

Controllable synthesis of metastable tetragonal zirconia nanocrystals using citric acid assisted sol–gel method

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Abstract

Metastable tetragonal ZrO₂ nanoparticles and nanosheets were synthesized with citric acid assisted sol–gel method. In this approach, zirconium acetylacetonato, Zr(acac)₂, citric acid (CA) and ethylene glycol (EG) were used as the source of Zr⁴⁺, the chelating, and solvent agent, respectively. The effects of heat treatment on zirconia phase evolution were investigated. We demonstrate that pure tetragonal nanocrystalline zirconia can be obtained with CA: EG mole ratio=5:1 and calcination temperature 490 °C. The microstructure of the products was characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and Raman scattering. Finally, Photoluminescence (PL) of nanosheets and nanoparticles were also investigated.

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1. Introduction

At atmospheric pressure, pure zirconia has three solid polymorphs which exhibit monoclinic structure [space group $P2_1/c$] (m-phase), that is, thermodynamically stable at the temperatures below 1172 °C, tetragonal structure [space group $P4_2/nmc$] (t-phase), stable at the temperature range of 1172–2347 °C, and cubic structure [space group $Fm3m$] (c-phase), stable above 2347 °C [1–3]. The applications of zirconia strongly depend on both crystal structure and phase transformations [3–5]. Cubic phase of zirconia is a good candidate for solid oxide fuel cells (SOFCs), oxygen sensors, electrochemical capacitor electrodes and ferrules due to its ionic, electrical [3,4,6] and optical [7] properties. Tetragonal zirconia can be used as an effective catalyst due to unique amphoteric characteristics and redox properties

[7,8]. The transformable tetragonal zirconia, such as yttria stabilized zirconia (YSZ) (called t-phase) used as engineering ceramic material since it shows high values of strength and hardness. This hardening mechanism is due to the transformation of the tetragonal phase into the monoclinic phase which implies a volume change associated with pseudo-plasticity [5,9]. The ‘non-transformable’ metastable tetragonal YSZ phase (called t′) [5] is remarkably resistant and does not undergo the transformation to the monoclinic phase under stresses. The t′ phase is widely used for thermal barrier applications due to the formation of a tweed microstructure which tends to increase the thermo-mechanical performances [10]. This microstructure corresponds to a three-dimensional pseudo-periodic lattice of high Y₂O₃ cubic particles within all of the t′ grains [5].

There are five techniques for obtaining metastable tetragonal phase of zirconia at room temperature: (1) stabilization with doping metal oxide, such as Y₂O₃ doped zirconia (YSZ) [10–15] (2) Using high rate deposition techniques, such as EBPVD, plasma spray method: In these techniques, the t′ phase is obtained via a displacive transformation by quenching liquid or cubic phase from high temperature

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[16,17](3) crystallization from amorphous phase [18,19] (4) particle or crystallite size reduction of zirconia to 8–29 nm and below 5 nm, respectively [5,20–23]; and (5) thermal decomposition of zirconium salts, alkoxides and hydroxide or by ball milling of monoclinic zirconia (m-ZrO₂). There are some evidences that metastable t-ZrO₂ can also be produced by ball milling of zirconium decomposition products of three different zirconium salts [7].

The high-temperature cubic and tetragonal phases can be stabilized at room temperature by incorporating dopants in the lattice, e.g., CaO, MgO, Y₂O₃ and CeO₂ [10–15]. However, it is difficult to stabilize these high-temperature phases at room temperature without any doping. Particle size reduction is known to stabilize the high-temperature modifications at room temperature. It has been reported in the literature that in the case of nanopowders above the critical size of 20–30 nm, the material reverts to monoclinic (m-) ZrO₂ [20–25]. It was concluded that the formation of t-ZrO₂ is dependent on the nature of starting salt, the type of synthetic method and the crystallite size of zirconia [9]. As it was said before, the stable phase of zirconia at room temperature (RT) is monoclinic. So, it is very important to control zirconia crystallite size to obtain tetragonal structure at RT. One of the effective methods is citric acid and ethylene glycol-based process, which is established for the preparation of fine ceramic oxide powders. In this technique, a uniform particle size powder is produced by means of a homogeneous distribution of metal ions in the polymeric gel. The polymeric (polyester) gel produced by the reaction of citric acid and ethylene glycol during heat treatment. Meanwhile, other elements such as C and H are easily removed during calcination. Therefore, the purity of the final powder will not get affected when citric acid and ethylene glycol are being used as chelating agents and template materials [24].

The main goal of the present research is the synthesis of nano size tetragonal zirconia powder via introducing zirconium acetylacetonato, Zr(acac)₂, as a new starting salt for producing homogenous gel. Also, the effects of particle size on the zirconia phase evolution are investigated. Finally, the optical properties of ZrO₂ nanosheets and nanoparticles are investigated.

2. Experimental

2.1. Materials

All of the materials purchase from Merck Company (Germany) and were used as received without further purification.

2.2. Characterization equipment

XRD patterns (X'Pert Pro, Philips, Holland) were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$), generator setting 40 kV and 30 mA and step size 0.05. Field emission scanning electron microscopy (FESEM) images were obtained on

S-4160 (Hitachi Ltd., Japan). Transmission electron microscopy (TEM) micrographs were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Samples for TEM were prepared by diluting the product with ethanol and placing a 6 μL drop onto a 200 mesh copper grid covered by a continuous amorphous carbon film. Analysis of particle size was done with the Scion image Beta 4.02 software for image processing. Crystallite sizes (D_c) were calculated from the line broadening of the X-ray diffraction peaks using the Debye–Scherrer Eq. (1) [3,20],

$$D_c = k\lambda/\beta\cos\theta \quad (1)$$

where β is the breadth of the observed diffraction line at its half-intensity maximum, k is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD.

2.3. Synthesis of nanocrystalline zirconia

In a typical experiment, 3 g Zr(acac)₂ and citric acid mono hydrate (C₆H₈O₇·H₂O) were dissolved in deionized water, and appropriated amounts of ethylene glycol (EG) were then added (EG:CA mole ratios=1:1, 5:1, 20:1) to form a sol at 50 °C for 1 h (The pH value of precursor was ~2). A white solution was obtained and further heated at 80 °C for 1 h to remove excess water. During continued heating at 140–150 °C for 1 h, the solution became more and more viscous and finally became a xerogel. To complete drying, xerogel was placed at 250 °C for 1 h. The result powder is a precursor. In the furnace, the precursor was calcined at 490–650 °C for 2 h, in an alumina boat, and then was cooled to reach room temperature. To investigate pH effect on the morphology and phase structure, in parallel reactions series, the pH value was changed from 2 (acidic medium) to 12 (alkali medium), by adding adequate liquor ammonia (for changing pH of precursor, 120 ml concentrated ammonia was added, so the final pH of solution was adjusted at 12.) and other parameters such as EG:CA ratio and calcination temperature were kept constant.

3. Results and discussion

3.1. The effect of the calcinations temperatures

It is well known that calcination can result in the growth of zirconia crystallite. In order to investigate the effect of temperature on the crystallization process of zirconia, XRD results of zirconia, calcined at 650, 540 and 490 °C for 2 h, respectively, were compared. Fig. 1a shows XRD of as-prepared products at 650 °C. This figure indicates that a mixture of monoclinic (m) and tetragonal (t) phase of zirconia was obtained. When calcinations temperature was reduced to 540 °C (Fig. 1b) the amount of m-phase was considerably reduced. Upon reducing temperature to 490 °C (Fig. 1c), no m-phase was obtained. The distinguishing characteristic peaks for t-phase occur at $2\theta=30.2^\circ, 34.9^\circ, 50.6^\circ$ and 60.08° for the (1 0 1), (0 0 2),

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