Novel Acrylamide Assisted Polymeric Citrate Route for the Synthesis of Nanocrystalline ZrO_2 Powders for Dental Applications

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ABSTRACT

The acrylamide assisted polymeric citrate route was investigated for the synthesis of nanocrystalline ZrO_2 powders, using zirconium oxychloride as the source for metal ion along with citric acid and acrylamide as chelating as well as polymerizing agents. The complete process for the synthesis of nanocrystalline ZrO_2 powders was monitored by TG/DTA, FTIR, XRD and TEM techniques. Thermal decomposition of the polymeric intermediate was investigated using TG/DTA analysis. Structural coordination and phase of the synthesized ZrO_2 powders were investigated by FTIR and XRD analysis respectively. The microstructure of the synthesized nanocrystalline ZrO_2 powder was identified using transmission electron microscopy, which showed ~10nm agglomerates of still finer ZrO_2 particles.

Keywords: Nanocrystalline ZrO_2, Acrylamide, combustion, TG/DTA, FTIR, XRD, TEM.

1 INTRODUCTION

Zirconium oxide has been found to have wider range of biomedical applications than other ceramic materials, because of its high mechanical strength, fracture toughness, bio-compatibility, etc. [1-3]. Also, zirconia powders have been shown to have enhanced performance as reinforcing fillers in dental composites due their physicochemical properties [4]. Recently it is found that the zirconia based biomaterials with nanocrystalline phase exhibits an enhanced performance due to the smallest crystallite size as well as larger surface area [5]. Synthesis of nanostructured zirconia powders with desired properties (size and shape) is often difficult, since nanoscale particles agglomerate easily due to the high surface reactivity [6, 7]. In order to overcome these disadvantages, wet chemical routes, such as sol-gel, combustion, etc., have been investigated for the preparation of a wide range of nano structured metal oxides, including nanocrystalline zirconia powders [8-12].

Among the available routes, the polymeric citrate process, which is also a combustion process, has been found to be a versatile route to the synthesis of a wide range of metal oxides with controlled morphologies [13, 16]. Basic principle of polymeric citrate process is to distribute the metal ions though out the polymeric network uniformly, which also inhibit the metal ion precipitation. Thermal decomposition of the polymeric intermediate lead to the formation of fine ceramic powders [17]. Recently, we found that addition of acrylamide to polymeric citrate enhances polymerization during the evaporation process and leads to the formation of a highly porous intermediate material. Thermal decomposition of the porous intermediate leads to the formation of non agglomerated, independent particles. Hence, in the present work, nanocrystalline ZrO_2 powders were prepared by the acrylamide assisted polymeric citrate route, and the complete synthesis process and the final product were investigated through TG/DTA, FTIR, XRD and TEM techniques.

2 EXPERIMENTAL TECHNIQUES

Fig 1 shows the schematic procedure for the synthesis of nanocrystalline ZrO_2 powders. Required amount of zirconium oxychloride (AR, Sd-Fine, India) was first mixed with concentrated nitric acid and boiled for 10 min. Citric acid (CA) (SQ grade, Qualigences, India) and acrylamide (ACD) (AR, Sd-Fine, India) solutions were added to the zirconium oxychloride and nitric acid mixture by keeping the total metal ions to CA ratio of 1:1 and total metal ions to ACD ratio of 1:0.5 and the resulting solutions were heated at 80^{o}C under constant stirring. Evaporation resulted in the formation of polymeric resin. This was dried at 150^{o}C for 24 hours and the resulting highly porous intermediate was calcined at 600^{o}C to obtained nano crystalline ZrO_2 powders, which were characterized using TGDTA, FTIR, and XRD, and TEM analysis.

Thermal behavior of the polymeric intermediate was investigated by simultaneous TG/DTA measurement using a Lybsys thermal analyzer (Setaram, France). Approximately, 3mg of polymeric intermediate was heated at a rate of 10^{o}C min^{-1} between 30 – 600^{o}C. All thermal studies were performed in flowing oxygen. Fourier transform infrared (FTIR) spectra were recorded using a FTIR - 8000 spectrophotometer (Shimadzu, Japan), to identify the structural coordination of as-prepared as well

as-calcined polymeric intermediate. The FTIR measurements were carried out between 400 and 4000 cm^{-1} with KBr dilution. X-ray diffraction (XRD) patterns were recorded using an X-ray powder diffractometer (Rigaku, Japan), employing Cu K_α radiation. The volume fraction of the monoclinic phase (V_m) was determined using the following empirical formula [18].

$$V_m = [I_m(111) + I_m(11\bar{1})]/[I_m(111) + I_m(11\bar{1}) + I_t(111)]$$

where $\boldsymbol{I_m}$ – intensities of the monoclinic peaks and $\boldsymbol{I_t}$ - Intensities of the tetragonal peaks. Microstructure of the polymeric intermediate was taken using transmission electron microscope (Jeol, Japan). The samples for TEM measurements were prepared by dispersing the polymeric intermediate powder in high purity acetone and sonicated for 2 min. Using tweezers, a carbon coated copper grid was immediately dipped into the sonicated suspension, then dried and TEM images collected.

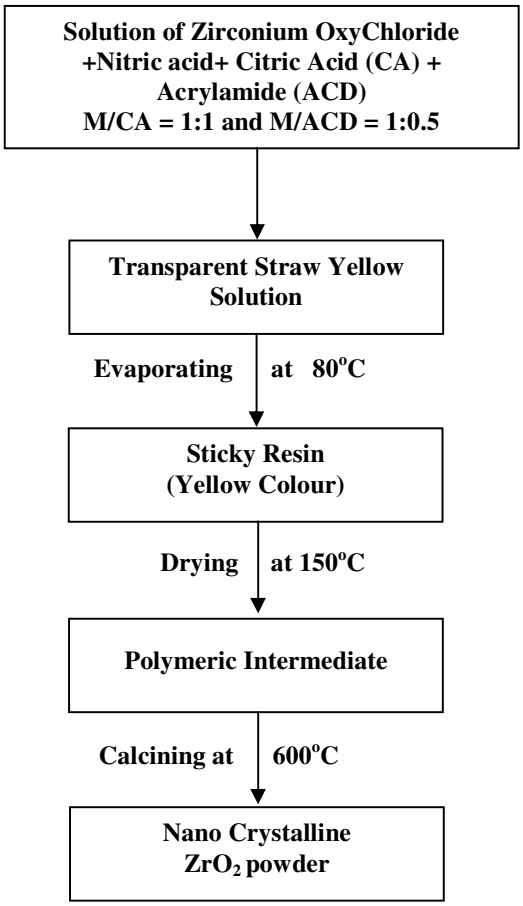

Figure 1. Schematic diagram for the synthesis of nanocrystalline ZrO_2 powder by the acrylamide assisted polymeric citrate route

3 RESULTS AND DISCUAAION

TG/DTA thermogram of the polymeric intermediate is shown in fig 2. The observed exothermic peak with a major weight loss of ~40% in the TGA curve indicates the combustion of organic derivatives, which begins at 300°C and is complete at 575°C. Also, the observed small exothermal peak between 500 and 575 °C, may be due to the crystallization of ZrO_2. No further weight loss is observed above 575 °C, which may indicate the formation of ZrO_2 structure. This is confirmed by FTIR and XRD analysis.

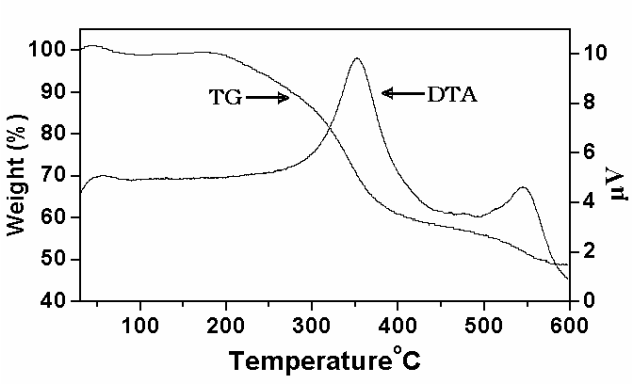

Figure 2 TG/DTA thermogram of the polymeric intermediate

Fig 3 shows the FTIR spectrum of the synthesized ZrO_2 powder. The observed IR peaks at 747-755 cm^{-1} and 498-502 cm^{-1} are attributed to the vibration modes of the ZrO_3^{2-} group, and confirm the formation of ZrO_2 [19, 20]. The observed FTIR spectrum does not show any peaks related to the organic derivatives, which confirm that complete decomposition occurred during the calcination process, as observed in the TG/DTA analysis.

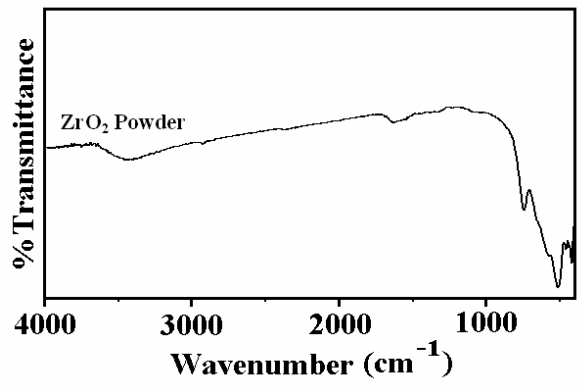

Figure 3 FTIR spectrum of synthesized ZrO_2 Powder

Figure 4 shows the XRD pattern of synthesized ZrO_2 powder prepared at 600 ^{0}C. From fig.4, the observed x-ray diffraction peaks are compared with the JCPDS data and confirm the formation of mixed phases of tetragonal (t-ZrO_2) and monoclinic (m-ZrO_2) zirconium oxides. The volume fraction was calculated using XRD data. The volume fractions obtained for the tetragonal and monoclinic phases are respectively 53.4 % and 46.6 %.

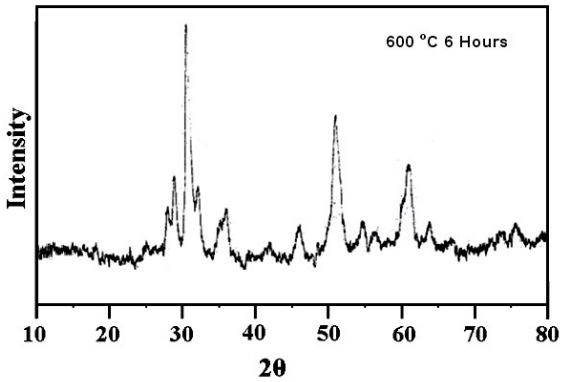

Figure 4 XRD pattern of synthesized ZrO_2 Powder

Microstructure of the synthesized ZrO_2 powder is identified through TEM analysis. Fig.5 shows the TEM micrographs of the synthesized ZrO_2 powder. The TEM images show <1000 nm agglomerations of primary ZrO_2 particles that are in the size range of ~10-20 nm. Synthesized ZrO_2 particles are planned for use in the development of nanocomposite resin materials for dental and other biomedical applications.

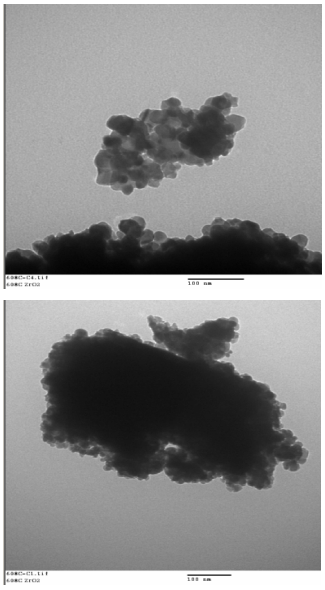

Figure 5 TEM micrographs of the nanocrystalline ZrO_2 powder

4 CONCLUSIONS

The acrylamide-assisted polymeric citrate route is an attractive means for the synthesis of nanocrystalline ZrO_2 powder. From TG/DTA, FTIR and XRD results, it is found that the organic-free nanocrystalline ZrO_2 particles are formed at 600 ^{o}C with two different phases of tetragonal and monoclinic. Their volume fractions were calculated using XRD data found to be 53.4 % for t-ZrO_2 phase and 46.6% for m-ZrO_2 phase. Transmission electron micrographs show that the synthesized ZrO_2 particles occur as agglomerates of ~1-=20 nm primary ZrO_2.

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