



Carbonated hydroxyapatite deposition at physiological temperature on ordered titanium oxide nanotubes using pulsed electrochemistry

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Abstract

The effect of temperature and nanotubular surface morphology on calcium phosphate deposition was investigated using a modified simulated body fluid and electrochemistry. Ordered nanotubular titanium oxide plates were coated by pulsed electrochemical deposition process, while titanium oxide and pure titanium surfaces were used as controls at 80 °C and 37 °C. The calcium phosphate deposit was characterized using XRD, FT-IR and FE-SEM. Carbonated hydroxyapatite was deposited at the physiological temperature of 37 °C on nanotubular surfaces, which provided a large surface area for hydroxide ion generation and a small volume for the confinement and concentration of hydroxide ions. Compounds containing carbonates and hydrogen phosphates were deposited on porous titanium oxide surfaces and flat titanium surfaces as the control group. This study demonstrates deposition of hydroxyapatite at physiological temperatures, which is essential for codeposition of organic bioceramics for medical use.

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1. Introduction

Biom mineralization organizes the mineral, the organic material and the tissue fluid hierarchically to form a natural composite material. Biomimicking biom mineralization has enabled the design and production of innovative nanomaterials and systems that contain a bioactive, biocompatible and osteoconductive calcium phosphate (Ca-P) layer, produced using an appropriate deposition method [1–11].

Coating methods can be grossly classified as wet chemistry, high temperature processes and electrochemical methods. The wet chemistry methods produce Ca-P by immersing the surface to be coated in a fluid consisting of anions found in the body and subsequently adding calcium, which results in dense

coatings with good biological performance [12]. The high temperature processes are as follows: plasma spray method, producing thick, inhomogeneous coatings; the ion-beam method, producing thin coatings; the laser method, producing thin coatings with diverse compositions, crystallinities and high fatigue strength; RF sputtering, producing thin, but dense and adhesive coatings; and hot-isostatic pressing of uniform Ca-P granules on titanium surface [13]. Electrochemical methods for depositing Ca-P coatings on implant surfaces are electrophoresis, i.e. deposition of negatively charged Ca-P particles migrating towards the cathodically polarized surfaces [14], and electrochemical deposition (ECD), or cathodic deposition as used here, enabling Ca-P coating of implant materials of any size and shape from an electrolyte solution containing calcium and phosphorus. The method involves various controllable factors, which determine the chemistry of Ca-P coating, e.g. current density, potential, length of cathodic and anodic deposition cycles, temperature and type of solution used [13,15–24].

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The biological performance of dental and orthopedic implants is determined by osteointegration, the ability of host tissues to form a functional interface with the implant without an intervening layer of connective tissue [25,26]. Implant success involves three major factors: mechanical stability, biological activity and chemical integration, which contribute to the osteointegration of implants. The mechanical stability is dependent on the mechanical strength and the correct placement of the implant as well as the surface coating. Biological fixation of the implant involves the microscopic surface topography of implants introduced as grooves, threads, or porous surfaces using micromachining, sand/grit blasting, rough polishing techniques, etc., in order to provide a scaffold for bone cells to attach [13,22]. Chemical fixation involves the processes that render surfaces a chemical base for osteointegration, i.e. presence of a biologically active oxide layer and a stable crystalline base for Ca-P deposition, which are of critical importance in shaping the cellular interaction between the host tissue and the implant, enabling transmission of forces and long-term implant success [11,13]. Crystalline hydroxyapatite (HA) coated implant surfaces have been shown to establish a firm layer of ossification and display approximately two or three times more rapid response and several-fold increase in interfacial strength compared to uncoated surfaces [11,13,25–27].

Currently, Ca-P coated titanium implants with microfunctionalized surfaces are commercially manufactured. Nanotubular titania surfaces, produced by anodization in fluoride-containing electrolytes, may emerge as a future implant surface design [28–32]. The original limitation of ionic diffusion into the nanotubes posing a constraint on Ca-P deposition has been overcome with the introduction of pulsed ECD (PECD) [20]. The PECD of HA begins with a prior alkaline surface preparatory treatment, a crucial step for galvanic reactions to take place on titanium oxide. These reactions have been described as formation, polymerization and condensation of sodium titanate and titanium hydroxide groups into negatively charged titanium oxide around pH 7.4 [11,20]. During the cathodic cycle, these compounds interact with calcium ions to form positively charged amorphous calcium titanate (ACT). During the cathodic deposition on nanotubular titania, the reduction of water to hydroxide takes place with the donation of electrons on cathodically polarized surface at pH values equal to or greater than 7.2. In the case of nanotubes, the large surface area enables generation of a high number of hydroxide ions, which may not only increase solution alkalinity, but also convert hydrogen phosphates to phosphate ions, which, then react with ACT to form ACP, which transforms into crystalline hydroxyapatite and grows by incorporation of calcium, phosphate and hydroxide ions [11,20].

Micro- and nanofunctionalized surfaces have been coated by this method using modified saturated simulated body fluid (SBF) with Ca/P atomic ratios of 1.5, 1.67 and 2.5, at pH ranging from 4 to 7.2, and temperature ranging from 5 to 200 °C [11,14–24,30–34]. Findings of these studies can be grossly summarized as follows: at pH above 7.2 and temperature above 60 °C, highly crystalline HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$)

and calcium deficient HA (CDHA) derivatives; while, at neutral to acidic pH (≤ 7.2) and temperature below 60 °C, poorly crystalline HA and other Ca-P compounds have been deposited on micro-structured or nanostructured substrates. To the best of our knowledge, there has not been any systematic study on the effect of surface morphology on the type of Ca-P deposited using ECD. This study aims to be the first controlled study on electrochemical deposition of HA, where surface micro/nanostructure is correlated with the type of Ca-P deposited using PECD both at 80 °C and at the physiological temperature of 37 °C on titanium substrates, which were (a) under as-received condition, (b) anodized in fluoride-free electrolytes and (c) anodized in fluoride-containing electrolytes (producing nanotubular titania).

2. Materials and method

2.1. Sample preparation and characterization

Commercially available pure titanium (CP grade) (250 by 250 mm by 1 mm) plates were metallographically ground and polished using #120 grit down to #1200 grit Emery paper and finally 1 μm diamond paste, washed with distilled water and sonicated in acetone. Three different types of surfaces were prepared: as the control surface, (1) flat titanium (unprocessed, polished pure titanium plate, referred to as Flatit from here on) and as experimental samples, (2) titanium anodized in fluoride-free electrolyte (referred to as Anotit from here on) and (3) titanium anodized in fluoride-containing electrolyte (referred to as Nanotit from here on). Anodization of titanium in fluoride-free electrolyte was conducted in 0.1 M KOH, in an electrochemical cell using a stainless steel cathode and applying an anodic voltage of 40 V at 20 °C for 3 min. Nanotubular titanium oxide surfaces were prepared in an electrochemical cell, using a stainless steel cathode with an anodic constant voltage of 40 V in 0.5 wt % NH_4F and 1 vol% water containing ethylene glycol solution at room temperature for 30 min. The total number of specimens for the three groups was 18 for each coating temperature. The surface morphology of the specimen was characterized using field emission scanning electron microscopy (FE-SEM) (JEOL JSM 7000F FEI).

2.2. Calcium phosphate coating and characterization

All substrate surfaces were bioactivated by immersion in 0.5 M NaOH for 2 min at 50 °C and rinsed with deionized water [35]. A modified simulated body fluid (SBF), containing reagent grade 0.15 M NaCl, 1.67 mM K_2HPO_4 and 2.50 mM CaCl_2 , pH buffered at 7.2 with the addition of 0.05 M Tris (hydroxyl aminomethane) (pH 7.4) and hydrochloric acid, was used as the electrolyte solution [20]. Deposition was conducted in a typical three-electrode electrochemical cell. The working electrode was the titanium substrate, the reference electrode was a standard silver–silver chloride electrode (Ag/AgCl in saturated KCl) and the counter-electrode was platinumized stainless steel. Deposition was carried out initially at 80 °C by pulsing the current density between -10 mA/cm^2 for 0.2 s and

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