



Short communication

A novel green nonaqueous sol-gel process for preparation of partially stabilized zirconia nanopowder

Guo Feng^{1,*}, Weihui Jiang^{1,2,*}, Jianmin Liu¹, Quan Zhang¹, Qian Wu¹, Lifeng Miao¹

¹National Engineering Research Center for Domestic and Building Ceramics, Jingdezhen 333000, PR China

²Department of Materials Science and Engineering Jingdezhen Ceramic Institute, Jingdezhen 333000, PR China

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Abstract

A novel green nonaqueous sol-gel process was developed to prepare 3 mol% Y_2O_3 -doped ZrO_2 nanopowder from zirconium oxychloride and without need for washing of the obtained particles. It was shown that highly dispersive nanometer-scale zirconia powder with the particle size of 15–25 nm and BET surface area of $41.2\text{ m}^2/\text{g}$ can be prepared. The sintering behaviour was also investigated. Density of the translucent body sintered at $1400\text{ }^\circ\text{C}$ is $98.7 \pm 0.3\%$ of its theoretical density and the surface and cross section areas are dense without holes or other defects. The bending strength of the sintered sample is $928 \pm 64\text{ MPa}$.

Keywords: zirconia, nonaqueous synthesis, fracture, crystal structure

I. Introduction

Zirconia is one of the most important ceramic materials. It has excellent combination of mechanical, optical, electrical and thermal properties, which makes it a good choice for applications such as structural, semiconductor, SOFC electrolyte and bio-material [1,2]. Zirconia powder can be prepared via various methods, such as emulsion [3], hydrothermal [4], combustion [5], thermal decomposition [6], sol-gel [7] and precipitation method [8]. Sol-gel method is one of the best methods for preparation of zirconia, titania and alumina nanopowder [9–11]. However, traditional sol-gel method takes water as medium, but its large surface tension inevitably leads to agglomeration during the drying process. In addition, widely used precursor, zirconium oxychloride, which is cheap and easy accessible, often needs repeated washing in order to avoid “salt bridge” effect of chloride ions [12]. Green synthesis route is environmentally friendly route known as “zero pollution, zero infection, zero emission” and “high utilization” [13,14]. Lydia *et al.* [14] developed a green route for synthesis of

ZrO_2 nanoparticles, however, they used $Zr(NO_3)_4 \cdot 4H_2O$ which is expensive and can involve ammonia pollution in environment.

In this work we develop a novel simple green nonaqueous sol-gel process to prepare highly dispersive yttria-stabilized zirconia nanopowder. Zirconium oxychloride was used as zirconium source since it does not need washing dechlorination because chloride can be expelled in the form of crystalline precipitate or molecule of ammonium chloride.

II. Materials and methods

Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and yttria (Y_2O_3) were supplied by Jiangxi Kingan Hi-Tech Co., Ltd. (China) and Fanmeiya (Jiujiang) High-tech Materials Co., Ltd. (China), respectively. Anhydrous ethanol, anhydrous acetic acid, glycerol and oleic acid were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water was used from a direct ultra-pure water system. All chemicals were used without further purification.

The used synthesis procedure for preparation of 3 mol% Y_2O_3 -doped ZrO_2 (C) powder is schematically presented in Fig. 1. Initially, zirconium oxychloride and yttria were dissolved in anhydrous ethanol by stirring

*Corresponding author: tel/fax: +86 798 8499328, e-mail: fengguo@jci.edu.cn (G. Feng), jwhjiang@163.com (W.H. Jiang)

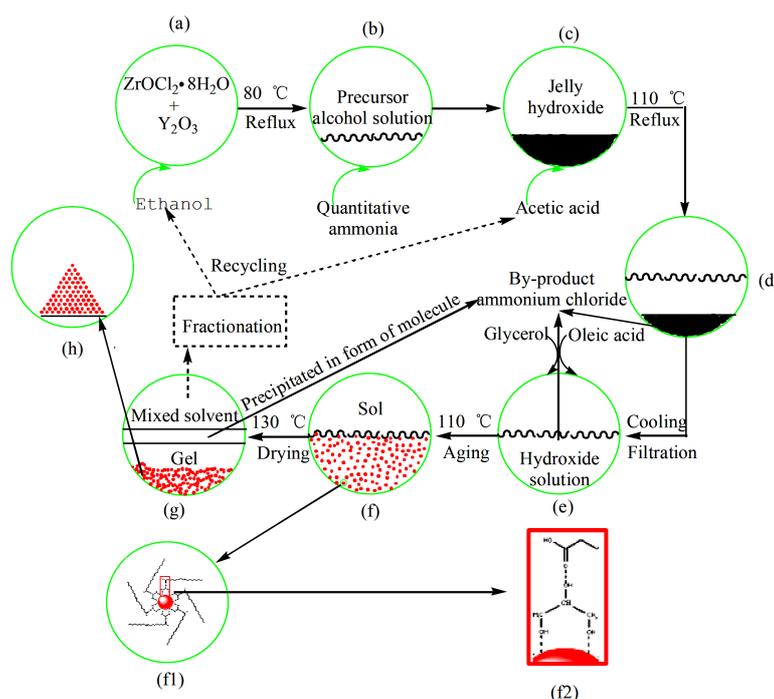
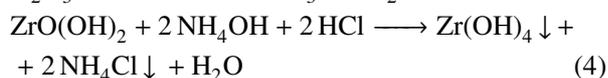
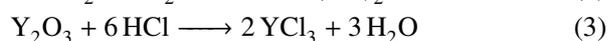


Figure 1. Process schematic diagram for zirconia nanopowder preparation via nonaqueous sol-gel method: a) precursors, b) precursor alcohol solution, c) jelly hydroxide, d) hydroxide solution with ammonium chloride precipitation, e) hydroxide solution, f) sol [stabilization of colloidal particles (f1) and particle functionalization (f1)], g) gel and h) zirconia powder

and refluxing at 80 °C for 0.5 h producing 0.5 M transparent precursor solution. Then, ammonia with molar ratio $\text{NH}_4\text{OH} : \text{ZrOCl}_2 = 2 : 1$ was introduced into the resulting solution, which can ensure that the chloride ion can completely precipitate in the form of ammonium chloride. After that jelly zirconium and yttrium hydroxides were formed. The whole process can be divided into the following three stages: i) the hydrolysis of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (equations 1,2); ii) the dissolution of yttria (equation 3); iii) further reaction and formation of hydroxides after the introduction of ammonia (equations 4,5) [15–17].



In the next step, anhydrous acetic acid was added to dissolve zirconium and yttrium hydroxides by refluxing at 110 °C for 1 h, and to form crystalline ammonium chloride precipitate in hydroxide-acetic acid solution. The final concentration of precursors was maintained at 0.2 M. The refining by-product was filtered and washed with anhydrous acetic acid and cooled down to room temperature. Stable hydroxide sol was formed after adding 1.5 mol% of glycerol and oleic acid to the filtered hydroxides and ageing at 110 °C for 24 h. Fi-

nally, the obtained zirconia gel, mixed solvents and a small amount of residual ammonium chloride were separated by distilling at 130 °C and condensed. The mixed solvents of ethanol and acetic acid can be re-utilized through further fractionation, and the residual ammonium chloride was precipitated in the form of crystalline molecules. The zirconia gel was finally calcined at 900 °C for 2 h and ground to get 3-YSZ nanopowder.

The translucent zirconia ceramic body was obtained by granulation by agate mortar grinding for 15 min, pressing into pellets under pressure of 8 MPa and sintering at 1400 °C [18] for 2 h in box-type high temperature muffle furnace (KBF1600). The temperature rise rates from 20 to 400 °C, 400 to 1050 °C, 1050 to 1400 °C and 1400 to 800 °C were 3.5, 5, 2 and -5 °C/min, respectively, and holding time at 1050 °C was 2 h and at 1400 °C it was 3 h.

The phase composition of the 3-YSZ powder was analysed by X-ray diffraction (XRD, D8 Advance, Bruker AXS Co. Ltd.) with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) and 2θ scanning range of 5–70°. The powder morphology was studied by transmission electron microscopy (TEM, JEM-2010, JEOL) and the specific surface area (SA) was measured using Brunauer-Emmett-Teller method (N_2 gas adsorption) (BET, ASAP 2020M, AMIC). The mean zirconia particle size D_B was calculated from the specific surface area and density ($\rho = 6.1 \text{ g/cm}^3$ [19]) using the following equation [20]:

$$D_B = \frac{6 \cdot 10^3}{\rho \cdot \text{SA}} \quad (6)$$

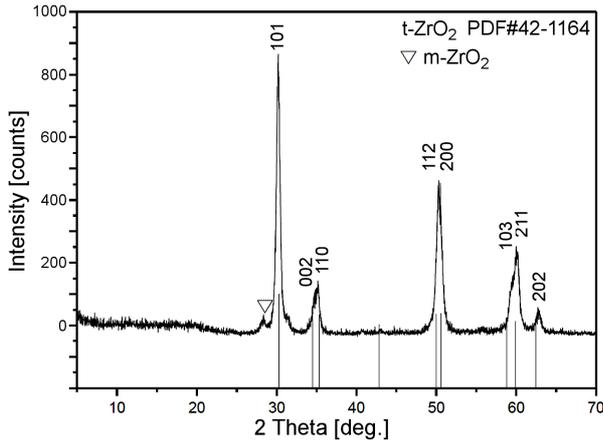


Figure 2. XRD pattern of zirconia nano powder

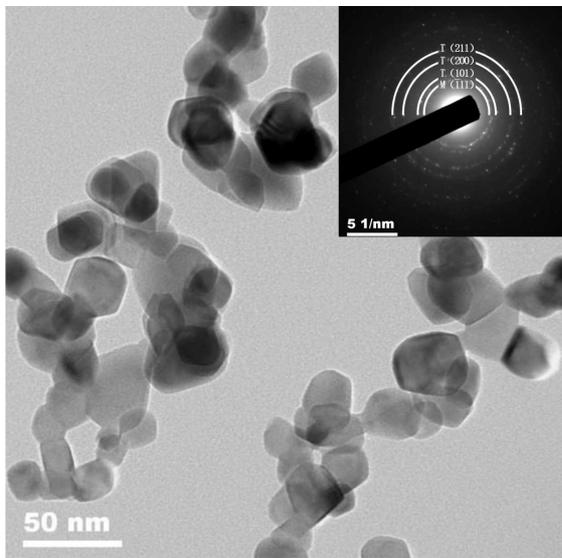


Figure 3. TEM micrograph and SAED pattern of zirconia particles prepared via nonaqueous sol-gel process

The density of the sintered zirconia bodies was calculated according to dimensional measurement and Archimedes' principle. The surface and cross section of the sintered 3-YSZ ceramics were observed by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). Three-point bending strength was measured by desktop mechanical tester (AG-IS, Shimadzu, Japan) at a cross-head speed of 1 mm/min. The dimensions of the test samples were 5×5×40 mm, and five samples were tested to obtain the average strength values.

III. Results and discussion

X-ray diffraction pattern of the powder obtained by calcination at 900 °C is shown in Fig. 2. The slight broadening of diffraction peaks in the XRD pattern indicates nanocrystalline nature of the product. The XRD pattern is quite similar to that of the standard tetragonal zirconia phase (PDF#42-1164). A very weak peak at 28.36°, which belongs to monoclinic phase, was de-

tected. Generally, tetragonal (T) zirconia phase is not thermodynamically stable at room temperature. However, it can be stabilized in the presence of Y^{3+} ion [21], while some monoclinic (M) zirconia phase is presented along with its tetragonal modification, which suggests that the meta-stable tetragonal phase can be retained during processing and may contribute to the increase in fracture toughness [22]. Also, as it can be seen from the XRD pattern, there is a slight shift of the tetragonal peaks, which could indicate changes of the lattice parameter. The crystallite size D_C of the sample was calculated using Scherrer formula [23]:

$$D_C = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (7)$$

where k is the shape factor (assumed to be 0.94), λ is the X-ray wavelength (0.154 nm), β is the full width at half maximum of m-ZrO₂ $\bar{1}11$ and t-ZrO₂ 101 diffraction peaks and θ is the Bragg angle of the corresponding plane. The obtained crystallite size values are 26 nm for m-ZrO₂ and 18 nm for t-ZrO₂.

Figure 3 shows the TEM micrograph and selected area electron diffraction (SAED) of the prepared zirconia particles by nonaqueous sol-gel process. As it can be seen, the sizes of zirconia crystallites are in the range of 15–25 nm, which is consistent with the crystallite size calculated from XRD data. Diffraction rings (SAED pattern) are indexed to M ($\bar{1}11$), T (101), T (200) and T (211) crystal planes and coincide well with the

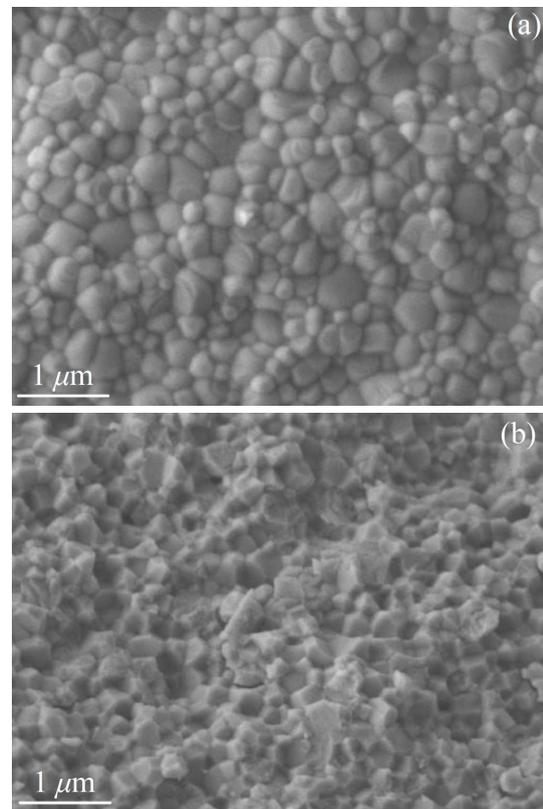


Figure 4. Surface (a) and cross section (b) morphology of sintered zirconia 3-YSZ ceramics

XRD results. BET surface area of the prepared zirconia sample is $41.2 \text{ m}^2/\text{g}$ and the corresponding mean particle size D_B is 23.9 nm. These sizes are relatively small in comparison to the literature data [24–26].

Density of the zirconia green body is relatively high, i.e. $53.5 \pm 0.6\%$ of theoretical density (TD). It is well known that the high green body density determines the excellent sintering performance. Thus, the zirconia sample sintered at 1400°C for 2 h in air has density of $98.7 \pm 0.3\%$ TD. In addition, FE-SEM micrographs of the typical surface and cross sections (Fig. 4) confirm an almost fully dense structure. It is clearly observed that both the surface and cross sections of the as-prepared zirconia sintered body are crack-free with small equiaxed grains of approximately 100–250 nm in diameter. A high tendency of zirconia grains for transgranular fracture shown in Fig. 4b increases the fracture strength of the sintered body and indicates an excellent toughening property. The bending strength of the sintered body is $928 \pm 64 \text{ MPa}$, which is comparable with the results of Sun *et al.*, who reported excellent result of $932 \pm 63 \text{ MPa}$ [27].

IV. Conclusions

Highly dispersive 3 mol% yttria-stabilized zirconia powder, with particle sizes of 15–25 nm and BET surface area of $41.2 \text{ m}^2/\text{g}$, was successfully synthesized by a novel green nonaqueous sol-gel process. The 3-YSZ ceramics obtained by sintering of pressed pellet at 1400°C have dense structure without pores or other defects, density of $98.7 \pm 0.3\%$ TD and bending strength of $928 \pm 64 \text{ MPa}$. The synthesis process is a green synthesis route, as it is not only simple, but also avoids the ammonia emission and water pollution caused by washing.

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