

Mechanism and kinetics of apatite formation on nanocrystalline TiO₂ coatings: A quartz crystal microbalance study

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Abstract

Apatite (Ca₅(PO₄)₃OH) has long been considered as an excellent biomaterial to promote bone repairs and implant. Apatite formation induced by negatively charged nanocrystalline TiO₂ coatings soaked in simulated body fluid (SBF) was investigated using in situ quartz crystal microbalance (QCM), scanning electron microscopy (SEM), Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) techniques, and factors affecting its formation such as pH, size of TiO₂ particles and thickness of TiO₂ coatings, were discussed in detail. Two different stages were clearly observed in the process of apatite precipitation, indicating two different kinetic processes. At the first stage, the calcium ions in SBF were initially attracted to the negatively charged TiO₂ surface, and then the calcium titanate formed at the interface combined with phosphate ions, consequently forming apatite nuclei. After the nucleation, the calcium ions, phosphate ions and other minor ions (i.e. CO₃²⁻ and Mg²⁺) in supersaturated SBF deposited spontaneously on the original apatite coatings to form apatite precipitates. In terms of the in situ frequency shifts, the growth-rate constants of apatite (K_1 and K_2) were estimated, respectively, at two different stages, and the results were $(1.96 \pm 0.14) \times 10^{-3} \text{ s}^{-1}$ and $(1.28 \pm 0.10) \times 10^{-4} \text{ s}^{-1}$, respectively, in 1.5 SBF solution. It was found that the reaction rate at the first stage is obviously higher than that at the second stage.

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1. Introduction

Many investigations have demonstrated that TiO₂ possesses excellent biocompatibility and bioactivity [1–5]. In fact, the well-known property of TiO₂ is closely related to the existence of abundant titanium hydroxide groups on its surface [6]. TiO₂ films are of interest as they can combine properties of optical transparency, nontoxicity, ease of fabrication, chemical stability and high surface area (often 1000 times higher than its geometric area) [7]. Recently, porous TiO₂ films produced by depositing the oxide in colloidal form onto a solid substrate have been widely

employed to immobilize proteins, enzymes or other biomolecules on an electrode surface for either mechanistic study of the proteins or fabricating biosensors [8–10]. Apatite, an excellent biomaterial, has been used intensively in such fields as bone repairs, bone implant and bioactive materials due to its excellent biocompatibility, slow biodegradation, osteoconductivity and mechanical properties [11–14]. It has been demonstrated that the apatite precipitates can be formed biomimetically on TiO₂ surface in SBF with ion concentrations nearly equal to those of human blood plasma [14–19]. The heterogeneous nucleation and growth of apatite induced by negatively charged TiO₂ surface is a complicated process. To our knowledge, previous investigation mainly focused on apatite preparation; the mechanism and kinetics of apatite precipitation on nanocrystalline TiO₂ coatings have not been explored in detail, so far.

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A piezoelectric quartz crystal microbalance (QCM) is an effective tool due to its extreme sensitivity to the nanogram level of mass change loaded onto its surface. As a mass sensor, QCM has been widely used in biochemistry, environment, food, and clinical analysis because the technology provides a label-less method for the direct study of biospecific interaction process [20–24]. With immobilized antibodies on the surface of crystal, some QCM immunosensors have been employed for the detection of viruses [25,26], proteins [27,28], bacteria [29,30], and DNA [31]. QCM has also been successfully used to investigate hydroxyapatite formation on self-assembled monolayers in supersaturated solution [32,33].

In the present study, to obtain a comprehensive understanding of the mechanism and kinetics of apatite formation on nanocrystalline TiO₂ coatings in SBF, a QCM device has been employed to in situ monitor the nucleation and growth of apatite. The obtained apatite was characterized by scanning electron microscopy (SEM), Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX).

2. Experimental

2.1. Materials

Anatase TiO₂ particles with 5 nm (P5) and 25 nm (P25) were purchased from Hangzhou Wanjing Co. (Hangzhou, China). All other chemicals were of analytical reagent grade obtained from Shanghai Chemical Reagent Co. (Shanghai, China). Deionized (DI) water (resistivity of 18 MΩ cm) was obtained from a Milli-Q system (Millipore Inc.), and was used for rinsing and for makeup of all aqueous solutions.

The SBF containing ion concentrations similar to those in human blood plasma was prepared by dissolving analytical-grade chemicals of NaCl, KCl, NaHCO₃, Na₂SO₄, K₂HPO₄ · 3H₂O, MgCl₂ · 6H₂O and CaCl₂ · 2H₂O into deionized water, and buffered at the desired pH (7.4) with tris(hydroxymethyl)aminomethane ((CH₂OH)₃CNH₂) and hydrochloric acid at 37 °C. The SBF with other concentrations was obtained by the same method and ion concentrations in the prepared SBF are shown in Table 1. SBF (1.5)

at pH 7.4 was employed in our experiments, unless otherwise stated.

2.2. Apparatus

QCM measurements were performed using a Q-sense instrument (Gothenburg, Sweden). Mechanically polished AT-cut 9 MHz quartz crystals (diameter of 12 mm, Beijing Chenjing Co., Beijing, China) were vacuum-deposited with gold electrodes (6 mm diameter) on both sides of the surface. To reduce background frequency drift, one electrode was completely insulated from the test liquid. This was accomplished by mounting a glass cover slip over one side of the quartz crystal, which was held in place by two silicon o-rings. The o-rings were large enough (10 mm) so that they could make contact only with the exposed quartz peripheral to the centrally located electrode and not with the electrode itself. Thus, the covered electrode was in contact only with air. This covering assembly was held in place using silicone glue. The electrical contacts were insulated from the test solution using silicon tubing and silicone glue, and only one electrode was exposed to the test solution. The working crystal was connected to a home-made oscillator. Both the detector cell and the oscillator were put in a copper Faradaic cabin to remove the surrounding electromagnetic noise. The frequency was monitored by a frequency counter (Iwatsu, Model SC-7201), and the recorded data were stored in a computer. The characteristic constant of the quartz crystal (*K*) was determined experimentally by electrodepositing Ag from a solution containing 40 mM of AgNO₃. Assuming that the Ag electrodeposition process is 100% efficient, the mass sensitivity of the quartz crystal was determined from the recorded frequency change and the charge obtained by integration of the current. The calibrated value of *K* was 5.7 ng Hz⁻¹ cm⁻² for the frequency change within 10⁴ Hz.

Apatite precipitates formed on TiO₂ coatings were characterized by SEM (JEOL JSM-5400, Japan), FTIR (Model 883, Perkin–Elmer Optoelectronics Inc., USA), XRD (Model RU 200, Rigaku Co., Tokyo, Japan) and EDX (VOYAGER, NORAN Instrument Co., Middletown, WI, USA). The changes in the concentrations of calcium and phosphate ions in SBF after soaking were measured

Table 1
Ion concentrations in human blood plasma (HBP) and simulated body fluid (SBF)

	Ion concentration (mM)							
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻
HBP	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5
0.6 SBF	142.0	5.0	1.5	1.5	147.8	4.2	0.6	0.5
1.0 SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5
1.5 SBF	142.0	5.0	3.75	1.5	147.8	4.2	1.5	0.5
1.5 SBF (Ca ²⁺ = 0)	142.0	5.0	0	1.5	147.8	4.2	1.5	0.5
1.5 SBF (HPO ₄ ²⁻ = 0)	142.0	5.0	3.75	1.5	147.8	4.2	0	0.5
1.8 SBF	142.0	5.0	4.5	1.5	147.8	4.2	1.8	0.5
2.5 SBF	142.0	5.0	6.25	1.5	147.8	4.2	2.5	0.5

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