

# Structural, Morphological and Mechanical Properties of Zirconia Nanostructures for Bone Implantations

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## ABSTRACT

Nanoparticles are currently superseding other prosthetic treatment particularly in the case of substituting anterior teeth. Zirconia is considered as bioactive material but biomaterial requires high biocompatibility and suitable mechanical properties for implants. Zirconia has outstanding esthetics and mechanical characteristics, including strength, hardness and fracture toughness. Among zirconia phases tetragonal zirconia is most biocompatible and higher strengthen phase. Tetragonal zirconia can be achieved by addition of additives, and the other is reduction the zirconia crystallite size. For this purpose different amounts of citric acid (1 to 5ml) was added in pre-synthesized zirconia sols. Sols were stirred at room temperature until formation of gels. Gels of citric acid added zirconia were dried at temperature 50°C and characterized under as-synthesized conditions. Citric acid amounts in zirconia strongly influence the crystal system. Pure tetragonal zirconia has been obtained in as-synthesized samples at citric acid content 3ml and remains stable. Smallest crystallite size has calculated for tetragonal phase of zirconia with reduced dislocation density. Structural morphology of the citric acid added zirconia results in nano dendrites with large surface area growth. Size of the stems of nano dendrites is in the range of 20-30nm. These large surface area dendrites show high value of hardness confirmed by micro Vickers hardness indenter.

## 1. INTRODUCTION

Zirconia ( $ZrO_2$ ) is a white powder having three different crystal structures: monoclinic, tetragonal, and cubic. Below 1100°C, monoclinic phase (m-phase) exists between 1100 °C and 2370 °C, tetragonal phase (t-phase) exists; while greater than 2370 °C, zirconia converts to cubic phase (Bashir et al. 2014). Zirconia is considered as biomaterials but biomaterials require high biocompatibility and suitable mechanical properties for implants. Zirconia has outstanding esthetics and mechanical characteristics, including strength, hardness and fracture toughness (Bashir et al. 2015a). Among zirconia phases tetragonal zirconia is most biocompatible and higher strengthen phase. Tetragonal zirconia can be achieved by doping, and the other is reduction the zirconia crystallite size (Cassiers et al. 2003, Chane-Ching et al. 2005, Su

et al. 2000). Actually crystallite size is a constraint for the transformation of tetragonal to monoclinic poly-crystals (Li et al. 2012). Organic additive was used due to make particles assume spherical shape and results in decreased crystallite size from 30 to 10 nm (Heshmatpour and Aghakhanpour 2011).

Thus, in view of above mentioned properties on  $ZrO_2$  nanostructures and its wide applications, it is thought worthwhile to study the effect of organic additives on structural (crystal phases), morphology and hardness. The object of the present research is the synthesis of nanostructures tetragonal zirconia via introducing citric acid additive. Also the effects of particle size on zirconia phases are investigated.

## 2. Experimental Details

### 2.1 Materials

Zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ , BDH, 99.99% pure) was obtained from Sigma Aldrich. Citric acid and aqueous ammonia (32%) were obtained from Merck. Deionized (DI) water was used as solvent.

### 2.2 Method

Zirconyl chloride octahydrate was dissolved in DI water to form 0.1M solution. This stock solution was stirred at room temperature. After that citric acid was added 1 to 5ml per 100ml of zirconia. Ammonia was added to vary the pH up to 9. Sols were stirred at room temperature for 4 hours for polymerization. Gels were dried in the temperature 60-70°C for powder formation.

### 2.3 Characterizations

Structure analysis of citric acid zirconia was obtained by X-ray diffractometer (Bruker D8 advance) using  $Cu\ \kappa\alpha$  radiation ( $\lambda=0.1540598\ \text{nm}$ ). Morphological characteristics were studied by Scanning Electron Microscopy (SEM). Shimadzu HMV-2 hardness micro Vickers indenter. For indentation powders were made in the form of pallets by using hydrolytic pressure of 1 Ton.

## 3. Results and Discussion

These synthesized zirconia powders were checked for their crystal structure at different content of methanol as shown in Fig. 2. XRD patterns of citric acid added zirconia powders are a mixture of m-phase and t-phase at low content of citric acid illustrated in Fig 1(a-b). Peaks at approximately  $23.2^\circ$  and  $31.6^\circ$  correspond to the (011) and (111) planes of monoclinic zirconia ( $m\text{-}ZrO_2$ ) [JCPDS card no. 13-307] respectively. However, peaks at  $30.4^\circ$ ,  $40.3^\circ$ ,  $47.1^\circ$ ,  $53.1^\circ$ ,  $68.5^\circ$ ,  $72.9^\circ$  and  $78.4^\circ$  correspond to the (111), (112), (202), (221), (113), (132), (004) and (114) planes of tetragonal zirconia ( $t\text{-}ZrO_2$ ) [JCPDS card no. 17-923]. As the citric acid content increases up to 3ml tetragonal zirconia has observed, which means sufficient amount of additive is available for coating of nanostructures. Phase pure tetragonal zirconia retain up to 5ml. Organic based additives acts as capping agent for zirconia crystallites and prevent them for aggregation. The increase in citric acid amount promotes the length of the organic chain by increasing the distance between cations (Quinelato et al. 1999). Thus, the interaction between particles becomes less strong by increasing the amount of citric acid. So addition of such organics is used to provide nanosized less agglomerated powders. Less agglomeration or soft agglomeration caused in formation of tetragonal zirconia.

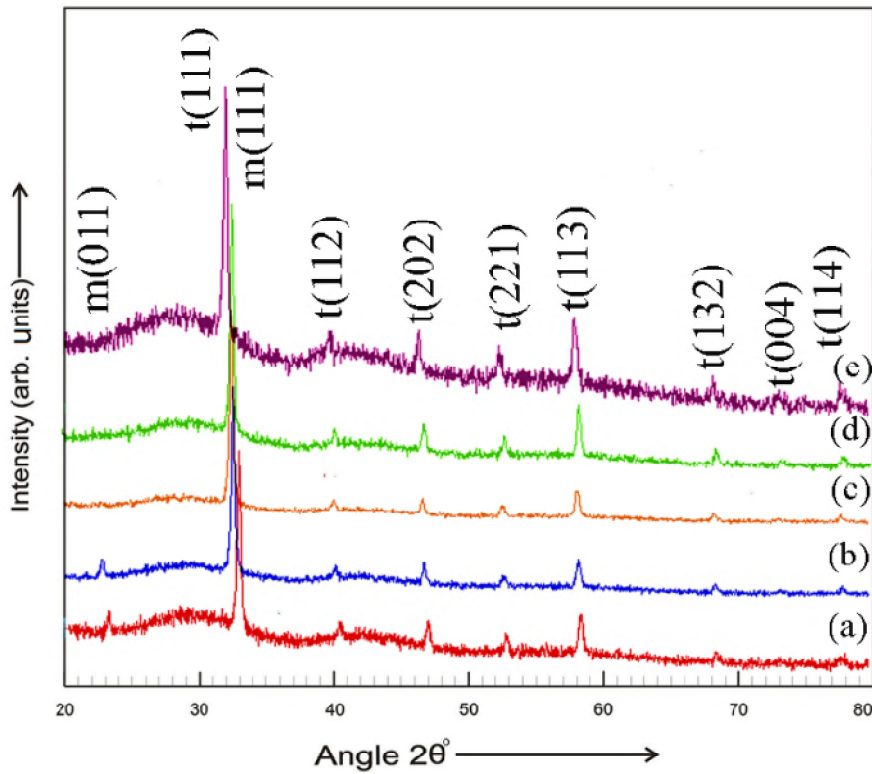


Fig. 1 XRD patterns at citric acid content (a) 1ml, (b) 2ml, (c) 3ml, (d) 4ml and (e) 5ml

Volume fraction monoclinic phase ( $V_m$ ) was calculated by the following equations, as given in Eqs. 1-3.

$$X_m = \frac{\Sigma I_m}{I_t + \Sigma I_m} \quad (1)$$

$$V_m = 1.311X_m / 1 + 0.311X_m \quad (2)$$

$$V_t = 1 - V_m \quad (3)$$

Where,

$I_m$  = m-phase integrated intensity

$I_t$  = t-phase integrated intensity

Volume fraction of monoclinic phase decreases with the additive for synthesis of zirconia as shown in Table 1.

**Table 1** tetragonal to monoclinic (t:m) of zirconia nanostructures at various citric acid content

Citric acid content (ml)	t:m
1	37:63
2	42:58
3	100:0
4	100:0
5	100:0

The crystallite size of the citric acid added zirconia nanostructures was estimated using the Eq. 4 (Cullity and Stock 2001). Crystallite size of  $ZrO_2$  powders synthesized by varying the citric acid content is shown in Fig. 2. It is evident from this Fig. 2 that there are two distinct varying regions (monoclinic-tetragonal phase and tetragonal phase. These variations are consistent with changes in the various phases with citric acid content. As additive content increases from 2 to 3ml there is a sharp decrease in crystallite size. There is every time decreases in crystallite size when phase change takes place and after stabilization crystallite size begin to increase. Structural changes might take place as a result of coalescence of two differently oriented crystallites. Surface diffusion and migration of grain boundaries can easily rotate smaller crystallites that may cause the structural changes (Riaz and Naseem 2007). Crystallite size is about ~ 23nm for tetragonal zirconia phase which is in close agreement with the Garvie et al. (1965) work for occurrence of t- $ZrO_2$ . Dislocation density of citric acid additives zirconia crystallites was calculated by using Eq. 5. Fig. 2 shows the few dislocation lines/ $m^2$ .

$$D = 0.9\lambda / B \cos \theta \quad (4)$$

$$\delta = 1/D^2 \quad (5)$$

For relatively lower citric acid content, samples have slight larger unit cell due to mix phases as depicted from XRD graphs. However, with the increase in additive content and stabilization of tetragonal phase leads to shrinkage in unit cell volume.

These volumetric changes results in densification of material as shown in Fig. 3. Moreover, high x-ray density of citric acid additive ZrO<sub>2</sub> nanostructures (~ 6 g/cm<sup>3</sup>) leads to higher hardness of the material; which is perquisite for implants.

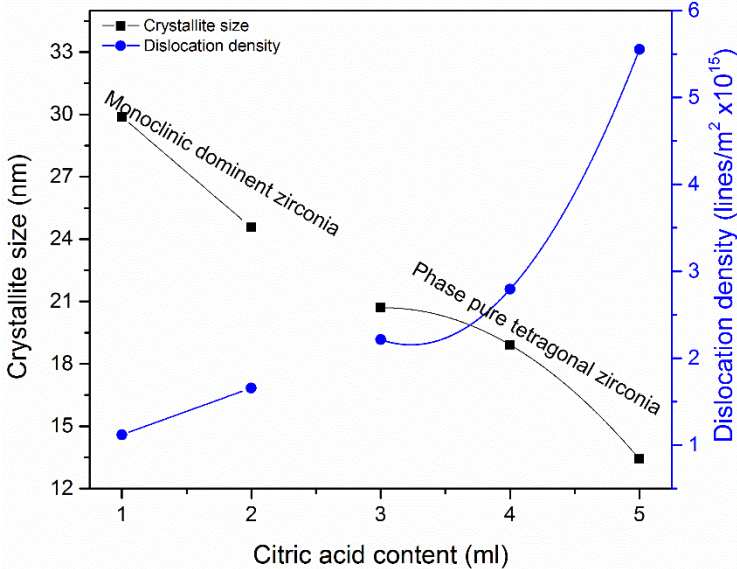


Fig. 2 Crystallite size and dislocation density of zirconia nanostructures as a function of citric acid content

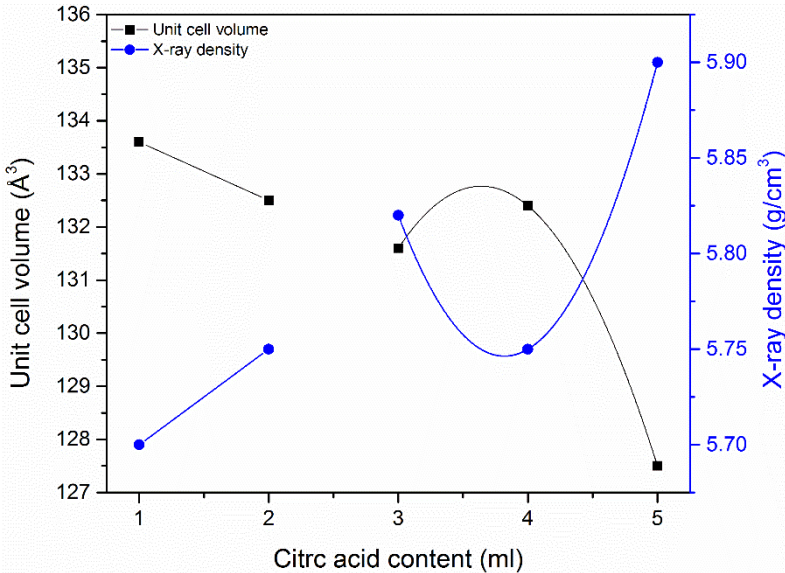


Fig. 3 Unit cell volume and x-ray density of zirconia nanostructures at various citric acid contents

For hardness measurement Vickers indentation under 4.9N load for 15 seconds dwell time was performed according to American standard testing machine (ASTM C-1327-99). Hardness of the samples was observed to be in the range of 954HV to 1150HV. A small variation in hardness was observed with the increase citric acid content. These results are in close agreement with the XRD data presented in Fig 1. Use of citric acid based additives provides long chain network and compact network of particles with negligible porosity, which enhances the hardness of the samples. Citric acid acts as anti oxidents which play a vital role in the prevention of cancer, stabilization of zirconia with reduced oxygen vacancies and high value of hardness for implantation as well. Table 2 summarizes the hardness values.

**Table 2** Hardness of zirconia nanostructures as a function of citric acid content

<b>Citric acid content (ml)</b>	<b>Hardness (HV) at constant load and time ASTM C- 1327-99</b>
1	989
2	850
3	954
4	1077
5	1150

Along with structural properties microstructural properties of zirconia has a strong impact on phase transformation and consequently to the hardness of the material. For investigation effect of citric acid content morphological properties of zirconia, SEM analysis was performed. Structural morphology of the citric acid added zirconia results in nano dendrites with large surface area growth. Size of the stems of nano dendrites is in the range of 20-30nm as shown in Fig. 4. Formation of nano dendrites is caused by the aggregation of small particles with large particles during sol gel process. However, present study shows that the amount of citric acid is a key parameter in the formation of zirconia nanoparticles with various sizes and shapes.

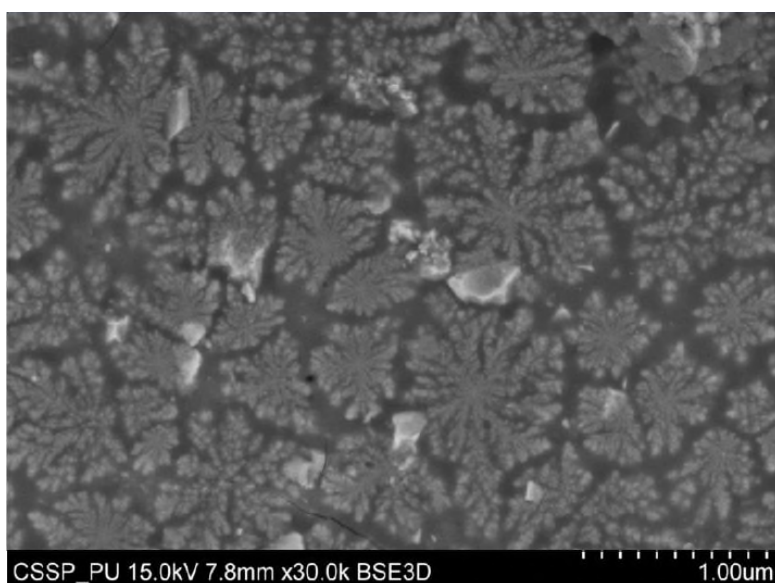


Fig. 4 Formation of dendrites using citric acid as additive

### 3. CONCLUSIONS

(1) Zirconyl chloride octahydrate was used as a starting material. Five different sols by varying the citric acid content 1 to 5ml were prepared. (2) XRD results showed that zirconia nanocrystallites are a mixture of monoclinic and tetragonal  $ZrO_2$  at low content of methanol whereas. Phase pure tetragonal zirconia has obtained at 3ml and retained its stability up-to 5ml (3) Crystallite size of the samples was in close agreement for the appearance of tetragonal zirconia. (4) Hardness of the samples was in the range of 954HV to 1150HV. Hardness of the samples increased with increased citric acid content after phase stabilization. (5) Zirconia powders showed formation of nanodendrites of size 20-30nm.

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