

Sol-Gel Synthesis of Zn doped HA Powders and their Conversion to Porous Bodies

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Abstract. The present study was aimed at fabricating porous ceramic scaffolds via polymeric sponge method for biomedical applications using as synthesized Zinc doped Hydroxyapatite (ZnHA) powders. Zn doped HA powders were prepared via sol-gel method using diammonia hydrogen phosphate $[(\text{NH}_4)_2\text{HPO}_4]$ and calcium nitrate tetrahydrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ as starting materials. The obtained powders were then used for the preparation of porous ZnHA scaffolds via polymeric sponge method. The green porous bodies so developed by impregnating cellulosic sponges with HA slurries, were subjected to sintering process at a temperature of 1300 °C. Field-emission scanning electron microscopy (FESEM) was used to observe the surface morphology of the powder and sintered porous sample. The structure and crystallinity of (Zn)HA powder and the sintered porous samples was analyzed using X-ray diffractometer whereas Fourier transform infrared spectroscopy (FTIR) was used to determine the presence of various phases in the powder. FESEM results showed the formation of agglomerates at an increased Zn concentration. The morphology of the porous samples showed high degree of fusion and densification with an increase in Zn concentration. Preliminary mechanical testing results show that maximum compression strength of HA porous bodies was 0.12 MPa.

Introduction

Bone grafting is a widely used technique for dealing with problems that are associated with bone loss, repair, and reconstruction. Several researches have been conducted for investigating the materials that have potential of triggering natural regeneration process of damaged or lost bone tissue. These materials have capability of being in contact with bodily fluids and tissues for prolonged periods of time. One of the key factors in a biomaterial's usage is its biocompatibility and functionality. Biomaterials used as bone grafts are identified on the basis of osteogenicity (presence of bone forming cells), osteoconductivity (ability to function as a scaffold) and osteoinductivity (ability to stimulate bone formation) [1]. Various biological and synthetic bone substitutes have been used so far for clinical applications. Calcium Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a synthetic biomaterial similar to biological HA, which forms the structural component of the human bone and teeth. Owing to its excellent biocompatibility and bioactivity, Calcium hydroxyapatite has been used widely for various bone and tooth implants. It bonds strongly to the bone and favours osseointegration of bone implant. Calcium phosphate-based

ceramics such as HA are available in porous as well as in dense form. Porous ceramic implants provide a surface for proliferation and growth of cells that are infiltrated from the surrounding tissues so that a new bone grows into the pores and prevent any movement or loosening of the implants. In fact porous HA ceramics are proven to mimic the porous structure of the mineral phase of the living bone [2]. However the structural and surface morphology of these ceramics have a considerable effect on bone growth mechanisms [3]. The structure and morphology of ceramic scaffolds play an important role in determining the growth and proliferation of cells around surrounding tissue [4]. Most of mammalian cells are anchorage dependent i.e. they need a substrate for growth. As a result numerous studies have been conducted in the field of tissue engineering for development of porous ceramic scaffolds for bone replacement applications. In the present study porous scaffolds have been prepared via polymeric sponge method using as prepared ZnHA powders by sol-gel technique.

Experimental Procedures

Materials. For preparation of Zinc-doped HA powders via sol-gel technique [5], calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (System), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) (Merck), zinc nitrate hexahydrate (Friendemann & schmidt), urea (System), EDTA (titriplex) (Merck) and ammonium solution (NH_4OH) (B&M Chemical) were used as starting materials. For preparation of porous sample, cellulosic sponge, used as a template for pore creation was purchased from Testafabrics Inc., USA whereas Dispersing agent (Duramax D3005) was purchased from Rohm and Haas, USA.

Powder Preparation. An ammoniacal solution (NH_4OH) was heated to 60°C and EDTA was added while stirring until it dissolved. This was followed by the addition of phosphorus precursor di-ammonium hydrogen phosphate, calcium precursor calcium nitrate tetrahydrate and Urea. The mixture was then refluxed at 110°C for 4–5h while maintaining the stirring until a white gel of Zn free HA was obtained. The obtained gel was dried at 340°C in furnace to form a black gel which was then crushed into powder. This black powder was calcined at 900°C in furnace to form a white powder that was further used for preparation of the slurry. Same procedure was followed to obtain

Zinc doped HA wherein zinc nitrate hexahydrate of varying concentrations was incorporated during stirring.

Porous Sample Preparation. The obtained powders of Zn free HA and ZnHA (8 g) were dissolved separately in distilled water (10 ml) with Duramax D3005 (10 ml) as a dispersion agent. This mixture was stirred for 24 h to obtain a homogeneous slurry. The cellulosic sponges were cut into circular samples of 1.5 cm diameter and then impregnated with the prepared slurry. After soaking into the slurry, the sponges were dried in ambient air for 72 h and then subjected to heat treatment at 600°C for 3h to eliminate organic matrix. This was followed by sintering at 1300°C for 3 h.

Characterization. The structure and crystallinity of (Zn)HA powder and the sintered porous samples was analyzed using X-ray diffractometer (Shimadzu, XLab XRD 6000). Fourier transform infrared spectroscopy (FTIR) was used to determine the presence of various phases in the powder. The porosity of all samples was determined by calculating its apparent and relative densities. Compressive strength of porous HA was measured using Lloyd LR10K mechanical tester. The compressive load was applied at a crosshead speed of 0.4 mm/min on the cylindrical samples until failure. Morphological evaluation of the HA powder and porous bodies was done using Field emission scanning electron microscope (JEOL, JSM 6700 F) and particle size distribution of the powder was analyzed using zetasizer nano-series (Nano S, Malvern Instrument).

Results and Discussion

Fig. 1 presents the XRD pattern of Zn-doped HA powders calcined at 900°C . The figure shows peaks attributed to ICCD standard data of HA (JCPDS 09-432) as the main phase. The figure also

confirms that at higher concentrations of zinc the synthesized powder tends to form β -TCP apart from HA. Moreover the relative intensity of peaks decrease as the concentration of dopant Zn is increased. These results are in good agreement with the previous results reported by Ren et al [6]. It thus indicates that crystallinity is decreased with an increase in Zn content. Change in crystallinity can be attributed to the fact that ionic radius of Zn^{2+} is less than Ca^{2+} , being 0.074 nm for Zn^{2+} and 0.099 nm for Ca^{2+} .

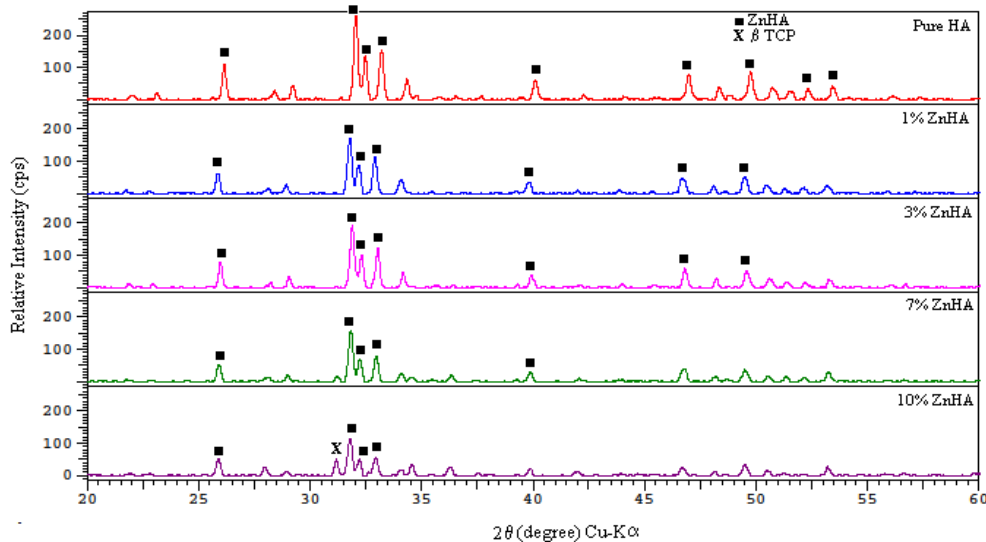


Fig. 1. XRD pattern of Zn-doped HA powders

Fig. 2 shows the FESEM micrographs of Zn-doped HA powders calcined at 900°C. The microstructure of the powders consists of fine particles tightly agglomerated into microscale aggregates. Moreover the size of the agglomerates tends to increase as the amount of dopant increases. The micrograph of 10 mol% ZnHA depicts a flat-like structure which results from the fusion of the spherical-particle agglomerates.

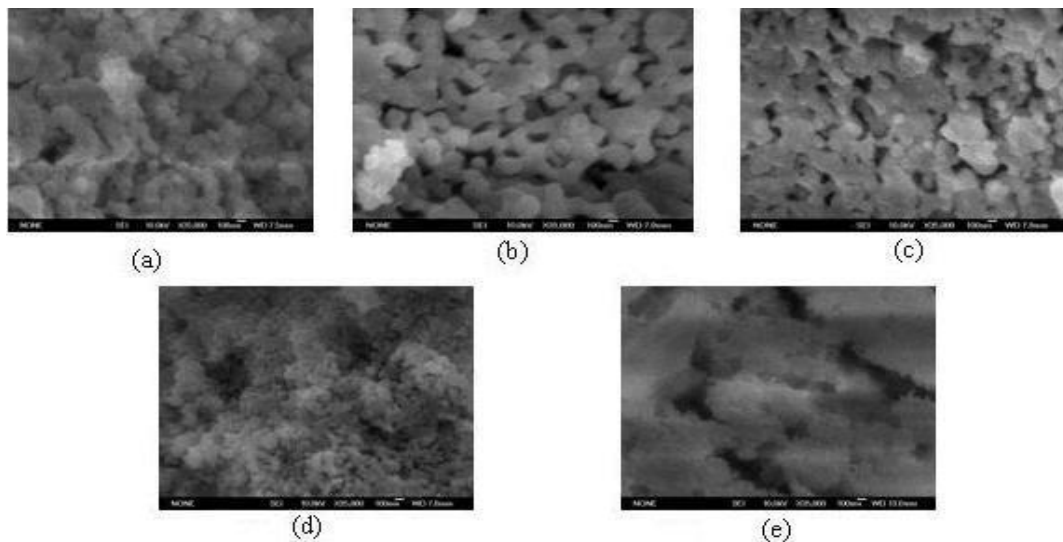


Fig. 2. FESEM micrograph of Zn doped HA powders (a) 2 mol% ZnHA (b) 3 mol% ZnHA (c) 5 mol% ZnHA (d) 7 mol% ZnHA (e) 10 mol% ZnHA

The reason for an increased rate of fusion is that the crystallite size decreases with an increase in Zinc concentration. This result is in confirmation with the XRD results and also results obtained from particle size analysis shown in Table. 1.

Table. 1. Crystal size of Zinc doped HA powders

Sample	Particle size (nm)
1% Zn- HA	185
2% Zn- HA	159
5% Zn- HA	149
10% Zn- HA	143

Fig. 3 shows FTIR spectra of Zn-doped HA powders calcined at 900°C. The spectra show vibrational characteristic of apatite phase. The characteristic phosphate (mode ν_4) vibrations of HA are spotted at 563 and 600 cm^{-1} and other mode ν_1 , and mode ν_3 of PO_4^{3-} peaks at 961, 1024 and 1085 cm^{-1} respectively [7, 8]. The bands at 1380-1550 cm^{-1} correspond to CO_3 groups while 1420 and 875 cm^{-1} to HPO_4^{2-} . As it can be seen from the figure, with an increase in Zn percentage, the separation of three PO_4^{3-} stretching peaks (961, 1024 and 1085 cm^{-1}) becomes indistinct, and the OH bending peak at 630 cm^{-1} becomes broad. This is due to decreased crystallinity at higher Zn percentages [9].

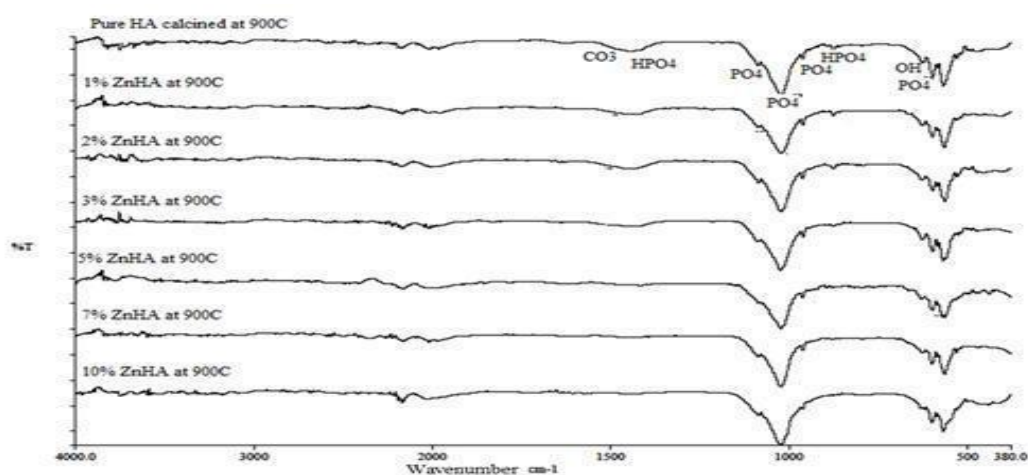


Fig. 3. FTIR spectra of Zn-doped HA Powders

Fig. 4 shows the XRD patterns of porous HA and ZnHA. XRD pattern of powder and porous sample was similar confirming that the sintering process did not disrupt the HA phase.

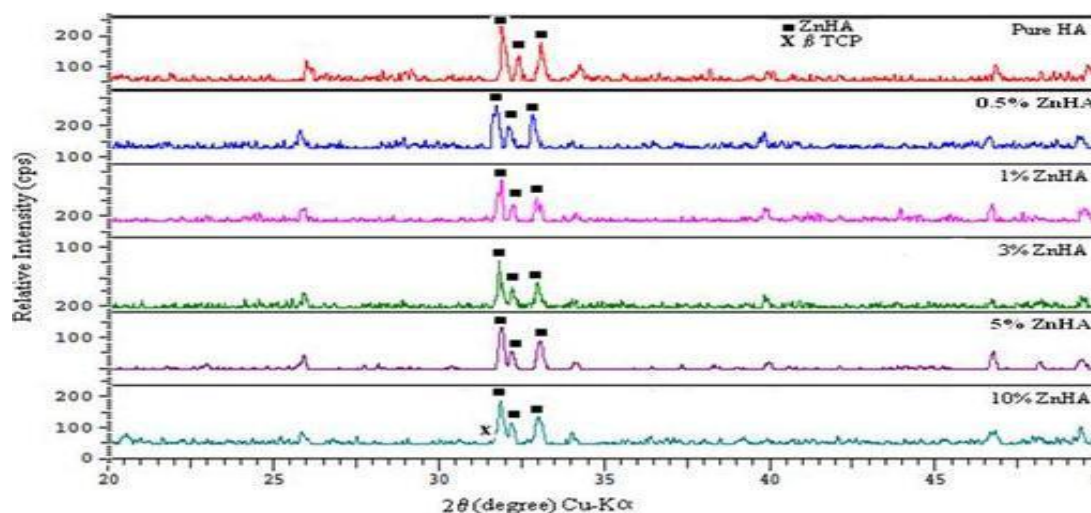


Fig. 4. XRD pattern of Porous Samples

Table 2 shows the apparent density and % porosity of porous samples. The apparent density was found to be between 2.06 - 2.31 g/cm³ whereas porosity of the samples ranged between 26-34%. It can be inferred that as the concentration of Zn increases the porosity of the samples decrease. This is also evident from the FESEM micrographs of porous samples as shown in fig 5.

Table. 3 Apparent Density and % Porosity of Porous Samples

Sample	Apparent density (g/cm ³)	Porosity (%)
Zn free HA	2.1	34
1% Zn- HA	2.19	31
3% Zn- HA	2.06	32
5% Zn- HA	2.31	26
10% Zn- HA	2.29	27

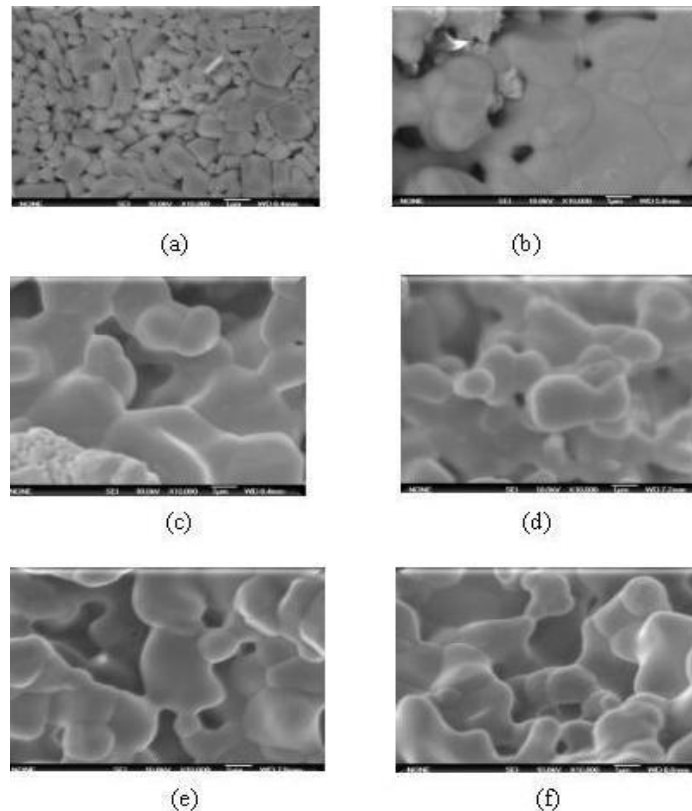


Fig. 5. FESEM micrograph of Porous Samples (a) Zn free HA (b) 1 mol% ZnHA (c) 3 mol% ZnHA (d) 5 mol% ZnHA (e) 7 mol% ZnHA (f) 10 mol% ZnHA

FESEM images of the porous samples reveal progressive densification and fusion with an increase in Zn concentration. Zn doped HA is denser as compared to Zn free HA. This is because Zn free HA still has some residual porosity due to incomplete densification during the sintering process. In other words, the density increases whereas porosity decreases with an increased Zn content.

From the preliminary compressive test results it was revealed that porous Zn free HA samples did not have a measurable compressive strength owing to its highly porous structure. However 3% ZnHA porous sample shows the maximum compressive stress of about 0.12 Mpa.

Summary

The conversion of Zn-doped HA fine powders into porous bodies have been successfully carried out via polymeric sponge method. The effect of dopant concentration on the phase behaviour and morphology of powders and porous bodies have been studied. FTIR analysis of the powders revealed that with an increase of Zn concentration, the separation of three PO_4^{3-} stretching peaks become obscure, and the OH bending peak at 630 cm^{-1} becomes broad. XRD results of porous bodies is similar to that of powders, confirming that the sintering process did not disrupt the HA. FESEM results confirmed that with an increase in the concentration of dopant Zn, the size of the agglomerates tend to increase. The morphology of the porous samples showed high degree of fusion and densification with an increase in Zn concentration.

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