Solar synthesis of nanostructured zirconia: microstructural and thermal characterization

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Abstract
The use of concentrated solar energy in processing ceramic materials is an attractive route to obtain these materials with low CO₂ emissions. In this work, nanostructures of monoclinic zirconia (m-ZrO₂) were obtained using concentrated solar energy provided by the IER-UNAM solar furnace as a heat source. In the first stage of the process, a Zr/O/C complex was obtained by sol-gel method at a temperature of 120 °C using zirconium n-propoxide and sorbitol as precursors reagents. This complex was used in a second stage to obtain m-ZrO₂ by heating it at a temperature of 1200 °C for one hour in air atmosphere. This last stage was performed in a solar furnace. Samples were analyzed by characterization techniques: FT-IR, TGA/DSC, XRD, TEM, and SEM confirming the formation of nanostructures of zirconia in monoclinic phase.

1. Introduction

Concentrated solar energy is a potential source of energy for developing materials reducing greenhouse gas emissions and other pollutants from the combustion of fossil fuels. Several researches study the synthesis and characterization of materials under concentrated solar radiation provided by a solar furnace [1–3]. Solar furnaces are research installations where it is possible to reach high temperatures in a few seconds [4]. Trefilov et al. [5] described seven solar furnaces and their respective applications in material science. Some materials that have been processed in solar furnaces are: crystalline glass based on residues of pyroxene [6], barium titanate [7], steel with TiB₂ [8], fullerenes [9–11], carbides [12–14], carburisation of metals [15, 16] and processing of metal oxides [17–19].

Nanostructured materials exhibit unique properties that can improve performance of various technologies in different fields, from catalysis to optics, from optoelectronics to structural applications [20]. Zirconium dioxide (ZrO₂) nanoparticles are considered attractive wideband semiconductors with extensive technological applications, due to their small size and high refractive index, these nanoparticles can be used as fillers in transparent coatings, such as anti-corrosive, anti-reflective and scratch-proof coatings [21]. ZrO₂ is a metal oxide ceramic material with unique physicochemical properties which depend on its crystalline phase, particle shape and size. This material exists in three crystalline phases: monoclinic (m-ZrO₂), tetragonal (t-ZrO₂) and cubic (c-ZrO₂). Both last two phases possess superior mechanical properties but are degraded at low temperatures in water or vapor [22], while the monoclinic structure is thermodynamically stable [23]. The transition from the tetragonal to monoclinic phase can improve zirconia mechanical properties with the introduction of compressive stress [24]. Zirconia also shows an excellent combination of strength, fracture toughness, ionic conductivity and low thermal conductivity [25, 26]. Nanostructured zirconia has optical and electric properties in applications of piezoelectric, dielectric, and nanocomposite materials, fuel cells and oxygen sensors, among others [27, 28].
Synthesis of ZrO₂ using several different methods has been reported. These include: sol-gel [29–32], hydrothermal [20, 27, 28, 33], solvothermal [34], micro-emulsion [35], oil/water interface [36], combustion synthesis [37], atmospheric plasma-spraying technique [22], direct nucleation [38] anodization [39], salt-assisted ultrasonic spray pyrolysis with a citrate precursor method [21], co-precipitation route using inorganic precursors [40], molten salt method [26], and in one pot at room temperature using an extremophilic Acinetobacter sp. KCSI1 [41], in which zirconia nanostructures such as nanorods, needles, nanobars, nanosheets, nanowires or nanoparticles are obtained.

In this work, we report for the first time the synthesis of zirconia nanostructures through a processing solar of thermal decomposition from a Zr/O/C complex obtained by sol-gel process, using zirconium n-propoxide and sorbitol as precursors reagents.

2. Materials and methods

2.1. Materials

Zirconium n-propoxide (a concentration of 70 wt% in 1-propanol, supplied by Aldrich®), boric acid, sorbitol, and acetic acid were used for solar zirconia synthesis.

2.2. Experimental procedure

Zirconium dioxide was synthesized through the two following stages. The first stage consists in Zr/O/C complex synthesis at low temperature (120 °C) by a sol-gel process, like that reported by Ji et al [42]. In this stage, boric acid (H₃BO₃) and sorbitol (C₆H₁₄O₆) were dissolved in acetic acid (C₂H₄O₂), with continuous stirring at 60 °C for 1 h. The obtained solution was cooled down to room temperature, then zirconium n-propoxide (Zr(OPr)₄) was added under constant stirring at room temperature. Subsequently, the sample was introduced in an electric furnace at 70 °C for 4 h; this material was dried at 120 °C temperature for 6 h, obtaining a light-yellow material with a vitreous consistency, resulting in Zr/O/C complex powders for ZrO₂ synthesis. The second stage comprises the high-temperature synthesis of solar ZrO₂ starting with the Zr/O/C complex powders obtained in the first stage. This synthesis was performed at different temperatures for 1 h: 400, 800 and 1200 °C, under air atmosphere. The high temperatures were obtained by direct solar irradiation provided by the IER-UNAM solar furnace.

ZrO₂ synthesis with solar processing was performed in a 10 kW cavity solar reactor. The reactor consists of a ceramic cylindrical cavity with a 15 cm-diameter aperture where the concentrated solar radiation is received. This cavity has been insulated by a surrounding layer of Al₂O₃-SiO₂ fibers to reduce conduction heat losses. A stainless-steel outer shell sheathed both, cavity, and insulation. The reactor front is closed with a 40 cm-diameter borosilicate glass window to maintain a controlled atmosphere in the reaction zone. Carrier gas was injected near the window through six radial inlet ports. Reaction gas product exited the reactor via an outlet port placed at the back of the reactor (figure 1). Sample temperature was measured by R-Thermocouple and gas flow was regulated by mass flow controllers (Bronkhorst EL-flow mass controller).

The sample was directly irradiated with concentrated solar energy provided by the IER-UNAM solar furnace. This solar furnace gives a maximal power of 25 kW with peak concentrations of 18,000 kW m⁻² in the focal zone. It consists of a flat heliostat of 81 m² surface area and a solar concentrator formed of 409 hexagonal...
mirrors \[43\]. Between the solar furnace and the concentrator, there is a shutter that regulates the amount of concentrated solar energy that the sample receives, and therefore the temperature in the sample.

2.3. Characterization
To confirm characteristic bonds, the material was analyzed by Fourier transform infrared spectroscopy (Bruker Fourier Transform Infrared Spectrophotometer, FT-IR, Alpha-model). To analyze thermal decomposition of the Zr/O/C complex and oxidation resistance of zirconia, thermal analysis was performed at a heating rate of 10 °C min \(^{-1}\), from ambient temperature to 1000 °C, under air atmosphere (TA Instruments SDT Q600, TGA/DSC). Crystalline phases of ZrO$_2$ powders and interplanar distances were identified by x-ray diffractometer (RIGAKU, Mod. DMAX-2200, XRD). Microstructure, particle size, and crystallinity were evaluated by transmission electronic microscopy and high-resolution transmission electron microscopy (JEOL 1400 of 120 kV, TEM, HRTEM). Surface of the powders was analyzed with a scanning electron microscope (JEOL JSM-7800F, SEM).

3. Results

3.1. Zr/O/C complex characterization
Figure 2 shows the FT-IR spectrum of Zr/O/C complex synthesized at 120 °C, showing peaks corresponding to stretching vibrations of the O–H bond and bending vibrations of water molecules adsorbed at 3417 and 1620 cm \(^{-1}\), respectively. Peak at 1413 cm \(^{-1}\) is assigned to the B–O–C bond found near the B–OH bond characteristic peak at 1370 cm \(^{-1}\), as reported \[42\], where B–OH bond was transformed into B–O–C due to the reaction that occurred between boric acid and sorbitol. Peak at 1174 cm \(^{-1}\) corresponds to the Zr–O–C–B bond, while two pairs of peaks at 1047 and 1096 cm \(^{-1}\), and at 803 and 857 cm \(^{-1}\) were attributed to Zr–O–C and Zr–O bonds, respectively, formed in the sol by hydrolysis process and condensation reactions as bond bridges with increased viscosity. These bonds allowed to stabilize and to standardize the sol. In addition, a pair of peaks was observed at 551 and 654 cm \(^{-1}\) formed by hydrolysis of Zr(OPr)$_4$ \[40, 41, 44\].

Thermogram in figure 3(a) shows TGA and DSC of Zr/O/C complex synthesized at 120 °C. There were four stages of mass loss: from room temperature to 200 °C, there was a 16% of mass loss due to propanol elimination and water absorption with an endothermic peak at 120 °C; between 200 °C–500 °C, 25% of mass loss was lost, corresponding to a small decomposition of boric acid crystals to boron trioxide (B$_2$O$_3$) \[33\], with exothermic peaks at 366 and 486 °C due to organic material combustion and decomposition of hydrated ZrO$_2$ into amorphous ZrO$_2$, respectively \[45–47\] and, after 500 °C a small mass loss of 7% appeared, associated with an exothermic peak at 700 °C, resulting from the transformation of amorphous ZrO$_2$ into m-ZrO$_2$, where B$_2$O$_3$ could have been volatilized above 600 °C\[33\]. Reduction of organic content is correlated with the crystallization process \[48\]. The XRD pattern (figure 3(b)) of Zr/O/C complex powders exhibits a mostly amorphous material presenting only a few peaks characteristic of B$_2$O$_3$ in 2θ at 14.6° and 27.9° (JCPDS No. 06-0297); the wide peak in 2θ = 6.6° indicates carbon presence \[49\] derived from sorbitol.
3.2. ZrO\textsubscript{2} characterization

3.2.1. X-ray diffraction analysis

Figure 4 shows the XRD patterns for Zr\textsubscript{}/O\textsubscript{}/C complex heated in a solar furnace at different temperatures for 1 h under air atmosphere. Figure 4(a) exhibits the formation of t-ZrO\textsubscript{2} and boron oxide (B\textsubscript{2}O\textsubscript{3}) at 400 °C, according to JCPDS 17-0923 and 06-0297, respectively. In figure 4(b), m-ZrO\textsubscript{2} and small traces of t-ZrO\textsubscript{2} \cite{40}, graphite, and B\textsubscript{2}O\textsubscript{3} were observed, indicating that zirconia tetragonal phase has been transformed mainly into monoclinic zirconia at 800 °C. Research on zirconia surface treatment to enhance the osseointegration behavior in implant dentistry, indicates that the transition from the tetragonal to monoclinic phase can improve mechanical properties of this material due to the introduction of compressive stress \cite{24}. When temperature reached 1200 °C, m-ZrO\textsubscript{2} was the only crystalline phase present (JCPDS 37-1484), without impurity (figure 4(c)), which means that the higher the synthesis temperature is, the more predominant the monoclinic phase is.

Precursor reagents were dissolved in the solution, but boric acid was not involved in the sol-gel network construction. Boron makes a sol more stable and uniform when temperature increases and, furthermore, Zr–O–C–B network structure fractures and forms crystallized B\textsubscript{2}O\textsubscript{3}, C and ZrO\textsubscript{2} \cite{41}. Therefore, the XRD results were consistent with the TGA/DSC analysis of Zr\textsubscript{}/O\textsubscript{}/C complex, confirming the ceramics crystallization at 1200 °C.

3.2.2. TEM and HRTEM analysis

Microstructural analysis of solar m-ZrO\textsubscript{2} was performed by TEM and HRTEM. Figure 5(a) shows TEM bright field image of m-ZrO\textsubscript{2} nanorods obtained at 1200 °C with a thickness around 300 nm and a 0.3–2 \textmu m length.
Figures 5(b), (c) exhibit nanostructures of solar m-ZrO$_2$ in different magnifications showing a mostly cubic morphology with a narrow range of sizes. Figure 5(d) shows corresponding HRTEM image with typical spacing for the monoclinic zirconia crystal lattice such as 0.284 and 0.221 nm, corresponding to the (1 1 1) and (−1 1 2) planes with $2\theta = 31.45^\circ$ and $2\theta = 40.7^\circ$, respectively (JCPDS 37-1484), which are shown in the Fast Fourier Transform (FFT) pattern (inset in figure 5(d)), as well as the corresponding (−2 0 2) and (−4 0 1) planes to $2\theta = 45.5^\circ$ and $2\theta = 71.3^\circ$, respectively. XRD analysis is consistent with the electron diffraction pattern generated by FFT from HRTEM.

3.2.3. SEM analysis
To obtain a clear understanding of the behavior of the ZrO$_2$ nanostructures synthesized in the solar furnace, SEM analysis was performed. SEM images of solar m-ZrO$_2$ nanostructures synthesized in the solar furnace are presented in figure 6. Figure 6(a) micrograph shows porous zirconia nanostructures with different morphology and sizes. As the temperature rises during the heat treatment process, it leads to the escape of CO, which eventually leads to the formation of a different pore size, resulting in a denser and porous ceramic. Figures 6(b)–(d) show the indicated amplified regions. Figure 6(d) exhibits monoclinic zirconia nanostructures where a spherical and cubic morphology predominates with dimensions of 100–200 nm thick and length ranging from nanometers to 1–2 μm (similar value to TEM analysis obtained). The zirconia nanomorphology has great application in dental implants to improve the osseointegration process, therefore this system can be used for the generation of biomaterials [50]. Kumari et al [28] has reported similar sizes with hexagonal shape ZrO$_2$ nanostructures but with sodium impurities, these researchers use different synthesis methods with conventional energy and longer synthesis time. Synthesis in a solar furnace of nanostructured zirconia has not been reported before, so it is possible to obtain similar results using solar and conventional energy.

3.2.4. Thermal analysis
Figure 7 shows the TGA of m-ZrO$_2$ synthesized in the HoSIER at 1200 °C. TGA showed a weight loss up to 170 °C of 5.2%, which is attributed to humidity, while from 170 °C–1000 °C mass was kept constant presenting good thermal stability. Previous results indicate that synthesized solar m-ZrO$_2$ shows better thermal stability and lower weight loss compared to what has been reported in the literature [48, 53–55], where m-ZrO$_2$ was obtained with hydrothermal treatment at synthesis times greater than 24 h.

3.2.5. FT-IR spectroscopy
Figure 8 shows the FT-IR spectrum of solar m-ZrO$_2$ with a band at 3218 cm$^{-1}$ due to O–H groups and absorbed humidity. The 1464 and 1196 cm$^{-1}$ bands are assigned to the bending vibrations of C–H bonds in the species linking. C–H bond was related to the carbon chain of the organic additives adsorbed on the surface of zirconia,
while the 750 cm\(^{-1}\) band is characteristic of m-ZrO\(_2\). Finally, the 537 and 648 cm\(^{-1}\) bands are assigned to Zr–O vibrations or ZrO\(_2\) phase [31, 51, 52].

4. Conclusions

Zirconia nanostructures were synthesized for the first time through processing solar, which was provided by the solar furnace, using a cavity solar reactor designed to work at high temperatures and controlled atmospheres. XRD and HRTEM analyses showed zirconia synthesized at 1200 °C with high crystallinity and unique crystalline structure: monoclinic zirconia. TEM micrographs revealed the formation of m-ZrO\(_2\) nanostructures with a 100–200 nm thickness and a 0.3–2 μm length, while SEM images showed the morphology of powders, predominating circular and rectangular nanostructures. According to TGA thermal analysis results, m-ZrO\(_2\) presented high thermal stability.

The reported process could be used for synthesizing other metal oxide nanostructures, reducing CO\(_2\) emissions by using concentrated solar energy in processing materials instead of conventional methods.
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Figure 8. FT-IR spectrum of m-ZrO2 synthesized at 1200 °C in HoSIER.
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