Hydroxyapatite Formation on the Antase Phasetitanium Dioxide Nanoparticles

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Abstract. The The objective of in-vitro study was aimed to synthesize and characterize the nanoparticles of Titanium dioxide (TiO_2) and Hydroxiapatite (Hap). The anatase phase Titanium dioxide nanoparticles were synthesized using chemical precipitation method. This study demonstrates the efficient growth of hyroxyapatite over the surface of TiO_2 nanoparticles under the medium of in-vitro studies of 1 SBF and 1.5 SBF separately at body temperature 36.5 °C using the BOD incubator. The growth of HAp over the surface of TiO_2 nanoparticles are confirmed by structural studies, surface morphology, chemical composition and vibrational stretching.While comparing the results of anatase phase of TiO_2 nanoparticles, anatase phase of TiO_2 nanoparticles in 1.5 SBF had higher growth of HAp than anatase phase TiO_2 nanoparticles in 1 SBF.

Keywords: TiO_2 nanoparticles, Anatase phase, Hydroxyapatite, 1 SBF, 1.5 SBF.

1 Introduction

Due to the high biotolerance, adequate mechanical properties, nontoxicalsoity and corrosion resistance of Titanium dioxide and alloys of TiO_2have been broadly used in orthopedic and dental fields as biomaterials for permanent implants materials (1,2). Due to the mechanical property, titanium shows a mechanically stable interface towards bone. The capacity of the bone bonding and bioactivity of implant surfaces has been developed by the TiO_2 (3,4). The major inorganic component of bones, teeth and hard tissue in mammals [Hydroxyapatite (HAp) ($Ca_{10}(PO_4)_6(OH)_2$)] (5) and also it is the most widely used bioceramics for orthopaedic and dental applications,which gives excellent bio-activity, biocompatibility and strong bonding natural bones.

In order to improve the capacity of bone-bonding ability, titanium and its alloys are often used to develop HAp. Implanting TiO_2-HAp over the surface of the bone tissue will form a chemical bond with the bone to motivate the promotion of bone growth. In recent decades, a number of researchers have concentrated on the interesting field of biological application. The arrangements of a bioactive surface layer directly on TiO_2substrate would prompt the apatite evolution in the living environment or simulated body fluid (SBF). In this study, the anatase phases of TiO_2 nanoparticles were prepared as a pellet form to investigate the in-vitro apatite arrangements in order to assess the calcium and phosphorous percentage in SBF, which is required to make bone-like apatite.

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2 Methods And Materials

In the present work, the prepared [6] anatase phase at an annealing temperature 450°C of TiO_2 nanoparticles are separately prepared to pellets by using hydraulic pressure pelletizer. One gram of TiO_2 powder (i.e., anatase phase) was pressed uniaxially to acquire disk-shaped pellet of 15 mm dia and 0.5 mm thickness preceding to an isostatic pressing at 100 MPa.

SBF (1 SBF and 1.5 SBF) aqueous solution was synthesised for the formation of apatite in one litre of solution by adding the reagents proposed by Kokubo and his colleagues [7]. A solution with ion concentrations 1 and 1.5 times of SBF (1.5SBF) can be synthesised, in order to stabilize the apatite formation.

The prepared anatase phases -TiO_2pellets were immersed in 50 mL of 1 SBF and also 1.5 SBF separately in the polyethylene container under body temperature 36.5 °C using the BOD incubator. For every 24 hours, the used solution was drained out and filled with another fresh solution. Exactly, after the 5^{th} day of immersing, the pellets were removed from the solution, washed with distilled water and dried below 50 °C for one hour to remove the moisture from the pellets. After that they were characterized.

The above procedure was repeated for the same characterized pellets to proceed up to 10^{th} day of immersing and 15^{th} day of immersing. Exactly, after the 10^{th} and 15^{th} day of immersing, the pellets were removed from the solution, washed with distilled water and dried below 50 °C for one hour to remove the moisture from the pellets. After that they were characterized.

In this study, XRD(X-ray diffraction) were observed using PANalytical X-ray diffractometer. The surface morphologies and energy dispersive X-ray energy spectroscope of synthesized nanoparticles was analysed by Field emission scanning electron microscope (FESEM) with EDX in CARLZEISS SIGMA version. Fourier Transform Infrared spectroscopy (FTIR) analyses were recorded by using SHIMKDZU IRAffinity – 1 instrument to confirm the compound and nanoparticles formation.

3 Result And Discussion

3.1 Structural Studies

The XRDformation of annealed at 450°C of TiO_2 samples after immersing into the 1 SBF and 1.5 SBF solution under body temperature shown in Figures 1.1 and 1.2 (a, b & c) are the diffraction peaks corresponding tothetetragonal BCC of the anatase phases of TiO_2(101), (004), (200), (105), (204), (220) and (107) crystal planes. The lattice constants were found to be a = 3.745Å and c = 9.510Å, and in good agreement with standard (JCPDS) card No. 89-4921. Along with this diffraction peaks there was presence of other diffraction peaks (211), (202) and (140) crystal planes of hexagonal primitive of the Calcium Hydroxide Phosphate ($Ca_{10}(PO_4)_6OH_2$ – Hydroxyapatite) represents in graph as HAp.The lattice constants have been found to be a = 9.248Åand c = 6.593Å which was with the standard (JCPDS) card No. 74-0565 (8).

From the XRD, the phase of the TiO_2 nanoparticles is mainly of nano-crystalline anatase type tetragonal symmetry with the presence of hexagonal symmetry of hydroxyapatite. The intensities of the peaks describes the hydroxyapatite were increased because the immersing period was increased by days.

The observation indicates that the growth of HAp increases with increase inthe immersing period of days from 5 to 15 days in both the concentration 1 SBF and 1.5 SBF. The growth of

HAp improvement is proportional to the increase in the intensity of the diffraction peak. The growth of the HAp in the concentration of 1.5 SBF solutions was higher than the concentration of 1 SBF solution.

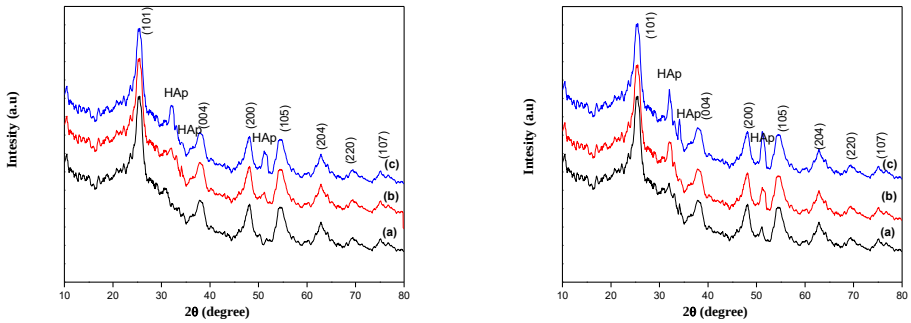

Figure 1.1 & 1.2 XRD Pattern of Anatase HAp-TiO_2 (Concentration of 1 SBF & 1.5 SBF immersed after(a) 5thday, (b) 10thday and (c) 15thday in SBF)

By comparing the XRD patterns of HAp on anatase phase-TiO_2nanoparticles in 1 SBF and 1.5 SBF. The anatase phase -TiO_2 nanoparticles in 1.5 SBF has more growth of HAp (calcium and phosphate) than the anatase phase -TiO_2 nanoparticles in 1 SBF.

4 Surface Morphological Studies

The formations of HAp over TiO_2 nanoparticles can be seen in FESEM Figures 2(a – f). The sample shows the agglomerated grains with random shapes and the distributions of grains were regular spherical shape through all the regions with the formation of calcium and phosphate (HAp) over the sample. Figure 2(a-c) FESEM images of anatase phase of HAp-TiO_2nanoparticles in the concentration of 1 SBF solution. The yellow colour circles in the image shows the formation of calcium and phosphate (HAp). The observation of Figure 2(a-c) indicates the increase in the formation of calcium and phosphatespersentage with increasingthe immersing period from 5 to 15 days in the concentration 1 SBF solution. Similarly Figure 2(d – f) depicts the FESEM images in the concentration of 1.5 SBF solution. The yellow circles of this image show that, there was increase in the formation of calcium and phosphate ratio with increase inthe soaking period from 5 to 15 days in the concentration 1.5 SBF solutions.

Figure 2.1 indicates the growth of HAp increases with increase in the soaking period from 5 to 15 days in both the concentration of 1 SBF and 1.5 SBF solutions. The growth of HAp improvement is responsible for the increase in the yellow marked circles. The growth of the HAp in the concentration of 1.5 SBF solutions was higher than the concentration of 1 SBF solutions in anatase phase of TiO_2 nanoparticles.

The FESEM images reveal the crystallites were nanoscale in size. Therefore, the growth of HAp was also in nanoscale range over the TiO_2 nanoparticles on the anatase phases under the concentration of 1 SBF and 1.5 SBF solutions. By comparing the FESEM images, the anatase phase-TiO_2nanoparticles in 1.5 SBF have more growth of HAp (calcium and

phosphate) than the anatase phase-TiO_2 nanoparticles in 1 SBF.The HAp-$TiO_2$is due to the increase in concentration of SBF with maximum soaking period as similarly shown in XRD results.

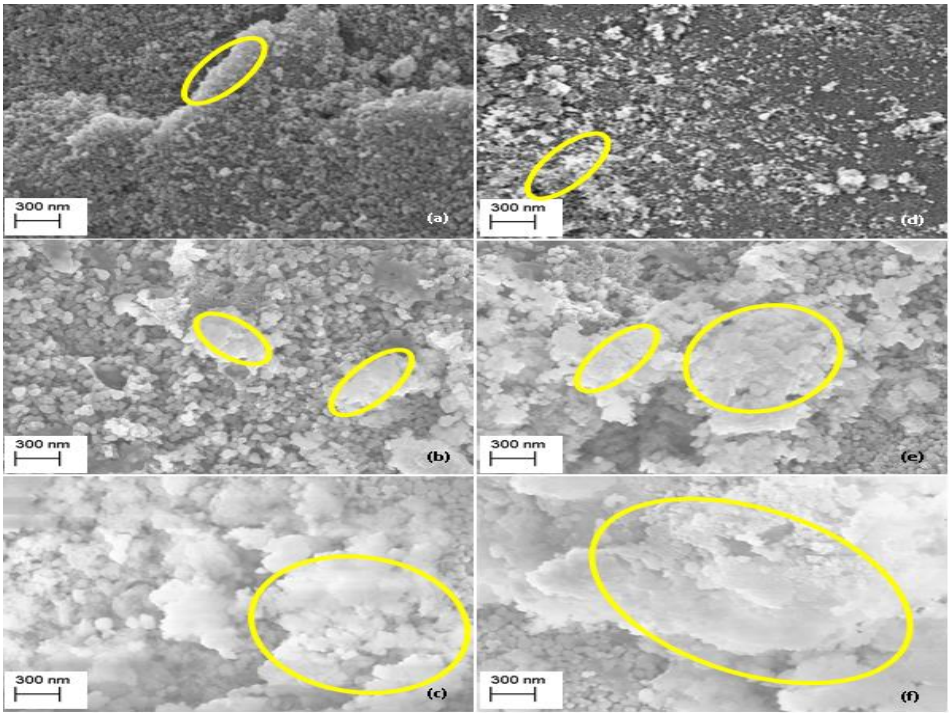

Figure 2FESEM images of AnataseHAp-TiO_2nanoparticles (immersed after in 1 SBF (a) 5thday, (b) 10thday and (c) 15thday& immersedafter in 1.5 SBF(d) 5th day, (e) 10thday and (f) 15th day)

5 Compositional Analysis

Energy dispersive X-ray energy spectroscopeanalysis was used to determine the composition of the TiO_2 nanoparticles with the presence of calcium and phosphate to justify the growth of HAp. Figures 3.1to 3.2 (a – c) show the elements of Ti, O, Ca and P presents. Thus, the spectroscopeanalysis indicates that the obtained HAp-TiO_2 nanoparticles were pure representing the growth of artificial bone. Figure 3.1 and 3.2 depicts the chemical composition of Ti, O, Ca and P with anatase phase in the concentration of 1 SBF and 1.5 SBF solutions. Mainly there was increase in the composition of Ca and P with increase in the soaking period and also in concentration.

When comparing the anatase phases of HAp-TiO_2 in both the concentration of 1 and 1.5 SBF solutions, the anatase phase of HAp-TiO_2 nanoparticles in 1.5 SBF has more growth of calcium and phosphate. HAp-TiO_2 concentration is raised due to the increase in concentration of SBF with maximum immersing period as similarly shown in XRD and FESEM results.

6 FTIR Spectral Analysis

Fourier transform infrared spectra were observed using a SHIMKDZU IRAffinity – 1 spectrometer(9). Figures 4.1&4.2 shows the spectrum of anatse phase HAp-TiO_2 nanoparticles of 1 SBF and 1.5 SBF solutions under different immersing period of days.

Figures 4.1 show the approximately similar bands occurred corresponding to the growth of HAp-TiO_2nanoparticles. The peak at 3500 cm^{-1}, were stretching vibration of OH groups and the symmetric and antisymmetric OH peaks of molecular H_2O with in TiO_2 nanoparticles.

The bending vibration to the molecular H_2O bending band is at 1600cm^{-1}. The TiO_2-OH bonds formed from the hydrolysis reaction. While the peakfrom 2800 to 2970 cm^{-1}corresponds to symmetric stretching of CH and CH_2 bands, the in-plane skeletal vibrations of aromatic ringsaroundthe peaks from 1300 to 1500cm^{-1}. The modes at 450 to840 cm^{-1} indicate the stretching vibrations of anatase phase TiO_2 nanoparticles along with the PO_4^{3-} and Ca^{2+}.

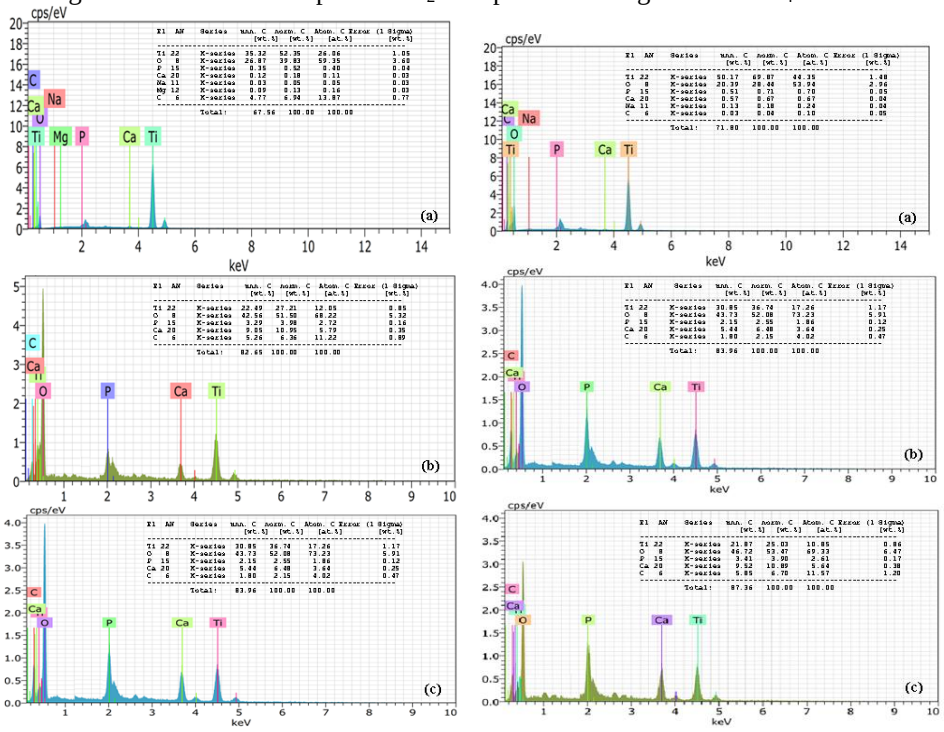

Figure 3.1 & 3.2EDAX pattern of AnataseHAp-TiO_2nanoparticles (immersed after in 1 SBF& 1.5 SBF(a) 5thday, (b) 10th day and (c) 15th day)

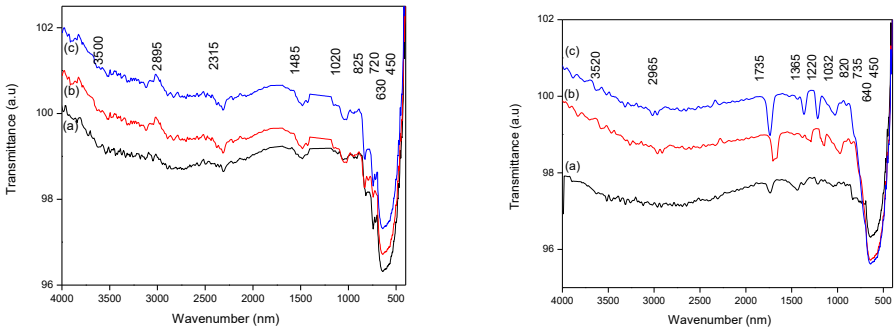

Figure 4.1 &4.2FRIR Pattern of Anatase HAp-TiO_2 (Concentration of 1 SBF & 1.5 SBF immersed after(a) 5thday, (b) 10thday and (c) 15th day in SBF)

In Figures 4.1 to 4.2, the FTIR peaks of anatase phase of HAp-TiO_2 nanoparticles in the concentration of 1 SBF and 1.5 SBF are shown. The FTIR result proves the formation of HAp over TiO_2 nanoparticles rises gradually while the period of soaking day increases.

7 Growth Mechanism of HAp on TiO2 Nanoparticles

In this study, crystal planes of hexagonal primitive of the Calcium Hydroxide Phosphate ($Ca_{10}(PO_4)_6OH_2$ – Hydroxyapatite) represents as HAp-TiO_2 nanoparticles under the SBF solution at a human body temperature. The prepared anatase phase of TiO_2 nanoparticles are taken for this study of bonelike apatite. The SBF (1 SBF and 1.5 1.5 SBF) aqueous solution with the ion concentration were prepared separately by adding the chemicals like NaCl, $NaHCO_3$, KCl, $K_2HPO_4.3H_2O$, $MgCl_2.6H_2O$, HCl, $CaCl_2$, Na_2SO_4 and $(CH_2OH)_3CNH_2$ in distilled water. This reagent is dissolved into an ion exchanged gives the concentration of distilled water ions as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, HPO_4^{2-} and SO_4^{2-} are clearly shown under the EDAX and FTIR analysis. The pellet of TiO_2 nanoparicles were immersed in 50 mL of 1 SBF and 1.5 SBF in a polystyrene container at body temperature under BOD incubator which has in-built of cooler, heater, UV lamp and illumination light. Due to the presence of aqueous solution TiO_2 nanoparicles tends to monitor the H_2O molecules over the surface to form TiO_2 group. UV illumination light was responsible to accelerate the formation of bone-like apatite. The bone-like apatiteis composed with the calcium and phosphates i.e., the Calcium (Ca^{2+}) and the phosphorous (HPO_4^{2-}) present in the SBF solution are deposited over the Ti-OH surface of TiO_2 nanoparicles as calcium (Ca^{2+}) and phosphates (PO_4^{3-}).

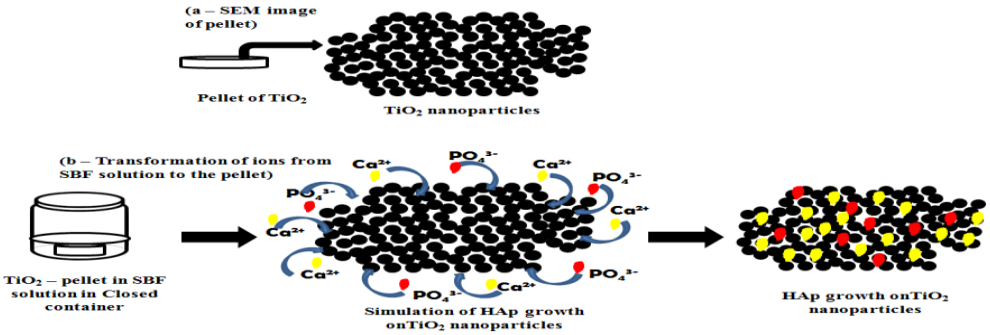

Figure 5.1 Schematic Growth Mechanism of HAp on TiO_2 nanoparticles in SBF Solution

Figure 5.1 depicts the mechanism of the bone like apatite growth over the TiO_2 nanoparticles. The powder form of TiO_2 nanoparicles were made to pellet form. The schematic image is given in Figure 5.1(a). The particles were closely arranged in a random manner. Figure 5.1(b) is the schematic diagram that represents the formation of bone like apatite i.e., Ca^{2+} and PO_4^{3-} simulated over the surface of TiO_2 nanoparicles. Thus, the growth of HAp over the surface of TiO_2 nanoparicles is finally shown.

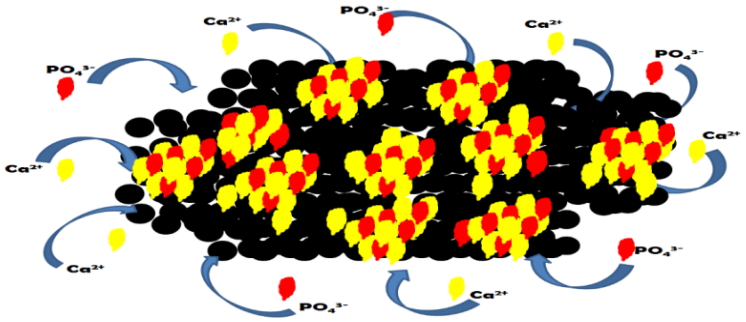

Figure 5.2 Schematic Picture of HAp Growth over TiO_2 nanoparticles

The FESEM images of the HAp over the TiO_2 nanoparicles were visible in Figures 5.1 and 5.2. In those figures, the HAp was seen like foam formation over the surface of TiO_2 nanoparicles. Thus, a similar mechanism was seen in Figure 5.2 as schematic representation of the HAp growth over the surface of TiO_2 nanoparicles.

8 Conclusion

The growth of HAp over the surface of TiO_2 nanoparticles is confirmed by the structural studies, surface morphology, chemical composition and vibrational stretching. While comparing the results of anatase phase of TiO_2 nanoparticles, anatase phase of TiO_2 nanoparticles in 1.5 SBF had higher growth of HAp than anatase phase TiO_2 nanoparticles in 1 SBF.

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