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Bioactive calcium phosphate coating prepared on H_2O_2-treated titanium substrate by electrodeposition

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Abstract

This study examined the characteristics of calcium phosphate coatings formed on untreated and H_2O_2-treated titanium substrates by electrodeposition in a modified simulated body fluid (SBF). A porous coating comprising of mainly hydroxyapatite (HA) was formed on the H_2O_2-treated titanium substrate by electrodeposition. This coating was transformed into carbonate and calcium-deficient HA layers with a bonelike crystallinity during immersion in the SBF. However, a uniformed coating comprising of amorphous calcium phosphate (ACP) formed on the untreated titanium substrate by electrodeposition was transformed into poorly crystalline HA during immersion in the SBF. This difference was attributed to the increased surface area of the titanium substrate after the H_2O_2 treatment as well as the OH^- ions released from this modified surface during electrodeposition. Therefore, it was shown that the H_2O_2 treatment prior to electrodeposition may be an effective method for preparing a potentially bioactive calcium phosphate coating by electrodeposition.

Keywords: Bioactivity; Coating; Electrodeposition; Hydroxyapatite (HA); Simulated body fluid (SBF)

1. Introduction

The bioactivity of a material is the ability to induce the direct, adherent, and strong bonding between the materials and the bone tissue [1]. In order to evaluate this bioactivity of materials, it has been proposed that the materials, which form a bonelike apatite on their surfaces in the simulated body fluid (SBF), can also form apatite in a living body and can bond to bone through the apatite layer. This means that the apatite-forming ability in the SBF is a measure of the in vivo bioactivity [2]. Recently, bioactive metal surfaces prepared by various chemical and heat treatments have been reported. The titanium surface after NaOH and heat treatments induced a bonelike apatite layer in the SBF within 7 days [3,4]. The titanium surface after $H_2O_2/TaCl_5$ or H_2O_2/HCl and heat treatments also showed apatite deposition ability in the initial stage of SBF immersion [5,6]. However, alkali ions released from the titanium surfaces prepared by chemical and heat treatments in the initial stages of implantation in a living body can have harmful effect on the surrounding tissues [7–9]. Therefore, the titanium surfaces already coated with bioactive materials were further encouraged when implanted in a living body.

Bioceramic coatings on metallic substrates have been widely used in medicine and dentistry to combine the excellent mechanical properties of metal alloys with the bioactive properties of bioceramics [10]. A hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) coating is preferable for the stability during the longer period, and an amorphous calcium phosphate (ACP) coating is advantageous for only the osteoconducive property in the initial fixation of porous materials [11]. In addition, an octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$) coating was recommended as a biomimetic coating for use in orthopedic surgery because OCP was known to be one of the precursors during the bone mineralization process [12]. Among these bioceramic coat-

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ings, this study focused on the rapid conversion of the HA coating into bonelike apatite in a physiological environment for the improvement of osseointegration.

The prevailing method for producing HA coatings is via plasma spraying. However, it is almost impossible accurately controlling the chemical composition, crystallographic phase and crystallinity of the coating with this method [13]. In addition, plasma spraying cannot produce a uniform coating on devices with complicated shapes. Therefore, in order to improve the disadvantages of plasma spraying, an electrodeposition method was introduced with good properties including quick and uniform coating of the substrates with complex shapes at low temperatures and the control of the film thickness and chemical composition of the coating [14–18]. With chemical treatments prior to deposition, the coating sometimes gets more uniform and well-adhered [19]. Moreover, a chemical treatment prior to electrodeposition aimed at the improvement of bioactivity of the coating as well as the physical properties is also necessary.

In this study, we used an H_2O_2 treatment as a chemical pretreatment to form bioactive calcium phosphate coatings by electrodeposition, and investigated the characteristics of the coatings that were formed on the untreated and H_2O_2-treated titanium substrates by electrodeposition in a modified SBF, and were subsequently transformed during immersion in a SBF for 5 days.

2. Experimental

Commercially pure titanium sheets (10×10×0.8 mm) were used as substrates for electrodeposition. Their surfaces were ground with #100 and #600 SiC paper, and cleaned ultrasonically in acetone and ethyl alcohol for 5 min, respectively, rinsed in double-distilled water, and finally dried. The edges of the titanium substrates were rounded to avoid an edge effect during electrodeposition. The H_2O_2-treated titanium substrate was prepared by immersing the titanium substrate in 10 ml of a 5 M H_2O_2 solution at 60 °C for 24 h. After the H_2O_2 treatment, the titanium substrate was washed with double-distilled water and dried.

The electrodeposition of calcium phosphates was performed at 60 °C for 1 h in a conventional cell fitted with a saturated calomel electrode (SCE) maintaining a cathodic potential of −2 V (vs. SCE). A modified SBF was used as the electrolyte for electrodeposition. The modified SBF was prepared by dissolving reagent-grade NaCl, $NaHCO_3$, $K_2HPO_4 \cdot 3H_2O$, and $CaCl_2$ into double-distilled water, which was buffered at pH 7.4 at 60 °C with tris-hydroxymethylaminomethane [$(CH_2OH)_3CNH_2$] and 1 M hydrochloric acid (HCl). The composition of this modified SBF is shown in Table 1. The untreated and H_2O_2-treated titanium substrates were used as cathodes for electrodeposition. A potentiostat/galvanostat (Model 263A, EG&G Instruments, USA) operating in potentiostatic mode was used to maintain the cathodic potential. The solution was stirred during electrodeposition. After electrodeposition, the coatings formed on the untreated and H_2O_2-treated titanium substrates were rinsed gently with double-distilled water and dried for 24 h.

Table 1
Compositions of the modified SBF as an electrolyte for the electrodeposition coating

Order	Reagent	Amount/1 dm^3 (H_2O)
1	NaCl	7.996 g
2	$NaHCO_3$	0.350 g
3	$K_2HPO_4 \cdot 3H_2O$	0.228 g
4	1 mol/dm^3 HCl	40 ml
5	$CaCl_2$	0.278 g
6	$(CH_2OH)_3CNH_2$	6.057 g

In order to evaluate the bioactivity of the coatings, the coatings formed on the untreated and H_2O_2-treated titanium substrates by electrodeposition were immersed in 20 ml of an acellular SBF with ion concentrations similar to that of human blood plasma at 36.5 °C for 5 days. The SBF was renewed each day. The SBF was prepared by dissolving reagent-grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 in double-distilled water and buffering at pH 7.4 at 36.5 °C with tris-hydroxymethylaminomethane [$(CH_2OH)_3CNH_2$] and 1 M hydrochloric acid (HCl) [20]. After immersion in the SBF for 5 days, the coatings transformed on the untreated and H_2O_2-treated titanium substrates were washed gently with double-distilled water and dried for 24 h.

The crystallinity and structure of the coatings were examined using X-ray diffractometer (XRD, D-Max Rint 240 Model, Rigaku, Japan) with Ni-filtered CuKα radiation generated at 30 kV and 30 mA as the X-ray source. The morphology of the coatings was observed using scanning electron microscope (SEM, S-800 Model, Hitachi, Japan). The chemical composition of the coatings was analyzed by energy dispersive spectroscope (EDS, Kevex Superdry Model, Kevex Instruments, USA) and Fourier transform infrared spectroscope (FTIR, Avatar 360, Thermo Nicolet, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the untreated titanium substrate prior to electrodeposition, the coating formed on the untreated titanium substrate after electrodeposition, and the coating transformed on the untreated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days. The XRD pattern of the coating formed on the untreated titanium substrate by electrodeposition did not exhibit any special peaks indicating dicalcium phosphate dehydrate (DCPD, $CaHPO_4 \cdot 2H_2O$), OCP, and HA. Therefore, this coating was expected to be ACP because calcium phosphate coating formed on the untreated titanium substrate right after electrodeposition was clearly observed

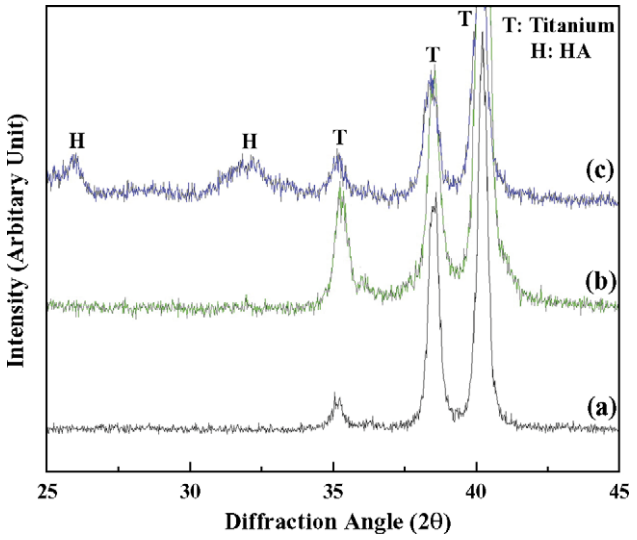

Fig. 1. XRD patterns of (a) the untreated titanium substrate prior to electrodeposition, (b) the coating formed on the untreated titanium substrate after electrodeposition, and (c) the coating transformed on the untreated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days.

by SEM. After immersion in the SBF for 5 days, the structure of the coating transformed ACP into mainly HA. The broad and weak peaks of the transformed HA indicate a low crystallinity and density. These results suggest that the coating formed on the untreated titanium substrate by electrodeposition does not have rapid bone-bonding ability in the initial stage of the implantation in living tissue because the ACP is transformed into bone-like apatite through various intermediates.

Fig. 2 shows the XRD patterns of the titanium substrate prior to the H_2O_2 treatment, the titanium substrate after the H_2O_2 treatment, the coating formed on the H_2O_2-treated titanium substrate after electrodeposition, and the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days. The main structure of the H_2O_2-treated titanium substrate surface was amorphous titanium oxide. In addition, the H_2O_2-treated titanium substrate surface was a light blue, which indicated that the H_2O_2 treatment produced a thicker and more porous titanium oxide layer ($\approx$0.06 μm) [21,22]. It is believed that this porous surface of the titanium substrate after the H_2O_2 treatment provides more favorable sites for calcium phosphate nucleation. The main structure of the coating formed on the H_2O_2-treated titanium substrate by electrodeposition was mainly HA with a low crystallinity and density. After immersion in the SBF for 5 days, the HA structure of the coating got more crystalline. The crystallinity and density of the transformed HA are similar to those of a bonelike apatite [23]. This change in the crystallinity and density is due to the dissolution and reprecipitation process of the HA during immersion in the SBF. Moreover, it was reported that only HA that was not crystallized highly was transformed into bonelike apatite even in the SBF including serum proteins [24]. Therefore, it is believed that the coating formed on the H_2O_2-treated titanium substrate by electrodeposition can induce stable bonding to the bone in the initial stage of the implantation in living tissue, being transformed into bonelike HA layers.

Fig. 3 shows the SEM images of the coating formed on the untreated titanium substrate after electrodeposition, and the coating transformed on the untreated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days. In Fig. 3, (a) and (b) show low magnification and high magnification of the morphologies of the coating formed on the untreated titanium substrate by electrodeposition, respectively. The sphere-shaped crystallites shown in Fig. 3(b) had an average crystallite size of 0.1 μm. In the same figure, (c) and (d) show low magnification and high magnification of the morphologies of the coating transformed on the untreated titanium substrate after electrodeposition and subsequent immersion in the SBF, respectively. The crystallites shown in Fig. 3(c and d) were distributed irregularly with an average grain size of 2 μm. In addition, the rod-shaped crystallites shown in Fig. 3(d) were larger and more densely distributed than those shown in Fig. 3(b). This indicates that the ACP was transformed into poorly crystalline HA after immersion in the SBF, as shown in the above-mentioned XRD results.

Fig. 4 shows the SEM images of the coating formed on the H_2O_2-treated titanium substrate after electrodeposition, and the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition with subsequent immersion in the SBF for 5 days. In Fig. 4, (a) and (b) show low magnification and high magnification of the morphologies of the coating formed on the H_2O_2-treated titanium substrate by electrodeposition, respectively. The porous structure

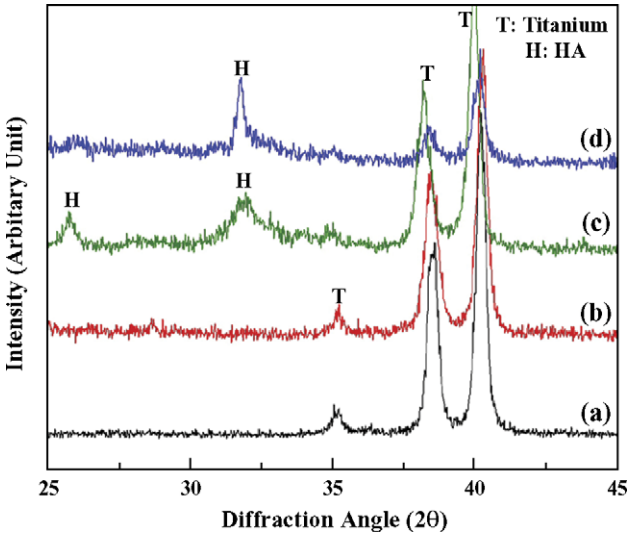

Fig. 2. XRD patterns of (a) the titanium substrate prior to the H_2O_2 treatment, (b) the titanium substrate after the H_2O_2 treatment, (c) the coating formed on the H_2O_2-treated titanium substrate after electrodeposition, and (d) the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days.

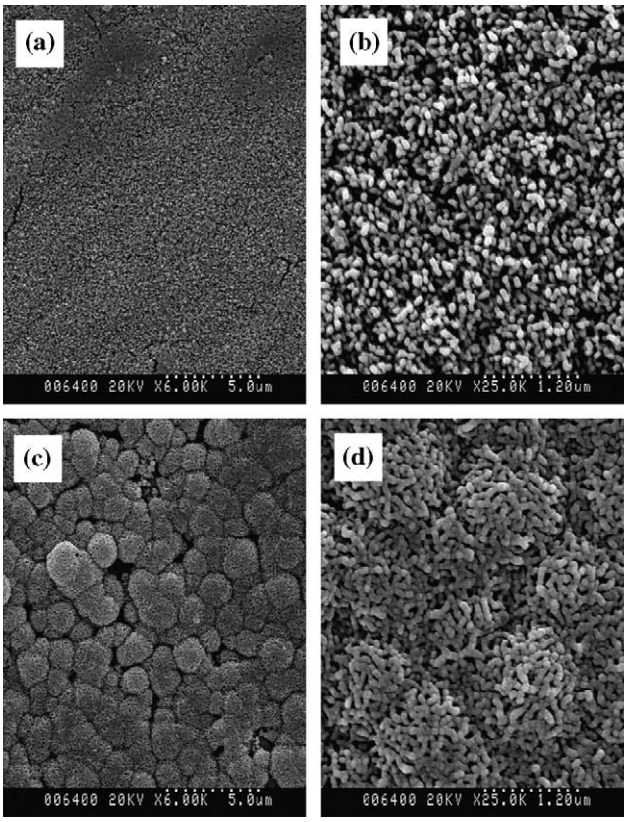

Fig. 3. SEM images showing the morphologies of (a) the coating formed on the untreated titanium substrate after electrodeposition, (b) high magnification of (a), (c) the coating transformed on the untreated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days, and (d) high magnification of (c).

shown in Fig. 4(a) had an average pore size of 4 μm. These pores were expected to help the dissolution and reprecipitation process to transform into more crystalline HA by allowing the body fluid to diffuse into the deeper spaces inside the coating. The crystallites shown in Fig. 4(b) had an average crystallite of 0.2 μm and were densely packed. In addition, this coating electrodeposited on the H_2O_2-treated titanium substrate with poorly crystalline HA is different from those showed by Wang et al. [25]. The electrolytic deposited carbonate apatite coatings of Wang et al. exhibited non-porous surface with flake-shaped crystallites indicating OCP, which was an intermediate during the transformation into bone-like apatite. It indicates that our coating is expected to show more excellent bond-bonding ability due to its pores and poorly crystalline HA structure, compared to those of Wang et al. In the same figure, (c) and (d) show low magnification and high magnification of the morphologies of the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF, respectively. The crystallites shown in Fig. 4(c and d) were distributed irregularly with various grain sizes. In addition, the rod-shaped crystallites shown in Fig. 4(d) were smaller and more uniformly distributed than those shown in Fig. 4(b). This indicates that the HA coating formed by electrodeposition was transformed into the HA with a bonelike crystallinity and density after immersion in the SBF, as shown in the above-mentioned XRD results.

Moreover, the average grain size shown in Fig. 4(c) was larger than that shown in Fig. 3(c). This means that the coating formed on the H_2O_2-treated titanium substrate by electrodeposition dissolved at a slower rate providing fewer nucleation sites where the nuclei could grow to a large size. In contrast, the coating formed on the untreated titanium substrate by electrodeposition dissolved faster thereby providing more sites for nucleation, which limited the growth of the nuclei [26]. In addition, the rod-shaped HA crystallites with large grain size shown in Fig. 4(c and d) were smaller and more densely interlocked than those with small grain size shown in (c) and (d), which indicates that the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF had crystallinity and morphology more similar to those of bone mineral compared to that transformed on the untreated titanium substrate.

Fig. 5 shows the FTIR spectra of the coatings transformed on the untreated and H_2O_2-treated titanium substrates after electrodeposition and subsequent immersion in the SBF for 5 days. All the coatings transformed on the untreated and H_2O_2-treated titanium substrates

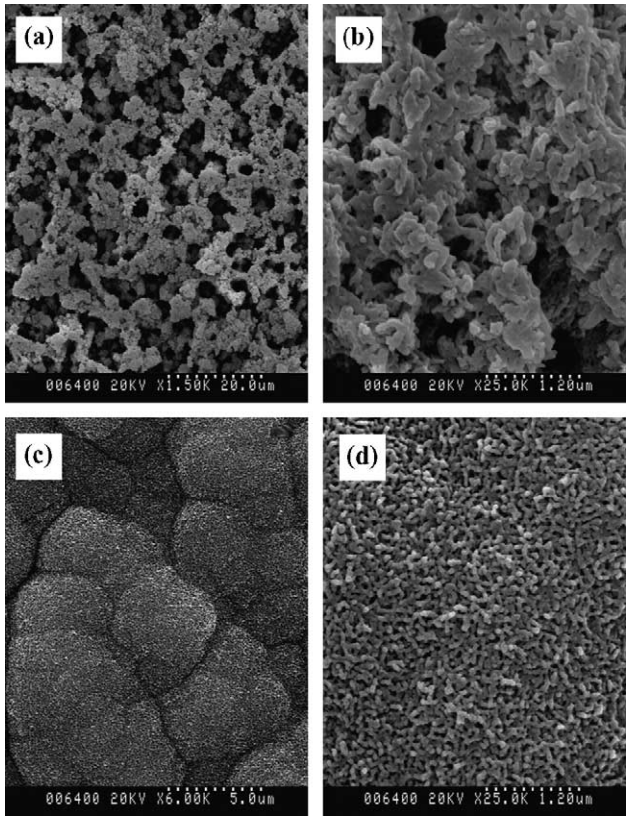

Fig. 4. SEM images showing the morphologies of (a) the coating formed on the H_2O_2-treated titanium substrate after electrodeposition, (b) high magnification of (a), (c) the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days, and (d) high magnification of (c).

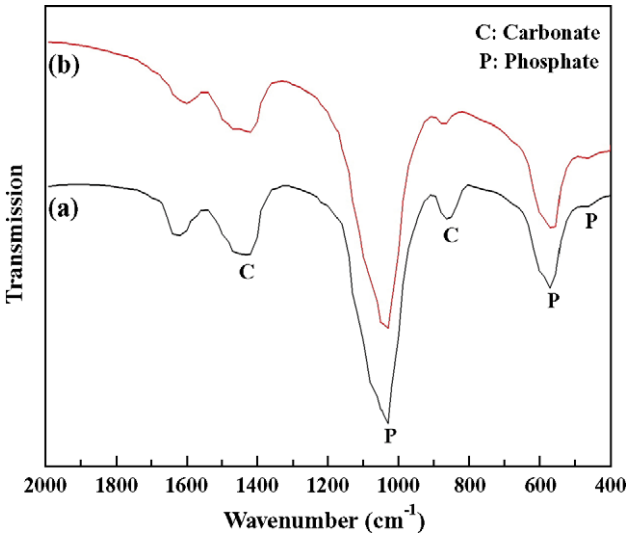

Fig. 5. FTIR spectra of the coatings transformed on the (a) untreated and (b) H_2O_2-treated titanium substrates after electrodeposition and subsequent immersion in the SBF for 5 days.

exhibited phosphate peaks at 560–630 and 960–1120 cm^{-1}, and carbonate peaks around 870 and 1400–1500 cm^{-1} [27]. The carbonate peaks in the spectra of the coating transformed on the untreated titanium substrate are more intense than those on the H_2O_2-treated titanium substrate. This indicates that the coating transformed on the untreated titanium substrate contains more carbonate ions and shows a lower crystallinity than that on the H_2O_2-treated titanium substrate, as shown in the above-mentioned XRD results, because carbonate ions contained in the HA disturb crystallization [28]. Therefore, these FTIR results show that the coating transformed on the H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF has proper carbonate content for a bonelike crystallinity.

The Ca/P atomic ratio of the coatings was measured to analyze the chemical composition of the coatings that had been transformed on the untreated and H_2O_2-treated titanium substrate after electrodeposition and subsequent immersion in the SBF for 5 days using EDS. The Ca/P atomic ratios of the HA transformed on the untreated and H_2O_2-treated titanium substrates after electrodeposition and subsequent immersion in the SBF were 1.55 and 1.63, respectively. The Ca/P atomic ratio of the HA transformed on the H_2O_2-treated titanium substrate was similar to that of bone apatite being slightly less than 1.67, which is the ratio of stoichiometric HA [23]. However, the Ca/P atomic ratio of the HA transformed on the untreated titanium substrate was much lower than 1.67. It is believed that this decrease in the Ca/P atomic ratio of the coating transformed on the untreated titanium substrate is due to minor intermediate phases in the HA, such as OCP and DCPD.

Generally, OH^- ions are present on the titanium substrate surface in the forms of acidic OH(s) and basic Ti–OH. OH^- ion in an acidic OH(s) is bound to two titanium atoms and OH^- ion in a basic Ti–OH is bound to one titanium atom [29]. Therefore, it is expected that basic Ti–OH groups are released from the surface more easily due to the single coordination with titanium atoms than the acidic OH(s) groups that are doubly coordinated with titanium atoms. The formation of the basic Ti–OH groups was accelerated by the chemical treatment with the H_2O_2 solution [30]. When the cathodic potential is loaded onto the H_2O_2-treated titanium substrate in the initial stages of the electrodeposition, the surface of the H_2O_2-treated titanium substrate releases more OH^- ions with the movement of H^+ ions to the cathode, compared to that of the untreated titanium substrate. H^+ ions are used mainly to form H_2 gas around the cathode. In addition, OH^- ions in the modified SBF as well as the OH^- ions, which are formed by the reduction of water during electrodeposition [17], migrate around the cathode because of the electrostatic effects between the anions and cations. Consequently, the pH around the cathode increases with increasing OH^- concentration and the insoluble calcium phosphate precipitates heterogeneously on the cathode. This sudden increase of the pH around the cathode in the initial stages of electrodeposition, which results from OH^- ions released from the surface of the H_2O_2-treated titanium substrate as well as OH^- ions formed by the reduction of water during electrodeposition, results in direct deposition of a more bioactive and porous calcium phosphate, which is easy to be transformed into the bonelike apatite layer in short period.

4. Conclusions

Calcium phosphate coatings were formed on the untreated and H_2O_2-treated titanium substrates by electrodeposition in the modified SBF at 60 °C for 1 h. The coating formed on the untreated titanium substrate consisted of ACP and DCPD, and the coating formed on the H_2O_2-treated titanium substrate consisted of mainly HA. The coatings formed on the untreated and H_2O_2-treated titanium substrates subsequently transformed during immersion in the SBF for 5 days. The coating formed on the untreated titanium substrate transformed into HA with a low crystallinity and large crystallites, whereas the coating formed on the H_2O_2-treated titanium substrate transformed into HA with a bonelike crystallinity and small crystallites. In addition, the coating transformed on the H_2O_2-treated titanium substrate consisted of calcium-deficient and carbonate HA. These results were attributed to the increased surface area of the titanium substrate after the H_2O_2 treatment as well as the OH^- ions released from this modified surface during electrodeposition. Overall, an H_2O_2 treatment is an effective surface pretreatment for producing more bioactive calcium phosphate coatings by electrodeposition.

Acknowledgements

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