

# Formation of hydroxyapatite within porous TiO<sub>2</sub> layer by micro-arc oxidation coupled with electrophoretic deposition

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## Abstract

Micro-arc oxidation (MAO) is commonly used to modify the surface of Ti-based medical implants with a bioactive and porous titanium oxide (TiO<sub>2</sub>) layer. This study reports a novel method of incorporating hydroxyapatite (HA) within the TiO<sub>2</sub> layer by coupling MAO with an electrophoretic deposition (EPD) process. A HA-incorporated, porous TiO<sub>2</sub> layer was produced successfully on the Ti substrate using the EPD-coupled MAO treatment, as confirmed by electron microscopy observations. Addition of ethanol to the electrolyte solution containing the fine HA particles was essential to reduce the level of gaseous emission on the anode, which obstructs the attachment of HA particles. In vitro cellular assays showed that the incorporation of HA significantly improved the osteoblastic activity on the coating layer.

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## 1. Introduction

Titanium (Ti) and its alloys are suitable materials for dental and orthopedic implants on account of their outstanding chemical stability, mechanical properties and biocompatibility, which are mainly due to the surface oxide layer formed naturally in air or in many aqueous environments [1,2]. Therefore, the properties of the surface oxide layer, such as roughness, topography and composition, play an important role in the biocompatibility of a Ti implant. Thus far, a number of techniques have been developed to improve the surface properties of Ti implants. These include blasting with hard particles, etching in an acidic solution, coating with bioactive materials and electrochemical treatments [3–6].

Micro-arc oxidation (MAO) is considered one of the most useful methods for surface modification because it can produce porous and firmly adherent TiO<sub>2</sub> films on Ti implants, which can not only enhance the fixation of the implants to the bone, but also improve their in vivo corrosion behavior [6–11]. This technique basically makes full use of the anodic oxidation of Ti by applying a positive voltage to a Ti substrate used as the anode immersed in an electrolyte. In particular, when an applied voltage is increased beyond a certain point, micro-arcs are generated as a result of the dielectric breakdown of the surface TiO<sub>2</sub> layer, whereupon Ti ions in the Ti implant and OH ions in the electrolyte move in opposite directions very quickly to form TiO<sub>2</sub> again.

Furthermore, bioactive materials or antibiotics can be incorporated into the coating layer during the MAO process by tailoring the composition of the electrolyte solution [6,7,12,13]. For example, Ca and P ions have been

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incorporated successfully into the TiO<sub>2</sub> layer using an electrolyte solution containing Ca and P sources, which resulted in a considerable improvement in the osseointegration ability of the implant in vivo tests [6,12,13]. In addition, these incorporated Ca and P ions can be crystallized to form hydroxyapatite (HA) or other calcium phosphate phases using a hydrothermal treatment [14–16]. More recently, it has been demonstrated that a thin calcium phosphate layer could be directly deposited onto a micro-arc oxidized Ti substrate using electron beam evaporation, which could enhance osseointegration of Ti implants [17]. However, it is still challenging to develop new methods that can allow the incorporation of bioactive materials, particularly in the form of crystalline phase, into the TiO<sub>2</sub> coating layer in an in situ manner.

Therefore, in this study, a new simple method was proposed to directly incorporate well-crystallized HA particles into the TiO<sub>2</sub> layer on Ti without significantly altering the microporous coating morphology. The strategy combined the principles of the MAO process with an electrophoretic deposition (EPD) process, which is often used to coat the surface of Ti materials with a HA layer [18–20]. In particular, a porous TiO<sub>2</sub> layer was formed via the MAO process, while, at the same time, negatively charged HA particles migrate toward the Ti anode through the EPD process, as illustrated in Fig. 1. These particles then become incorporated into the pores formed in the TiO<sub>2</sub> layer, resulting in the formation of a bioactive HA-incorporated TiO<sub>2</sub> coating layer on the Ti substrate. For the successful use of the newly developed MAO-EPD treatment, ethanol was added to the electrolyte containing the fine HA particles in order to retard the evolution of the gas at the anode,

which would otherwise obstruct the attachment of HA particles [21]. The morphology, composition and phase of the coating layer were examined at different ethanol concentrations in the electrolyte and applied voltages during the MAO-EPD treatment. The biological properties of the coating layers were evaluated using in vitro cell growth and osteoblastic differentiation assays.

## 2. Materials and methods

### 2.1. Preparation of electrolytic solution containing HA particles

For successful use of the MAO-EPD treatment, it is essential to prepare a suitable electrolyte solution, in which nanosized HA particles are dispersed homogeneously without severe agglomeration. To achieve this, commercially available HA powder (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>; Alfa Aesar Co., Milwaukee, WI, USA) was calcined at 900 °C for 3 h to improve the rheological behavior of the suspension [22]. Subsequently, the calcined HA powders were ball-milled for 48 h in a mixture of deionized water and ethanol with various ethanol concentrations ranging from 0 to 50 vol.%. The amount of HA powder in the slurry was 20 g l<sup>-1</sup>. After achieving a stable solution with fine HA particles for the EPD process, the suspension was transferred to a beaker and mixed with 0.08 mol l<sup>-1</sup> disodium β-glycerophosphate pentahydrate (C<sub>3</sub>H<sub>7</sub>Na<sub>2</sub>O<sub>6</sub>P·5H<sub>2</sub>O, β-GP, Tokyo Kasei, Japan) for 1 h using a magnetic stirrer to prepare the electrolyte solution. In addition, ammonium hydroxide (NH<sub>4</sub>OH, Sigma–Aldrich, St. Louis, MO, USA) was used to adjust the pH to 11. Before each coating treatment, the solutions were agitated using an ultrasonic cleaner for 1 h to prevent settling and agglomeration of the HA particles.

### 2.2. MAO-EPD treatment

Commercially pure (CP) Ti (Grade 2, Ka-Hee Metal Industry Co., Seoul, Korea) was used as the substrate. Plates, 10 × 10 × 1 mm<sup>3</sup> in size, were ground using 2000 grit SiC sandpaper and cleaned ultrasonically in acetone, ethanol and deionized water in series. The MAO-EPD treatment was carried out in the prepared electrolyte solutions by applying a pulsed DC field to the specimen using a pulsed DC power supply (Model-P6214, Auto Electric Co., Seoul, Korea). The frequency and duty cycle of the pulsed DC power were 660 Hz and 60%, respectively. The roughness and thickness of the oxide layer were controlled by applying a wide range of DC fields (300, 350, 375 and 400 V) to the specimens for either 3 or 10 min.

### 2.3. Characterization of oxide layer

An electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Co., Japan) was used to examine the zeta

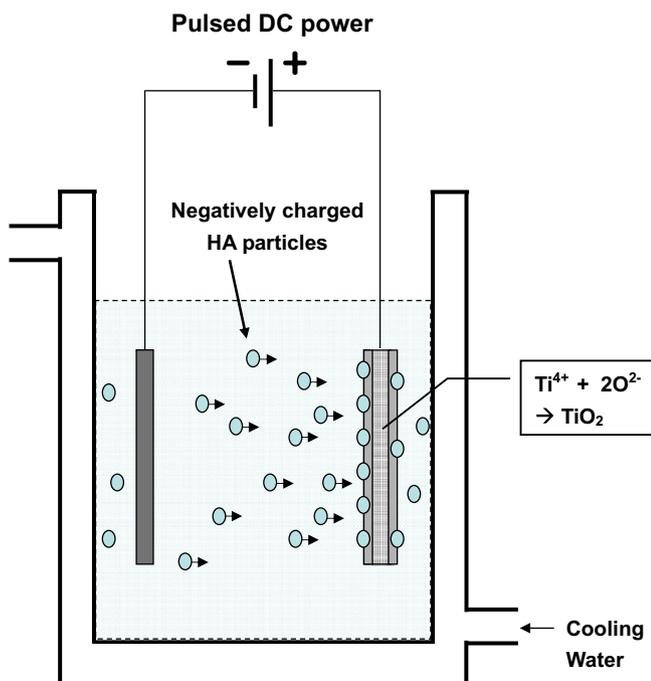


Fig. 1. Schematic diagram showing the experimental set up used for the MAO-EPD treatment.

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