

# Influence of calcium ion deposition on apatite-inducing ability of porous titanium for biomedical applications

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## Abstract

In the present study, the influence of calcium ion deposition on the apatite-inducing ability of porous titanium (Ti) was investigated in a modified simulated body fluid (m-SBF). Calcium hydroxide (Ca(OH)<sub>2</sub>) solutions with five degrees of saturation were used to hydrothermally deposit Ca ions on porous Ti with a porosity of 80%. Apatite-inducing ability of the Ca-ion-deposited porous Ti was evaluated by soaking them in m-SBF for up to 14 days. Scanning electron microscopy (SEM) and X-ray diffractometry (XRD) confirmed that a thin layer of calcium titanate (CaTiO<sub>3</sub>)/calcium oxide (CaO) mixture with a nanostructured porous network was produced on porous Ti substrates after hydrothermal treatment at 200 °C for 8 h. X-ray photoelectron spectroscopy results demonstrated that the content of the Ca ions deposited on Ti and the thickness of the CaTiO<sub>3</sub>/CaO layer increased with increasing saturation degree of the Ca(OH)<sub>2</sub> solution. The thickest (over 10 nm) CaTiO<sub>3</sub>/CaO layer with the highest Ca content was achieved on the Ti treated in an oversaturated Ca(OH)<sub>2</sub> solution (0.2 M). SEM, XRD, transmission electron microscopy and Fourier transformed infrared spectroscopy analysis indicated that the porous Ti samples deposited with the highest content of Ca ions exhibited the best apatite-inducing ability, producing a dense and complete carbonated apatite coating after a 14 day soaking in m-SBF. The present study illustrated the validity of using Ca ion deposition as a pre-treatment to endow desirable apatite-inducing ability of porous Ti for bone tissue engineering applications. Crown Copyright © 2009 Published by Elsevier Ltd. on behalf of Acta Materialia Inc. All rights reserved.

**Keywords:** Porous titanium (Ti); Calcium (Ca) ion deposition; Hydrothermal treatment; Apatite; Modified simulated body fluid (m-SBF)

## 1. Introduction

Titanium (Ti)-based metals have been extensively used in orthopaedic and dental implants areas [1]. Their excellent mechanical properties, good corrosion resistance [1] and superior biocompatibility [2] have enjoyed widespread clinical success. The problem with current Ti-based heavy-load-bearing implants lies in the fact that the mismatch of Young's modulus between Ti-based metals (90–110 GPa) and bones (0.3–30 GPa) can cause severe “stress shielding”, leading to bone resorption [3]. However, Young's modulus can be significantly reduced by introducing a porous structure [4–6]. Minimizing or eliminating the

stress-shielding to the bone tissues adjacent to the implant material can effectively prolong the implant lifetime [7]. The pore morphology, pore size, porosity and chemical composition of the porous scaffolds are basic parameters that affect their biomechanical properties, biocompatibility and bioactivity. Furthermore, it has been documented that the optimal pore size for the cell attachment, differentiation and ingrowth of osteoblasts and vascularization is approximately 200–500 μm [8]. Wen et al. have successfully fabricated a porous Ti with a porosity of 78% (pore size in the range of 200–500 μm) and a low Young's modulus (5.3 GPa) that exhibits a unique open-cell porous structure using a special powder metallurgy technique [4,5].

The use of porous Ti-based materials is constrained by their bioinert feature, when a strong interface bonding between implant and living bone tissue is strongly

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expected. Hydroxyapatite (HA), having a similar structure to the major mineral constituent of human hard tissue, can be steadily adapted to the surrounding bone tissues after implantation into the human body and shortens the recovery time. However, the mechanical weakness of HA limits its practical applications in load-bearing implants. Thus, bioinert Ti-based implants coated with HA or apatite have attracted much attention because the resultant composite combines the advantages of both the mechanical strength of metals and the biological affinity of HA to surrounding bone.

Recent advancements in developing chemical surface modification to induce biomimetic calcium phosphate (CaP, e.g. HA or apatite) coatings on Ti-based materials include sol-gel [9,10],  $H_2O_2$  [11], alkali-heat [12–15] and acid [16] treatments. Of these processes, the alkali-heat treatment technique proposed by Kokubo's team [14] is a cost-effective and efficient way to induce apatite coating formation on Ti-based substrates. However, the safety of the release of alkali ions from alkali-heat-treated metallic implants into the human body environment is still of concern. Meanwhile, it has been shown that removing alkali cations from the surface layer improves both the apatite-inducing ability of Ti in simulated body fluid (SBF) in vitro [17] and the bone-bonding ability of potential implant materials in vivo [18]. Moreover, the mechanical strength of porous Ti can be significantly degraded by alkali-heat treatment [19]. Yang et al. [20] revealed that Ca and  $PO_4$  ions deposit in an orderly fashion onto the alkali-heat treated Ti surface, and Ca ion precipitation is a prerequisite for  $PO_4$  ion deposition. Thus, incorporating Ca ions in the Ti surface with solutions containing Ca ions (CaO, calcium nitrate ( $Ca(NO_3)_2$ ), calcium chloride ( $CaCl_2$ ), etc.) might be a desirable approach to improve the ability to induce apatite formation both in vitro and in vivo, while simultaneously avoiding degradation of the mechanical properties incurred by alkali-heat treatment while using a highly concentrated NaOH/KOH solution ( $\geq 2.0$  M).

It has been found that, via Ca ion deposition techniques, titanium dioxide ( $TiO_2$ ) can be transformed into calcium titanate ( $CaTiO_3$ ), which exhibits excellent bone conductivity (apatite-inducing ability) [21–23]. However, such apatite precipitation was inhibited by the Ti surface which was deposited with  $CaCl_2$  due to the decrease in the surface layer thickness and the deficiency of Ca ions contained in the surface layer [23]. Coreño et al. [24] proposed that increasing the content of Ca ions embedded in  $TiO_2$  significantly enhances apatite precipitation. Implant materials would be isolated by fibrous tissues if the growth of the tissues around the implant materials is faster than the apatite precipitation on the implant surfaces [25,26]. Therefore, it is far preferable to have implant materials that have the capability of inducing quicker apatite formation on their surfaces than the growth of fibrous tissues. Though Kokubo [27] proposed that early bonelike apatite formation on the material surface in SBF is an indicator of bone

bonding through the apatite layer in the living body, the bone-forming ability of materials still needs to be tested by in vivo experiments.

The conventional ion-implantation technique [21], which can incorporate a vast amount of Ca ions onto metallic substrates, is a line-of-sight process that poses a practical difficulty when treating medical implants with a complex shape, like porous scaffold [28]. Nevertheless, hydrothermal practice is suitable to deposit Ca ions onto Ti-based biomaterials with complex geometries as aqueous solution can easily reach every region within the geometry. Investigation of the hydrothermal Ca ion deposition technique with a saturated  $Ca(OH)_2$  solution (0.02 M), developed by Hamada et al. [23], has proved that the  $CaTiO_3$  layer generated on a Ti surface promotes apatite precipitation, though research about the influence of the content of deposited Ca ions on apatite precipitation is still rare. It was reported that a hydrothermally produced  $CaTiO_3$  layer on a commercially pure Ti implant by a mixture of NaOH and  $Ca(OH)_2$  enhances osteoconductivity of the commercially pure Ti implant with microrough surface. The  $CaTiO_3$  layer shows good mechanical properties and provides the Ti implant with apatite-inducing ability [29]. A highly adhesive apatite coating was produced on a Ca-ion-deposited Ti substrate, which was attributed to the formation of a  $CaTiO_3/TiO_2$  interlayer between the substrate and the resultant coating [30]. Three different saturated Ca aqueous solutions, namely  $Ca(NO_3)_2$ ,  $CaCl_2$  and  $Ca(OH)_2$ , were used to deposit various Ca ion contents on Ti under ambient conditions [31]. The best apatite-inducing ability was found on the Ti with the highest Ca content after soaked in the saturated  $Ca(OH)_2$  solution (0.02 M), though the Ca/Ti molar ratio on the Ti surface was far less than 1 (ca. 0.11). There have been few other efforts to intensify the Ca content.

In the present study, porous Ti substrates were fabricated by a special powder metallurgical method and then Ca ions were deposited hydrothermally in  $Ca(OH)_2$  solutions to five degrees of saturation at 200 °C for 8 h. The exact Ca ion content and surface morphology change on the Ti substrates generated by the different  $Ca(OH)_2$  solutions were examined by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. After soaking in m-SBF for different periods of time, SEM, X-ray diffraction (XRD), transmission electron microscopy (TEM), inductive coupled plasma spectrometry (ICP) and Fourier transform infrared spectroscopy (FTIR) were used to comprehensively characterize and determine the dependence of apatite-inducing ability on the Ca ion content of the Ti surfaces.

## 2. Materials and methods

### 2.1. Materials preparation

Porous Ti discs were prepared by a special powder metallurgical method which includes the burn-out of a space-

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