

# Bioactive Calcium Phosphate Coating on Sodium Hydroxide-Pretreated Titanium Substrate by Electrodeposition

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**This study examined the characteristics of calcium phosphate coatings deposited on a NaOH-pretreated titanium substrate by electrodeposition in a modified simulated body fluid (SBF) immediately after electrodeposition as well as after the coatings had been immersed in the SBF for 5 d in order to determine the effects of a NaOH pretreatment on the bioactive coating prior to electrodeposition. The results showed that a dense and uniform coating that consisted of brushite and hydroxyapatite had formed on the NaOH-pretreated titanium substrate by electrodeposition. This coating had transformed to a bonelike apatite during immersion in the SBF. This was attributed to the increased surface area of the modified titanium formed after the NaOH treatment as well as the Na<sup>+</sup> ions released from that surface. Therefore, a NaOH pretreatment is recommended as an effective method for preparing a bioactive calcium phosphate coating by electrodeposition.**

## I. Introduction

CALCIUM PHOSPHATE-BASED BIOCERAMICS have been widely used in medicine and dentistry for almost 20 years. Among the various calcium phosphate-based bioceramics, stable hydroxyapatite (HA, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) has been used the most in body fluid because of its excellent bioactivity and biocompatibility.<sup>1</sup> However, HA has had many problems as a large-loaded structure during long-term implantation because of its inferior mechanical properties, and it has been used mainly as a coating material in the biomaterials field.<sup>2</sup>

Plasma spraying is the most often used method for obtaining an HA coating. An HA coating by plasma spraying exhibits excellent mechanical strength and adhesion between the coating and the substrate as well as good bioactivity, which bonds directly to the bone after implantation.<sup>3</sup> However, the plasma-spraying method does not allow the accurate control of the chemical composition, crystallographic structure, and crystallinity of the coating.<sup>4</sup> In addition, plasma spraying cannot produce a uniform coating of devices with complicated shapes. Recently, electrodeposition has been introduced with good properties, such as a quick and uniform coating of the substrates with complex forms at low temperatures and the control of the film thickness and chemical composition of the coating.<sup>5–10</sup> However, few chemical pretreatments to improve the bioactivity of the electrodeposited coating have been reported, except for basic pretreatments, such as grit blasting and passivation.

Kim and co-workers<sup>11,12</sup> reported the formation of bonelike apatite on a NaOH and thermal-treated titanium substrate after soaking it in a simulated body fluid (SBF) for 7 d. In the current study, a NaOH pretreatment was used as a chemical pretreatment to form a bioactive calcium phosphate coating by electrodeposition, and the calcium phosphate coatings that formed on the NaOH-pretreated titanium substrate by electrodeposition in the modified SBF with a subsequent transformation during immersion in the SBF for 5 d were characterized.

## II. Experimental Procedures

A commercially pure titanium plate (10 mm × 10 mm × 0.8 mm) was used as a substrate. Its surface was ground with No. 100 and No. 600 SiC paper and cleaned ultrasonically in acetone and ethyl alcohol for 5 min, rinsed in double-distilled water, and finally dried. To avoid an edge effect during electrodeposition, the edges of the samples were rounded. To evaluate the effect of the NaOH pretreatment on electrodeposition, the samples were immersed in 10 mL of a 5M NaOH solution and kept at 60°C for 24 h. After immersion in the NaOH solution, the samples were washed with double-distilled water and dried.

Electrodeposition of calcium phosphates was performed at 60°C for 1 h in a conventional cell fitted with a saturated calomel electrode (SCE). A modified SBF was used as an electrolyte for electrodeposition. The modified SBF was prepared by dissolving reagent-grade NaCl, NaHCO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, and CaCl<sub>2</sub> in double-distilled water and buffered at pH 7.4 at 60°C with tris-hydroxymethylaminomethane ((CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub>) and 1M hydrochloric acid (HCl). This modified SBF was stirred at room temperature for 1 h. The composition of this modified SBF is shown in Table I. The untreated and NaOH-treated titanium samples were used as the cathodes for electrodeposition. A potentiostat/galvanostat (Model 263A, EG&G Instruments, Princeton, NJ) operating in potentiostatic mode was used to maintain the cathodic potential of –2 V (versus SCE). The solution was stirred during electrodeposition. After electrodeposition, the coated samples were rinsed with double-distilled water and dried for 24 h.

To evaluate the bioactivity of the coatings, the untreated and NaOH-treated samples coated by electrodeposition were immersed in 20 mL of an acellular SBF with ion concentrations

**Table I. Compositions of the Modified Simulated Body Fluid for Electrodeposition Coating**

Order	Reagent	Amount (g)
1	NaCl	7.996
2	NaHCO <sub>3</sub>	0.350
3	K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O	0.228
4	CaCl <sub>2</sub>	0.278

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close to that of human blood plasma at 36.5°C for 5 d. The SBF was prepared by dissolving reagent-grade NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub> in double-distilled water and buffered at pH 7.4 at 36.5°C with tri-hydroxymethylaminomethane and 1M HCl.<sup>13</sup> After they were immersed in the SBF for 5 d at 36.5°C, the samples were washed gently with double-distilled water and dried for 24 h. The SBF was renewed each day.

The crystallinity and structure of the coatings was examined using X-ray diffractometry (XRD; Model D-Max Rint 240, Rigaku, Tokyo, Japan) at room temperature with Ni-filtered CuK<sub>α</sub> radiation generated at 40 kV and 50 mA. The morphology of the coatings was examined using scanning electron microscopy (SEM; Model S-2700, Hitachi, Tokyo, Japan), and the chemical composition of the coatings was analyzed using energy-dispersive spectroscopy (EDS; Model Superdry, Kevex Instruments, Waltham, MA).

### III. Results and Discussion

Figure 1 shows the XRD spectra of the untreated sample surface before and after electrodeposition as well as after immersion in the SBF for 5 d. The main structures of the coating that formed on the untreated sample by electrodeposition were amorphous calcium phosphate and dicalcium phosphate dehydrate (brushite, CaHPO<sub>4</sub>·2H<sub>2</sub>O). After this coated sample was immersed in the SBF at 36.5°C for 5 d, the coating transformed to mainly HA with a minor concentration of brushite. The broad and weak peaks of the HA transformed during immersion in the SBF suggested the poor crystallinity and density of the HA coating. Therefore, it is believed that the transformed HA is unstable in the body fluid and may easily dissolve.

Figure 2 shows the XRD spectra of the NaOH-pretreated sample surface before and after the NaOH pretreatment, after electrodeposition, and after immersion in the SBF for 5 d. The sample pretreated in 5M NaOH solution at 60°C for 24 h showed a weak anatase titanium oxide (TiO<sub>2</sub>) peak and a weak and broad sodium titanate (Na<sub>2</sub>Ti<sub>5</sub>O<sub>11</sub>) peak.<sup>12</sup> The main structures of the coating that formed on the NaOH-pretreated sample by electrodeposition were HA and brushite. After this coated sample was immersed in the SBF at 36.5°C for 5 d, the transformed coating showed that the main structure was HA. The broad and high peaks of the HA transformed during immersion in the SBF suggest that the HA has a bonelike crystallinity and density.<sup>14</sup>

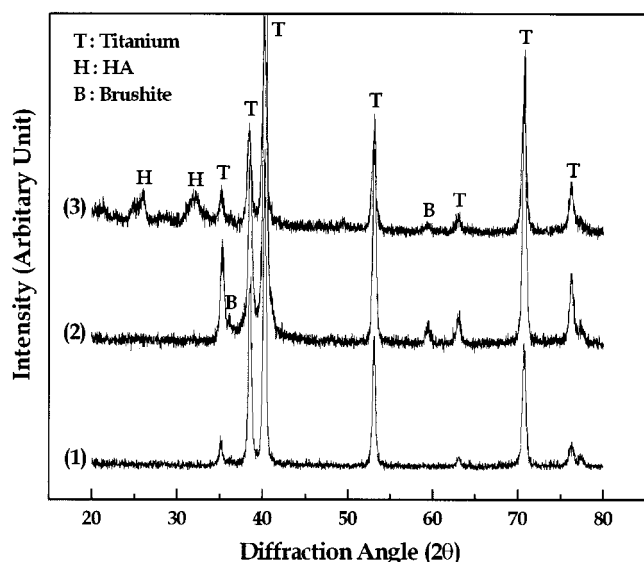


Fig. 1. XRD spectra of the untreated sample surfaces (1) before electrodeposition, (2) after electrodeposition, and (3) after immersion in the SBF for 5 d.

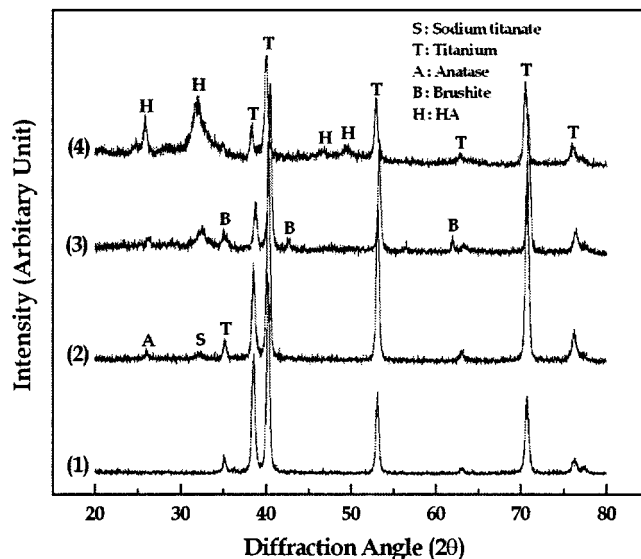


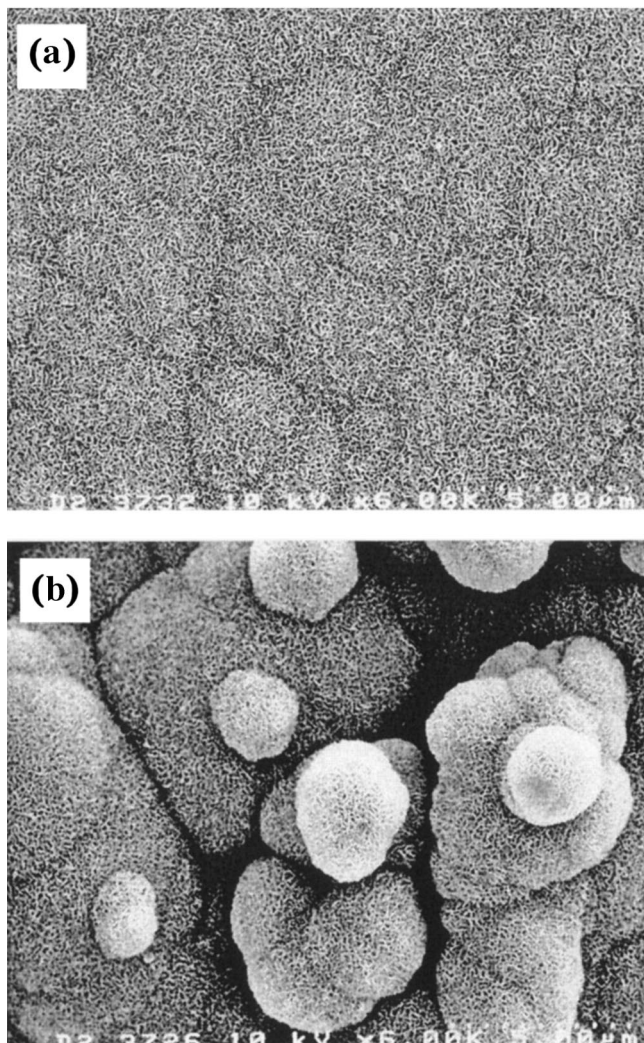
Fig. 2. XRD spectra of the NaOH-pretreated sample surfaces (1) before NaOH pretreatment, (2) after NaOH pretreatment, (3) after electrodeposition, and (4) after immersion in the SBF for 5 d.

The differences between the structures of these electrodeposited and transformed coatings indicated that the surface of the NaOH-pretreated sample was more suitable for electrodeposition of calcium phosphate, which could be transformed to a bonelike apatite, than that of the untreated sample. Brushite and HA that formed on the NaOH-pretreated sample by electrodeposition transformed to a bonelike apatite more easily and faster than the amorphous calcium phosphate and brushite on the untreated sample.

Figure 3 shows SEM images of the coatings transformed on the untreated and NaOH-pretreated samples during immersion in the SBF for 5 d after electrodeposition. For the untreated sample, the surface transformed during immersion in the SBF consisted of needle-shaped crystallites distributed irregularly with an even morphology and indistinguishable grains. No secondary rugged or island-shaped structures were observed on this surface. It is believed that the formation of an even structure is not sufficient for strong bone bonding to occur in the initial stages of implantation. For the NaOH-pretreated sample, the surface transformed during immersion in the SBF consisted of needle-shaped crystallites with large and clearly differentiated grains that had formed in the initial stages of the HA transformation. Secondary island-shaped HA structures that formed on the grains also were observed. The needle-shaped crystallites of the NaOH-pretreated sample were interconnected more densely than those of the untreated sample. Moreover, the secondary island-shaped HA structures that formed on the NaOH-pretreated sample after immersion in the SBF for 5 d were expected to show strong bone-bonding in the initial stages of implantation.

The small and dense needle-shaped crystallites that transformed on the NaOH-pretreated sample increased the contact surface area of the HA in the initial stages of SBF immersion and accelerated the formation of secondary HA precipitation with increased calcium- and phosphate-ion dissolution in the solution from the coating. The solubility of the coating decreased with increased crystallite size and crystallinity of the coating, because the coating with a larger crystallite size had less contact surface area with the solution, and a higher crystallinity prevented calcium and phosphate ions from being dissolved in the solution. Although HA and brushite that formed on the NaOH-pretreated sample by electrodeposition showed a lower solubility than the amorphous calcium phosphate and brushite that formed on the untreated sample, active transformation to the bonelike apatite could occur on the HA and brushite of the NaOH-pretreated sample, because





**Fig. 3.** SEM images showing the morphologies of the coatings transformed on the (a) untreated and (b) NaOH-pretreated samples during immersion in the SBF for 5 d after electrodeposition.

the crystallite size was more important in the initial stages of dissolution than the actual crystallinity.<sup>15</sup>

The Ca/P atomic ratio of the coatings was measured using EDS to analyze the chemical composition of the coatings that had transformed during immersion in the SBF for 5 d. For the untreated sample, the Ca/P atomic ratio of the HA and brushite transformed during immersion in the SBF for 5 d was 1.55. For the NaOH-pretreated sample, the Ca/P atomic ratio of the HA transformed during immersion in the SBF for 5 d was 1.62, which was lower than that of stoichiometric HA (Ca/P = 1.67). The Ca/P atomic ratio of the HA transformed on the NaOH-pretreated sample was similar to bone mineral, which was calcium deficient.<sup>14</sup> Therefore, it was concluded that the calcium phosphate coating that formed on the NaOH-pretreated sample by electrodeposition induced the formation of bonelike apatite in the acellular SBF.

The surface formed after the NaOH treatment consists of anatase titanium oxide and amorphous sodium titanate with a porous network.<sup>12</sup> If the cathodic potential is loaded onto the surface of the NaOH-pretreated sample in the initial stages of the electrodeposition, this surface releases Na<sup>+</sup> ions from the sodium titanate in association with the movement of H<sup>+</sup> ions to the cathode. H<sup>+</sup> ions are used mainly to form H<sub>2</sub> gas around the cathode. In addition, as the concentration of the released Na<sup>+</sup> ions

increases around the cathode, OH<sup>-</sup> ions in the modified SBF as well as OH<sup>-</sup> ions that are formed by the reduction of water during electrodeposition<sup>8</sup> migrate around the cathode because of the electrostatic effects between the anions and cations. Consequently, the pH around the cathode increases with increasing OH<sup>-</sup> concentration. As a result, the insoluble calcium phosphate precipitates heterogeneously on the cathode. Through this process, a calcium phosphate coating can be formed on the NaOH-pretreated sample by electrodeposition. The increase in the Na<sup>+</sup> concentration around the cathode in the initial stages of the electrodeposition helps coat the NaOH-pretreated sample with a denser and more uniform calcium phosphate than the untreated sample. In addition, the porous network of the titanium surface formed after the NaOH pretreatment provides more favorable sites for calcium phosphate nucleation.

#### IV. Conclusions

A coating with HA and brushite structures was formed on a NaOH-pretreated sample by electrodeposition in modified SBF at 60°C for 1 h. This coating was denser and more uniform and was transformed to a bonelike apatite more quickly during immersion in the SBF for 5 d than that on an untreated sample. Therefore, it was expected that bonding with the surrounding bones in the initial stages of implantation would form faster and more strongly on the coating that formed on the NaOH-pretreated sample by electrodeposition. This was due to the increased surface area of the modified titanium that formed after the NaOH treatment as well as the Na<sup>+</sup> ions released from that surface. Overall, a NaOH pretreatment was an effective surface pretreatment for producing more bioactive calcium phosphate coatings by electrodeposition.

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