Research Article

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

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ABSTRACT

Hydroxyapatite (HAp) is a nano-biomaterial incorporated as bone and teeth implants in the human body. The present work was aimed at the synthesis and characterization of pure and zinc-doped HAp nanoparticles prepared 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 samples were characterized by XRD, SEM, EDAX and UV analysis techniques. 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 determined using Ultraviolet spectroscopy and Photoluminescence analysis.

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

1. INTRODUCTION

Nanotechnology deals with materials in the size of one-billionth of a meter. While this is the most common definition of nanotechnology, researchers with various focuses have slightly different definitions.

Several free nanoparticles (NPs) are being generated in nanotechnology processes and are intentionally or unintentionally released into the environment or actually delivered directly to individuals through the functioning of a nanotechnology-based product. Of special concern would be those individuals whose work places them in regular and sustained contact with free nanoparticles (Uota *et al.* 2005; Shojai *et al.* 2013; Mohamed *et al.* 2013).

Acetates are salts or esters derived from acetic acid composed of two carbon atoms ionically bound to three hydrogen and two oxygen atoms (CH_3COO) for a total formula weight of 59.05. Phosphoric acid, which is also a mineral acid, is represented by the formula H_3PO_4, contains one atom of phosphorus, four atoms of oxygen and three atoms of hydrogen (Kalaiselvi *et al.* 2014; 2017a).

Calcium hydroxide, commonly referred to as slaked lime, is described by the chemical formula $Ca(OH)_2$ (Kalaiselvi *et al.* 2017b; 2018; Khan *et al.* 2013). It is an inorganic compound that has a white, powdery appearance in its solid state (Gobi *et al.* 2014). However, $Ca(OH)_2$ has a colourless appearance in its crystalline form (Gobi *et al.* 2014; Khataee *et al.* 2014a).

2. MATERIALS AND METHODS

2.1 Preparation of Pure HAp NPs

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 was dissolved with 50 ml of distilled water. Both solutions were stirred for 30 minutes. Then the orthophosphoric acid was added drop-wise into the calcium hydroxide solution and stirred for 30 minutes; this was followed by adding NaOH solution drop-wise to maintain the pH level at 12. This was continuously stirred for half an hour. 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 ground in a mortar to get white color pure Hydroxyapatite nanoparticles (Khataee *et al.* 2014b; Mahapatra *et al.* 2016).

2.2 Preparation of Zinc-doped HAp NPs

The pure HAp nanoparticles were prepared by taken 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 stirred for 30 minutes. Then the orthophosphoric acid was added drop-wise into the calcium hydroxide solution and 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 at 12, and it was continuously stirred for 30 minutes. The precipitate was dried in a microwave oven at 75 W for 30 minutes. Then the dried powder was ground by mortar and kept in a muffle furnace at 400 ºC for one hour, to get fine zinc-doped Hydroxyapatite nanoparticles.

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 and 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 Debye-Scherrer'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 CuKλ radiation source (1.54Å), β represents the full width at half-maximum and θ denotes the angle of diffraction.

3.2 SEM AND EDAX

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

4. RESULT AND DISCUSSION

4.1 XRD Analysis

The XRD patterns of prepared pure HAp and Zn-doped HAp were shown in Fig. 1. The prepared samples confirmed the presence of hexagonal structure, and it is well-matched with JCPDS File No.: 09-0432. The broad diffraction peaks of the samples were obtained at 2θ = 42.130, 54.370 and 75.490. The indexed hkl planes are (302), (104), and (602). No impurity peaks were detected. The average crystalline size (D) of pure and Zn-doped HAp NPs were 20.04 and 16.71 nm. Thus, the average crystalline size of Zn-doped HAp was small compared with pure HAp due to the presence of polyphenols in the doped sample. The unit cell volume (V) and the lattice parameters a and c decreased due to an increase in crystalline size (Table 1).

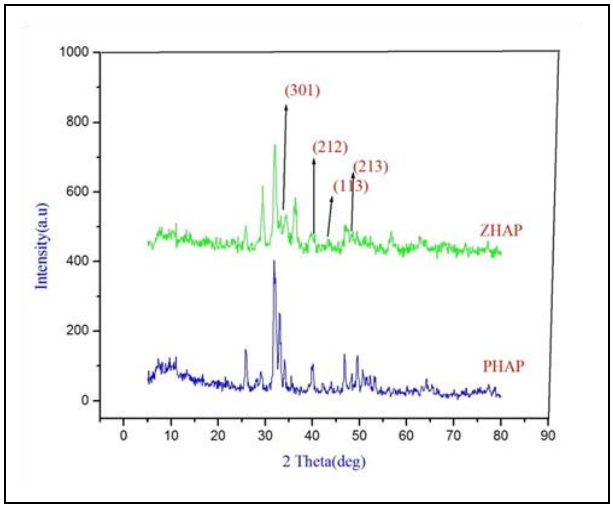

Fig. 1: XRD Analyses of Pure and Zn-doped HAp Nanoparticles.

4.2 SEM Analysis

The morphology of the synthesized nanoparticles was determined by Scanning Electron Microscopy (SEM). The pure hydroxyapatite nanoparticles exhibited clusters with agglomerated shapes with a size range of 51 to 71 nm. Zn-doped HAp nanoparticles have the cluster morphology in the range of 43 to 72 nm.

4.3 EDAX Analyses

Energy-dispersive X-ray spectroscopy (EDX) provides a quantitative analysis. The purity and elemental composition of the sample were detected by this technique. From EDAX analysis, the existence of Ca (Calcium), P (Phosphorus), O (Oxygen) and Na (Sodium) confirmed the presence of pure HAp nanoparticles. Zn-doped HAp NPs were identified from the elements of Zn (Zinc), Ca (Calcium), P (Phosphorus) and O (Oxygen), as shown in Fig. 3.

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

Sample	2θ (deg)	Crystalline size (nm)	Average crystalline size (nm)	hkl	Lattice constants		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

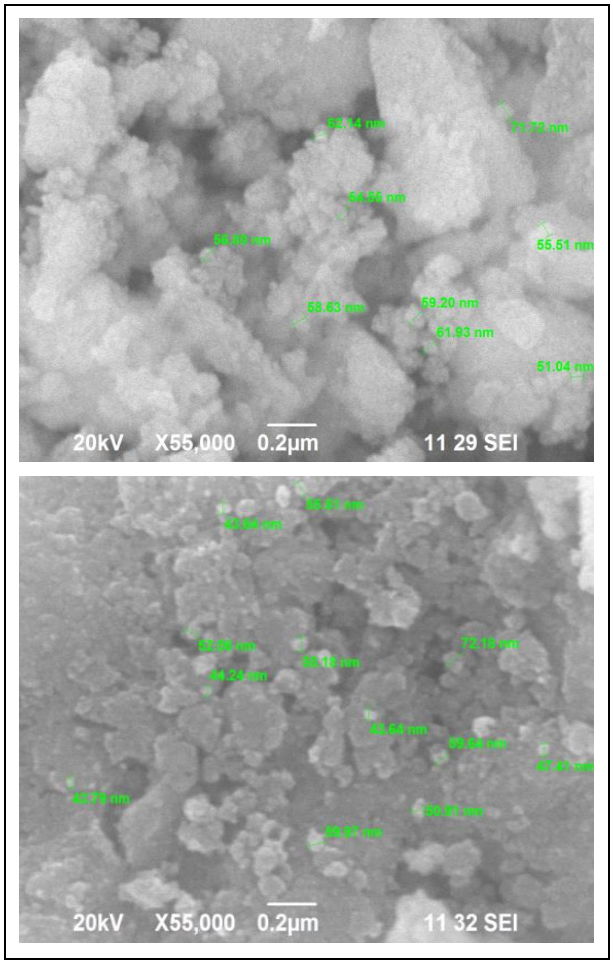

Fig. 2: SEM analysis of: (a) Pure and (b) Zn-doped Hap NPs.

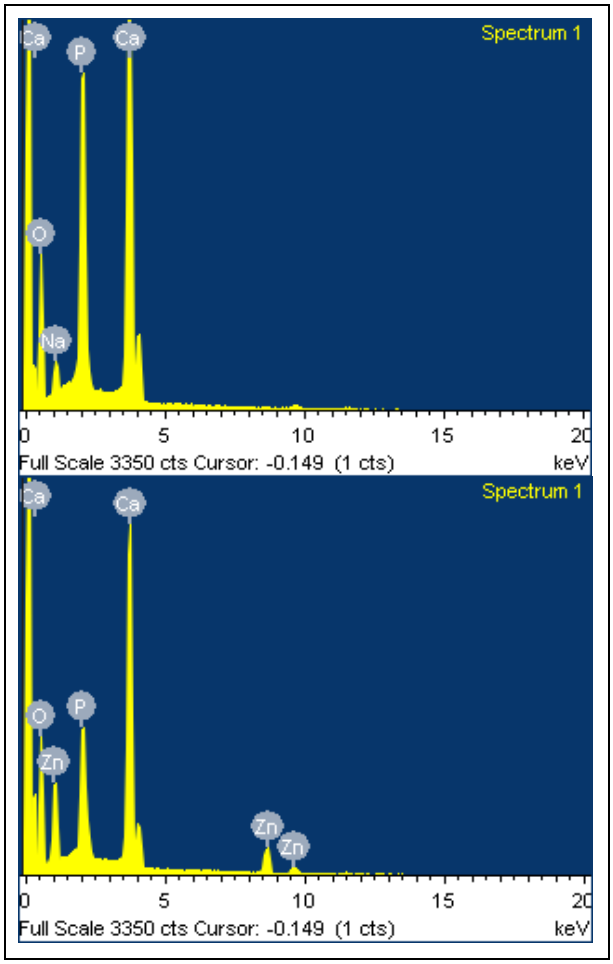

Fig. 3: EDAX analysis of: (a) pure HAp NPs and (b) Zn-doped HAp NPs.

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Table 2. EDAX analysis of pure HAp 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

4.4 FTIR Analysis

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} represented the CH_3 stretching of carboxylic acid. The present groups were given in Table 3 and Fig. 4.

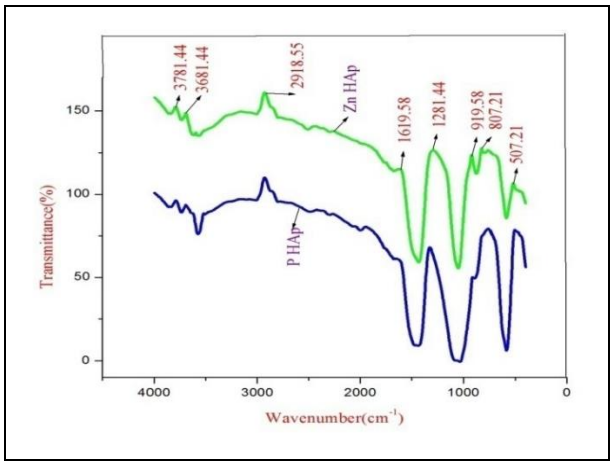

Fig. 4: FTIR Analyses of Pure and Zn-doped HAp Nanoparticles

4.5 UV and PL Analysis

UV-Vis. spectroscopy investigates 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 due to the quantum size effect and electronic structure modification. The bandgap and absorption wavelength of the sample are given in Table 4. The spectra of pure and Zn-doped HAp are shown in Fig. 5.

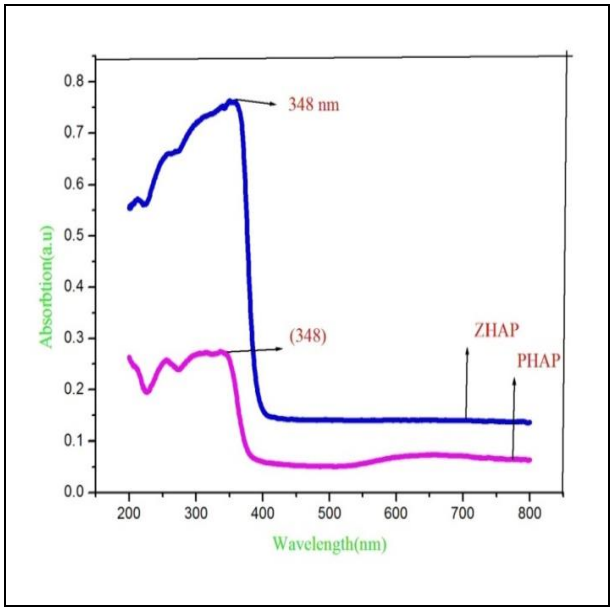

Fig. 5: UV-Vis. Analyses of HAp and Zn-doped HAp Nanoparticles

4.6 Photoluminance Spectroscopy

The emission radiations of HAp and Zn-HAp are shown in Fig. 6. The excitation wavelength for both samples occurred at 383 nm. T0he calculated bandgap energies of the samples are shown in Fig. 6.

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 NPs.

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

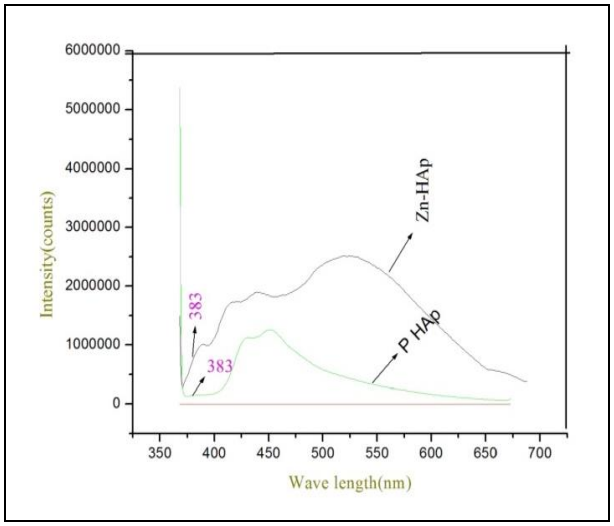

Fig. 6: PL analyses of pure and Zn-doped HAp nanoparticles.

6. CONCLUSION

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

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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