Assimilation of Zinc Metal Ion With Hydroxyapatite for Impedance Studies

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Research Article

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Abstract

The aim of the present work is to examine the doping outcome of Zn metal ions on hydroxyapatite for different concentrations (0.2, 0.4, 0.6, and 0.8). The samples for the pure and Zn doped HAp are synthesized by wet chemical precipitation method. The properties and the particle size are identified by using XRD. The functional bands of PO, CO and OH are analyzed through FTIR and the surface morphology and particle shapes are studied through SEM. The elemental analysis such as zinc, calcium and phosphates are analyzed by EDAX. All the designed elements are studied and confirm the (Ca+Zn)/PO ratio is nearly 1.67 and no other elements were identified in this study. The morphological particles of needle shape and the nanoscale particle size and shapes are studied by using TEM. The electrical conductivity of the synthesized ZnHAp ceramic is mainly related to width of the channel and the polarizability. The frequency dependence of the electric and dielectric properties was studied by using impedance spectroscopy.

Introduction

Hydroxyapatite [HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is the primary mineral for teeth and bone materials with properties such as the bioactive, biocompatible, non-immunogenic agent and osteoconductive. HAp has wonderful efficient properties due to its grain size, ultra-fine structure like a biological apatite when the particle size is at nano level [1,2]. The stoichiometric HAp belongs to a hexagonal crystal system with two major crystal planes such as *a* and *c* planes. Most of the plane *a* is intense with calcium and is referred as positively charged, while the *c* plane is wealthy in phosphate and hydroxide ions and hence referred as negatively charged [3]. The surfaces of HAp exhibit anisotropic characteristics due to adsorption of bio molecules [4]. The ion composition on the surface of the HAp in an aqueous medium varies according to the composition of the medium, because of ion exchange and gradual dissolution [5, 6]. The present study focuses on the doping of Zn^{2+} ions because Zn^{2+} ions are promoting for bone configuration among the exterior ions which commonly built into the HAp bioceramics. The solubility of zinc in HAp display a variation from a few to 15 mol % due to an incorporation of Zn^{2+} is reported experimentally [7]. The crystal lattice affects the solubility or mechanical strength of apatite that depends on the presence of minor cations or anions which is incorporated into the apatite [8]. Zinc is found in all human tissues and bones as a trace element and it is closely related to bone metabolism. Zinc can also promote osteoblasts cell proliferation and differentiation as well as for bone formation. It is utilized for orthopedic and dental materials because zinc plays an important role in HAp containing bioceramics [9-11]. The ionic radius of zinc (0.074 nm) is insignificant than the calcium atoms (0.099 nm) based on their interatomic potential [12]. The electrical properties of HAp based ceramic composites are adopted to tailor the properties which are suited for the technological applications like designing of a biological sensor, ferment sensor, ion sensitive field effect transistor etc. [13]. HAp can also be utilized as an insulating coating for electrical devices and associated circuitry. Such coatings are an asset in designing of biomedical devices where biocompatibility is an indispensable requirement of required application [14]. The electric property of calcium orthophosphate bio ceramics has an impact in the applications of biomedical field. The surface

charges are generated due to polarization of HAp bio ceramics by the application of electric fields at an elevated temperature of 200 °C and it shows a significant effect in the crystallization of biological apatite. Furthermore, the augmentation of bone appears to be accelerated on negatively charged surfaces and decelerated at positively charged surfaces of HAp bio ceramics. The dielectric constant of the ceramics varies with the frequency of the applied electric field and the molecules of HAp oscillate with the frequency of that applied field. Due to these oscillations of the dipoles, the dielectric constant of HAp is changed. The frequency dependencies of the real and imaginary parts of the dielectric constant for the undoped and doped materials are studied. The second relaxation frequencies were appeared around 3 MHz for undoped material and 4 MHz for the doped ones. The dielectric mechanism of ceramics is analysed by Cole-Cole plots. The plot exhibits semicircle and their diameter is changed depending on the concentration of doping [15-16].

Materials And Methods

The ZnHAp is synthesized by co-precipitation method using calcium nitrate, orthophosphate, zinc nitrate, and ammonia solution. A 10-X mol calcium zinc solution was prepared by using calcium nitrate and zinc nitrate for various concentration, X (Zn) = 0.2, 0.4, 0.6, 0.8 mol. The prepared phosphate solution $[(\text{NH}_4)_2\text{HPO}_4]$ are added by drop wise into the calcium zinc mixer solution with vigorous stirring for 70° C. During this reaction, the pH of the solution is maintained at 10-12 by using the ammonia solution. After mixing, the precipitated solution was centrifuged with 3500 RPM / 5min and the centrifuged Zn-HAp samples are collected and kept in a freezer for at least 24 hours. Then filter the melting content by using a filter paper at room temperature and the filtered mass is kept in an oven for 24 hours at 100 °C. Take out the oven ZnHAp samples were dried and the collected. The collected ZnHAp samples were again grinded by using the mortar-pestle and thus ZnHAp samples were prepared.

Results And Discussion

3.1 XRD analysis

Fig. 1 shows the XRD patterns of ZnHAp as dried at 100° C for 12 h. All the peaks were assigned to hydroxyapatite using the JCPDS card number: 09-0432. It is noticed that the XRD peaks of ZnHAP become broader with increasing Zn content. The spectra also provided support that all the doped formulations were crystalline. Table 1 contained the particle size, the parameters a , c values of all samples were noted. It also indicates the shortage of calcium site. Therefore, the added Zn^{2+} ions were all involved in the formation of the HAp lattice. when Zn ion content were increased then the Ca/P atomic ratio naturally decreased. This indicates that the samples were all deficient in cations, Ca, and Zn. Changes in general volume may involve that each doping substituted for calcium in the HAp lattice since Zn^{2+} smaller than calcium, corresponded with a shrinkage in crystal volume. It is also possible that crystal volume changes occurred due to doping ion clustering and/or other site substitutions in the crystal lattice. Synthesized samples contained for noise, that reason using the ammonia solution

maintaining the pH value. This may not be desirable, as the pure, clean powder is an essential criterion for any implantology in biomedical application. B-TCP peaks were not found for without sintering samples.

3.2 FTIR analysis

ZnHAp synthesized samples were studied using FT-IR and were shown in Fig.2. The bands assigned to the hydroxyl stretching and bending modes are at around 3450 cm^{-1} . In ZnHAp possibly caused by the hydroxyl groups. The band around 1000 cm^{-1} and around 600 cm^{-1} were attributed to the phosphate groups. The peak intensity at around 1000 cm^{-1} decreases when the zinc concentration increases. The band at 2400 cm^{-1} is considered being caused by adsorbed water. When zinc concentration increases, the band moves to 3500 cm^{-1} and finally disappears when increasing the Zn ion content. The bands around at 1654 cm^{-1} may be caused by impurities, which become weaker or even disappear when the zinc concentration increases. For all samples, the bands of carbonate groups are observed at around 1400 cm^{-1} , for higher zinc concentration (ZnHAp- 4) these bands disappear. The band at 1425 cm^{-1} assigned to the C-O bending mode also shows similar trends. It is observed the band at 962 cm^{-1} assigned to the PO_4^{3-} symmetric stretching mode becomes stronger due to the decreased hydrogen bonding with the HAp minerals. All samples are smooth and the nanosized particles are highly packed. The disappearance of peaks assigned to consider to be related to the morphology changes. Another possible reason for the disappearance is that the increased zinc concentration results in less-OH groups on the surface, and as a result, given in Table 2.

3.3 Impedance measurements

The frequency dependence of the electric and dielectric properties of all the samples are shown in Fig. 3(a-d). The AC conductivity swiftly increases in the low frequency region and then slowly increases with frequency. This means that the Zn doping did make an important contribution to the electrical resistance in the low frequency ranges because HAp is an insulating material. The impedance of the studied bio ceramics is connected to dispersal of the electromagnetic wave which is accountable for the relative permittivity of the bioceramic material. Therefore, the impedance values of the bioceramics were measured and discussed. Fig. 3(b) observed variations which were related to the polarizability of Ca^{2+} and to the quivering types of H^+ with the nearest anions [18]. However, they forwarded two conduction mechanisms in HAp. In one of the mechanisms, he proposed that the proton (H^+) hopped along the c-axis between the electro active O^{2-} anions. It was concluded that the hydrogen bond in HAp was very weak and the proton conduction through the inter-hydroxyl hydrogen bond along the -OH channel may be very difficult in Fig. 3(c). Thus, even from the crystallographic aspect. Fig. 3(d) shows that the alternating current conductivity linearly increases with increasing frequency for all the samples and obeys the universal power law behaviour. Furthermore, ZnHAp 0.6 sample increasing the maximum conductivity compare to other samples due to the maximum number of free dipoles. So, enormous number of

electrical polarizations takes place. Hence it shows superior conductivity then the rest of three. The result is in good agreement with previous studies [19].

3.4 SEM/TEM measurements

Fig. 4(a-d) shows the SEM photomicrographs of ZnHAp as dried at 100 °C. It is noticed that the unshaped particles were studied its causes by hand grained using mortar and pestle. The Ca/P was calculated from the integrated intensities of Ca and P and found to 1.52 - 1.80 to the ideal ratio of 1.667. The corresponding EDX spectrum confirms the materials comprise of ZnHAp in Fig. 4(a-d). Fig. 5(a-f) shows TEM micrographs of ZnHAp as dried at 100 °C for 12 h. The average particle size of HAp was about 100 nm and it was needle-like in shape. While increasing the Zn content more needle shapes were found. Indeed, the particle sizes of samples are (samples 1-4) smaller than 50 nm. These results indicate a lower crystalline and a smaller crystallite for ZnHAp and are in good agreement with the results of the XRD measurement presented in Fig. 1. Neither the amorphous phase nor any other zinc compounds were observed in any of these particles, and these ZnHAp samples were similar in shapes for all samples. In Fig. 1 are in good agreement with the results of TEM observation. The ZnHAp powders are produced by and are dependent on agglomeration of the primary particles.

Conclusion

The Zn doped HAp samples were prepared from $[\text{CaNO}_3\cdot 4\text{H}_2\text{O}]$, and $[(\text{NH}_4)_2\text{HPO}_4]$ by co-precipitation method. It was phase pure at temperature 100°C without an appearance of -TCP phase. Synthesized ZnHAp samples were examined by FT-IR and studied bands wavelength of OH, CO, PO_4^{3-} . Unshaped particles were studied from SEM and it was confirmed that it was due to mortar and pestle grained particles. From EDX the molar ratio was found to vary from 1.52 - 1.80 as an average of 1.67 which is the ideal molar ratio. According to the impedance studies the AC conductivity quickly increases in the low frequency region and then leisurely increases with frequency. This means that the Zn doping did make an important contribution to the electrical resistance in the low frequency ranges. TEM studies were confirmed that the needle shapes and d-spacing in synthesized ZnHAp samples.

Declarations

There is no conflict between the authors

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Tables

Table 1. Calculation for particle size, a-axis, and c-axis values.

	Description	Zn-HAp1	Zn-HAp2	Zn-HAp3	Zn-HAp4
1	Position 2 θ	31.8491	31.7931	31.8623	31.8302
2	Particle Size – D (211)	41.2388	41.0699	55.973	41.979
4	a (Å)	9.4129834	9.491577	9.43843	9.4463
5	c (Å)	6.6192606	6.512253	6.6271	6.6358

Table 2: Wavenumber corresponding to their respective functional groups in the FTIR spectrum

Functional groups	Wave number (cm ⁻¹)			
	Zn-HAp1	Zn-HAp2	Zn-HAp3	Zn-HAp4
OH	3415	3433	3425	3412
C=O	1419	1421	1419	1421
PO ₄ ³⁻	605	609	605	607

Figures

Figure 1

XRD Pattern of ZnHAp Synthesized samples

Figure 2

FTIR spectrum of ZnHAp synthesized samples

Figure 3

(a). Log F vs Loss tangent for impedance studies of ZnHAp synthesized samples (b). Log F vs Log sigma for impedance studies of ZnHAp synthesized samples (c). Real and imaginary part of the frequency in impedance studies of ZnHAp synthesized samples (d). Frequency vs sigma for impedance studies of ZnHAp synthesized samples

Figure 4

(a-d). SEM & EDAX image of ZnHAp synthesized samples

Figure 5

(a-f). TEM and size distribution spectrum of ZnHAp synthesized samples