



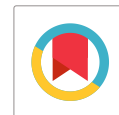
Synthesis and Characterization of Pure and Zn-doped HAp Nanoparticles by Microwave Irradiation Method

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ABSTRACT

Nanotechnology is an emerging field of science and technology. Hydroxyapatite (HAp) is a nano biomaterial incorporated as bone and teeth implants in the human body. The present work deals with the synthesis and characterization of pure and zinc-doped HAp nanoparticles prepared by using chemical co-precipitation method, associated with the microwave irradiation process. The HAp was prepared using calcium hydroxide as a calcium source and orthophosphoric acid as the phosphorous source. The prepared sample was characterized by XRD, SEM, EDAX and UV analysis. The X-ray Diffraction pattern revealed the crystalline size of the nanoparticles. Size and morphology of samples were examined by Scanning Electron Microscopy and Energy Dispersion X-ray Diffraction analysis was used to investigate the purity and elemental composition of the sample. Then the optical properties and bandgap energy were carried out using Ultra-Violet spectroscopy and photoluminescence analysis.

Keywords: Co-precipitation method; Morphology; Optical Properties; Pure Hydroxyapatite; Zinc doped Hydroxyapatite.

1. INTRODUCTION

Nanomaterial is defined as a structure or device or system having the size 1-100 nm with abnormal characteristics than that of the bulk material. While this is the most common definition of nanotechnology, researchers with various focuses have slightly different definitions (Uota *et al.* 2005). These possibilities may well be focused on the nature of free nanoparticles generated in nanotechnology processes and either intentionally or unintentionally released into the environment or actually delivered directly to individuals through the functioning of a nanotechnology-based product (Sadat-Shojai *et al.* 2013). Of special concern would be those individuals whose work places them in regular and sustained contact with free nanoparticles. Acetates are salts or esters derived from acetic acid composed of two carbon atoms ionically bound to three hydrogen and two oxygen atoms (Symbol: CH₃COO), for a total formula weight of 59.05. Phosphoric acid, which is also a mineral acid, is represented by the formula H₃PO₄ and it contains one atom of phosphorus, four atoms of oxygen and three atoms of hydrogen. Calcium hydroxide, commonly referred to as slaked lime, described by the chemical formula Ca(OH)₂, is an inorganic compound that has a white, powdery appearance in its solid state. However, Ca(OH)₂ has a

colourless appearance in its crystalline form (Kalaiselvi *et al.* 2017)

2. MATERIALS AND METHODS

2.1 Preparation of Pure HAp nanoparticles

Hydroxyapatite (HAp) was synthesized by the chemical precipitation method. 3.7 g of calcium hydroxide was dissolved with 50 ml of distilled water, and 2.9 g of orthophosphoric acid dissolved with 50 ml of distilled water (Kalaiselvi *et al.* 2018) and both were stirred for 30 minutes. Then the orthophosphoric acid was added drop-wise into the calcium hydroxide solution. The mixture was stirred for 30 minutes. Then NaOH solution was added drop-wise to maintain the pH level as 12. This was continuously stirred for 30 minutes. The mixture was allowed to settle; then, the precipitate was washed with double distilled water, and finally, it was kept in a microwave oven at 75 W for 20 minutes. Then it was kept in a muffle furnace for 4 hours. The dried sample was grained in a mortar to get white colour pure Hydroxyapatite nanoparticles (Khataee *et al.* 2014; 2015).

2.2 Preparation of Zinc-doped HAp nanoparticles

The pure HAp nanoparticles were prepared by taking 0.4 g of calcium hydroxide and 3 g of orthophosphoric acid in separate beakers. Both solutions were dissolved in 50 ml of distilled water, and were

stirred for 30 minutes. After the orthophosphoric solution was added into the calcium hydroxide solution, it was stirred for 30 minutes. 2 g of zinc acetate dihydrate was dissolved in 50 ml of distilled water and stirred for 30 minutes. Then the solution of zinc acetate dihydrate was added into the above mixture and stirred for 30 minutes. NaOH was added drop-wise into the solution to maintain the pH of 12 and continuously stirred for 30 minutes. The precipitate was dried in a microwave oven at 75 W for 30 minutes. Then the dried powder was grained by mortar and kept in a muffle furnace at 400 °C for one hour to get fine zinc-doped Hydroxyapatite nanoparticles (Gopi *et al.* 2012; Khan *et al.* 2013; Mohamed *et al.* 2013).

3. CHARACTERIZATION TECHNIQUES

3.1 XRD-Analysis

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. The lattice parameter of the sample was calculated using the following equation:

$$1/d^2 = (4(h^2+hk+k^2)/3a) + (1^2/c^2)$$

where, d is the spacing between the planes, a and c are the lattice parameters. The unit cell volume (V) of the sample was described using the equation:

$$V = (\sqrt{3}/2) + a^2 + c^2$$

The average crystalline size of the sample was determined by using Scherer's formula.

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

where, D denotes the average crystalline size of the sample, K represents the broadening constant, λ denotes the wavelength of CuK α radiation source (1.54Å⁰), β represents full width at half maximum and θ , the angle of diffraction.

3.2 SEM and EDAX

The surface morphologies of synthesized Cu HAp samples were analysed using Scanning Electron Microscopic (SEM). Energy dispersive spectroscopy (EDAX) was used to identify the elemental composition of the sample.

4. RESULT AND DISCUSSION

4.1 XRD analysis

The XRD analysis was used to determine the crystalline size and phase identification of the prepared nanoparticles. The crystalline size of the particle was defined from Debye - Scherrer's formula $D=K\lambda/\beta \cos \theta$, where λ is the wavelength of XRD, β is the full-width half-maximum and θ is the Bragg's angle.

The XRD pattern of prepared pure HAp and Zn-doped HAp were shown in Fig. 1. The prepared sample confirms the presence of hexagonal structure and is well-matched with JCPDS file No: 09-0432. The broad diffraction peaks of the prepared HAp and Zn-doped HAp at $2\theta = 42.130, 54.370$ and 75.490 were clearly deducted. The indexed hkl planes were (302), (104) and (602). No impurity peaks were detected. The average crystalline size (D) of HAp and Zn-doped HAp was 20.04 and 16.71 nm. Thus the average crystalline size of Zn-doped HAp was small compared with pure HAp, owing to the presence of polyphenols in the doped sample (Mahapatra *et al.* 2016). The unit cell volume (V) and the lattice parameters (a and c) decreased due to an increase in crystalline size and were shown in Table 1.

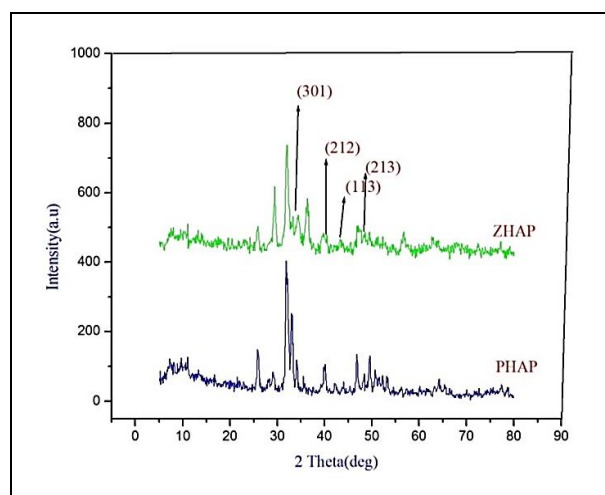


Fig. 1: XRD analyses of pure and Zn-doped HAp nanoparticles.

4.2 SEM analysis

The morphology of the synthesized nanoparticles was determined by SEM. The pure hydroxyapatite nanoparticles exhibited clusters with agglomerated shape with a range of 51 to 71 nm. Then the Zn-doped HAp nanoparticles have the cluster morphology in the range of 43 to 72 nm (Fig. 2).

4.3 EDAX analyses

EDAX provides a quantitative analysis. The purity and elemental composition of the sample were detected by this technique. From EDAX analysis, the existence of elements Calcium, Oxygen and Sodium confirmed the presence of pure HAp nanoparticles. Then Zn-doped HAp was identified from the elements of Zn (Zinc), Ca (Calcium) and O (Oxygen), as shown in Table 2 and Fig. 3.

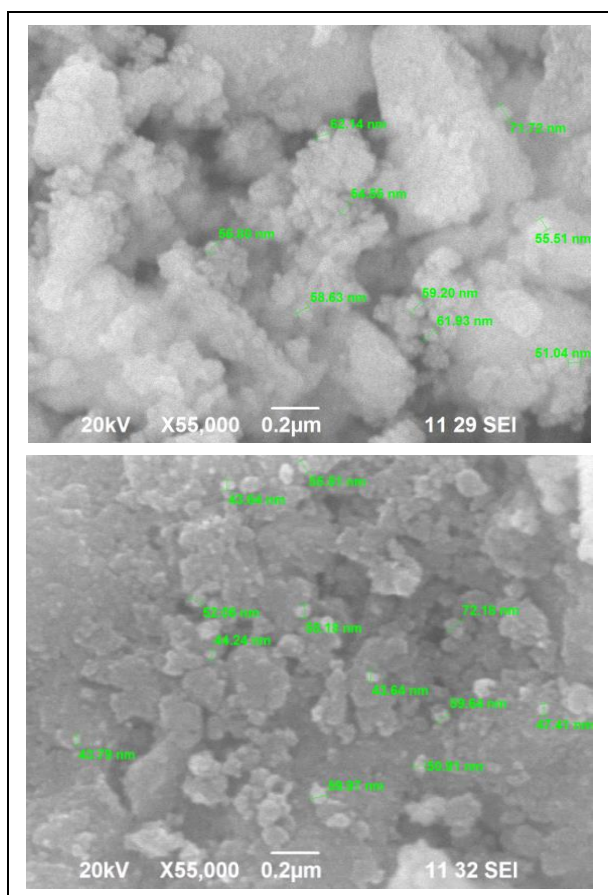


Fig. 2: SEM analyses of pure and Zn-doped HAP nanoparticles.

4.4 FTIR analyses

The FTIR spectra predicted the functional groups present in the sample. The FTIR spectrum of pure HAP has shown the vibration modes of phosphate at 870.70 cm^{-1} , 570.82 cm^{-1} and 1044.26 cm^{-1} . Hydroxyl groups for pure HAP were revealed at 3454.85 cm^{-1} and 3744.12 cm^{-1} . The vibration modes at 569.86 cm^{-1} , 872.631 cm^{-1} and 1043.31 cm^{-1} revealed the presence of phosphate group and Hydroxyl groups at 3456.78 cm^{-1} and 3636.12 cm^{-1} for Zn-doped HAP. The peaks at 1421.28 cm^{-1} and 1420.32 cm^{-1} represent the CH_3 stretching of carboxylic acid. The present groups were shown in Table 3 and Fig. 4.

4.5 UV and PL analysis

UV-Vis. spectroscopy was used to investigate the optical properties and bandgap energy of the sample. The absorption spectra of pure and Zn-doped HAP nanoparticles were found in the wavelength of 348 nm. The bandgap energy of both samples were similar in nature due to the quantum size effect and electronic structure modification. Table 4 shows the bandgap and absorption wavelength of the sample. The spectrum of pure and Zn doped Hap was shown in Fig. 5.

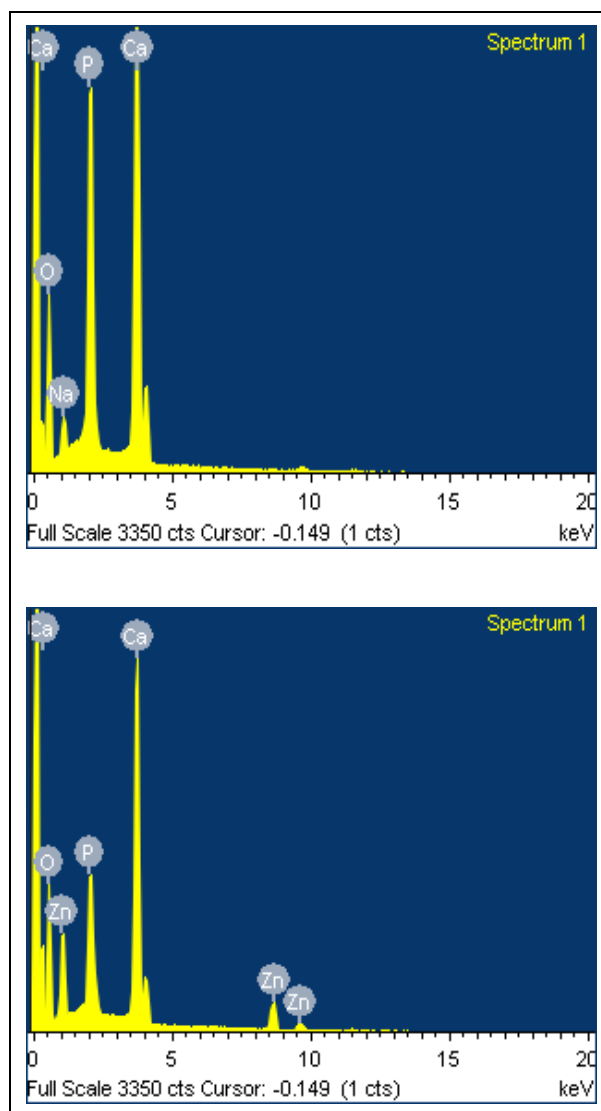


Fig. 3: EDAX analyses of pure HAP and Zn-doped HAP nanoparticles.

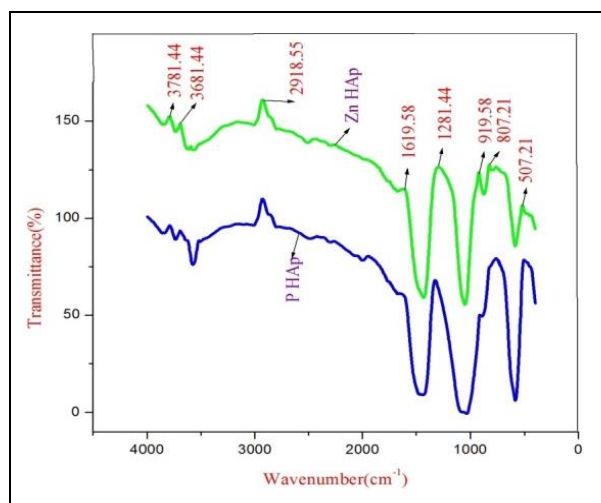


Fig. 4: FTIR analyses of pure and Zn-doped HAP nanoparticles.

Table 1. XRD analyses of pure and Zn-doped HAp nanoparticles.

Sample	2 θ (deg)	Crystalline size (nm)	Average crystalline size	hkl	Lattice constant		Unit cell volume
					a = b	c	
HAp	39.10	21.1135	19.1441	212	9.5492	6.8938	532.84
	43.22	19.7615		113			524.98
	49.50	16.5575		213			526.50
Zn-HAp	39.60	9.7443	14.2583	212	9.4033	6.8966	510.94
	43.35	13.1534		113			591.91
	49.40	19.8773		213			531.72

Table 2. EDAX analyses of pure and Zn-doped HAp nanoparticles.

Sample	Element	Weight %	Atomic Wt. %
HAp	OK	51.23	70.08
	NaK	2.93	2.79
	PK	13.05	9.22
	CaK	32.79	17.91
Zn-HAp	OK	52.76	74.84
	PK	6.89	5.05
	CaK	27.86	15.78
	ZnK	12.49	4.34

Table 3. FTIR analyses of pure HAp and Zn-doped HAp nanoparticles.

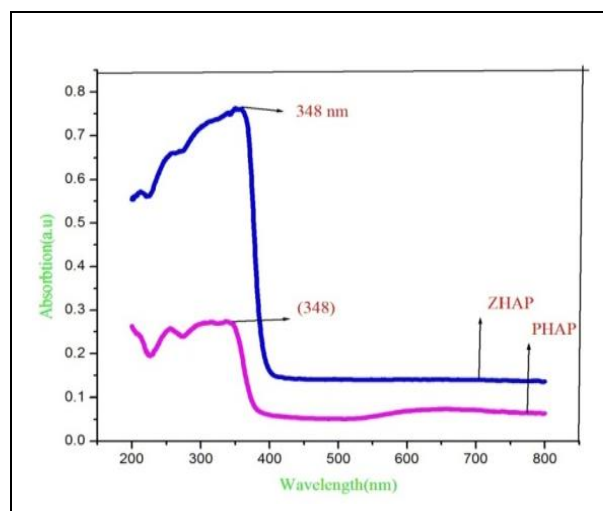
S. No.	Sample	WAVE NUMBER (cm ⁻¹)				
		O-H stretching vibration	C-H stretching vibration	C=C stretching vibration	CH ₃ stretching vibration	P-O stretching vibration
1.	HAp	3766.76	2918.88	1673.03	1320.47	797.04
2.	Zn-HAp	3781.44	2918.55	1619.58	1281.44	807.21

Table 4. Wavelength and bandgap energy of HAp and Zn-doped HAp.

S. No.	Sample	Wavelength (nm)	Bandgap energy (eV)
1	HAp	348	3.56
2	Zn-HAp	348	3.56

4.6 Photo Luminescence Spectroscopy

The intensity of emission radiations was observed using Photoluminescence spectroscopy. The excitation wavelength occurred at the range for both samples is 383 nm. The calculated bandgap energy of the samples is shown in Fig. 6.

**Fig. 5. UV analyses of HAp and Zn-doped HAp nanoparticles.**

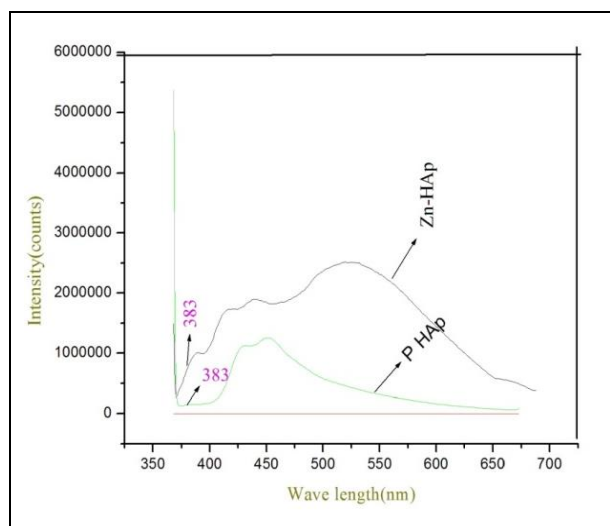


Fig. 6: PL Analyses of Pure and Zn-doped HAp nanoparticles.

5. CONCLUSION

The present work deals with the synthesis of pure and Zn-doped Hydroxyapatite nanoparticles using the microwave irradiation method. The XRD pattern confirmed the crystalline size of the sample. The average crystalline size (D) of pure HAp and Zn-doped HAp were 20.04 and 16.71 nm. The crystalline size decreased in Zn-HAp when compared with pure HAp. Then FTIR spectrum revealed the functional groups present in the sample. SEM predicted the spherical-shaped morphological structure and EDAX confirmed the elemental composition of calcium and phosphate and zinc groups present in the sample. The bandgap energy and optical absorption were determined from UV and PL analyses. The observed bandgap energy for both samples was 3.56 eV.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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