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Short communication

Preparation and characterization of tetragonal-ZrO_2 nanopowders by a molten hydroxides method

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Abstract

Pure tetragonal-ZrO_2 nanopowders are prepared by a molten hydroxides method, using hydrated zirconium nitrate as the starting material at 200 °C. X-ray diffraction analysis and transmission electron microscopy observation reveal that the nanopowders exhibit poor crystalline quality. After heat treated at 400 °C for 10 h in air, the nanopowders are crystalline with size range of ~10–12 nm and most of them are agglomerated. The formation mechanism of the ZrO_2 nanopowders has been proposed. The heat treated nanopowders have a BET surface area of ~27.3 m^2/g due to agglomeration. The photoluminescence of the heat treated nanopowders has been investigated at room temperature.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; B. Grain size; D. ZrO_2

1. Introduction

ZrO_2 is an important oxide due to its high strength and toughness, good corrosion and abrasion resistance, high melting point, refractory and low thermal conductivity [1]. ZrO_2 is usually used as a second phase to enhance mechanical properties of ceramics [2]. Recently, it has attracted much attention as a functional material. For example, ZrO_2 deposited metal implants can be used as biomedical ceramics [3]; sulfated ZrO_2 is recognized as a solid superacid [4] and has been used as catalytic support and catalyst [5]; stabilized cubic ZrO_2 (c-ZrO_2) can be used as an oxygen sensor [6].

In order to prepare pure ZrO_2 nanopowders, many methods, such as hydrothermal synthesis [7], microwave irradiation [8], solid-state synthesis [9], and sol–gel combined with solvothermal synthesis [10] have been developed. However, the product is usually mixed with another crystallographic phase of ZrO_2.

Liu et al. [11] have recently developed a molten hydroxides method to prepare complex oxides. This method is based on the reaction of source materials in a solvent of eutectic composite-hydroxides at a temperature of ~200 °C and atmosphere pressure. Zhang et al. [12] synthesized Ba-doped CeO_2 nanowires by the same method, using CeO_2 particles and $BaCO_3$ as the starting materials. In this paper we used this method to synthesize pure tetragonal ZrO_2 (t-ZrO_2) nanopowders using hydrated zirconium nitrate as the starting material.

2. Experimental

Chemicals with analytical grade were used as received. 8.62 g NaOH, 0.43 g $Zr(NO_3)_4\cdot5H_2O$, and 11.38 g KOH were put in sequence into four 25 mL Teflon vessels, and each vessel was covered and then shaken for about 30 s. The four vessels were put in an oven and heated to 200 °C, with a rate of ~10 °C/min, and held at 200 °C for 16, 24, 48, and 96 h, respectively, and finally cooled naturally. During the holding stage, the vessels were shaken for about 30 s in every 12 h. The products were washed with hot deionized water until the pH value of the lotion reached 7.0, and then separated by centrifugation for 5 min at 4000 rpm. The products were dried in vacuum at 70 °C for 12 h. Some dried powders were heat treated at 400 °C for 10 h. The products before and after the heat treatment were characterized by X-ray diffraction (XRD, Bruker D8 Advanced), transmission electron microscope (TEM) and high-resolution TEM (HRTEM, Philips TECNAI-20) equipped

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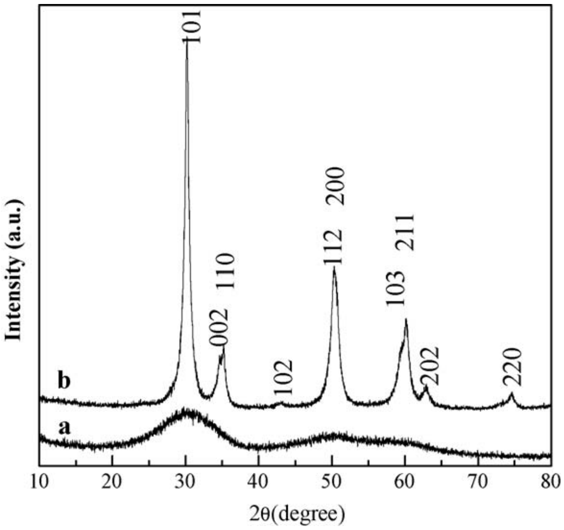

Fig. 1. XRD patterns for (a) the dried powders and (b) the heat treated powders.

with energy dispersive X-ray spectroscopy (EDS), respectively. BET measurements were performed in a liquid nitrogen bath with a Micromeritics TriStar 3000. The photoluminescence (PL) of the heat treated powders was observed under excitation at 254 and 412 nm in air with a PerkinElmer LS55 fluorescence spectrophotometer.

3. Results and discussion

XRD analyses reveal that the XRD patterns for all the dried powders are quite similar. As an example, Fig. 1(a) shows the XRD pattern for the powders synthesized at 200 °C for 48 h. The pattern has three very broad peaks at $2\theta = \sim 30^\circ$, 50°, and 60°, respectively, which can be indexed to the (1 0 1), (1 1 2), and (2 1 1) plane peaks for either c-ZrO_2 or t-ZrO_2 due to the similarity in their patterns [7]. This indicates that the powders are very fine or incomplete crystallization and that prolonging the holding time does not improve the crystallinity of the powders. However, the amount of the powders synthesized at

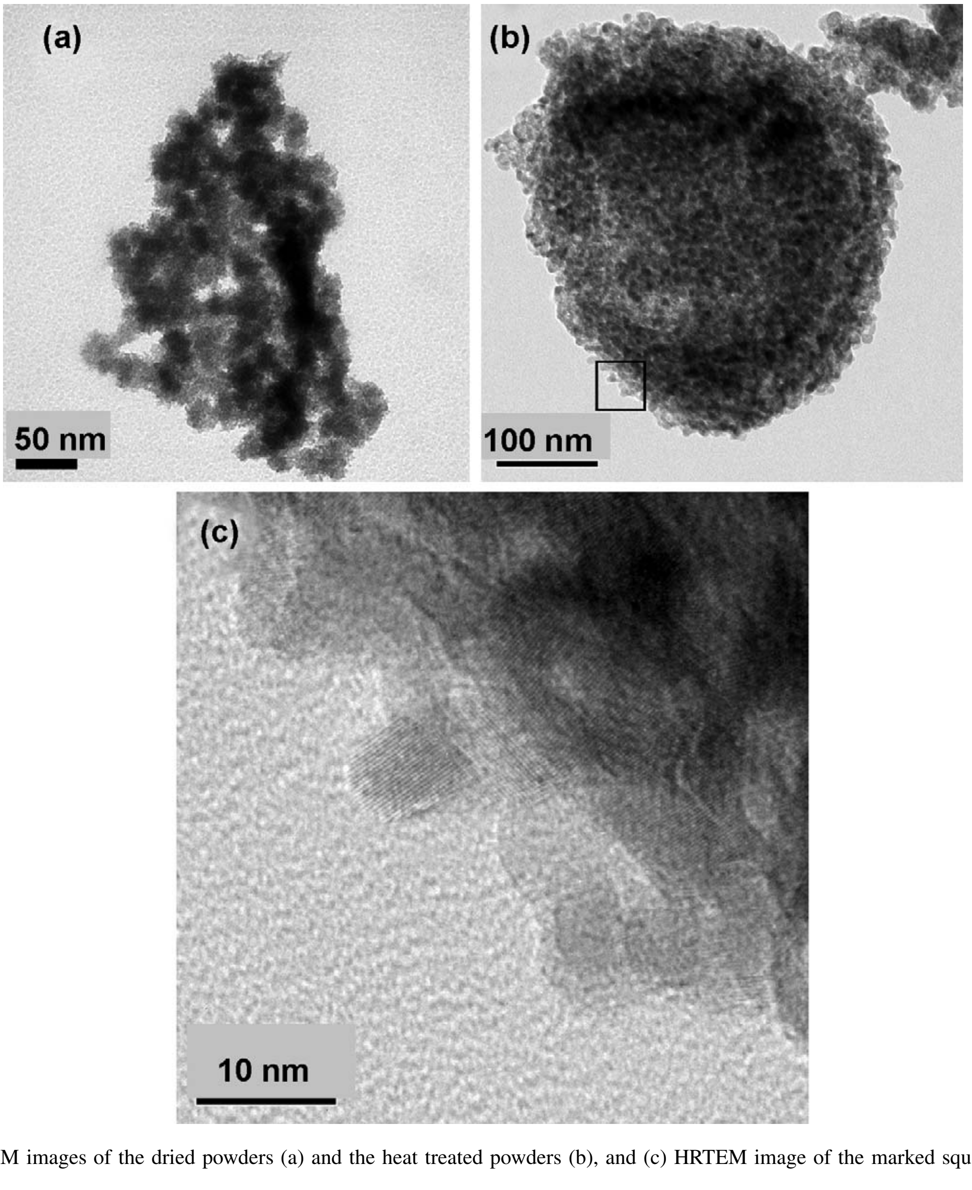

Fig. 2. TEM images of the dried powders (a) and the heat treated powders (b), and (c) HRTEM image of the marked square in (b).

200 °C for 16 h is less than that of the others, indicating that the reaction is incomplete. After the heat treatment the crystallization of the powders is much better, as the corresponding XRD peaks become sharp (see Fig. 1(b)). All the peaks in Fig. 1(b) can be indexed to t-ZrO_2 (JCPDF card file, no.79-1771).

Fig. 2(a) shows a typical TEM image for the dried powders. The powders are very fine and agglomerated. Electron diffraction analysis reveals that they are amorphous. EDS analysis indicates that the dried powders only contain zirconium and oxygen, which further confirms that the powders are ZrO_2. TEM observation indicates that the heat treated powders are mainly agglomerated. Fig. 2(b) shows a TEM image of a typical aggregate that consists of numerous nanoparticles. Fig. 2(c) is an HRTEM image of the zone marked by the black square in Fig. 2(b), which clearly shows that the nanoparticles are single crystalline. The size of the nanoparticles is estimated to be in the range of ~8–12 nm. The distance between two adjacent lattice planes is about 0.3 nm (see Fig. 2(c)), which is close to the spacing of (1 0 1) planes of the t-ZrO_2.

As the eutectic point at NaOH/KOH = 51.5:48.5 is about 165 °C, the hydroxides play a role not only as the solvent but also as the reactant [11]. In the molten hydroxides, zirconium nitrate reacts with hydroxides as follows:

$$Zr(NO_3)_4{\cdot}5H_2O + NaOH(KOH) = Zr(OH)_4 + 4NaNO_3(KNO_3) + 5H_2O\uparrow \quad (1)$$

$$Zr(OH)_4 = ZrO_2 + 2H_2O\uparrow \quad (2)$$

The ZrO_2 nuclei grow up to form ZrO_2 nanoparticles. Because the viscosity of the molten hydroxides is large, the formation of ZrO_2 nanoparticles is slow and it is difficult for them to agglomerate. The agglomeration should occur during drying and heat treatment.

The BET surface area of the heat treated powders is 27.3 m^2/g, which is lower than the reported data, 100 m^2/g, for the ZrO_2 nanopowders with size of ~10 nm [7]. The main reason for the difference is the agglomeration of the as-synthesized nanopowders.

Fig. 3(a) and (b) shows the PL spectra with excitation wavelength of 254 and 412 nm, respectively. Two strong emission peaks at 391 and 397 nm in Fig. 3(a), and a broad emission peak centering at ~534 nm in Fig. 3(b) could be observed. Liang et al. [8] studied the PL properties of the polymer-stabilized t-ZrO_2 nanopowders with average size of ~2 nm and found three emission peaks at 402, 420 and 459 nm, and a strong emission peak at 608 nm with a weak peak at 530 nm when the powders were excited by a 254 nm line and a 412 nm line, respectively. The different PL properties between the two t-ZrO_2 nanopowders should be due to their different synthesis routes.

The starting materials of the method are easy to obtain and the processing is very simple and environment-friendly.

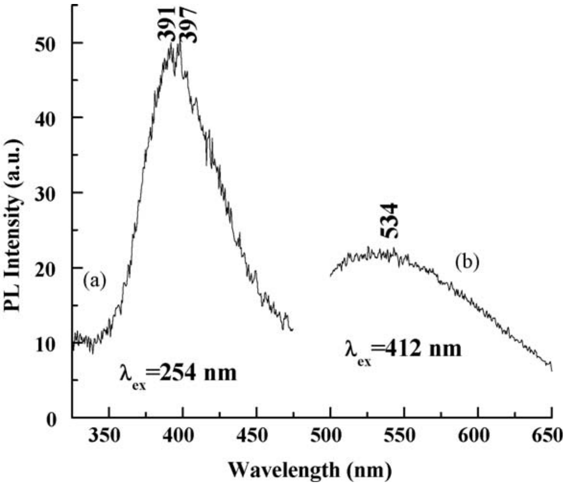

Fig. 3. PL Spectra of the heat treated powders excited at 254 nm (a) and 412 nm (b).

4. Conclusions

A simple and convenient route to pure t-ZrO_2 is presented. The t-ZrO_2 nanopowders from the molten hydroxides method showed poor crystalline quality. After heat treated at 400 °C for 10 h, the powders were crystalline with size range of ~8–12 nm, and most of them were agglomerated. The powders exhibited two strong emission bands at 391 and 397 nm when they were excited by a 254 nm line.

Acknowledgments

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