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Effect of Titanium Dioxide Doping on Nano Hydroxyapatite Synthesised From Egg Shells Via Wet Chemical Method

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ABSTRACT:

Among different available forms of Calcium Phosphate, Hydroxyapatite (HAP) plays a vital role in the field of medicine specifically in bone repair and tissue regeneration. The use of eggshell to generate hydroxyapatite will reduce the pollution effect of the waste and the subsequent conversion of the waste into a highly valuable product. In this study, pure hydroxyapatite (HAP) powder and Titanium dioxide doped hydroxyapatite was successfully synthesized using egg shell as calcium source and orthophosphoric acid as phosphorous source by novel wet-chemical method. The synthesized samples are characterized by XRD, SEM, FTIR and EDS. X-ray diffraction studies reveals that the prepared HAP is well crystalline in nature. The microstructural characterization of SEM studies reveals that the synthesized HAP nano particles are in the range of <100nm. The functional groups and element compositional analysis are studied from FTIR and EDX respectively.

KEYWORDS:

Hydroxyapatite, Egg shells, TiO2, XRD, Nano-biomaterials.

1.Introduction:

Hydroxyapatite [Ca10 (PO4) 6 (OH) 2, HAp] is known as the mineral component of the bone. Bone is an organ that not only provides a basic mechanical support to the body by generating and transferring forces that are involved in the locomotion but also has various other functions. Bone consist s of approximately 8wt% water, 22wt% protein and 70wt% minerals[1]. The mineral component of the bone is a form of calcium phosphate which presents the main mineral reservoir for the body. Among all biomaterials calcium phosphate areattractive biomaterials owing to its excellent biocompatibility and its non- toxicity.

It is a very good drug delivery carrier and possesses the following advantages, like biodegradability, biocompatibility, solu-bility. Calcium phosphate based system, particularly those with Ca/P molar ratio close to the one of hydroxyapatite are negligibly soluble in blood which is by itself supersaturated with respect to hydroxyapatite®. Calcium phosphate exists in different forms according to Ca/P ratio, such as hydroxyapatite, Octacalcium phosphate, Tri-calcium phosphate, Di-calcium phosphate dehydrate and Di-calcium phosphate[2].

Among these hydroxyapatite with hexagonal crystalline structure accounts 65 wt% of bone and provides most of its strength and stiffness. Hydroxyapatite crystals in bone are generally in the form of rod like crystals in the nanometer size range of less than 100nm®. Also this hydroxyapatite has excellent bio-compatibility and Osteoconductivity. This property of Osseo integration is needed to minimize discharge to surrounding tissues and to increase the implant efficiency.

The preparation of hydroxyapatite powder with controlled morphology, stoichiometry crystallinity and crystallite size in nano range has the main role in the production of biomaterials[3]. The main limitation of hydroxyapatite bio ceramic is that it has poor mechanical properties. Hydroxyapatite on the other hand has high bioactivity non-toxic with many medical application in the form of porous dense and granule forms[4].

A study has suggested that the recycling of chicken eggshells is a way of improving the ecosphere; it reduces the need of management of waste and the eggshells can serve as useful raw materials for nanomaterial. Fresh eggshell consists of a typically three-layered structure; the foamy cuticle layer on the outer surface resembles a ceramic; the middle layer is spongy; the inner layer consists of lamellar layers®. It represents almost 11% of the egg total weight®. Calcium carbonate (calcite) is the main component in eggshells and is the major inorganic substance

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found in an egg and it makes up about 94% of chemical composition of eggshell®. This makes it an essential material for hydroxyapatite production. Others are organic matter which makes up 4%, magnesium carbonate (1%), and calcium phosphate (1%) as well as insoluble proteins[5]. Here we are doping Titanium ions to identify the effect of titanium ions while reacting with Pure Hap. Titanium was chosen because of its importance in orthopedic field®. Since Hap is brittle in nature it was doped with titanium to improve its handling capacity also Ti is very friendly to human bones and teeth so it is readily acceptable as it has proven to be more bio compatible than other materials®. It is strong, light weight, corrosion resistant, cost effective, nontoxic, bio compatible, long lastingsimilar to that of human bone®.

Several methods of chemical synthesis have been developed to prepare HAP powder using various types of calcium and phosphor sources. The eggshell consists of about 94-97% of CaCO3 and the other 3% is organic matter and egg pigment. It was found to be a waste material®. Hence in this study the eggshell has been used as a calcium precursor to synthesize pure and Ti doped HAP with Ca/P ratio through wet chemical method[6]. The present work was aimed to determine the crystallite size, structural morphology and functional groups of pure and Ti doped hydroxyapatite. The powders were characterized by X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), Energy Dispersive spectroscopy(EDS).

Experimental Procedure
Materials:

Egg shells, Orthophosphoric acid(99%SIGMA ALDRICH), Titanium dioxide (99%SIGMA ALDRICH),Ammonia solution.

Pure Hydroxyapatite synthesis:

Cleaned and Uncrushed eggshells were calcined in air atmosphere at 900 ºC for 1h, organic materials will decay during heating of first 30 minutes, later on the egg shells will be recovered as calcium oxide. Then the calcined eggshells are grinded into very fine powder using mortar. 5gms of egg shell powder were dispersed in distilled water.To this2M of Ortho phosphoric acid is added drop by drop with continuous stirring for 1hr such that Ca /P ratio is 1:67.

The pH is found to be 8.5 at the end of the reaction.The precipitate formed was subjected to aging treatment for 24 hrs in ice. Later it is washed several times using double distilled water and filtered. The final precipitate is dried at 80 ºC for 2 h using Hot air oven and calcined at 900 ºC for 1h in muffle furnace to get fine HAp Nano powder.

Titanium dioxide doped Hydroxyapatite synthesis:

4gms of egg shell powder and 0.1M of titanium dioxide were dispersed in distilled water under continuous stirring for 30 minutes.To this 2M of Ortho phosphoric acid is added drop by drop with continuous stirring for 1hr such that (Ca + Ti)/P ratio is 1:67.The pH is found to be 11 at the end of the reaction. Ammonia is summated to reduce the pH to 8.5.The precipitate thus formed was subjected to aging treatment for 24 hrs in ice. Later it is washed several times using double distilled water and filtered. The final precipitate is dried at 80 ºC for 2 h using Hot air oven and calcined at 900 ºC for 1h in muffle furnace to get fine Ti doped HAp Nano powder.

Characterization and discussion of results:
1.X Ray diffraction (XRD):

The crystallite size (D) of the particle was calculated from XRD line broadening measurement from the Debye Scherer equation

$$D = 0.89\lambda / \beta\cos\theta \qquad (1)$$

Where λis the wavelength of the CuKαline,
β is the full width at the half maximum of the hydroxyapatite line and
θ is the diffraction angle(7).
The lattice parameter ‘a’ and ‘c’ of the HAp nanoparticle and volume were calculated using the standard equation

$$1/d2\ hkl = 4/3\ [\ h2 + hk + l2\ ]\ a2 + l2/c2. \qquad (2)$$

$$V = 2.589\ a2\ c \qquad (3)$$

Figure 1 (a,b) shows the XRD pattern of the prepared Pure& Ti doped HAp powder. The obtained XRD data Matches well with the standard JCPDS file no: 09 -0432.
XRD Table: 1

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Sample	Crystalline size	Cell parameters		c/a	Unitcell volume V(°A)^3
		a(°A)	c(°A)		
Pure HAp	28nm	9.9110	6.1051	0.6159	1552.60
Ti doped HAp	21nm	9.5486	7.0486	0.7381	1663.85

These values were found to be matching well with standard values.

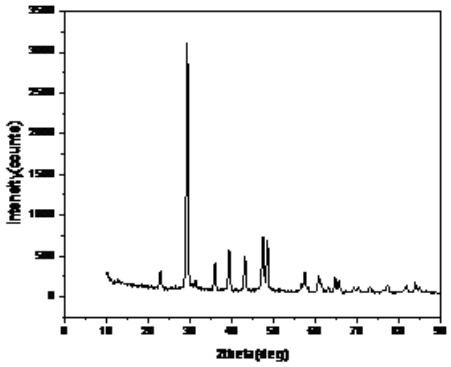

Fig 1(a)

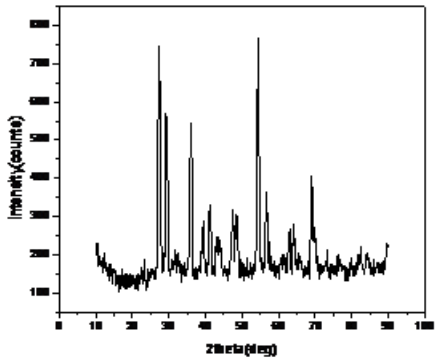

Fig 1(b)

2.Fourier Transform Infrared (FTIR) spectroscopy:

The formation of the HAp phase was tested by FT-IR spectral analysis. The elemental composition and Functional groups were investigated by FTIR spectra over the range from 400–4000 cm-1in pellet form for 1mg powder samples mixed with 200 mg spectroscopic grade KBr. Spectra were measured in the transmission mode(8).

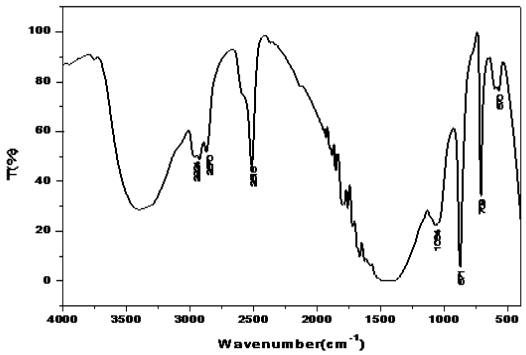

Fig 2(a)

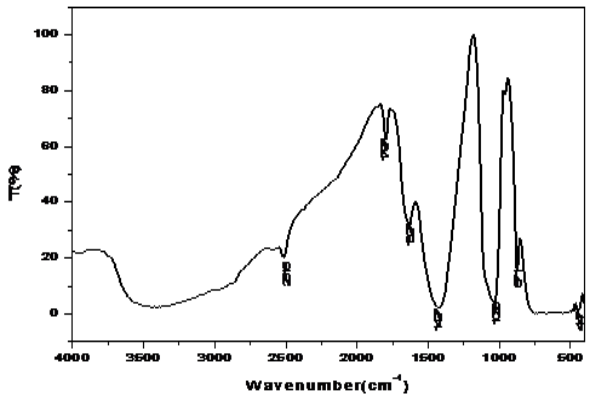

Fig 2(b)

Figure 2(a,b) represents the FTIR image of Pure and Ti doped HAP respectively.
FTIR Table:1

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SAMPLE NAME	P-O BENDING cm^{-1}	P-O STRETCHING cm^{-1}	C-O STRETCHING cm^{-1}	O-H STRETCHING cm^{-1}
HAP	570	871.82	1404	3749
HAP-TiO_2	671	871.82	1427	3865

Pure HAp fig 2(a):

The characteristic frequencies of P-O bending modes of vibration are seen around 570cm-1.The P-O stretching vibration are identified at 871.82 cm-1

The strong intensity of C-O stretching vibration modes are indicated at 1404 cm-1.The stretching peak value of 3749cm-1 is assigned to hydroxyl O-H functional groups. The adsorbed H2O in the sample is observed at 1627, 1666 cm-1 and 3394cm-1.

Ti doped HAp fig 2(b):

The P-O bending modes are indicated by the peak value 671cm-1. The presence of P-O stretching modes of vibration is observed at 871.82cm-1. The C-O stretching modes are observed at 1427 cm-1The O-H functional groups are assigned at 3865 cm-1. The P-O stretching modes are observed at 493 cm-1.

Thus FTIR proves that there are no obvious peaks found for any other impurities and introduction of TiO2 does not damage the back bone structure of HAp. There found a slight shift between the spectrums. The peaks between 400- 450 cm-1 indicates the presence of TiO2 in the synthesized sample.

3. Scanning Electron Microscope (SEM)

The surface morphology and crystallite morphology of the synthesized particles were investigated by scanning electron microscope (SEM) operating at an accelerating voltage of 20KV.Figure 3(a,b) shows the SEM image of Pure and Ti doped HAP

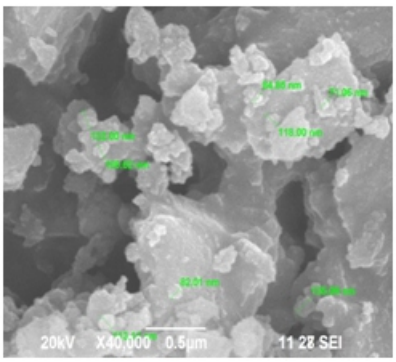

Fig 3(a)

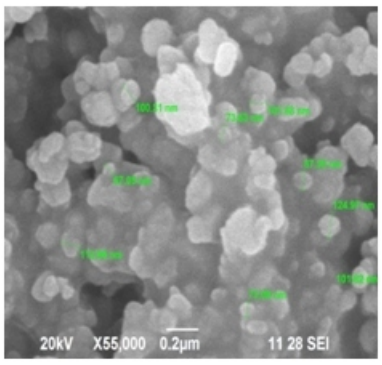

Fig3(b)

The size and shape of the HAp and TiO2 doped HAp was visualized by SEM. The Pure HAp exhibitsconglomerated structure ranges between 71 to 131 nm. TiO2 doped HAp shows cluster like structure (9) which ranges between67 to 124 nm.The SEM image helps us to draw a conclusion that the doping of TiO2has a strong effect on the morphology of Pure HAp.

4.Energy Dispersive xray Spectroscopy (EDS)

This is a qualitative and quantitative X- ray micro analytical technique that can provide information on the chemical composition for the elements with atomic number greater than 3. Fig 4(a) represents the EDS images of Pure and Ti doped HAP which predicts the higher concentration of Ca and P elements in pure HAp. In figure 4(b), the presence of Ti peaks determines the presence of this element in material constitution.

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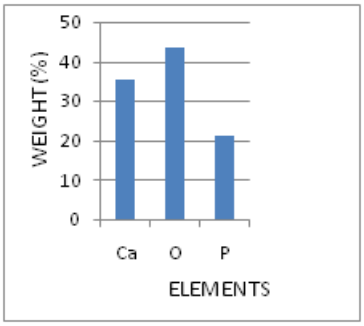

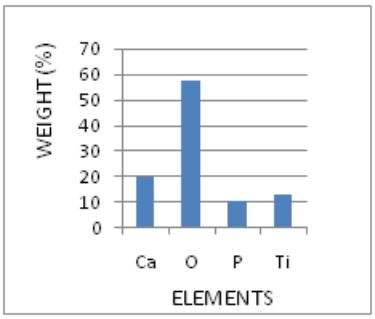

The Ca/P ratio of pure HAP is 1.67& and Ti doped HAP is 1.89 which is close to the expected value (1.67)[10]. The small difference in the value can be attributed to impurities in the eggshells. Therefore the images have provided the evidence that TiO2 has been successfully incorporated into the composites.

Conclusions:

Thus using egg shells Pure and Ti doped HAP was synthesized by wet chemical method. X-ray diffraction analysis confirmed the grain size, cell parameters, unit cell volume of the Pure and Ti doped HAP nanoparticles.FTIR showed the presence of Phosphate and Hydroxyl groups in both the samples.

The SEM results showed that the formation of conglomerated and cluster like structure in pure and doped samples.EDS reveals the composition of the elements. Thus by recycling and waste management method egg shells can be utilized as source for HAP synthesis. Egg shell based HAP is an inexpensive ceramic biomaterial can be produced in masses.

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