



Hydrothermal growth and characterization of zirconia nanostructures on non-stoichiometric zirconium oxide

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Abstract

Powder of nominal composition ZrO, which is a mixture of at least two different phases, was treated hydrothermally to grow zirconia nanostructures. The processes were performed in an autoclave using NaOH as the mineralizer at concentrations between 0 M and 25 M, at a fixed temperature of 200 °C and during 7 days. X-ray diffraction reveals the transformation of raw compound to monoclinic zirconia (ZrO₂) phase for all the concentrations of NaOH, which is confirmed by Raman spectroscopy. Transmission electron microscopy (TEM) indicates the formation of nanobars with diameter between 20 and 50 nm and length from 100 nm up to 200 nm. The growth of nanostructures was favored at higher concentrations, whereas the nanostructure length saturates at around 200 nm. Scanning electron microscopy (SEM) suggests that the growth of the nanostructures is perpendicular to the surface of raw powders. An emission peak of around 490 nm is observed in the photoluminescence (PL) spectra of zirconia nanostructures assigned to blue emission, with a red-shift at an increasing NaOH concentration. This is attributed to oxygen vacancies and a quantum size effect originated from the nanostructures produced during the hydrothermal treatment.

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1. Introduction

Zirconium dioxide ZrO₂ (zirconia) is monoclinic at room temperature, with tetragonal and cubic phases at higher temperatures. Nevertheless, cubic and orthorhombic phases have been detected in nanosized zirconia [1]. Nanosized zirconia has optical and electrical properties that may be used in transparent optical devices [2], electrochemical capacitor electrodes, oxygen sensors [3], fuel cells [4] and catalyst support [5]. As a biomaterial, coating with nanostructured zirconia by surface modification may improve the biocompatibility of implants [6].

A preferred method of growing zirconia nanostructures is by electrochemical treatments, which is limited to substrates of

low resistivity. Hydrothermal treatment of insulating zirconium oxide substrates has been reported by Kanade et al. [7], who modified the surface of commercial monoclinic zirconia powders (500 nm particle size) in a solution of NaOH, using an autoclave at 120 °C for 70 h, and obtained spherical particles in the range of 24–36 nm. Their X-ray diffraction (XRD) measurements showed the coexistence of monoclinic and cubic zirconia, while the selected area electron diffraction (SAED) corresponds to monoclinic nanoparticles. They also report the formation of disordered Zr–Na–O phases.

Starting with a different material, Espinoza et al. [8] treated nominal zirconium monoxide ZrO in a NaOH solution in the range of 15–25 M at 200 °C for one week, growing zirconia nanobars with monoclinic structure. One of the main advantages of hydrothermal processes is its comparatively lower environmental impact. Prof. Yoshimura illustrated the environmental

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impact, mainly reflected in the energy cost of a process, by displaying the temperature and pressure of different processes on a pressure–temperature diagram [9]; if ambient temperature and pressure are put at the center of the diagram, points far away represent processes expensive in energy. It is straightforward to expand this idea including the duration of the process, roughly proportional to the energy cost, as the third axis, or the cost of the chemicals and the environmental charge of the remnants. So, the advantage of the rather benign hydrothermal process is hindered because of the long treatment. The situation is even worse if we add the amount of mineralizer and the residuals released after the process.

In this article, we report the synthesis of zirconia nanostructures prepared by the hydrothermal method on a non-stoichiometric zirconium oxide (nominally ZrO) using an alkali solution of sodium hydroxide (NaOH) varying the concentration of NaOH. The structural and morphological properties of the nanostructures have been measured by X-ray diffraction (XRD), electron microscopy (SEM, TEM), and Raman spectroscopy (RS). The optical properties were studied as well.

2. Experimental

Commercial ZrO (99.3%, BALZERS) and sodium hydroxide (NaOH, 98%, Sigma-Aldrich) were used as starting material. 30 mL of basic solution was prepared at different concentrations of NaOH (0, 5, 10, 15, 20 and 25 M), with deionized water previously boiled to eliminate CO₂, in which the NaOH was introduced at 90 °C. The solutions were mixed in a Teflon vessel with 0.4 g of ZrO for each experiment. The vessel was introduced in an autoclave, sealed and heated up to 200 °C during 7 days, after which the autoclave naturally cooled down to room temperature. The resultant product was washed with deionized water several times until neutral pH was achieved, and finally dried in an oven at 200 °C during 15 min. Considering the different NaOH concentrations, the

samples were named Z-0 M, Z-5 M, Z-10 M, Z-15 M, Z-20 M and Z-25 M.

Samples were characterized by X-ray diffraction (XRD) in a Bruker D8 diffractometer using CuK $\alpha_{1,2}$ radiation. The data were collected at room temperature with a step size and scan rate of 0.01° and 0.1 s, respectively. The X-ray tube was operated at 40 kV and 30 mA. Rietveld refinements of XRD patterns were performed using TOPAS software, with a pseudo-Voigt function as a profile function. The obtained powders were also characterized using a Tecnai F20 G² transmission electron microscope (TEM) operated at 200 kV, equipped with an EDX detector. The TEM samples were ultrasonically dispersed in isopropyl alcohol and then collected in an ultrathin holey carbon-coated Cu grid. A FEI NOVA NanoSEM 30 scanning electron microscope (SEM) was used to study the surface of the powders. Raman spectra were recorded at room temperature in a backscattering geometry using a WITec alpha300R spectrometer, model CRC200, and a micro-Raman RM1000 Renishaw system. Radiation at 633 nm (1.96 eV) from a He–Ne laser was focused on the sample using a 100× objective. Photoluminescence (PL) measurements were performed at room temperature in a Perkin-Elmer spectrofluorometer LS-55, equipped with a Xenon lamp. All photoluminescence (PL) measurements were performed using a 10 mm/10 mm quartz cuvette.

2.1. Characterization of starting material

Since the oxidation states of zirconium are (0) and (IV), initial ZrO (named ZrO(i) sample) was characterized before hydrothermal treatments to elucidate the actual composition of raw powders. The initial powders were grinded in agate mortar and analyzed by XRD, TEM and Raman spectroscopy.

Fig. 1 displays the XRD pattern of ZrO(i) sample, indicating the existence of two crystalline phases identified as monoclinic ZrO₂ (m-ZrO₂, JCPDS 88-2390) and hexagonal ZrO_{0.27}

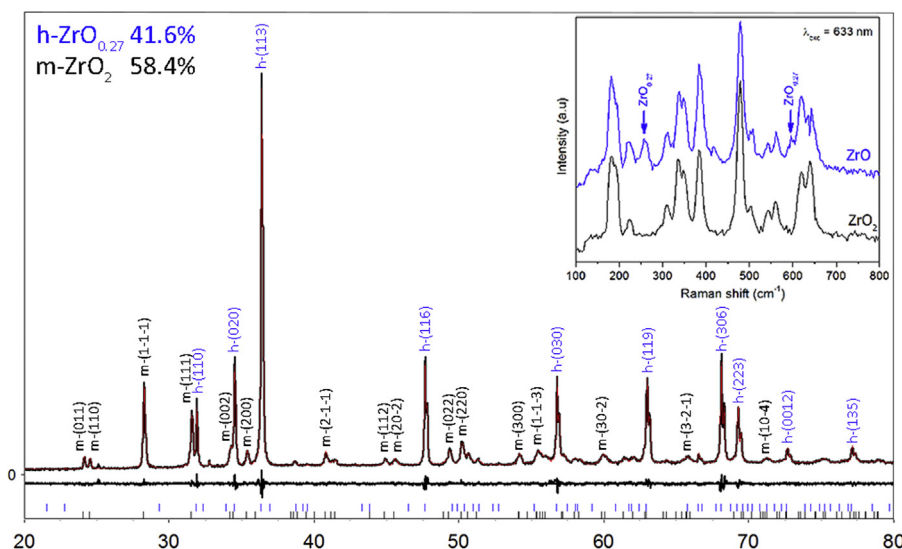


Fig. 1. XRD pattern of starting material, ZrO(i) sample. Hexagonal h-ZrO_{0.27} and monoclinic m-ZrO₂ phases are identified through indexed planes. Inset corresponds to Raman spectra of ZrO(i) sample and commercial ZrO₂.

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