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Hydroxyapatite electrodeposition on anodized titanium nanotubes for orthopedic applications

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ABSTRACT

Nanotubes modification for orthopedic implants has shown interesting biological performances (such as improving cell adhesion, cell differentiation, and enhancing osseointegration). The purpose of this study is to investigate effect of titanium dioxide (TiO_2) nanotube feature on performance of hydroxyapatite-coated titanium (Ti) bone implants. TiO_2 nanotubes were prepared by anodization using ammonium fluoride electrolyte (NH_4F) with and without modifiers (PEG400 and Glycerol) at various potential forms, and times. After anodization, the nanotubes were subsequently annealed. TiO_2 nanotubes were characterized by scanning electron microscope and X-ray diffractometer. The amorphous to anatase transformation due to annealing was observed. Smooth and highly organized TiO_2 nanotubes were found when high viscous electrolyte, NH_4F in glycerol, was used. Negative voltage (−4 V) during anodization was confirmed to increase nanotube thickness. Length of the TiO_2 nanotubes was significantly increased by times. The TiO_2 nanotube was electrodeposited with hydroxyapatite (HA) and its adhesion was estimated by adhesive tape test. The result showed that nanotubes with the tube length of 560 nm showed excellent adhesion. The coated HA were tested for biological test by live/dead cell straining. HA coated on TiO_2 nanotubes showed higher cells density, higher live cells, and more spreading of MC3T3-E1 cells than that growing on titanium plate surface.

1. Introduction

Biomaterials are artificial or natural materials used to replace the lost or infected biological structure. Commonly-used biomaterials for orthopedic implants are 316L stainless steels, cobalt–chromium alloys, and titanium and its alloys. Among these materials, titanium is preferred for orthopedic implants because it possesses closer elastic modulus to that of bone than other [1,2]. However, using titanium as bone implant often fails after long-term use due to an incomplete osseointegration (incomplete bonding between the implant and surrounding bone) [3,4]. Surface treatments such as roughening by sand blasting, formation of anatase phase TiO_2 [5], hydroxyapatite coating, or chemical treatment [6–10] have been used to improve bioactivity of titanium and to enhance bone growth. Webster et al. reported that nano-grained ceramics (with surface structures less than 100 nm) can improve bioactivity of titanium implants and enhance osteoblast adhesion [11,12]. In this aspect, nanoscaled modification is an alternative to improve osseointegration of titanium-based orthopedic implants [13,14]. Therefore, nanotubular TiO_2 arrays are highly interested in this study because of its nanoscale and high surface area.

Titanium oxide nanotubes can be prepared by various techniques, such as sol–gel method [15], electrophoretic deposition [16] and anodization [17]. Among these methods, fabrication of vertically aligned TiO_2 nanotubes on titanium substrate could be easily obtained by anodization [17]. Various researchers prepared the nanotubular structures by electrochemical anodization in hydrofluoric acid containing electrolytes [18,19]. However, to be non-toxic and environment friendly, neutral fluoride solution (NH_4F) was used as the electrolyte in this work. Metal oxide formation and nanotube self-assembly are formed by carefully balancing between the electrochemical processes (field-assisted oxide growth and metal etching) and chemical dissolution of the substrate (the presence of an acidic or complex-forming electrolyte)

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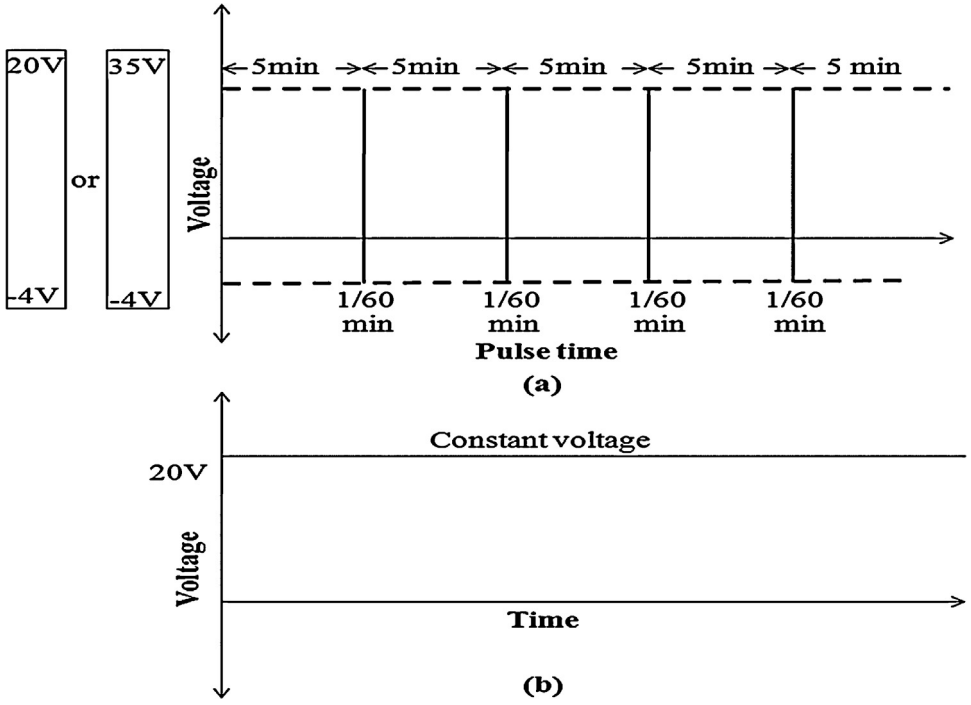

Fig. 1. Potential pulse waveform (a) and constant potential (b) used for anodic growth of TiO_2 nanotube arrays.

[20,21]. To obtain this balance, pulse anodization was used to control chemical dissolution [22]. In the other works, micrometer-long TiO_2 nanotubes with uniform or smooth tube walls were formed when high viscous electrolytes containing fluoride ions were used [23,24]. Therefore, to achieve uniform and well oriented TiO_2 nanotube array, pulse anodization and viscous electrolyte were used in this study.

Another approach to enhance osseointegration of Ti implants is coating titanium with nanostructured hydroxyapatite (HA) (main mineral in bones with the molar Ca/P ratio of 1.67 in stoichiometric hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$)[25]). The HA-coated titanium was shown to have excellent corrosion resistance and good biocompatibility [2]. With electrodeposition, HA with complex shapes can be obtained and thickness of coating can be easily controlled at low temperature. In this work, to search for the optimum conditions for fluoride anodization, the growing of TiO_2 nanotube layers in different viscous electrolytes, various times and pulse anodization were studied. Nanostructured HA coatings were electrodeposited on TiO_2 nanotube arrays after anodization and surface alkali treatment, respectively. After that, adhesion of HA electrodepositions coating on the nanotube from each anodization conditions were measured by ASTM D 3359-02: Standard Test Methods for Measuring Adhesion by Tape; cross-cut tape test (B). Finally osteoblast cells behavior on HA coated anodized titanium surface (ATi) was investigated.

2. Experimental

2.1. Preparation of titanium

Titanium plate with 1.0 mm. thickness (Alfa Aesar, 99.2 wt.%) was used as a substrate to grow oxide nanotube arrays. The surface was polished to mirror quality using silicon carbide paper (TOA, Thailand) of successively finer roughness (400, 600, 800, 1000, 1500 and 2000 grits), and following by polishing with 0.05-μm alumina powder (Allied, USA). After polishing, the titanium plate was washed with deionized (DI) water and was sonicated for 5 min in acetone and another 5 min in ethanol.

2.2. Anodization to form TiO_2 nanotube arrays

The titanium nanotube layers were prepared by electrochemical method. Platinum wire and the titanium plate were used as negative and positive electrodes, respectively. All films were grown at approximately 25 °C in 0.36 M ammonium fluoride (NH_4F) electrolytes (viscosity of 0.764 cP) with and without modifiers: 10% (NH_4F in H_2O):90% Glycerol, (viscosity of 300 cP) or polyethylene glycol 400 (viscosity of 133.71 cP). The viscosity of electrolyte was measured by cylinder rotation viscosity technique (Viscometer DV II+ (Brookfield, USA). Anodization was conducted with two different potential forms: pulse (20/−4 V) and constant (20 V) voltage, as shown in Fig. 1. Anodization time was varied as 0.5, 1.5 and 2.5 h. After anodization, samples were carefully cleaned with DI water and then were dried by nitrogen gas. The grown porous layers were annealed at 450 °C for 30 min to obtain anatase phase.

2.3. Electrodeposition of hydroxyapatite

It was reported that HA coating on ATi, anodized titanium, from electrodeposition without any surface treatment was not homogenous [26]. To obtain homogenous HA, the ATi samples were treated by 1 M NaOH solution at 50 °C for 2 min prior to electrodeposition. After the pre-treatment, the HA deposition was conducted. The electrolyte was prepared by dissolving 1.67 mM phosphate containing salt in the form of $NH_4H_2PO_4$ (Sigma, Thailand) and 2.5 mM calcium containing salt in the form of $Ca(NO_3)_2$ (Sigma, Thailand) in distilled water. To increase ionic conductivity, 0.15 M NaCl was dissolved in the electrolyte and the pH of electrolyte was buffered at 7.2 by tris(hydroxyl aminomethane), and hydrochloric acid [26]. The pre-treated ATi and platinum were used as a cathode and an anode, respectively. The electrodeposition of HA was carried out at a constant potential, −2.5 V, at 80 °C for 10 min.

2.4. Morphological and structural characterization

The surface morphology of ATi was investigated by a scanning electron microscopy (FE-SEM, CamScanMX2600) with a nominal