



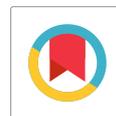
Efficient Zinc Oxide Incorporation in Nano Hydroxyapatite by Sol-Gel Synthesis

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ABSTRACT

Hydroxyapatite (HA) has widely used in bone tissue engineering due to their biocompatibility and biodegradability. The natural apatites contains minor constituents such as cations (Mg^{2+} , Mn^{2+} , Zn^{2+} , Na^{2+} , Sr^{2+}) and these ionic substitutions changes the structural, mechanical and biological properties of HA. Currently, the metals are widely used to increase the bioactivity of Hydroxyapatite. The aim of this study is to synthesis pure Hydroxyapatite nanoparticles and zinc doped Hydroxyapatite nanoparticles by sol-gel method. Zinc incorporated Hydroxyapatite gave better mechanical strength of calcium phosphate implants. Zn doping of HA is a major interest because biological tissues like bone and enamel of human teeth or composed of HA containing Zinc. Calcium nitrate tetrahydrate, Diammonium hydrogen phosphate and Zinc oxide are used as a precursor for calcium, phosphate and zinc. The prepared nanopowders were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction pattern (XRD), and Scanning electron microscopy (SEM) analysis.

Keywords: Fourier Transform Infrared Spectroscopy (FTIR); Scanning Electron Microscope (SEM); X-Ray Diffraction (XRD).

INTRODUCTION

Hydroxyapatite is a calcium phosphate and chemically similar to the mineral component of bones and having formula $Ca_{10}(PO_4)_6(OH)_2$. It has an ability to integrate in bone structures and support bone ingrowths without breaking down or dissolving. Hydroxyapatite is a thermally unstable compound, decomposing at temperature from 800 - 1200 °C depending on the stoichiometry. Particularly it has a hexagonal structure and a stoichiometric Ca/P ratio of 1.67 which is identical to bone apatite (Mestres *et al.* 2012).

Hydroxyapatite is a hydroxyl end member of the complex apatite group. The OH^- ion can be replaced by fluoride, chloride or carbonate, producing flourapatite or chlorapatite. It crystallizes into hexagonal crystal system (Reichert and Binner, 1996). HAp has absorbability with amino acid, protein, fat and sugar. Therefore, it is used as a bulking agent of column chromatography used for disrupting biomolecules or used for cosmetics through its adsorption removal of extra fat and waste. The chemical nature of hydroxyapatite lends itself to substitution, meaning that it is not uncommon for non-stoichiometric hydroxyapatites to exist (Reichert and Binner, 1996).

HAp has an ion- exchange performance, which exchanges calcium ion site with anion. Hexagonal HA structure enables some ionic substitutions according to charge type, charge size and ionic radii. Currently, the metals are widely used to increase the bioactivity of

Hydroxyapatite (Naruporn Monmaturapoj and Klong Luang, 2008). Zn ion has +2 charge and can be incorporated to the HA structure by replacement with Ca^{2+} ion. Zn^{2+} incorporation decreased the grain sizes and increased the solubility of pure or carbonated HA. Zn doping of HA is of major interest because biological tissues like bone and enamel of human teeth are composed of HA containing zinc (Naruporn Monmaturapoj and Klong Luang, 2008). This crucial element has an important role in the activity of many enzymes and its uptake and release are strongly mediated by the bone reservoir in the body (Atsuo *et al.* 2002). The aims of this research are to synthesis zinc oxide doped hydroxyapatite nanoparticles and examine their crystallinity and functional group.

2. MATERIALS & METHODS

Calcium nitrate tetra hydrate and Diammonium hydrogen phosphate are used as precursor for calcium and phosphate. 1M of calcium nitrate tetra hydrate and 0.6 M of diammonium hydrogen phosphate were used as precursors and stirred for half an hour. pH of the solutions were maintained separately at 10 using ammonium hydroxide solution. Then the phosphate solution is added drop wise to the calcium solution with vigorous stirring for 1 hour in room temperature. The resultant gel prepared was aged for 24 hours in room temperature. The impurities in the gel was removed by washing 4 times with double distilled water and finally filtered using Whatsmann filter paper. The produced HAP gel was

dried at 100 °C for 10 hours. The dried powder was grained with agate mortar and pestle into fine powder and subjected to calcinations at 250 °C temperature for 2 hrs using electrically heated muffle furnace. For Zn-HAP 0.05M of Zinc oxide is added with 0.95M of calcium solution with separately stirring for 10 minutes. Then the same procedure was repeated.

3. RESULTS & DISCUSSIONS

3.1 X-RAY Diffraction (XRD)

The crystallographic analysis was carried out by X-ray diffraction method. The average crystallite size is determined using scherrer formula (Ren *et al.* 2009) Xin,)

$$D = K\lambda / \beta \cos \Theta$$

Where, D is crystallite size in nanometer, λ is wavelength of the monochromatic, β is full width at the half maximum for the diffraction peak under consideration (rad), θ is diffraction angle (deg). The average crystallite size for pure HAp is found to be 30.18 nm and for ZnO doped HAp is 24.25 nm. The straight and sharp peaks from XRD studies reveal that the HAp and ZnO doped HAp were nanocrystalline in nature. The crystallite size was decreased with the additive of dopant. The XRD pattern of Pure HAp and ZnO doped HAp are shown in Fig. 1.

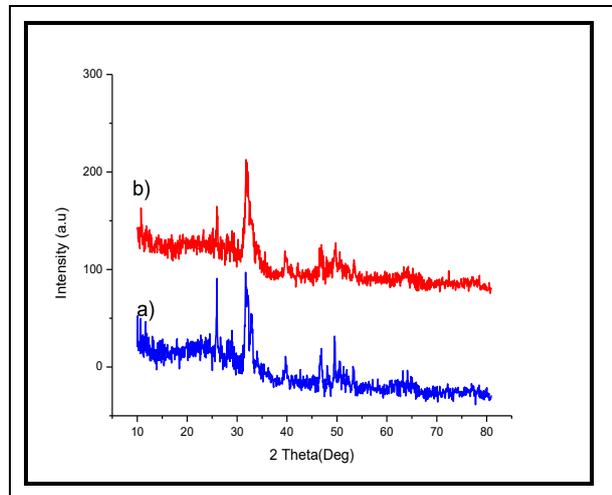


Fig. 1: a) XRD of Pure HAp b) XRD of ZnO doped Hap.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy was used to identify the elemental composition of pure and ZnO doped HAp nanopowders (Bish and Post, 1989). The FTIR spectra of pure and ZnO doped HAp nanopowders as shown in the fig. 2. For pure HAp the FTIR bands observed at 3428.98 cm^{-1} were assigned to presence of hydroxyl group. The peaks observed at

565.63 cm^{-1} were assigned to $\text{PO}_4^{3-}(\nu^4)$. The bands observed at 1072.91 cm^{-1} assigned to phosphate stretching vibration.

For ZnO doped hydroxyapatite, the bands observed at 566.11 cm^{-1} assigned to $\text{PO}_4^{3-}(\nu^4)$. The peaks observed at 1096 cm^{-1} were assigned to $\text{PO}_4^{3-}(\nu^3)$. The bands observed at 3432.84 cm^{-1} assigned to the presence of hydroxyl group. The intensity of the peaks increases with adding dopant.

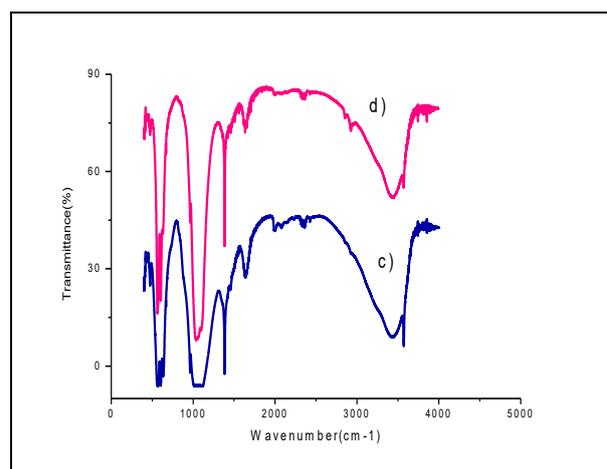


Fig. 2: FTIR Spectrum for c) Pure & d) ZnO Doped Hap.

3.3 Scanning Electron Microscope (SEM)

The surface morphology of pure and ZnO doped HAp powder were examined using scanning electron microscope. The SEM images of HAp are shown in fig. 3& fig.4. It was observed that for pure HAp the particles exhibit nearly platelet shape and the particles agglomerated due to vanderwaals force of attraction. There is improvement in the morphology due to incorporation of ZnO and the particles exhibit nearly spherical shape.

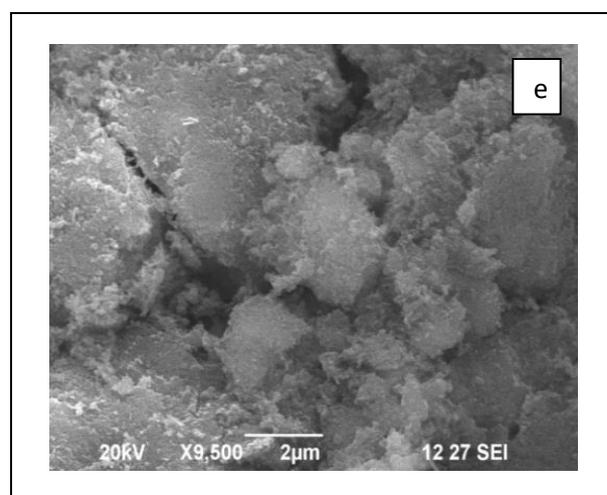


Fig. 3: SEM images for (e) Pure.

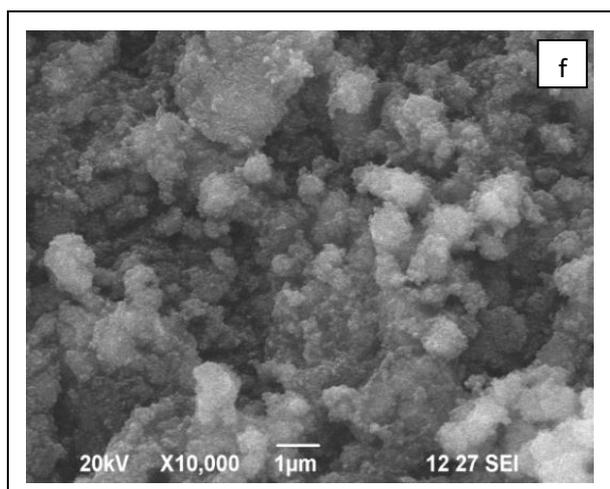


Fig. 4: SEM images for (f) ZnO doped Hap.

4. CONCLUSION

HAp and ZnO doped HAp nanoparticles were prepared using sol-gel method. The prepared nanoparticles were analyzed using the characterization techniques. The straight and sharp peaks from XRD studies reveal that the HAp and ZnO doped HAp were nanocrystalline in nature. Average crystallite size was calculated using scherrer formula and it was found for pure HAp is 30.18 nm and for ZnO HAp it was found to be 24.25 nm. The crystallite size is decreased when the dopant is added. The FTIR spectrum confirms the presence of functional group and their vibration mode in pure HAp and ZnO doped HAp were analyzed. The intensity of the peaks increases with addition of dopant. The surface morphology of synthesized nano HAp and ZnO HAp was confirmed by SEM analysis.

For the pure HAp the particles exhibit nearly platelet in shape and there is improvement in the morphology due to incorporation of ZnO and the particles exhibit nearly spherical shape.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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REFERENCES

- Atsuo, I., Haruo, Kawamura., Makoto, O, Masako, I., Hajieme, O., Kunio, I., Kazuo, O., Noriko, K., I., Yu, S. and Noboru, I., Zinc releasing calcium phosphate for stimulating bone formation, *Mater. Sci. Eng. C.*, 22(1), 21-25(2002).
[https://doi.org/10.1016/S0928-4931\(02\)00108-X](https://doi.org/10.1016/S0928-4931(02)00108-X)
- Bish, D. L. and Post, J. E., Modern powder diffraction, Reviews in Mineralogical Society of America, (1989).
- Mestres, G., Le Van, C. and Ginebra, M. P., Silicon stabilised tricalcium phosphate and its use in a calcium phosphate cement: Characterization and cell response, *Acta Biomaterialia.*, 8(3), 1169-1179 (2012).
<https://doi.org/10.1016/j.actbio.2011.11.021>
- Naruporn Monmaturapoj and Klong Luang, Nano-size Hydroxyapatite Powders Preparation by Wet-Chemical Precipitation Route, *J. Met. Mater. Miner.*, 18(1), 15-20(2008).
- Reichert, J. and Binner, G. P., An evaluation of hydroxyapatite-based filters for removal of heavy metal ions from aqueous solution, *J. Mater. Sci.*, 31(5), 1231-1241(1996).
<https://doi.org/10.1007/BF00353102>
- Ren, F., Xin, R., Ge, X. and Leng, Y., Characterization and structural analysis of Zinc substituted hydroxyapatites, *Acta Biomaterialia.*, 5(8), 3141-3149(2009).
<https://doi.org/10.1016/j.actbio.2009.04.014>