

# Fluoridated hydroxyapatite coatings on titanium obtained by electrochemical deposition

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## Abstract

Hydroxyapatite (HA) and fluoridated hydroxyapatite (FHA) coatings were deposited on titanium substrates using an electrochemical technique. Different concentrations of  $F^-$  ions were incorporated into the apatite structure by adding NaF into the electrolyte. Typical apatite structures were obtained for all the coatings after electrodeposition and subsequent post-treatment, including alkaline immersion and vacuum calcination. The coatings were uniform and dense, with a thickness of  $\sim 5 \mu\text{m}$ . When the F-concentration was higher than 0.012 M in the electrolyte, a saturation of F in the coating occurred and the F/Ca ratio in the coatings became almost constant (F/Ca ratio = 0.125). The FHA coatings showed higher bonding strength and lower dissolution rate than HA coating, particularly for those with a fluoridation level of 0.5–0.625. Compared with pure Ti, FHA and HA coatings exhibited higher biological affinity like cell proliferation and alkaline phosphatase activity. Regarding clinical application, it is suggested that a moderate content of F, such as  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})_{0.375-0.5}\text{F}_{0.5-0.625}$ , be most suitable as a compromise among cell attachment, cell proliferation, apatite deposition and dissolution resistance.

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**Keywords:** Fluoridated hydroxyapatite; Electrochemical deposition; Dissolution rate; Cellular responses

## 1. Introduction

Hydroxyapatite (HA,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) has been developed as a coating on metallic implants in the field of orthopedics and dentistry due to its chemical and biological similarity to human hard tissues as well as direct bonding capability to the surrounding tissues [1,2]. It has been established that HA coating can promote more rapid fixation and stronger bonding between the host bone and the implant [3]. In addition, HA coating provides protection to the titanium substrate against corrosion in the biological environment, and acts as a barrier against the release of metal ions from the substrate into the environment [4]. What is more inspiring is that HA coating can enhance bone growth across a gap of 1 mm between the bone and the implant and it is capable of limiting the formation of

any fibrous membrane and converting a motion-induced fibrous membrane into a bony anchorage [5].

However, pure HA coatings suffer relatively high dissolution rate in the biological environment, especially for those fabricated by plasma spraying, which contain a high concentration of the amorphous phase [6]. High dissolution may lead to the disintegration of the coatings and hinder the fixation of implant to the host tissue [7]. Fluorine, which exists in human bone and enamel, can be incorporated into HA crystal structure by substituting  $\text{OH}^-$  groups with  $F^-$  ions to form fluoridated hydroxyapatite (FHA,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})_{1-x}\text{F}_x$ , where  $0 < x < 1$  is the degree of fluoridation). FHA possesses lower solubility than pure HA while maintaining the comparable bioactivity and biocompatibility [8]. Recently, many researchers focused on the application of FHA as bioactive coatings to provide both early stability and long-term performance [9–13]. In comparison with HA coating, FHA coatings could provide lower dissolution, better apatite-like layer deposition, better

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protein adsorption, comparable or better cell attachment and improved alkaline phosphatase activity in cell culture.

Most HA and FHA coatings are now obtained using the plasma-spraying technique. However, plasma spraying is a high-temperature and line-of-sight process, which has some potential problems including exposure of substrates to intense heat, residual thermal stresses in coatings, and the inability to coat complex shapes with internal cavities [6]. In comparison, electrochemical deposition of HA coating has recently attracted considerable attention due to (1) a relatively low process temperature, (2) the ability to deposit on non-line-of-sight, porous or complex shapes of substrate, (3) the convenience to control the coating properties, (4) the possible improvement of the substrate/coating bond strength, and (5) the availability and low cost of equipment [6,14,15].

However, reports on the fabrication of FHA coatings using electrochemical deposition are scarce at present. Therefore, the purpose of this study is to deposit FHA and HA coatings on Ti substrates by electrochemical deposition technique, and furthermore, the film characteristics, bonding strength, dissolution rate and in vitro biological affinity of the coatings were also evaluated.

## 2. Materials and methods

### 2.1. Electrochemical deposition of FHA and HA coatings

Commercially pure titanium sheets ( $10 \times 10 \times 0.6$  mm, Non-ferrous Metals Corporation, Baoji, China) were used as substrates for electrodeposition. Their surfaces were ground with #100 and #600 SiC papers, etched in 4% HF solution for 2 min, ultrasonicated in acetone and ethyl alcohol for 15 min, respectively, rinsed in double-distilled water, and finally dried.

The electrolyte used for deposition contained 0.042 M  $\text{Ca}(\text{NO}_3)_2$ , 0.025 M  $\text{NH}_4\text{H}_2\text{PO}_4$ , 0.15 M  $\text{NaNO}_3$  and 6%  $\text{H}_2\text{O}_2$  (mass fraction).  $\text{NaNO}_3$  was added to improve the ionic strength of the electrolyte, and  $\text{H}_2\text{O}_2$  was added to erase the evolution of  $\text{H}_2$  gas and promote the deposition of dense coatings. As for the fabrication of FHA coatings, NaF ( $[\text{F}^-] = 0.001, 0.004, 0.008, 0.012$  and  $0.016$  M, respectively) was added into the electrolyte to deposit FHA coatings with different F contents. The electrolyte was prepared with analytical reagent grade chemicals (Kelong Chemical Reagent Corporation, Chengdu, China) and deionized water. The pH of the electrolyte was adjusted to 6.0 at 25 °C, so that the electrolyte was saturated with calcium and phosphate ions, and stoichiometric hydroxyapatite can be directly deposited on the cathodes without the formation of a precursor phase [6,16].

The electrodeposition was carried out at 65 °C in a three-electrode cell fitted with a graphite rod acting as the counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. An electric heater and magnetic agitation (Electrical Appliances Co., Changzhou,

China) was used to maintain the temperature of electrolyte and stir the electrolyte at a speed of 180 rpm. The deposition was carried out in galvanostat mode and the cathodic current density was kept at  $0.6 \text{ mA cm}^{-2}$  for 30 min.

After deposition, the specimens were rinsed in distilled water, soaked in 0.1 M NaOH solution at 60 °C for 48 h, and finally calcined in vacuum at 650 °C (heating rate =  $5 \text{ }^\circ\text{C min}^{-1}$ , maintaining time = 2 h, and cooling rate =  $1 \text{ }^\circ\text{C min}^{-1}$ ).

According to the concentration of NaF which was added into the electrolyte for FHA coatings deposition, the experimental groups were referred to as FHA0.001, FHA0.004, FHA0.008, FHA0.012 and FHA0.016, respectively, and pure HA coating was designated as control.

The thermodynamic calculation for the electrolyte was performed to evaluate the effects of solution conditions on the precipitation of calcium phosphates. A geochemical program, PHREEQC Version 2 [17], was employed to study the ionic strength of the electrolyte and the saturation index (SI) for the precipitation of calcium phosphate. SI is a good indicator to show the thermodynamic driving force for the precipitation of a calcium phosphate phase. When  $\text{SI} = 0$ , the solution is in equilibrium; when  $\text{SI} < 0$ , the solution is undersaturated and precipitation is impossible; and when  $\text{SI} > 0$ , the solution is supersaturated and precipitation is spontaneous [15].

### 2.2. Coating characterization

The phase and composition of the coatings were analyzed by means of X-ray diffraction (XRD, D/max-rA, Rigaku Co., Japan), Fourier transform infrared spectroscopy (FT-IR, MX-1E, Nicolet Co.), and X-ray photoelectron spectroscopy (XPS, PHI 5600, Physical Electronics). The surface and cross-sectional morphology was observed by means of field-emission scanning electron microscopy (SEM, JEM-5900LV, JEOL, Tokyo, Japan).

### 2.3. Bonding strength test

The bonding strength of the coatings was examined using a Universal Instron Mechanical Testing System (Instron 5569, Instron Co.) according to ASTM F1044 standard. The coating surface of the  $10 \times 10$  mm specimen was bonded to another metal surface with epoxy adhesive. The loading was applied in the in-plane direction with a crosshead speed of  $10 \text{ mm min}^{-1}$ . Five tests were conducted for the same type of coating in order to obtain an average value of bonding strength.

### 2.4. Dissolution test

The dissolution behavior of the FHA coatings was investigated by soaking in a tris-buffered physiological saline solution (0.9% NaCl, pH 7.4) at a constant temperature of 37 °C for predetermined periods of time. At the end of

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