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Dependence of ion concentration in simulated body fluid on apatite precipitation on titania surface

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ABSTRACT

Titanium and its alloys are used as biomaterials, because of their high biocompatibility. Apatite precipitates on a titania surface in vivo, and living bone and titanium alloy are coupled through the thin apatite layer. The initial precipitation behavior of apatite on titania in simulated body fluid (SBF) solutions was evaluated and the effect of inorganic ions in the SBF was investigated. Measurement using the SPR phenomenon was used to evaluate the initial apatite precipitation. An SBF containing approximately equal ion concentrations to those in blood plasma was added to a titania surface and the SPR profile was obtained, from which the initial apatite precipitation rate was found to be 1.14 nm/h. Furthermore, the relationship between the inorganic concentration and the precipitation rate was determined for SBFs with different Na^+ and Ca^{2+} concentrations. Apatite precipitation did not occur in the SBF with a low Na^+ concentration, whereas the initial apatite precipitation rate in the SBF that did not contain Ca^{2+} was 0.32 nm/h. According to these results, Ca^{2+} has little effect on the initial apatite precipitation. In the initial reaction of apatite precipitation, sodium titanate is formed by the absorption of Na^+. Next, calcium titanate precipitates upon the substitution of Na^+ with Ca^{2+}. Finally, Na^+, phosphate ions and hydroxyl ions are attracted to the surface and apatite is formed. Thus, the rate-limiting factor in the initial nucleation of apatite is the Na^+ concentration.

1. Introduction

Titanium (Ti) metal and its alloys exhibit high corrosion resistance and biocompatibility, and are thus used as biomedical implants such as artificial human bone [1], dental implants [2] and artificial hip joints [3]. The titanium surface is covered by a titanium oxide (titania) film of 1–5 nm thickness [4]. When considering the use of a Ti alloy as a biomaterial, it is important to investigate the surface reaction of titania in vivo. When titanium is embedded in a living body, hydroxyapatite is deposited on the titania on the titanium surface [5]. Hydroxyapatite has a similar chemical composition and crystal structure as the apatite in the human skeletal system [6]. Therefore, it is suitable for bone substitution and reconstruction. The precipitation reaction of apatite is as follows [5].

$$10Ca^{2+} + 6PO_4{}^{3-} + 2OH^- \rightleftarrows Ca_{10}(PO_4)_6(OH)_2 \quad (1)$$

First, titania absorbs water in the air or solution and titanium hydroxide is formed on the titania surface [7]. Hydroxyl groups are negatively charged; thus, Ca^{2+} in body fluids is bound and calcium titanate is formed. Next, $PO_4{}^{3-}$ is bound and calcium phosphate is formed. Finally, Ca^{2+} and $PO_4{}^{3-}$ are absorbed at the surface and the calcium phosphate changes to crystalline apatite [8].

The Na^+ and Ca^{2+} concentrations in normal human plasma are 135–145 and 8.2–10.0 mmol/L, respectively [9]. Because these are individual differences in inorganic ion concentrations in the plasma of normal humans, there are individual differences in the fixing rate of biological materials in vivo. It is important to determine which inorganic ions in body fluid are affected by apatite precipitation on a titania surface. Some researcher indicated dependence of these ionic concentrations. Effect of ions concentration such as Ca or Na on apatite formation was studied by observation images of scanning electron microscope (SEM) [10–13]. In these reports, the observed apatite participations are above nanometer which is enough to observe by SEM. Important point for the participation control is an initial participation such as nucleation less than sub-nanometer that is atomic level.

In the evaluation of the biocompatibility of a biomaterial with bone, the in vivo method of embedding the biomaterial in the body has been used [14]. Furthermore, in vitro evaluation methods using a simulated body fluid (SBF) have also been used [15].

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An SBF has ion concentrations approximately equal to those in human blood plasma [16]. The conventional methods of evaluating apatite precipitation take a long time; thus, the initial behavior of apatite precipitation has not been accurately elucidated [17]. And these reports also investigated by observations for the formation of the apatite which is above 1 nm or more in size. Mcleod et al. reported an initial apatite participation by X-ray photoelectron spectroscopic analysis [18]. In their report, participation rate depended on the SBF type and the initial participation of apatite was started at 30 min after the immersion test using these SBFs. From these reports, it can be considered that an initial participation of apatite such as sub-nanometer-thick was affected by contents of SBF solution.

An initial participation such as nucleation less than sub-nanometer is required to understanding influence of these ionic elements. A real-time measurement method using the surface plasmon resonance (SPR) phenomenon is well known as detected able method for the change in sub-nanometer. [19,20].

SPR is the resonance between a surface plasmon wave and an evanescent wave [21–24]. An incident *p*-polarized light wave is totally reflected at the surface of a thin metal film such as a gold or silver film through an optical prism. Then an evanescent wave is generated at the metal surface [23]. The evanescent wave penetrates the metal film and excites a surface plasmon wave [24]. By solving the Maxwell equations with suitable boundary conditions, the dispersion relation of a surface plasmon wave is obtained as follows:

$$K_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_s}{\varepsilon_m + \varepsilon_s}}. \quad (2)$$

where K_{sp} is the wave number of the surface plasmon wave, ω is the angular frequency of the light, c is the velocity of light in vacuum, and ε_m and ε_s are the complex dielectric constant of the metal and the dielectric constant of the sensing medium, respectively [25]. The dispersion relation of an evanescent wave at the interface between metal and a sensing medium is

$$K_{ev} = n_p \frac{\omega}{c} \sin\theta. \quad (3)$$

where K_{ev} is the wave number of the evanescent wave, n_p is the reflective index of the optical prism and θ is the incident angle [26]. When K_{sp} and K_{ev} are equal, SPR is excited. When the electric field energy of the incident light is at this resonance condition, the intensity of the reflected light is significantly reduced. SPR occurs under this condition [27]. The SPR angle under the resonant condition is expressed as follows from Eqs. (2) and (3):

$$\theta_{SPR} = \sin^{-1}\left(\frac{1}{n_p}\sqrt{\frac{\varepsilon_m \varepsilon_s}{\varepsilon_m + \varepsilon_s}}\right). \quad (4)$$

By sweeping the incident angle of the laser light, the SPR angle is obtained from the profile of the reflected light intensity. The SPR angle depends on the dielectric constant of the space above the metal film. Thus, the change in the complex reflective index above the metal film is obtained by measuring the SPR angle. SPR measurement can be used to detect the adsorption of a substance on an inorganic material surface with high accuracy [28,29]. The dielectric constant of a solid is higher than that of a liquid. When a solid is precipitated above a metal, the dielectric constant increases and the SPR angle is shifted. Hence, it is possible to detect the initial precipitation of a solid.

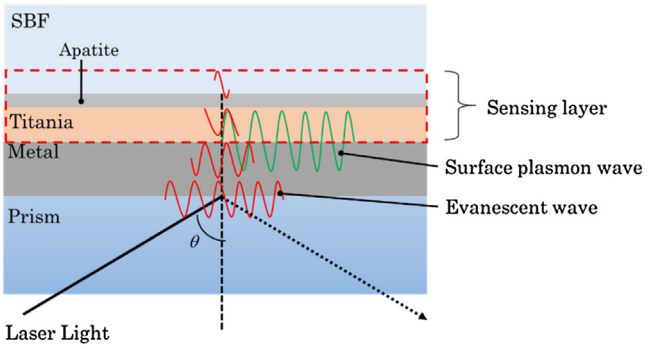

Fig. 1. The schematic illustration of penetration depth of evanescent wave. θ; incident angle of laser light.

In this study, titania was deposited on a Ag layer and an SBF was placed on the titania layer surface, as shown in Fig. 1. The system shown in Fig. 1 can be used to evaluate initial apatite precipitation by observing changes in the complex dielectric index of the system, which contains a titania layer, an apatite layer and the SBF above the metal surface. The complex dielectric constant on the metal layer increases upon apatite precipitation and the SPR angle also increases.

2. Experimental method

The device used for SPR detection had a multilayer structure. An S-TIH-11 optical glass substrate with dimensions of 25 mm × 25 mm × 1 mm and a refractive index of 1.778 was used as a substrate. A Ag layer of 35 nm thickness was deposited on the glass substrate followed by a titania layer of 10 nm thickness. The Ag layer was deposited by magnetron sputtering using Ag target (99.99%). The Ti layer was deposited by the same magnetron sputtering system using a Ti target (99.5%). After that, the Ti layer was oxidized by oxygen plasma irradiation. The deposited Ti sample was put in to vacuum chamber. An oxygen gas was introduced to chamber by 20 cm_3/min, and a pressure was controlled to 4 Pa by valves connected to vacuum pumps. A 10 kV 2 kHz pulse voltage was applied between the chamber and the substrate. Machine detail was shown the our old paper [30]. An oxygen plasma was generated around the substrate holder. A titania film was synthesized by the diffusion of oxygen ions into the Ti film.

The Kretchmann configuration was adopted for the SPR sensing system to achieve a resonant condition [31]. This Kretchmann configuration is mainly used in SPR measurement because it can be

Table 1
Ion concentrations of blood plasma and SBFs.

	Ion concentration (mM)							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO^{3-}	HPO_4^{2-}	SO_4^{2-}
Blood Plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5
m-SBF	142.0	5.0	1.5	2.5	103.0	10.0	1.0	0.5
SBF(0NaCl)	35.0	5.0	1.5	2.5	11.0	10.0	1.0	0.5
SBF(0.5NaCl)	96.3	5.0	1.5	2.5	57.2	10.0	1.0	0.5
SBF(1.5NaCl)	188.7	5.0	1.5	2.5	149.7	10.0	1.0	0.5
SBF(0$CaCl_2$)	142.0	5.0	1.5	0.0	100.4	10.0	1.0	0.5
SBF(1.5$CaCl_2$)	142.0	5.0	1.5	3.8	104.3	10.0	1.0	0.5