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Nanocrystalline ZrO_2 powder preparation using natural cellulosic material

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Nanocrystalline zirconia powder has been successfully prepared using a precursor calcination process involving hydrolysis of zirconium(IV) isopropoxide and utilizing *Oryza Sativa* pulp (Merang Pulp) as the cheapest natural template. The potential of *Oryza Sativa* pulp as a template in the preparation of nanocrystalline zirconia is investigated in this research. It is also shown that the presence of the pulp can produce zirconia in nanocrystallites because the agglomeration tendency has been reduced in the as-synthesized ZrO_2 particles. The effect of the calcination temperature on this zirconia preparation is found out by variation of the applied calcination temperature. XRD characterization shows monoclinic zirconia as a fully dominant phase, and the largest ZrO_2 crystallite is found to be 42.7 nm. However, the zirconia crystallite size will increase with an elevation of the calcination temperature.

Key words: Nanocrystalline, powder, zirconia, precursor calcining process, *Oryza Sativa* pulp.

Introduction

Zirconia is well known as a material for structural applications due to its excellent properties, such as high mechanical strength, fracture toughness, and hardness [1]. Zirconia exhibits three well-defined polymorphs: monoclinic (m), tetragonal (t), and cubic (c) phases. [2-5]

$$\text{Monoclinic} \xleftrightarrow{950\text{–}1170\,^{\circ}\text{C}} \text{tetragonal} \xleftrightarrow{1170\text{–}2270\,^{\circ}\text{C}} \quad (1)$$

$$\text{Cubic} \xleftrightarrow{2270\text{–}2680\,^{\circ}\text{C}} \text{melting point.} \quad (2)$$

The tetragonal-to-monoclinic phase transformation in ZrO_2 has become very important in engineering ceramic materials. It has been used to increase the fracture toughness, strength, and hardness of oxides (alumina) as well as non oxides (carbides, borides, and nitrides) ceramics, using tetragonal-ZrO_2 as a dispersed phase. Tetragonal-ZrO_2 is also used for other applications such as a catalyst, while cubic-ZrO_2 finds other applications in the automobile industry as an oxygen sensor and in the fabrication of fuel cells [5, 6].

Controlled structures, large interfaces, density power and other unique characteristics are examples of the superiority of nano-materials properties so that they can access new and improved properties and functionalities. Therefore, nano-ZrO_2 exhibits more excellent chemical and physical properties as compared to normal or coarse ZrO_2 powder, due to the small particle diameter and will result in a better sintering ability [7-9].

The most common methods that have been used to synthesize nano ZrO_2 are a "sol-emulsion-gel technique" and a "sol-gel method" [1, 2]. Several methods have been used to synthesize or to prepare nanoparticles of zirconia namely: 1) Roy has synthesized tetragonal zirconia using poly-acryl amide as a gel and matrix, and the average particle size of tetragonal zirconia synthesized was about ~20 nm [5]; and 2) Shukla, *et al*. has prepared nano-sized zirconia powder using a sol gel technique involving hydrolysis and condensation of zirconium (IV) n-propoxide in an alcohol solution, utilizing hydroxypropyl cellulose (HPC) polymer as a steric stabilizer, then a calcination process was performed at a temperature of 400 °C for 2 hours, and the crystalline phase was tetragonal zirconia having a crystallite size of 65 nm [6]. Both of the nano-sized zirconia preparation methods use a synthetic template material, which is not economical and relatively more expensive. Therefore, the present study tries to apply a simple precursor method and to utilize a natural template such as *Oryza Sativa* pulp (Merang Pulp) on the preparation of nanocrystallline ZrO_2, which consists of a cellulosic structural coating on ZrO_2 particle surfaces which results in reduced particle-particle aggregation due to the steric hindrance provided by the polymer [6]. The benefits of using *Oryza Sativa* pulp are that it is easy to obtain and very cheap. The potential of *Oryza Sativa* pulp as a template in the preparation of nanocrystalline zirconia is investigated in this research and the effect of the calcination temperature is identified

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by variation of the applied calcination temperature at 900 °C, 1000 °C, and 1100 °C.

Experimental Procedure

Materials

Zirconium (IV) chloride was obtained from Merck; whereas isopropyl alcohol, ethanol, methanol, and an ammonia solution were obtained from Aldrich Co.; and the *Oryza Sativa* pulp (Merang Pulp) was obtained from the local pulp and paper industry.

Synthesis of Precursor

9.83 grams of $ZrCl_4$ as precursor was reacted with *isopropyl alcohol* to produce *zirconium isopropoxide* ($Zr(i\text{-}C_3H_7O)_4$). The product then was dissolved in a mixture of 300 ml *ethanol* and 300 ml *methanol* along with stirring by a magnetic stirrer for 15 minutes. Then, 19.6 grams of *Oryza* Sativa pulp was put into the solution slowly along with stirring for 15 minutes. The weight ratio of precursor to pulp was 1 : 2. Hereinafter, ammonia solution was poured slowly into the mixture until hydrolysis occurred by checking the pH, the process was carried out until the solution pH was equal to 6. Then an aging process was conducted for 48 hours. After that, the solution was filtered until a gel of zirconium hydroxide-pulp was obtained. The sample from the filtration was divided into three parts; the carbon content of each sample had to be removed by oxidizing it at a temperature of 400 °C for 3 hours in an oxidation furnace.

Precursor calcination process

After the oxidizing process, calcination was performed at the temperatures of 900 °C, 1000 °C, and 1100 °C for 90 minutes. The samples were given labels based on the temperature calcination, namely ZrO_2-900 °C, ZrO_2-1000 °C, and ZrO_2-1100 °C.

Characterization

All synthesized sample, ZrO_2-900 °C, ZrO_2-1000 °C, and ZrO_2-1100 °C were characterized by XRD, SEM and TEM. The crystalline phase of calcined powder and the average crystallite size were determined by X-ray powder diffraction using a PAN analytical X-ray instrument. Meanwhile, a scanning electron microscope (SEM, JEOL JSM-35C) was used to observe the morphology and the sizes of crystallites. TEM characterization was also performed to observe the crystallite size of the synthesized zirconia.

Result and Discussion

Zirconia precursor phase transformation

Fig. 1 shows XRD patterns of ZrO_2 samples calcined at the temperatures of 900 °C, 1000 °C, and 1100 °C. According to three XRD patterns, two phases of ZrO_2 have been formed namely the t-ZrO_2 and m-ZrO_2 phases. Nevertheless, the existence of the t-ZrO_2 phase in the samples is at a very small level. This is shown by the small diffraction main peak intensity of t-ZrO_2 at a 2θ angle of 30.25° and the intensity becomes lower with an elevation of the calcination temperature. The main phase, m-ZrO_2 is shown by two main peaks at diffraction angles of 28.21° and 31.45°, from crystals planes of $(\bar{1}11)$ and (111) respectively. The peak intensity from t-ZrO_2 becomes lower with an elevation of the calcination temperature, because during the thermal treatment of the amorphous zirconia gels at assorted temperatures above 400-600 °C, the crystallization is occurred via a thermodynamically metastable tetragonal phase, whilst at temperatures above 600 °C, the tetragonal-to-monoclinic phase transformation occurred [12]. The peak intensity from the m-ZrO_2 is becoming sharper with the elevation of the calcination temperature as shown in Fig. 1.

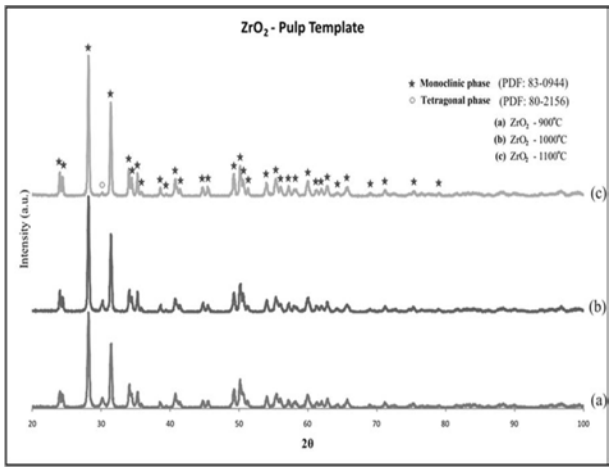

Fig. 1. XRD patterns of ZrO_2, (a) T = 900 °C, (b) T = 1000 °C, (c) T = 1100 °C.

Crystal Size

Crystal sizes are calculated using the Scherer equation based on the main peaks of the XRD patterns [2, 10]:

$$D = \frac{\kappa\lambda}{\beta cos\theta} \tag{3}$$

where D is the crystal size, K is a shape factor with a value of 0.9-1, λ is the wavelength of the X-rays (1.54056 Å), and β is the value of the *full width half maxima* (FWHM). According to the Scherer equation, the crystal size of the three zirconia samples can be calculated and is presented in Table 1.

Table 1 shows the crystals size from two m-ZrO_2 main peaks with crystal planes of $(\bar{1}11)$ and (111). The crystal

Table 1. Crystal size of two main peaks of m-ZrO_2

Crystal plane	ZrO_2 900 °C	ZrO_2 1000 °C	ZrO_2 1100 °C
$(\bar{1}11)$	34.1 nm	39.2 nm	42.7 nm
(111)	31.9 nm	37.4 nm	39.5 nm

sizes for the ZrO_2 sample calcined at the temperature of 900 °C for planes of ($\bar{1}$11) and (111) are 34.1 nm and 31.9 nm respectively. Whereas the crystal sizes for the ZrO_2 sample calcined at the temperatures of 1000 °C and 1100 °C are about 39.2 nm for ($\bar{1}$11), 37.4 nm for (111) and 42.7 nm for ($\bar{1}$11), 39.5 nm for (111), respectively. When the peak of an XRD pattern is more broadened and has a lower intensity, the crystal size is becoming smaller. By contrast, if the peak of an XRD pattern is becoming sharper, crystal sizes will be bigger and its crystallinity will be better. This is in conformity with the three XRD patterns of the ZrO_2 samples in Fig. 1.

Morphology

According to the SEM micrographs given in Fig. 2, the size of ZrO_2 powders are found in the range of 47-76 nm at a calcination temperature of 900 °C, 76-94 nm at a calcination temperature of 1000 °C, and 88-141 nm at a calcination temperature of 1100 °C. As the temperature increases, the crystallite grains grow and crystal size becomes larger. A typical TEM image of the zirconia powder at calcination temperature of 900 °C for 90 minutes is given in Fig. 3. The image represents a small region of the ZrO_2 powder having an average size near 50 nm.

The size of nano m-ZrO_2 products is sensitive to the calcination temperature. This research has shown the potential of *Oryza Sativa* pulp as a template of a precursor calcining process in the preparation of nanosize ZrO_2. The above results are indicative that the overall process represents an effective and a low cost methodology; however, further experiments are needed to provide more comprehensive results for a full understanding of the nanosize zirconia preparation process.

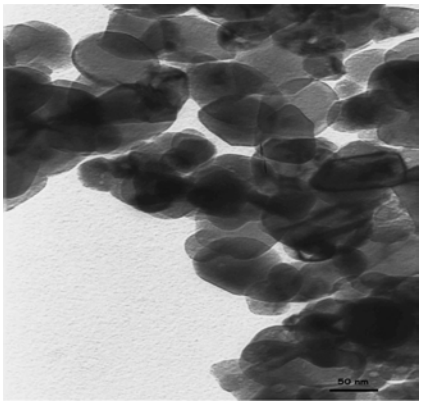

Fig. 3. TEM images for a sample of (a) ZrO_2-900 °C.

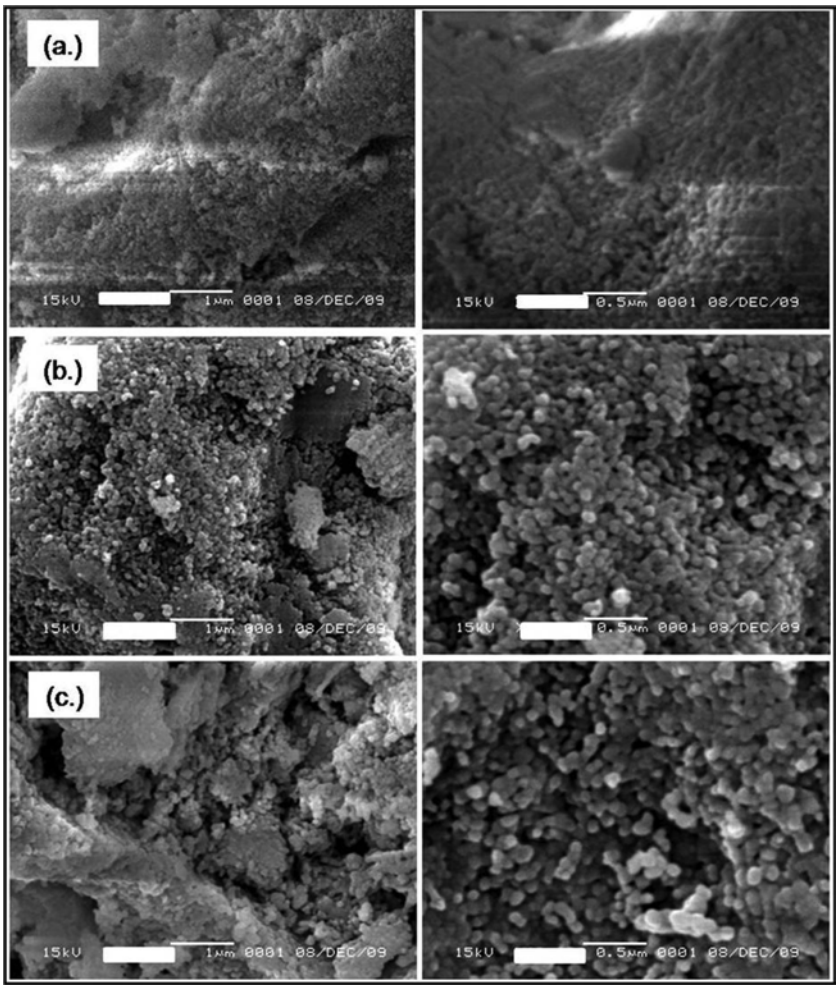

Fig. 2. SEM images for samples of (a) ZrO_2-900 °C, (b) ZrO_2-1000 °C and (c) ZrO_2-1100 °C.

The formation of "Zirconium-cellulonates"

The rate of a chemical reaction depends on the following : (*a*) pH, (*b*) concentration, and (c) solution [1]. In the case of the preparation of the 'zirconia powder' from a zirconium salt, the reactions are assumed as follows:

$$ZrCl_{4(s)} + 4(i\text{-}C_3H_7OH)_{(l)} \rightarrow Zr(i\text{-}C_3H_7O)_{4(s)} + 4HCl_{(l)} \quad (4)$$

$$Zr(i\text{-}C_3H_7O)_{4(s)} + 4H_2O_{(l)} \xrightarrow{NH_4OH} Zr(OH)_{4(aq)} + 4i\text{-}C_3H_7OH_{(l)} \quad (5)$$

The reaction occurs step by step and slowly based on the addition of ammonia.

The presence of cellulose, during the preparation, significantly reduces the tendency to agglomeration in the as-synthesized ZrO2 particles. The cellulose contains hydroxyl and ether groups in its structure, which hydrogen bond with the hydroxyl groups from the particle surfaces (Fig. 4). As a result, the surface hydroxyl groups get capped with the glucose polymer (cellulose). The cellulose coating on the ZrO_2 particle surfaces results in reduced particles aggregation due to the steric hindrance provided by the polymer [6]. In this case, cellulose is not only capable of masking salt molecule in the surfaces, but also forms "zirconium-cellulonates".

$$nZr(OH)_{4(aq)} + [Cellulose]_n \rightarrow [zirconium\text{-}cellulonates]_{n\ (gel)} + 4nH_2O_{(l)} \quad (6)$$

At a calcination temperature above 900 °C (Fig. 5), zirconium cellulonates are decomposed becoming zirconia particles, carbon dioxide and water molecules.

Conclusions

Nanocrystalline zirconia powders were successfully prepared using natural cellulosic material (*Oryza Sativa* pulp). The presence of the pulp can produce zirconia in a nanocrystallite form because it can reduce the tendency for agglomeration in the as-synthesized ZrO2 particles.

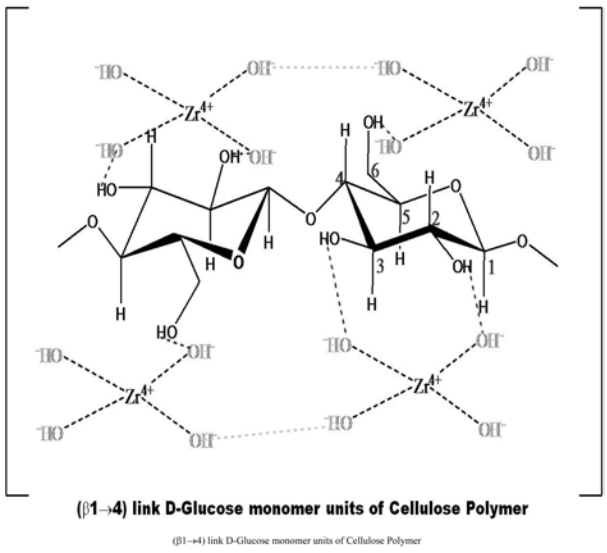

Fig. 4. Mechanism of the formation of zirconium-cellulonates.

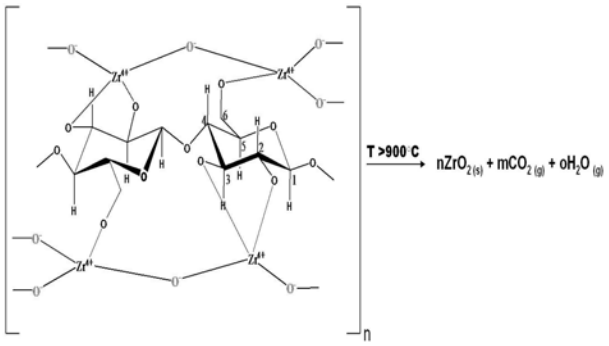

Fig. 5. Reaction occurring at a temperature above 900 °C.

However, the size of the nanocrystalline ZrO_2 powder is sensitive to the calcination temperature. The higher the temperature applied, the larger the crystal size will be produced. The optimum calcination temperature of the precursor for nano ZrO_2 crystallization is found at the temperature of 900 °C for 90 minute where the crystallite sizes based on the $(\bar{1}11)$ and (111) planes are 34.1 nm and 31.9 nm, respectively. Whereas, the ZrO_2 crystallite particle sizes at this calcination temperature are from 47 to 76 nm as given by SEM.

The experimental results are indicative that the overall process represents an effective and a low cost methodology. Therefore, *Oryza Sativa* pulp has the potential to be used as a template in nanocrystalline ZrO_2 preparation.

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