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In vitro electrodeposition of Hydroxyapatite coatings on Ti-6Al-4V for biomedical applications

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Abstract: The current paper focuses on enhancing the Osseo integration of Ti based orthopedic implants. This will be achieved by the deposition of nanoceramic coatings using Electrodeposition technique. Hydroxyapatite coatings on titanium implant have received more attention because of the combined effect of mechanical and enhanced biocompatibility. The uniform and well adhered HAP coating was prepared by electrodeposition technique. The formed coating was characterised by FT-IR, XRD and SEM analysis.
Keywords: Electrodeposition, biocompatibility, XRD and SEM.

Introduction

Titanium and its alloys like Ti-6Al-4V, Ti-6Al-7Nb, Ti-13Nb-13Zr and Ti-12Mo-6Zr are widely used in load-bearing orthopedic implants because of their high corrosive resistance, increased mechanical strength and bio-inert in nature. Such properties of titanium and its alloy made them to be the better choice for hard tissue replacements and in dentistry[1,2]. These specific properties of titanium alloys make them important in biomedical applications, even though they have a limitation that is lack of bioactive sites on their surfaces responsible for making bond with the natural bone and tissues. The osteoinductive properties of the titanium can be enhanced by coating its surface with a bio ceramic layer. Considering bio ceramics, Hydroxyapatite (Ca_{10} $(PO_4)_6$ OH_2) is extensively used in coating of metal implants for orthopedic applications. Because, of their close resemblance of chemical composition and structure with human bone. In addition, it has ability to promote the bone tissue-metal interaction and growth of bone tissues at the beginning stage of implantation[3,4,5].

In present scenario, various coating techniques like plasma spraying, sol-gel, electrophoretic deposition, electro deposition have been employed to deposit hydroxyapatite on titanium implants. Plasma spraying was most widely used technique for coating of HAp on implants surface. But plasma spray technique leads to decomposition of HAp and implants due to high generation of temperature. As a line -in-sight process it cannot be employed for complex structures. In electrophoretic deposition, high voltage was applied to the metal surface to attract the dispersed particles which leads to anodic polarization of metal substrate. This may increase the corrosion risk of metal adhesion and suppress the adhesion of HAp particles[6,7,8].

When comparing to other coating techniques, electro deposition has unique attractions which can be operated in low temperatures and capability for giving uniform coatings to complex shapes and heterogeneous surfaces. In addition, it shows minimal corrosion risk when compared to electrophoretic deposition because the metal substrate was polarized cathodically[9]. By adjusting the pH, electrolyte concentration, time and electrode

potential we can control the thickness and morphology of the coatings[10]. So a careful study to be done in order to find out the optimal condition for deposition of HAp coatings on implants with desired thickness and morphology by varying these parameters.

In this present work our aim is to develop well adhered and uniform deposition of hydroxyapatite coatings on Ti-6Al-4V substrates for biomedical applications, through *in-vitro* electro deposition method and was characterized by FT-IR, XRD and SEM Analysis.

Experimental

Cathode preparation

Commercially available Ti-6Al-4V were cut down into area of 10 x 10 x 2mm specimens and used as substrates (cathode material) for coating HAp. The substrates surfaces were polished to mirror finish using silicon carbide emery sheets ranging from 120 to 1200 grit and diamond lubricant. Finally the metal substrates were ultrasonically degreased with acetone for 15 minutes and washed in distilled water, then dried.

Electrolytic deposition of HAp

The electrodeposition process was carried in electrolyte containing 0.6M $Ca(NO_3)_2.4H_2O$,0.36M$(NH_4)_2HPO_4$, 1M $NaNO_2$, 6% H_2O_2 and pH of the solution was adjusted to 6 using ammonia and HCl. Sodium nitrate was added to increase the ionic activity of the electrolytes. Ti-6Al-4V was used as cathode, platinum (Pt) electrode acts anode and Ag-AgCl electrode as reference. The schematic diagram of three electrode set up was shown in Fig.1. The deposition process was carried out with Biologic SP-150 by applying different electrode potential of -0.5V, -1.0 V, -1.5V,-2.0V and -2.5V at the temperature of 80^0C. After deposition specimens were taken out dried and sintered at 400^0 C for 2 hours.

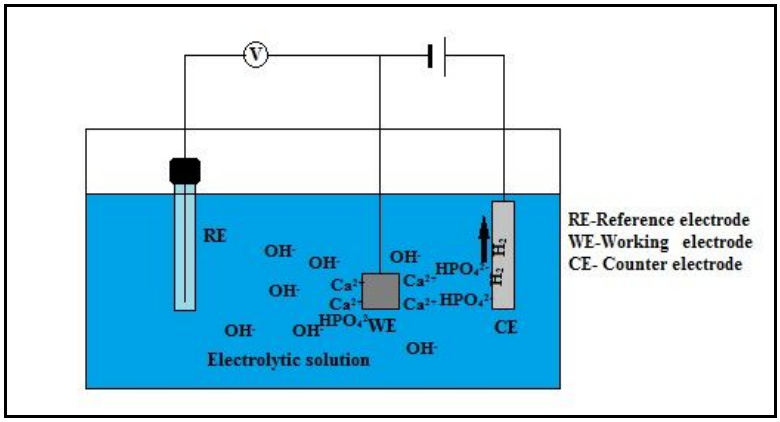

Fig.1. Schematic representation of electrodeposition setup

Materials characterization

The presence of functional groups was obtained using Fourier Transformer Infrared spectroscopy (Shimadzu –IR Affinity-1 Spectrometer, Japan. The FT-IR spectra were obtained over the region 400–4,000 cm^{-1} using KBr pellet technique. The resolution of spectrometer was 4cm^{-1}. The crystallographic phase analysis of the HAp coatings was determined by using X-ray diffractometer, Bruker D8 Model, Germany in reflection mode with Cu Kα (λ=1.5405 Å) radiation. The diffraction pattern was collected from 2Θ range from 10º to 80º with a scanning speed of 1º/min. Surface morphology and shape of the coatings formed was observed using scanning electron microscopy, Zeiss EVO 18 Research (SEM). The samples are scanned at the operating voltage of 10 KV with a working distance of 12.5 mm from low to higher magnification ranges.

Results and discussions:

FT-IR Analysis

The FT-IR pattern of HAp coating formed through electrodeposition at the voltage of -1.5V is shown in Fig 2. From the Fig.2 it is indicated that there is a board envelope of peak between 3827 cm^{-1} and 2765 cm^{-1}. The peaks at 3570 cm^{-1} arise due to the stretching mode of hydrogen bonded OH^- ions. The bands from 960 to 1091 cm^{-1} was corresponds to the P-O symmetric stretching mode of PO_3^{4-} ions. The band arises at 474 cm^{-1}, 563 cm^{-1} and 601 cm^{-1} indicates the bending mode of P-O in PO_3^{4-} ions. The peaks appear at around 3442 cm^{-1} and 1637 cm^{-1} are due to the bending mode of water molecules. This is due to the presence of small amount of moisture absorbed form the atmosphere. A weak band of carbonate apatite was detected in the region around 1400 cm^{-1} and 873 cm^{-1} in the sample. This might have originated due to the absorption of carbon di oxide from environment on handling. This characteristic band indicates the presence HAp with only trace amount of impurities.

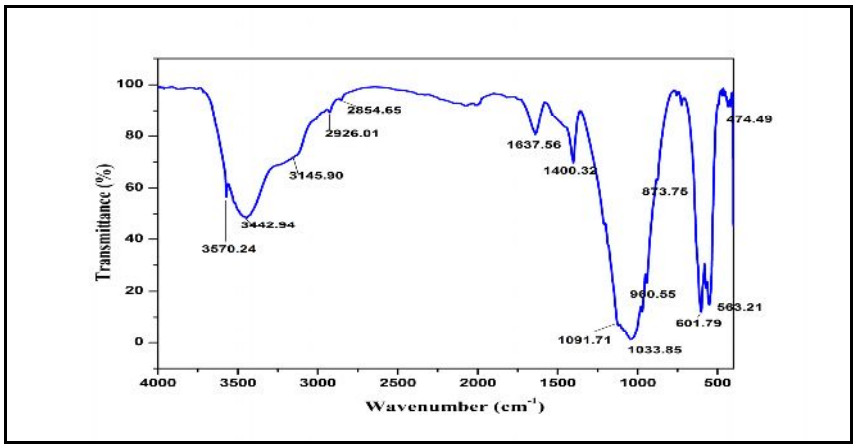

Fig.2. FT-IR pattern of HAp coatings formed through electrodeposition

X-ray diffraction analysis

The peaks obtained for electrodeposited HAp particles were shown in Fig.3. The EL deposited HAp compared with standard references in JCPDS file available in software for hydroxyapatite (09-0432). XRD pattern of the electrodeposited HAp showed the structure similar to that of hydroxyapatite standard. There is a higher consistency between the data of HAp that form and with the standard data. XRD pattern indicates the formation of the pure hydroxyapatite inorganic phase without any other major impurities.

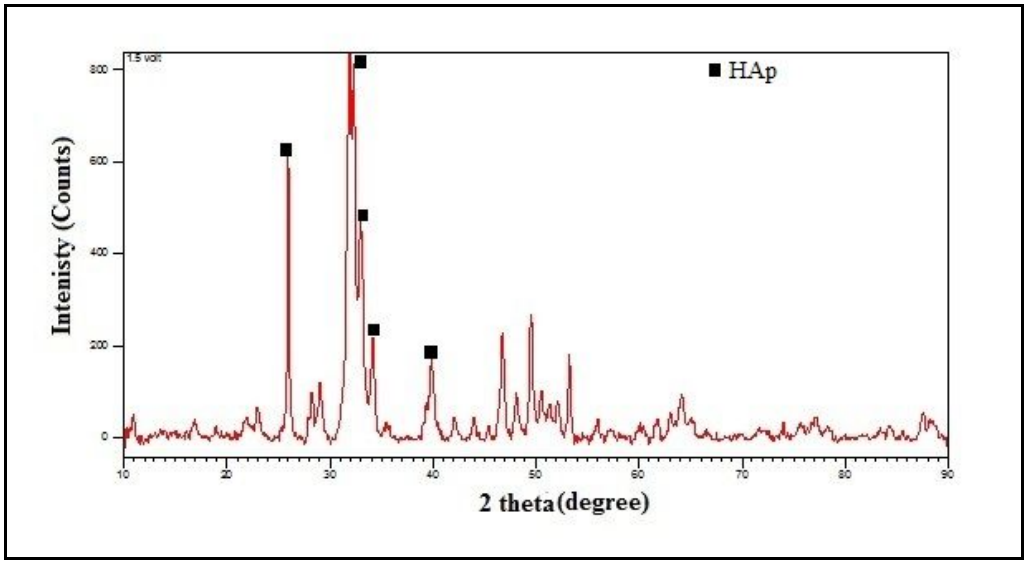

Fig.3. XRD pattern obtained for electrolytic deposited HA particles at 1.5V.

SEM studies of HAp coating

SEM images shows the clear morphology of the HAp coatings formed by electrodeposition in Fig .4.(a), (b) and (c). The SEM image shows flower like-lamellar structures of HAp coatings formed on the implant substrate. The image Fig4.(a) & (b) shown at magnification of 5 K X and 10 K X respectively confirms that HAp coating formed was homogenously dispersed on the substrate with a size ranged from 100-200 nm . It indicates that the majority of the particles were regular in shape, dense and with no aggleromation, which can be highly applicable for biomedical applications.

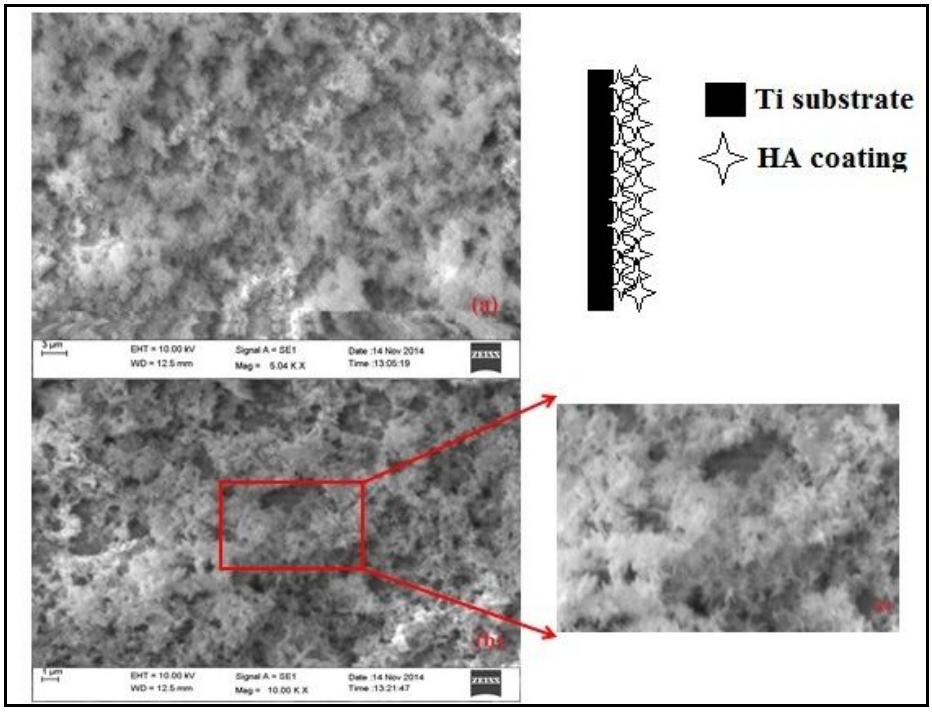

Fig.4. SEM images of electrolytic deposited HAP-Ti6Al4V at different magnifications (a) 5 K X (b) 10.00 K X (c) 20.00 K X

Conclusions

The nanosized hydroxyapatite coating was obtained using the in-vitro electrolytic deposition with calcium nitrate and di- ammonium hydrogen phosphate as precursor. Hydroxyapatite coatings developed by this method have shown good purity, regular size distribution, dense and flower like structure. We have carried out the deposition at various voltages ranging from -0.5 to -2.5V and the uniform distribution were arrived at the voltage of -1.5 V. The developed coating was further confirmed by SEM Analysis. This concludes that the *in-vitro* electrodeposition method can be employed for development of nanoceramic thin film coatings on metal implants which can be potentially used for biomedical applications.

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