence of the amount of the tetragonal phase on the dosage of NaCl. The sols were formed at 130 °C,