



# Hydroxyapatite formation on titania-based materials in a solution mimicking body fluid: Effects of manganese and iron addition in anatase



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## ARTICLE INFO

### Article history:

Received 30 July 2014

Received in revised form 12 November 2014

Accepted 7 December 2014

Available online 9 December 2014

### Keywords:

Titania

Surface characteristic

Zeta potential

Hydroxy group

Hydroxyapatite formation

## ABSTRACT

Hydroxyapatite formation on the surfaces of implanted materials plays an important role in osteoconduction of bone substitutes in bone tissues. Titania hydrogels are known to instigate hydroxyapatite formation in a solution mimicking human blood plasma. To date, the relationship between the surface characteristics of titania and hydroxyapatite formation on its surface remains unclear. In this study, titania powders with varying surface characteristics were prepared by addition of manganese or iron to examine hydroxyapatite formation in a type of simulated body fluid (Kokubo solution). Hydroxyapatite formation was monitored by observation of deposited particles with scale-like morphology on the prepared titania powders. The effect of the titania surface characteristics, i.e., crystal structure, zeta potential, hydroxy group content, and specific surface area, on hydroxyapatite formation was examined. Hydroxyapatite formation was observed on the surface of titania powders that were primarily anatase, and featured a negative zeta potential and low specific surface areas irrespective of the hydroxy group content. High specific surface areas inhibited the formation of hydroxyapatite because calcium and phosphate ions were mostly consumed by adsorption on the titania surface. Thus, these surface characteristics of titania determine its osteoconductivity following exposure to body fluid.

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## 1. Introduction

Titanium and its alloys are widely used in biomedical applications because of their high biological affinity in the body [1]. However, these materials do not directly bond to a living bone. Therefore, the biological affinity of titanium and its alloys can be enhanced by appropriate chemical treatments on their surfaces to achieve direct bonding to the living bone, a process termed as osteoconduction [2,3]. Chemical treatments on the surfaces of titanium and its alloys generate formation of amorphous titania (TiO<sub>2</sub>) hydrogel layer with Ti–OH groups on their surfaces by a suitable heat treatment. Ti–OH group works as a site of heterogeneous nucleation of hydroxyapatite under physiological conditions. Accordingly, chemically treated titanium can induce deposition of hydroxyapatite under physiological conditions [2–4]. Bone-like apatite formation on the surface of a substrate when implanted in bone defects is an indicator of osteoconductivity [5]. Accordingly, the osteoconductivity of hydrated titania substrates when implanted in bone tissues can be assessed by monitoring hydroxyapatite deposition on the titania surface. Hydrated titania is an important matrix employed to achieve high biological affinities, i.e., osteoconduction on its surface.

Treatment of titanium substrates with chemicals was followed by a heat treatment formed titania layer on their surface. This treatment

afforded the formation of hydroxyapatite with a similar inorganic phase to that of natural bone using a type of simulated body fluid (Kokubo solution) [2]. The formed hydroxyapatite is referred as bone-like apatite. Treatments of titanium substrates enabled osteoconduction in vivo on their surface [6] and the manufacture of a commercial prosthesis with trademark AHFIX® (KYOCERA Medical Co., Japan). Treatment of titanium substrates with H<sub>2</sub>O<sub>2</sub> solution also enabled osteoconduction [7–9]. Recent studies have proved that thermal oxidization of Ti–15Zr–4Ta–4Nb alloy with specific grooves results in hydroxyapatite formation in Kokubo solution [10]. Moreover, titania nanoparticles can induce hydroxyapatite formation when used as fillers in bioactive composites comprising high-density polyethylene [11]. The above reports suggest that titania has potential for inducing heterogeneous nucleation of hydroxyapatite under physiological conditions. Hydroxyapatite formation is influenced by the composition and crystalline phase of the titania substrate. Previously, we reported that the addition of aluminum (Al) and silicon (Si) in titania inhibited calcium phosphate surface deposition in Kokubo solution. In contrast, additive-free titania generated precipitates rich in calcium and phosphorus that were attributed to the formation of bone-like apatite following exposure of the titania substrate to the solution [12].

The effects of major parameters, i.e., crystal structure, zeta potential, and hydroxy group content, on the heterogeneous nucleation of hydroxyapatite on titania substrates have been extensively discussed. However, to date, the mechanism relating to the induction of

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hydroxyapatite formation remains unclear. To investigate the relationship between the characteristics of titania surfaces and their ability to induce hydroxyapatite formation, modification of the titania surface with additives can be performed to prepare titania substrates with varied characteristics. Previous reports indicated that the introduction of additives in titania using a sol–gel process led to a variation of surface characteristics of the resulting powders [13–16]. For instance, the surface charge of Al-added titania displayed a positive charge, whereas that of Si-added titania displayed a negative charge [12]. However, despite the anatase characteristic of the differently charged titania surfaces, the powders did not show potential for apatite formation in Kokubo solution.

In this study, titania powders were prepared with additives, manganese (Mn) or iron (Fe), and their ability to induce surface hydroxyapatite formation in Kokubo solution was examined. Primary anatase-form titania was obtained using 0–10 mol% additive, followed by firing at 600 °C. The performance of the Mn- and Fe-added titania samples was compared with that of additive-free and Al- and Si-added titania samples.

## 2. Experimental

### 2.1. Preparation of titania powders

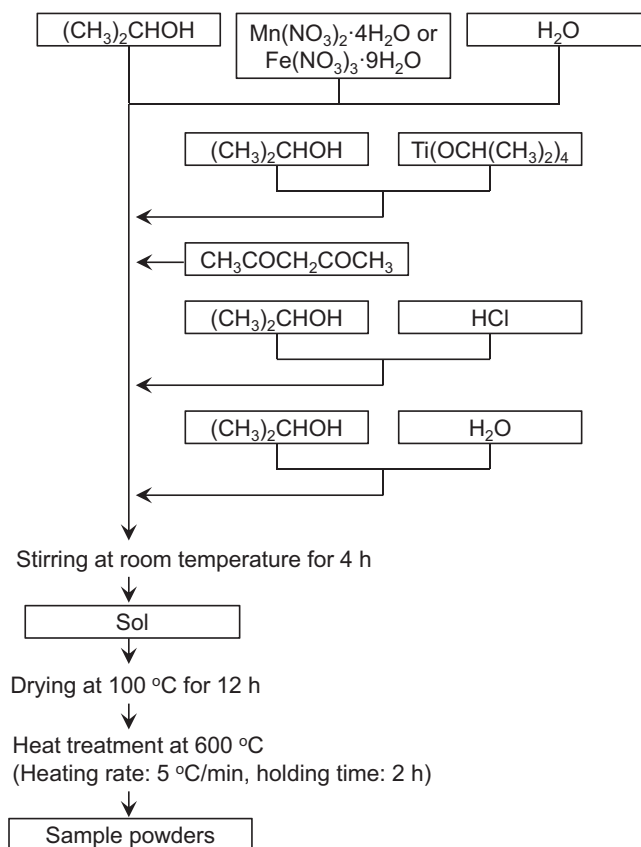
Titania powders containing either Mn or Fe were prepared by a sol–gel method. The additive was incorporated at a nominal composition ranging from 0 to 10 mol%. The theoretical compositions of the samples are summarized in Table 1. The synthetic procedure is shown in Fig. 1. All the chemicals were used as received without further purification. Titanium isopropoxide ( $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ; 97%, Sigma-Aldrich Co., LLC.), manganese(II) nitrate tetrahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; 98%, Sigma-Aldrich Co., LLC.), and iron(III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; 99%, Wako Pure Chemical Industries Ltd., Japan) were purchased as reactants.  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$  was mixed with acetylacetone ( $\text{CH}_3\text{COCH}_2\text{COCH}_3$ ; 99%, Sigma-Aldrich Co., LLC.) in isopropyl alcohol (iPrOH,  $(\text{CH}_3)_2\text{CHOH}$ ; 99%, Kishida Chemical Co., Ltd., Japan) under stirring at room temperature for 60 min to obtain  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$  solution.  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in iPrOH solution under stirring at room temperature for 30 min to obtain the additive precursor solution. Then, the latter precursor solution was mixed with the  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$  solution, after which dilute hydrochloric acid (HCl; 37%, Nacalai Tesque Inc., Japan) and ultra-pure water were added. The resulting solution was stirred at room temperature for 120 min. The obtained titania sol was dried at 100 °C and then calcined in an electric furnace. The sample was heated to 600 °C at a rate of 5 °C/min, maintained at 600 °C for 120 min, and then allowed to naturally cool. The resulting powders with Mn or Fe are denoted as TM<sub>x</sub> and TFe<sub>x</sub>, respectively, where *x* refers to the nominal concentration (mol%) of the additive.

### 2.2. Analysis of the powders

The crystalline phase of TM<sub>x</sub> and TFe<sub>x</sub> was determined by powder X-ray diffraction (RINT-2000, Rigaku Co., Ltd., Japan) with Cu K $\alpha$  radiation source. The surface of the powders was observed under a scanning

**Table 1**  
Starting compositions of the powders.

Sample	Reactant (molar ratio)		
	$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
TMn01	99	1	0
TMn03	97	3	0
TMn05	95	5	0
TMn10	90	10	0
TFe01	99	0	1
TFe03	97	0	3
TFe05	95	0	5
TFe10	90	0	10



**Fig. 1.** Synthetic procedure of the powders containing either Mn or Fe at varying compositions.

electron microscope (SEM; JSM-5600, JEOL Co., Ltd., Japan) and their finer morphology was observed under a transmission electron microscope (TEM; H-800, Hitachi Co., Ltd., Japan). The actual compositions of the powders were determined by energy-dispersive X-ray (EDX; JEM 2300, JEOL Co., Ltd., Japan) spectroscopy. The Brunauer–Emmett–Teller (BET) method was applied to measure the specific surface area of the powders on a NOVA1000e (Quantachrome Instrument, USA). Zeta potential analysis of the powders was conducted in 10 mol/m<sup>3</sup> sodium chloride (NaCl) solution at pH 7.4, adjusted with dilute sodium hydroxide (NaOH), using a flow-type cell on a zeta potential analyzer (ELS-Z1, Otsuka Electronics Co., Ltd., Japan). X-ray photoelectron spectroscopy (XPS; JPS-9000MC, JEOL Co., Ltd., Japan) using Al K $\alpha$  X-ray source was employed to determine the relative amount of hydroxy groups in the titania samples.

### 2.3. Evaluation of hydroxyapatite formation

Hydroxyapatite formation on the surface of the prepared powders was investigated using Kokubo solution. According to a previous report [17], 1 dm<sup>3</sup> Kokubo solution was prepared by dissolution of 7.996 g NaCl, 0.350 g NaHCO<sub>3</sub>, 0.224 g KCl, 0.228 g K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, 0.305 g MgCl<sub>2</sub>·6H<sub>2</sub>O, 0.278 g CaCl<sub>2</sub>, 0.071 g Na<sub>2</sub>SO<sub>4</sub>, and 6.057 g tris(hydroxymethyl)aminomethane ((CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub>); appropriate amounts of HCl were used to adjust the solution pH to 7.4 at 36.5 °C. Then, 0.1 g of the prepared powder was immersed in 30 cm<sup>3</sup> of Kokubo solution, and the temperature was maintained at 36.5 °C. After soaking for 14 days (d), the powders were removed from the Kokubo solution by filtration and washed adequately with ultrapure water. The powders were then dried at 50 °C for 24 h.

Deposition of hydroxyapatite on titania surface was determined by selected area electron diffraction (SAED; H-800, Hitachi Co., Ltd., Japan). The concentrations of calcium (Ca) and phosphorus (P) of the

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