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Preparation of Hydroxyapatite-titanium Dioxide Coating on Ti6Al4V Substrates using Hydrothermal-electrochemical Method

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Abstract: Ti6Al4V substrates were anodized in a 0.5 mol/L H_2SO_4 solution at applied voltages of 90-140 V. A hydroxyapatite-titanium oxide (HA-TiO_2) coating was then deposited on the anodized Ti6Al4V substrates via a hydrothermal-electrochemical method at a constant current. The obtained films and coatings were characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Fourier-transform infrared spectrometry. The microstructures of the porous films on the Ti6Al4V substrates were studied to investigate the effect of the anodizing voltage on the phase and morphology of the HA-TiO_2 coating. The results indicated that both the phase composition and the morphology of the coatings were significantly influenced by changes in the anodizing voltage. HA-TiO_2 was directly precipitated onto the surface of the substrate when the applied voltage was between 110 and 140 V. The coatings had a gradient structure and the HA exhibited both needle-like and cotton-like structures. The amount of cotton-like HA structures decreased with an increase in voltage from 90 to 120 V, and then increased slightly when the voltage was higher than 120 V. The orientation index of the (002) plane of the coating was at a minimum when the Ti6Al4V substrate was pretreated at 120 V.

Key words: Ti6Al4V; HA-TiO_2 coating; anodic oxidation; hydrothermal-electrochemical method

1 Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$)) coatings have been widely used in dental and orthopaedic implants as a result of their high degree of biocompatibility and their osteoconductive properties[1,2]. However, these coatings are not suitable for use under load-bearing conditions because they display poor mechanical performance resulting from a high degree of brittleness and low fatigue resistance[3,4]. An effective method to overcome this problem is to deposit HA onto the surface of biocompatible metals, such as titanium alloys. These coated products not only demonstrate the excellent mechanical performance of the metal, but also the good bioactivity of HA.

Various methods of depositing HA onto the surface of titanium alloys have been tested, including plasma-spraying[5], the use of sol-gel films[6], biomimetic solution methods[7], electrophoretic deposition[8] and electrochemical methods[9]. Of these methods, the plasma-spraying technique is currently used commercially for the fabrication of HA coatings. However, there are several major problems in this technique, such as the decomposition and phase transformation of HA at high temperatures, the discontinuous deposition of HA when using a line-of-sight process, limitations in the deposition of HA on complex metal implants and poor adhesion between the HA coating and the substrate[10,11]. It is therefore desirable to develop a method to deposit HA on titanium surfaces with both good bonding and good bioactivity. Hydrothermal-electrochemical techniques (soft solution processing) have attracted much attention[12]. These methods are a combination of electrochemical deposition and a hydrothermal treatment technique, and offer many advantages, such

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as a low process temperature, the ability to produce continuous deposition on the substrate regardless of its shape, easy control of the microstructure and thickness, and a highly crystalline coating. This process is not only simple and easy to operate, but also convenient, economic and environmentally friendly.

However, HA coatings often flake off the substrate as a result of the large thermal stresses caused by the difference in the thermal expansion between the HA and the substrate, which may result in failure of the implant[13]. The idea of coating HA with a tough secondary phase, such as TiO_2, to form a composite coating has therefore been investigated. Anodic oxidation is a simple and highly efficient method of surface modification, and can be used to form porous TiO_2 structures directly on titanium surfaces. The porous three-dimensional structure can improve the bioactivity of titanium by forming a rutile and/or anatase oxide film on the surface of the substrate. The surface characteristics of the films can be controlled by varying the processes used, in particular, by varying the anodizing voltage. The porous oxide film can produce Ti-OH groups by ion exchange under physiological conditions, greatly promoting the growth of HA into the open pore space. The oxide film can also supply space for the adsorption of proteins and the attachment of cells, improving the bonding between the biological tissues and the implants[14,15].

The formation of porous oxide films by micro-arc oxidation in an electrolyte containing calcium and phosphorus at voltages higher than 350 V has been reported previously[16-18]. Porous oxide films can also be obtained by anodic oxidation in an electrolyte without calcium and phosphorus at low voltages, although this has been studied less often[19,20]. We report here a novel approach in which a Ti6Al4V substrate underwent anodic oxidation in a solution of H_2SO_4 at 90-140 V. An HA-TiO_2 coating was then deposited on the anodized Ti6Al4V surface via a hydrothermal-electrochemical method. This approach makes full use of the advantages of anodic oxidation to modify the titanium surface and a hydrothermal-electrochemical method to prepare the HA coating. Therefore, it may provide an effective method to coat HA onto metallic substrates used for implantation. We systematically evaluate how the oxidation voltage influences the surface morphology of the Ti6Al4V substrate. The effects of the applied voltage on the characteristics of HA and the precipitation of HA during the hydrothermal-electrochemical process are also studied.

2 Experimental

2.1 Sample preparation and anodic oxidation

Commercially available medical Ti6Al4V alloy plates with dimensions of 25 mm × 25 mm × 2 mm were used in this study. The samples were first polished using $200^\#$, $400^\#$, $600^\#$, and $800^\#$ abrasive papers and then washed ultrasonically for 10 min each with acetone, ethanol and distilled water. The Ti6Al4V plate was anodized in 0.5 mol/L H_2SO_4 solution for 10 min using a direct current power supply (SW171500SL, 0-150 V, Shanghai). The applied voltages were 90, 100, 110, 120, 130, and 140 V. The titanium plate was used as the anode and a platinum plate was used as the cathode. During the anodic oxidation process, the solution was stirred magnetically at a constant speed to accelerate the escape of the gas produced in the reaction. After pretreatment, the samples were washed thoroughly with distilled water.

2.2 Hydrothermal-electrochemical depositions

The electrolyte used for HA deposition was heated at 120 °C in a stainless-steel autoclave. The cathode was the anodized Ti6Al4V plate and the anode was a platinum plate. The electrolyte contained 0.138 mol/L NaCl, 0.016 mol/L $K_2HPO_4{\cdot}3H_2O$ and 0.02 mol/L $CaCl_2$. The current density between the cathode and anode was 1.25 mA/cm^2 and the current loading time was 120 min.

2.3 Surface characterizations

The crystal phases of the coatings were characterized by X-ray diffraction (XRD) on a D8-Advanced diffractomer (Bruker, Germany) using Cu Kα radiation at a scan speed of 4.0 °/min in the 2θ range of 20°-60°. The crystal morphologies were observed by scanning electron microscopy (SEM) on a Quatan 450 instrument (FEI, The Netherlands). The chemical composition of the coating was characterized by energy-dispersive X-ray spectroscopy (EDS). The functional groups of the HA-TiO_2 coating were characterized by Fourier-transform infrared spectrometry (FTIR) on a Vertex 70 instrument (Bruker, Germany). The Fourier-transform infrared spectra were obtained in the region 400-4 000 cm^{-1} using the KBr transmission technique.

3 Results and discussion

3.1 Anodic oxidation pretreatment of Ti6Al4V substrates

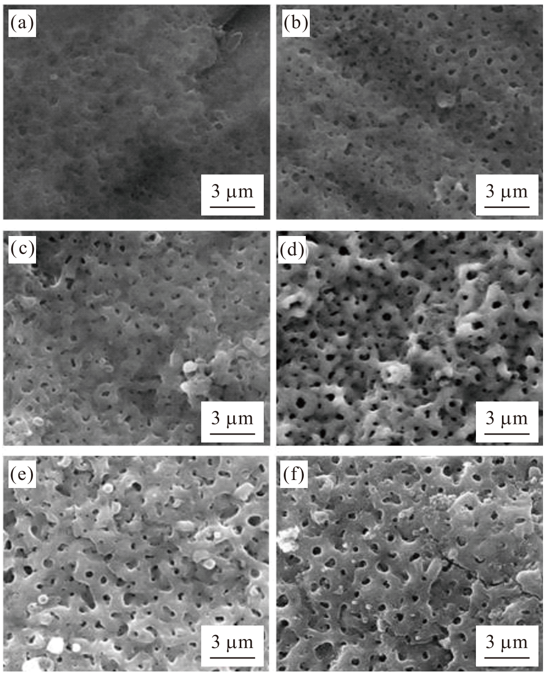

Fig.1 SEM images of Ti6Al4V substrates anodized in H_2SO_4 solution for 10 min at (a) 90 V; (b) 100 V; (c) 110 V; (d) 120 V; (e) 130 V; and (f) 140 V

Fig.1 shows images of the porous films obtained at 90, 100, 110, 120, 130, and 140 V. The images show that porous structures formed on the Ti6Al4V surface after anodic oxidation. Several layers formed when the surface was anodized at low voltages (Figs.1(a)-1(c)). In contrast, uniform and large pores were homogeneously distributed throughout the Ti6Al4V surface when the applied voltage was 120-140 V (Figs.1(d)-1(f)). These results confirm that the pore size increases as the applied voltage increases. Wang *et al* showed that this type of three-dimensional structure stimulates the nucleation of HA anchored to the substrate as a result of the increase in the specific surface area[21].

Yi *et al* have used XRD to detect the presence of a TiO_2 phase on the surface of the Ti6Al4V substrate after anodic oxidation in H_2SO_4 solution at a constant voltage[22]. This implies that this porous layer is composed of TiO_2. The TiO_2 phase has reported to enhance the formation of HA and the bond strength between the substrate and the coating[23].

3.2 Hydrothermal-electrochemical deposition method

Fig.2 shows SEM images of the morphologies of the HA-TiO_2 coatings precipitated on the Ti6Al4V substrates. It can be seen that both the microstructures and the layered growth patterns of the coatings are affected by the voltage of the anodic oxidation. An HA layer with uniform and compact structures completely covered the surface of the substrates and the XRD results confirmed that the HA was characterized by typical needle-like crystals growing perpendicular to the substrate. The edges of the needle-like HA suggested a defined hexagonal crystal habit. A large amount of nucleation was seen to develop further into another film at the top of the needle-like HA when the underlying needle-like HA layer grew to a certain size. The second layer was identified as cotton-like HA. This presence of a new second layer may be attributed to the crystal density of the needle-like HA precipitated during the hydrothermal-electrochemical process. The substrate surface was not completely covered by the first layer of needle-like HA crystals as the density of the first layer of crystals was low. Hence the substrate came into direct contact with the electrolyte in some places where there was a large gap in the layer, resulting in a stronger electrochemical reaction in these interspaces. The pH near these interspaces increased gradually, stimulating new nucleation and eventually leading to the formation of the cotton-like HA.

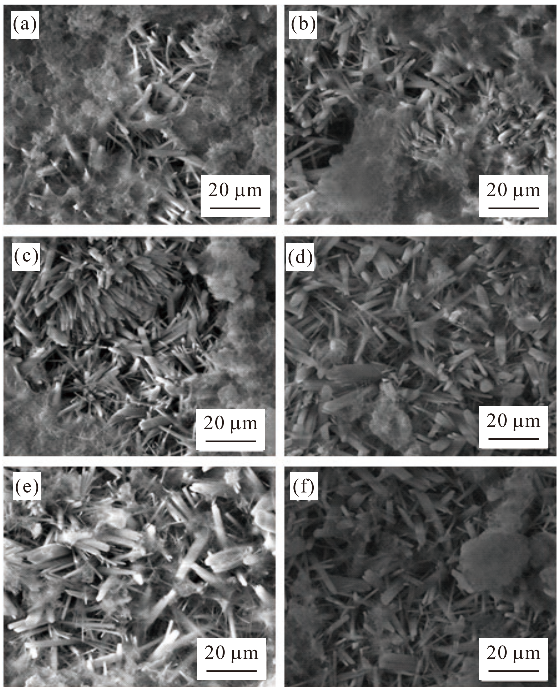

Fig.2 SEM images of HA-TiO_2 coated substrates after anodic oxidation at (a) 90 V; (b) 100V; (c) 110 V; (d) 120 V; (e) 130 V; (f) 140 V, and hydrothermal-electrochemical depositions

The amount of cotton-like HA decreased as the oxidation voltage increased up to 120 V and then increased only slightly at higher voltages. It is possible that the surface characteristics of the oxide film on the anodized substrate significantly affected the amount of cotton-like HA. When the applied voltage was 90

V, the oxide film was thin and there were few holes, which resulted in a lower level of crystallization of the needle-like HA, thus promoting the growth of the second layer of cotton-like HA. With increasing voltage, the amount of porous oxide film increased, allowing more nucleation of the needle-like HA structures. Consequently, the amount of cotton-like HA reached a minimum at 120 V. Then it slightly increased at voltages higher than 120 V. This may be related to the cracks on the surface of the oxide films that occur at high voltages, resulting in a relative decrease in the number of holes in the oxide and reducing the amount of precipitation of the needle-like HA. This results in the cotton-like shape of the HA in the second layer.

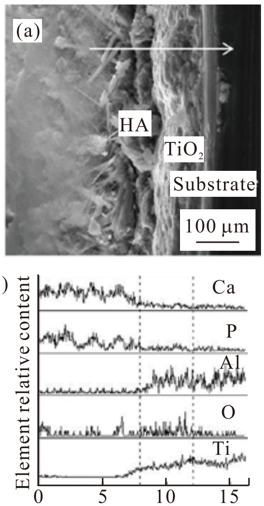

Fig.3 Cross-sectional morphology of the interface and EDS linear scanning across the HA-TiO_2 coating at 120 V pretreatment, and hydrothermal-electrochemical deposition

Fig.3 shows the cross-sectional morphology of the interface and the results of linear scanning by energy-dispersive X-ray spectroscopy across the HA-TiO_2 coating obtained with pretreatment at 120 V and hydrothermal-electrochemical deposition. The coating is mainly composed of multilayer films and has an obvious gradient structure. The functionally graded composite coating with HA as the top layer and porous TiO_2 as the intermediate layer uniformly covers the substrate. The linear scanning chemical analysis of elemental Ca, P, Ti, O, and Al in the coating is shown in Fig.3(b), corresponding to the scanning range marked in Fig.3(a). These results indicate that the content of HA increased gradually from the interface to the surface, whereas the concentration of TiO_2 decreased gradually. The presence of the TiO_2 layer reduced the discrepancy in the thermal expansion coefficients between the HA coating and Ti6Al4V substrate, significantly improving the interfacial bond strength and the overall performance of the HA-coated Ti6Al4V system[24,25].

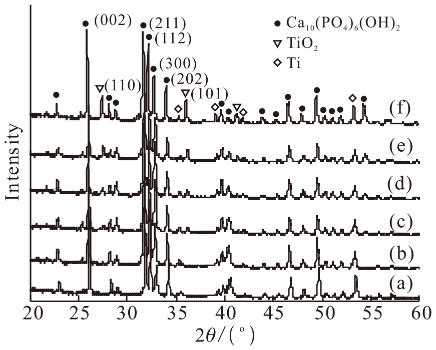

Fig.4 XRD patterns of HA-TiO_2 coated substrates after anodic oxidation at (a) 90 V; (b) 100V; (c) 110 V; (d) 120 V; (e) 130 V; (f) 140 V, and hydrothermal-electrochemical depositions

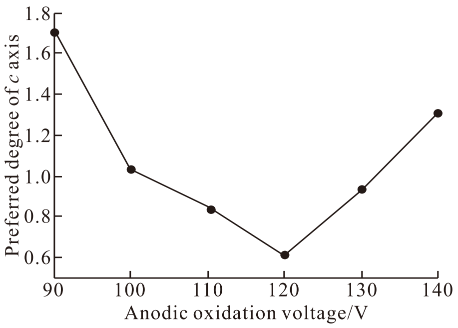

Fig.5 The orientation values of the (002) plane of the HA-TiO_2 coatings at different anodic oxidation voltages

Fig.4 shows the XRD patterns of the HA-TiO_2 coatings after hydrothermal-electrochemical deposition. These patterns show that HA has formed according to the standard JCPDS file No. 09-0432[26]. When the anodic oxidation voltage reached 110 V, a TiO_2 phase was detected in the deposited films. This result shows that the TiO_2 was an amorphous phase at low voltages. It can also be clearly seen that the three most intense diffraction peaks of HA corresponding to the (211), (112), and (300) planes narrowed significantly, indicating the high crystallinity of the HA precipitated by this hydrothermal-electrochemical method[27].

With respect to the standard intensity of HA, the precipitated coatings grow along the *c*-axis[28], as evidenced by the larger intensity ratio of the (002) diffraction peak. One possible mechanism of HA growing along the *c*-axis can be summarised below. It has been reported that a large aspect ratio of nanomaterials can be obtained when the reaction system has a high chemical potential[29], as in this study, with the preferred orientation of HA along the c-axis. HA with an anisotropic structure has a higher crystal energy on the (002) plane. During the hydrothermal-electrochemical deposition, when the chemical potential of the reaction system was higher than that of the (002) plane at a certain temperature, HA grew exclusively along the c-axis as a result of the release of the stored metastable chemical energy. It can be inferred that both the anisotropic structure of HA and the higher chemical energy of the solution play critical parts in the growth of HA along the c-axis.

Compared with the intensity of the three most intense peaks (211), (112), and (300), the relative intensity of the (002) peak (*RI*) is defined as:

$$RI = \frac{I_{(002)}}{I_{(211)} + I_{(112)} + I_{(300)}} \tag{1}$$

In this study, the preference (*P*) is evaluated according to the following relationship:

$$P = \frac{RI - RI_{\mathrm{s}}}{RI_{\mathrm{s}}} \tag{2}$$

where, $I_{(002)}$, $I_{(211)}$, $I_{(112)}$, and $I_{(300)}$ are the diffraction peak intensities of the (002), (211), (112), and (300) planes, respectively. The relative intensity of the (002) peak of HA from the data in JCPDS No. 09-0432 was used, yielding RI_{s}=0.1818[30].

Fig.5 shows the orientation values of the (002) plane of the HA-TiO_2 coatings calculated based on the XRD data. It can be observed that the orientation index first decreased and then increased as the anodizing voltage increased. The minimum preferred degree of HA was 0.6104 when the pretreatment voltage was 120 V. The variation in the orientation value with applied voltage may be a result of the amount of Ti-OH groups produced during the hydrothermal-electrochemical process. When Ti6Al4V was anodized at a low voltage, such as 90 V, only a few Ti-OH groups formed because of the presence of a thin oxide film and few pores on the substrate. As the pretreatment voltage increased, the oxide film became thicker and the pore size on the surface also increased, resulting in a higher number of Ti-OH groups, which allowed the more effective formation of HA. At the same time, the concentration of the electrolyte in the reaction system decreased, leading to a lower chemical energy. Consequently, the growth rate of HA along the c-axis slowed down. As a result, the orientation value decreased with applied voltage up to 120 V. It then slightly increased as the pretreatment voltage increased. According to previously reported research[31], HA in bone has no obvious preferred orientation. The coating precipitated by the hydrothermal-electrochemical method on the anodized Ti6Al4V substrate at 120 V showed a lower orientation value. Therefore, it can be concluded that by controlling the anodic oxidation voltage, HA similar to natural bone with a lower preferred orientation can form; this is expected to improve its performance in practical applications.

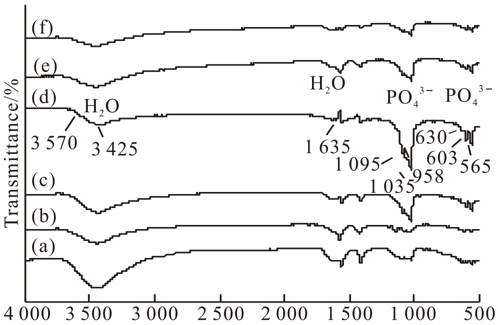

Fig.6 FTIR spectra of HA-TiO_2 coatings at different anodic oxidation voltages: (a) 90 V; (b) 100V; (c) 110 V; (d) 120 V; (e) 130 V; (f) 140 V

Fig.6 shows the results of the Fourier-transform infrared spectrometry measurements of the coatings at different pretreatment voltages. In all the spectra, the PO_4^{3-} absorption bands occur at 565 (v_4), 603 (v_4), 958 (v_1), 1 035 (v_3), and 1 095 cm^{-1} (v_3). Stretching and bending absorption bands of OH^- can be clearly seen at 3 570 and 630 cm^{-1}, which are the characteristic wavenumbers for HA. The absorption peak for PO_4^{3-} is significantly split in the range 1 000-1 100 cm^{-1}, suggesting a higher crystallinity of the HA[32], which agrees with the XRD results (Fig.5).

3.3 Mechanism of formation of the porous oxide film and HA

There are two steps in the formation of the TiO_2 porous films in H_2SO_4 solution: chemical etching and chemical dissolution. The chemical reactions can be described as follows[33,34]:

$$\mathrm{Ti} \rightarrow \mathrm{Ti}^{4+} + 4\mathrm{e}^- \tag{3}$$

$$2\mathrm{H_2O} \rightarrow 2\mathrm{O}^{2-} + 4\mathrm{H}^+ \tag{4}$$

$$\mathrm{Ti}^{4+} + 2\mathrm{O}^{2-} \rightarrow \mathrm{TiO_2} \tag{5}$$

$$\mathrm{TiO_2} + 2\mathrm{H_2SO_4} \rightarrow \mathrm{Ti(SO_4)_2} + 2\mathrm{H_2O} \tag{6}$$

When the anodizing voltage is applied, TiO_2 forms via reactions (3)-(5) as a result of the enhanced electrical field. After that, the TiO_2 layer is gradually dissolved, resulting in the formation of $Ti(SO_4)_2$, as in reaction (6), and pits form on the surface of the substrate. As these processes continue, these pits form into pores and extensive TiO_2 pores finally form.

It is reported that substrates with functionalised surfaces, such as –OH, facilitate the rapid formation of HA[35]. Once the TiO_2 oxide films are immersed in the electrolyte, the ionic exchange process between the oxide layers and the calcium ions in the solution takes place during the hydrothermal-electrochemical process. As a result, a large number of Ti-OH groups form on the surface. Thereafter, Ti-OH becomes $Ti\text{-}O^-$ by the discharge of a proton and the porous film surface becomes negatively charged. The following reactions could occur on the surface[36,37]:

$$TiO_2 + 2H_2O + e^- \rightarrow Ti(OH)_3 + OH^- \quad (7)$$

$$Ti\text{-}OH + H_2O + e^- \rightarrow Ti\text{-}O^- + H_3O^+ \quad (8)$$

The mechanism of deposition of HA on the surface of the porous oxide film during hydrothermal-electrochemical process includes electrochemical, acid-base and precipitation reactions. As the current is applied, the electrolysis of water takes place at the electrode surface as follows[38]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (9)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (10)$$

As a result of reactions (9) and (10), a localized increase in pH occurs near the cathode, resulting in the formation of PO_4^{3-} ions:

$$HPO_4^{2-} + OH^- \rightarrow PO_4^{3-} + 2H_2O \quad (11)$$

When the concentration of PO_4^{3-} increases to a certain level, the Ca^{2+} absorbs PO_4^{3-}. The degree of supersaturation of the electrolyte increases in the vicinity of the cathode, promoting the nucleation of apatite and the precipitation of HA:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (12)$$

4 Conclusions

a) A porous TiO_2 film with a three-dimensional structure formed on the Ti6Al4V surface in a simple H_2SO_4 electrolyte at different applied voltages. The anodizing voltage played an important role in determining the morphology of the films. The pore size of the porous films increased with increasing applied voltage. A higher voltage favoured the formation of the oxide film.

b) HA-TiO_2 coatings with gradient structures were produced directly on the surface of anodized Ti6Al4V substrates via a hydrothermal-electrochemical method. The phase composition and microstructure of the HA-TiO_2 coating were both affected by the pretreatment voltage in the hydrothermal-electrochemical deposition process. The TiO_2 phase in the coatings developed when the applied anodizing voltage was 110-140 V. The coating showed a layered structure with the main component being a needle-like HA, together with a small amount of a cotton-like HA layer. And the amount of cotton-like hydroxyapatite decreased firstly and then slightly increased as the pretreatment voltage increased.

c) The orientation value of the HA-TiO_2 coating firstly decreased with the increase of pretreatment voltage, reaching a minimum when the anodizing voltage was 120 V, and then increased with higher pretreatment voltage.

d) The XRD and FTIR spectra both showed a high crystallinity of the HA precipitated by this hydrothermal-electrochemical method.

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