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**Synthesis and characterization of hydroxyapatite/alumina composite
nanopowders with various alumina content**

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Abstract

Preparation of hydroxyapatite - based nanocomposites and the use of α - Al_2O_3 particles as reinforcing phase, including ways to improve the mechanical properties of apatite bioceramics. In this study, hydroxyapatite /alumina composite nanopowders with alumina content of 10,20 and 30% wt was synthesized via colloidal sol - gel method. Structural evolution during the synthesis of HAp/ Al_2O_3 composite nanopowders is investigated by using simultaneous thermal analysis (STA), X-ray diffraction (XRD) and infrared spectroscopy (FT-IR). The microstructural and morphology were studied using scanning electron microscopy (SEM). This study showed the successful formation of HAp phase after a low temperature calcination process at 300 °C. Increasing Al_2O_3 content has no effect on decomposition rate of HAp in to beta tri-calcium phosphate (β -TCP) and presence of Al_2O_3 particles among hydroxyapatite particles resulted in grain growth inhibition of HA particles.

Keywords: hydroxyapatite, alumina, sol-gel, nanopowders, composite

1.Introduction

Hydroxyapatite bioceramics due to ability of establish good biocompatibility with bone tissue are among the most important bioceramics that have been studied in recent years. Hydroxyapatite bioceramics are used extensively in medical applications for repair or replacement of bone tissues[1]. However these bioceramics exhibit low toughness and strength due to its brittleness. Several solutions have been proposed to improve the mechanical properties of these bioceramics [2].

Coating of bioactive hydroxyapatite on metallic implants or preparation of hydroxyapatite-based composites using metal fibers, zirconia (ZrO_2) silicon nitride (Si_3N_4), Titan (TiO_2) and alumina (Al_2O_3) as reinforcing phase improve mechanical properties of hydroxyapatite bioceramics [2-4]. Hydroxyapatite-based nanocomposites have better mechanical properties and biocompatibility due to nanoparticles high surface area [5]. One of these nanocomposite, hydroxyapatite / alumina (HAp- Al_2O_3) is a compilation of the bioactivity of hydroxyapatite and mechanical properties of alumina. In this study, HAp- Al_2O_3 composite nanopowders were synthesized via colloidal sol-gel method. In colloidal sol-gel method, besides high purity and uniformity of powders, there is no need to control or maintain PH in high values [6].

2. Experimental

HAp- Al_2O_3 composite nanopowders containing 10, 20 and 30 wt% Al_2O_3 were synthesized via colloidal sol-gel method.

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, MERCK) and phosphorus pentoxide (P_2O_5 , MERCK) with an atomic ratio of Ca / P =1.67 were dissolved separately in absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, MERCK) and after dissolving above precursors, the solution containing phosphorus penta-oxide was added to the solution of calcium nitrate tetrahydrate (solution A). Nanometric alumina powder (α - Al_2O_3 (TAIMEICRON TM-D SERIES 100 nm average particle size) was poured in absolute ethanol and ultrasonicated

for 10 minutes to minimize the degree of agglomeration. The suspension was added to solution A and the mixture was stirred for about 3 h at room temperature and aged for 24 h before drying; here a white gel was obtained. The gel was dried at 80 °C for 24 h in oven following which as-dried gel was subsequently heat-treated at a rate of 10 °/min up to 900 °C for 1 h.

In order to study the phase evolution and formation of crystalline HAp, the as-dried powdered was analysed by differential thermal analysis /thermo gravimetric (DTA/TG) in stagnant air using NETZSCH(PC/PG STA900). FT.IR was performed to study the chemical bonds in calcined powders. Phase formation and crystallinity was characterized by X-ray diffraction (XRD) using diffractometer Philips Expert (Cuk $\alpha = 0/154$ nm). The microstructure and morphology of composite nanopowders was observed by Scanning electron microscopy (SEM,VEGA/TESCAN).

3. Results and Discussion

3.1. thermal analysis of the as-dried gel (DTA/TG)

Fig. 1 shows the (DTA/TG) curves of the HAp- Al₂O₃ with Al₂O₃ content 20% wt composite dried gel measured at a rate of 10 °/min.

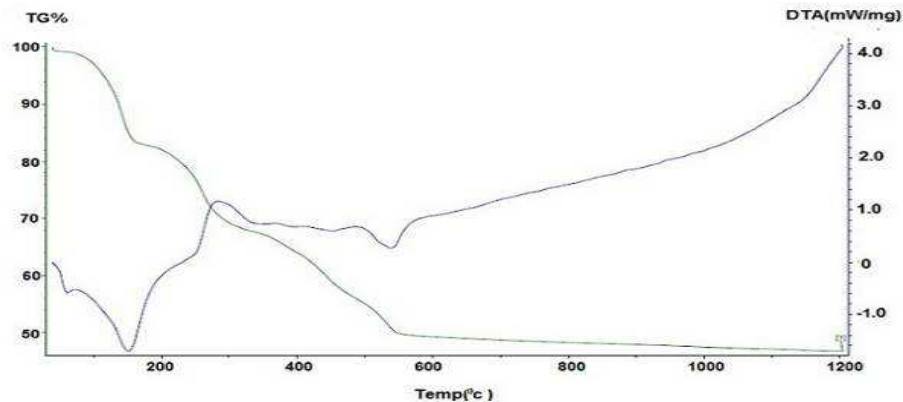


Fig.1 . Typical DTA and TG curves of HAp- Al₂O₃ with Al₂O₃ content 20% wt from room temperature to 1200°C .

Figure 1. curve shows about 51% total weight loss in temperatures range of 25 to 1200 °C. 17% weight loss with an endothermic peak at about 70 – 150 °C correspond to the evaporation of ethanol remaining in the sample and crystalline water in calcium nitrate using as the precursor. Since all calcium nitrate is not transformed in to alkoxy-nitrates, the unreacted crystalline salt manifests its self in the gel [7]. X-ray diffraction pattern (XRD) in Figure 2 confirms the presence of crystalline calcium nitrate in the as-dried gel . 34% weight loss occurs in the temperature range 170 to 550°C with endotherms (310, 420 ,550°C) imply removal of the groups such as (—OEt) and NO₃ .

Sharp exotherm at about 300 °C is related to crystallization of HAp that observed by others[7].

3.2. X-Ray diffraction(XRD) phase analysis

XRD patterns of the as-dried and calcined composite powders of HAp- Al₂O₃ containing 20% Al₂O₃ are shown in Fig 2 and 3, respectively.

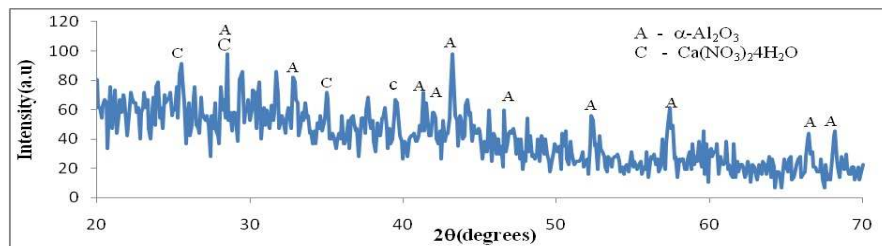


Fig. 2. XRD pattern of as-dried HAp- Al₂O₃ with Al₂O₃ content 20% wt composite nanopowders

The as-dried composite powders exhibits the peaks of calcium nitrate and alumina phases. There is no crystalline HAp phase observed in the XRD pattern of this sample. After calcination at 400°C XRD pattern (Figure. 3) shows the formation of HAp (JCPDS # 9-432) as the dominant phase (all peaks with no sign corresponds to HAp phase). Broad and non-obvious peaks are due to poorly crystalline HAp. Increasing the temperature to 600°C the width of the peaks is reduced and became obvious. Formation of beta tricalcium phosphate (β-TCP) phase after calcination at 600 °C is due to HAp decomposition according to following reaction[8]:

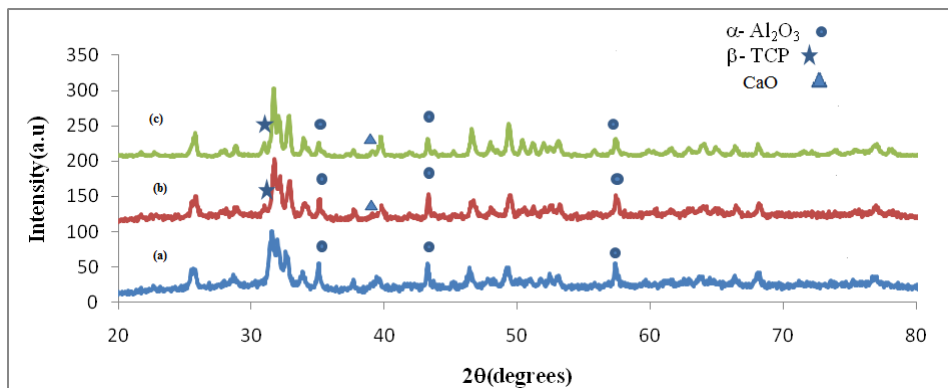
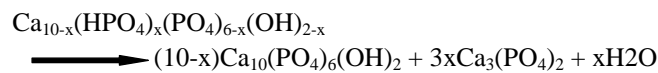


Fig 3. XRD patterns of HAp-Al₂O₃ composite nanopowders with Al₂O₃ content 20% wt heated at (a) 400, (b) 600 (c) 900 °C for 1h

Decomposition of hydroxyapatite at a temperature of 600⁰C shows the non-stoichiometric lattice of HAp[9]. According to thermal analysis and XRD pattern(fig.1 and 2) the presence of free calcium nitrate tetrahydrate implying the incomplete reaction with P₂O₅ during the gel formation and caused lack of Ca⁺² cation positions in the hydroxyapatite lattice and reducing Ca / P atomic ratio. The CaO phase observed after heat-treatment at 600⁰C corresponds to the product of the decomposition of calcium nitrate that remains unreacted in the gel. XRD patterns of pure HAp and HAp/Al₂O₃ composite samples with Al₂O₃ content 10,20 and 30% wt% after calcination at 900⁰C are shown in Figure. 4. Volume fraction of β-TCP (X_β) was calculated Using Eq(1) [10]. Finally X_β values for the powders with Al₂O₃ content of pure HAp and 10,20 and 30% wt was determined as 0.45,0.47,0.45 and 0.46, respectively. The values indicate that presence of α-Al₂O₃ phase has no effect on the decomposition rate of HAp in to β-TCP and Unlike other reinforcements, such as ZrO₂[10] Al₂O₃ is Chemically inert and does not react with the HAp phase up to 900⁰C.

$$X_{\beta} = \frac{P \cdot W_{\beta}}{1 + (P-1)(W_{\beta})} \quad (1)$$

Where

$$P = \frac{I_{H(211)}}{I_{\beta(0210)}}, \quad W_{\beta} = \frac{I_{\beta(0210)}}{I_{\beta(0210)} + I_{H(211)}}$$

Here I_{β(0210)} and I_{H(211)} are the XRD integrated intensity values of β-TCP(0210) and HAp(211).

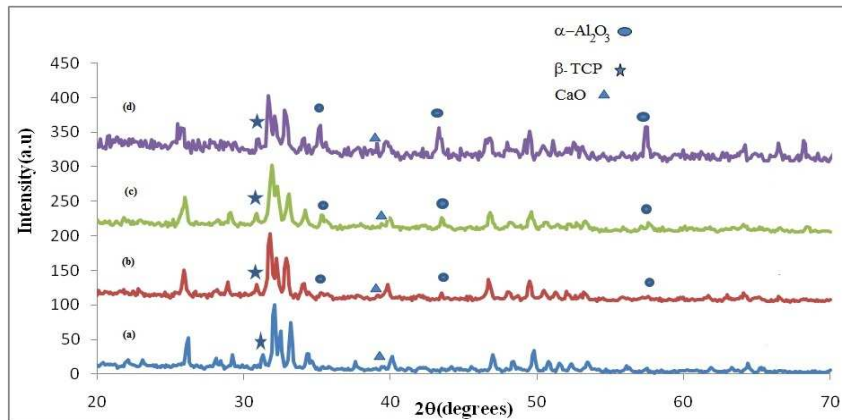


Fig. 4 . XRD patterns of HAp-Al₂O₃ composite nanopowders heated at 900 for 1 h with Al₂O₃ content (a) pure HAp (b) 10 , (c) 20 , (d) 30% wt

3.3. FT-IR analysis

FT-IR spectrum of the hydroxyapatite and composite nanopowders prepared via sol-gel are shown in Fig.5. Band absorption in regions 601 and 570 cm^{-1} are the typical bands of phosphate bending vibration, while the bands at areas 962 and 1042 cm^{-1} are due to phosphate stretching vibration [11]. Bands at 1412, and 1450 cm^{-1} are related to the carbonate group. Since the decomposition of CaCO_3 is reported to occur at 580 $^{\circ}\text{C}$ [12], carbonate stretching should be absent in the spectra of the materials calcined at 900 $^{\circ}\text{C}$ but in this spectra the peaks are evident. It might be due to chemisorptions of atmospheric CO_2 on the surface of HAp[12]. Peaks appeared in the areas of 3570 and 630 cm^{-1} belong to hydroxyl stretching vibration[11]. These spectra indicate the formation of a HAp structure containing sharp O—H and P—O bands, as reported by XRD pattern of Fig. 3 and 4. The appearance band in the region of 808 cm^{-1} is attributed to the Al—O bond stretching vibrations in the Al_2O_3 structure[13]. Resolution and sharpness of the band increases in the case of increasing Al_2O_3 content to 30% wt.

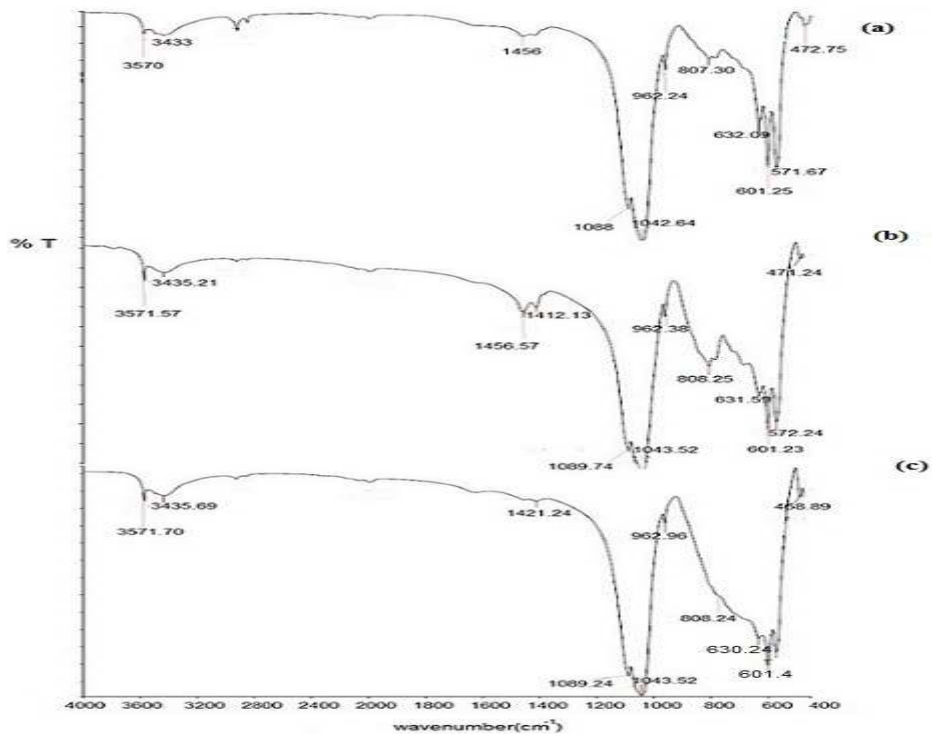


Fig .5 . FT-IR spectra of the HAp- Al_2O_3 composite nanopowders after heat-treatment at 900 $^{\circ}\text{C}$ for 1h with Al_2O_3 content (a) 10 , (b) 20 ,(c) 30% wt

3.4. SEM analysis

The SEM micrographs of the HAp- Al_2O_3 are presented in Fig.7. It can be seen that the samples are composed of tiny spheres which attached together and form agglomerates. Due to the high surface area of nanoparticles, particle size was calculated by analysis of SEM images. The mean particle size of the samples with Al_2O_3 content 10 , 20 and 30 %wt were approximately 60-110nm, 52-107nm and 38-103 nm. The presence of Al_2O_3 among hydroxyapatite particles inhibited HAp grain growth during heat-treatment.

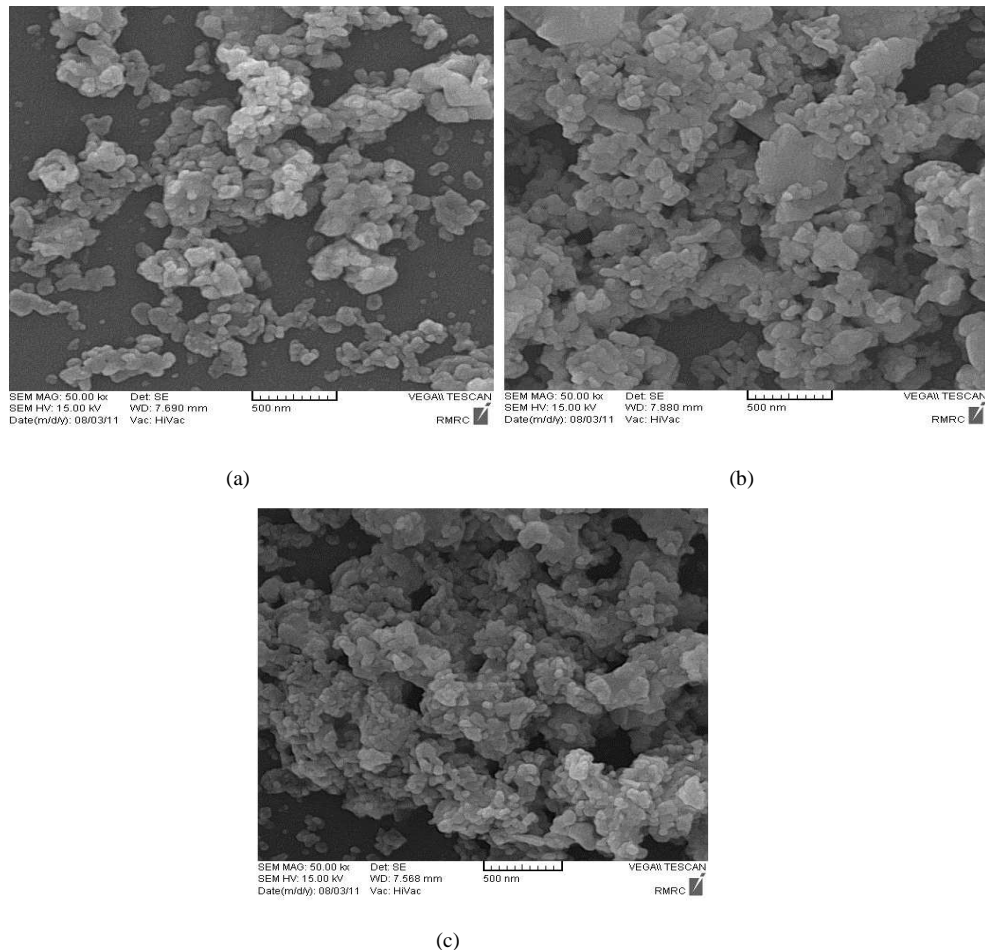


Fig. 6. SEM micrographs of the samples with Al_2O_3 content (a) 10 ,(b) 20 ,(c) 30 % wt heated at 900 °C for 1h

4. Conclusions

Composite nanopowders of hydroxyapatite/alumina containing 10, 20 and 30% wt Al_2O_3 were successfully synthesized via simple sol – gel by reacting $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and P_2O_5 and adjusting sol-gel parameters. XRD result of the as-dried gel indicate no crystalline HAp phase. According to thermal analysis(DTA/TG) and XRD patterns, HAp crystallization temperature was about 300°C .

Increasing Al_2O_3 content to 30% wt in HAp- Al_2O_3 composite nanopowders has no effect on decomposition rate of HAp in to β -TCP. All the powders studied consist of big agglomerates composed of tiny sphere nanoparticles. Presence of Al_2O_3 nanoparticles among HAp particles inhibited HAp grain growth during heat-treatment.

Acknowledgements

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Synthesis and characterization of hydroxyapatite /alumina composite nanopowders with various alumina ...

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