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Apatite formation on titania–vaterite powders in simulated body fluid

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Abstract

Titania–hydroxyapatite composites were prepared by soaking compacts of a powder mixture consisting of crystalline titania and calcium carbonate (vaterite) to form apatite in simulated body fluid (SBF). The apatite crystal formed on compacts in SBF at 37 °C within 2 days. The apatite-forming ability of the mixtures was much higher than that of titania crystals such as anatase or rutile on their own. Calcium carbonate (vaterite), which has high solubility in the aqueous solution, plays an important role in the apatite formation; the dissolution is suggested to increase the supersaturation of the apatite in SBF. Formation of titanium hydroxide groups, which may induce the apatite formation, is drastically promoted on the powder-compacts by the soaking in SBF, independently of the structures of the titania crystals (anatase or rutile). The apatite formation on the compact of the titania–calcium carbonate (vaterite) powder mixture containing the anatase phase occurs in a shorter period than that on the one of titania (rutile)–calcium carbonate (vaterite). Crystalline titania (anatase phase) is suggested to be particularly effective in inducing the apatite nucleation.

Keywords: Apatite; Composites; Functional applications; TiO_2; Vaterite

1. Introduction

When titania crystals are illuminated with light, they oxidize organic chemicals in water and air;[1,2] they can be used for environmental purification or as an antibacterial material. Hydroxyapatite, on the other hand, was reported to be useful in absorption of bacteria, viruses, NO_x, and/or ammonia.[3,4] Titania–hydroxyapatite composites were suggested to be applicable as environmental materials having the abilities to absorb bacteria and/or organic matters and subsequently to decompose them using photocatalytic activities.[5] The composites can be prepared by soaking crystalline titania (anatase) in a tris-buffer solution containing calcium and phosphorous ions.[5]

Titania has a tendency to adsorb water at the surface, resulting in formation of titanium hydroxide groups, i.e., acidic TiOH groups and basic Ti–OH groups.[6] pK_a values for the acidic TiOH group and basic Ti–OH group are 2.9 and 12.7, respectively.[7] In a tris-buffer solution with pH ~7.4, the TiOH group is suggested to be neutralized and the Ti–OH group has to dissociate; the surface of titania is then negatively charged. We previously reported that light-illumination in simulated body fluid (SBF),[8] which is a tris-buffer solution with inorganic ion concentrations almost equal to those of human plasma, when applied to crystalline titania powder-compacts having high photocatalytic activities, enhances apatite formation. Numerous Ti–OH groups form on the surface after the light-illumination in SBF.[9] The Ti–OH group at the surface is suggested to induce nucleation of apatite.[10] Another condition needed for the apatite formation is an increase in the supersaturation of the apatite.[11]

We reported earlier that composites consisting of poly(lactic acid) (PLA), which hydrolyzes to form carboxy groups that are known to induce the apatite nucleation,[12] and calcium carbonates containing a large amount of vaterite with a large surface area have extraordinarily high apatite-forming ability in SBF.[13] Some of the carboxy groups bond with Ca^{2+} ions and the supersaturation of apatite in SBF increases much rapidly due to the faster dissolution of the nano-sized

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vaterite. As a result, the apatite forms on the composites in SBF within 3 h.

In the present work, the apatite deposition on powder-compacts consisting of titania (anatase) and calcium carbonate (vaterite) during soaking in SBF was examined for preparation of titania–hydroxyapatite composites. Apatite formation on titania consisting of the rutile phase was also examined to clarify the importance of the phase type.

2. Experimental procedure

Calcium carbonates consisting predominantly of vaterite were prepared via a carbonation process in methanol.[14] CO_2 gas was blown for 1 h at a flow rate of 300 ml/min into the suspension consisting of 4.6 g of $Ca(OH)_2$ in 120 ml of methanol at room temperature in a Pyrex© beaker. The specific surface area of the obtained calcium carbonates was determined to be 40

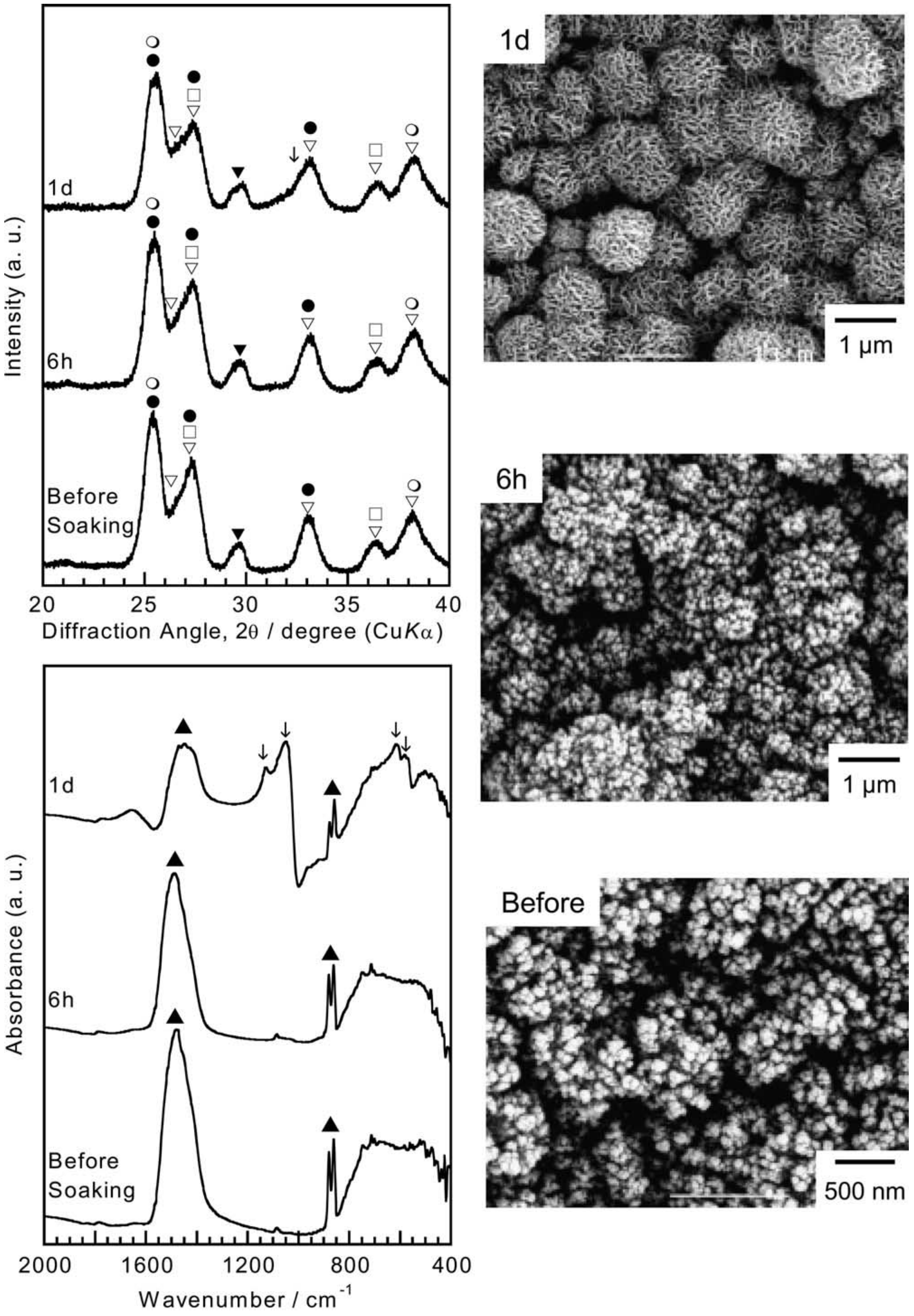

Fig. 1. TF–XRD and FT-IRRS spectra, and SEM micrographs of T(A)-C powder-compacts before and after soaking in SBF. In TF–XRD spectra; (↓) apatite, (○) anatase, (□) rutile, (●) vaterite, (▼) calcite, and (▽) aragonite. In FT-IRRS spectra; (↓) apatite and (▲) CO_3^{2-}.

m^2/g by a nitrogen gas sorption analysis. After CO_2 bubbling, 2 g of titania powder was added to the suspension and mixed with a magnetic stirrer for 5 min. The ratio of titania/calcium carbonates in the mixtures was 1/3 by weight. The mixtures were dried at 100 °C for 1 day. Two kinds of TiO_2 powders (P25S6, received from Nippon Aerosil, and TiO-3, received from JRC) were used in the present work. P25S6 contains crystalline phases of 80% anatase and 20% rutile with an average primary particle size of 21 nm and a surface area of 50 m^2/g. TiO-3 consists of crystalline rutile with an average primary particle size of ~30 nm and a surface area of 40 m^2/g. Roughly, these powders are comparable in having a large surface area and fine-sized particles. P25S6 and TiO-3 are denoted by T(A) and T(R), respectively. Average cluster particle sizes of T(A) and T(R) were measured to be 2.2 and 3.4 μm, respectively, by a light-scattering method. The powder mixtures consisting of titania and calcium carbonate were pressed isostatically at 100 MPa to obtain disk-shaped compacts of 20 mm diameter×1.6 mm thickness. The powder-compacts containing T(A) or T(R) are denoted by T(A)-C or T(R)-C, respectively.

T(A)-C and T(R)-C powder-compacts were soaked under static conditions in a 100 ml of SBF (consisting of 2.5 mM of Ca^{2+}, 142.0 mM of Na^+, 1.5 mM of Mg^{2+}, 5.0 mM of K^+, 148.8 mM of Cl^-, 4.2 mM of HCO_3^-, 1.0 mM of HPO_4^{2-}, and 0.5 mM of SO_4^{2-} that included 50 mM of $(CH_2OH)_3CNH_2$ and 45.0 mM of HCl) at pH 7.4 at 37 °C. The ratio of sample surface area (S) to SBF volume (V), S/V, was adjusted to be 0.16 cm^{-1}. After the soaking, the samples were removed from the SBF and were gently washed with distilled water. They were dried at room temperature. Surface of the compacts before and after the soaking was analyzed by a X-ray diffractometer equipped with a thin-film attachment (TF–XRD), at a glacing angle of 1° and by Fourier transform infrared reflection spectroscopy (FT-IRRS). The surface morphology was observed by scanning electron microscopy (SEM). X-ray photoelectron spectra (XPS) of the O_{1s} level for the compacts before and after soaking in SBF were measured under an ultra high vacuum (~10^{-7} Pa) using monochromatized Al-$K\alpha$ X-ray irradiation. The binding energy was normalized to the C_{1s} energy.

3. Results and discussion

3.1. Apatite formation on powder-compacts consisting of titania containing anatase and calcium carbonate containing vaterite

Fig. 1 shows TF-XRD and FT-IRRS spectra, and SEM micrographs of T(A)-C powder-compacts before and after soaking in SBF. Numerous nanoparticles with diameters of ~100 nm can be seen in the SEM micrograph before the soaking. The TF–XRD spectrum before the soaking show that T(A)-C consists of anatase, rutile, and vaterite, with small amounts of calcite and aragonite. In the TF–XRD and FT–IRRS spectra and the SEM micrograph after 6 h of the soaking, almost no significant change is observed. The spectra show that the apatite forms after soaking for 1 day. In the SEM micrograph after 1 day of soaking, the surface of T(A)-C is completely covered with the leaf-like nanodeposits, which are hydroxyapatite, judging from the morphology and the TF-XRD and FT-IRRS spectra. Newly formed calcite was not observed via the SEM and TF-XRD analysis. A large amount of Ca^{2+} ion from dissolution of vaterite with a large surface area is suggested to increase the supersaturation of the apatite in the SBF, resulting in the precipitation of the apatite prior to conversion of vaterite into calcite. In our preliminary experiments, on the T(A) compacts, no apatite formed even after soaking for 30 days.[9] In comparison with the T(A) compacts, the T(A)-C compacts have much higher apatite-forming ability.

Changes in the amounts of titanium hydroxide groups on the surface of the T(A) compacts were examined using XPS of the O_{1s} levels before and after the soaking in SBF. The spectra were deconvoluted into three Gaussian component peaks as reported by Sham and Lagarus:[15] 529.5 eV; O in surface oxide lattices (denoted by TiO_2), 531.4 eV; O in acidic TiOH groups and physisorbed H_2O (denoted by TiOH, bridging OH groups) and 532.2 eV; O in basic Ti–OH groups (denoted by Ti–OH, terminal OH groups). Since the spectra of the T(A)-C compacts also include information on calcium carbonates consisting predominantly of vaterite, they were deconvoluted into four Gaussian component peaks, including 531.8 eV; O in vaterite.[16] Fig. 2 shows O_{1s} XPS spectra of the T(A)-C compacts before and after soaking in SBF. As found in Fig. 1, no apatite

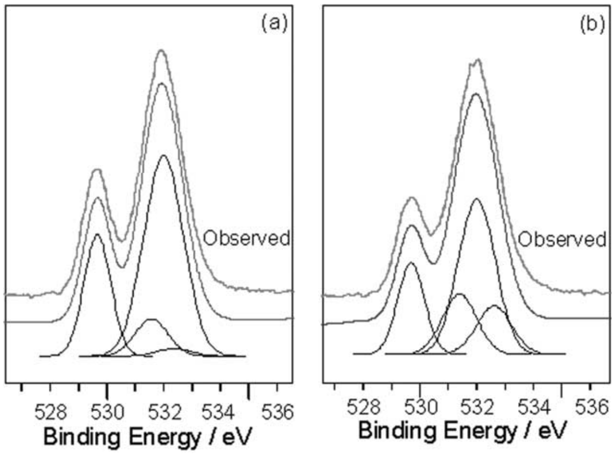

Fig. 2. XPS O_{1s} spectra of the surfaces of T(A)-C powder-compacts. (a) before and (b) after 6 h of the soaking in SBF.

formation occurs after 6 h of soaking. However, significant differences between the spectra can be seen. To emphasize this, the relative ratios of their peak areas are shown in Table 1. Almost no changes in the ratios are seen between before and after soaking T(A). Since the XPS spectra were measured for the dried samples under an ultra high vacuum, water adsorbed at the surface was supposed to decrease during the XPS measurements. The relative ratios of titanium hydroxide groups on the T(A)-C compacts before the soaking are comparably small. After 6 h of the soaking, the ratios of titanium hydroxide groups on the compacts increase and they are comparably higher than those on the T(A) compacts. Vaterite peaks of the compacts decrease extremely due to the dissolution. It is proposed that the amount of titania particles, which come into contact with water,

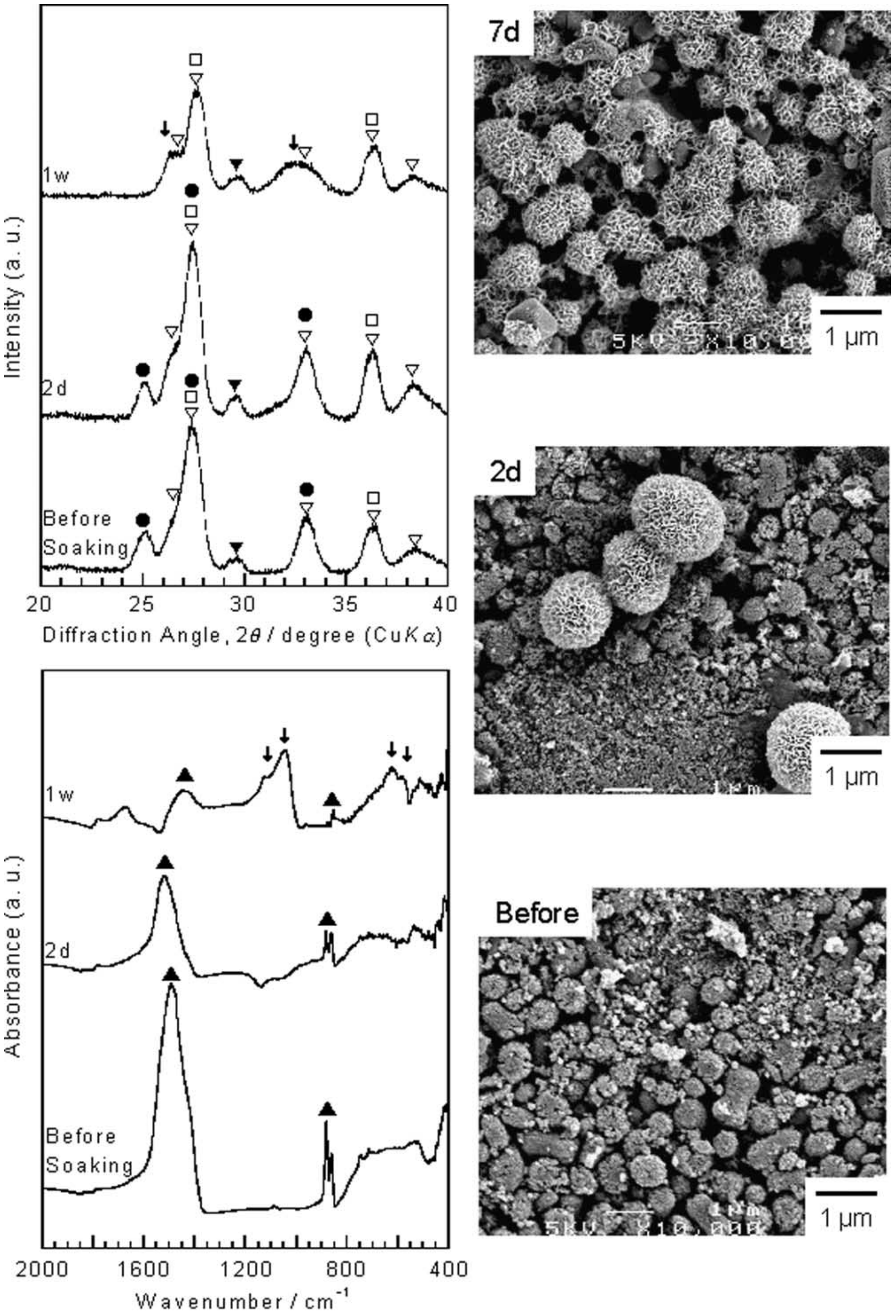

Fig. 3. TF–XRD and FT-IRRS spectra, and SEM micrographs of T(R)-C powder-compacts before and after soaking in SBF. In TF–XRD patterns; (↓) apatite, (□) rutile, (●)vaterite, (▼) calcite, and (▽) aragonite. In FT-IRRS spectra; (↓) apatite and (▲;) CO_3^{2-}.

Table 1
Percentage areas of the TiO_2, TiOH, and Ti–OH and calcium carbonate (vaterite) peaks obtained by deconvoluting the XPS O_{1s} spectra of the surface of the T(A) and T(A)-C compacts before and after soaking in SBF

Sample	Percentage area of the deconvoluted peaks			
	TiO_2	TiOH	Ti–OH	Vaterite
T(A) before soaking	93.3	4.2	2.5	
T(A) after soaking for 6 h in SBF	87.8	9.3	2.9	
T(A)-C before soaking	25.8	9.8	2.1	62.3
T(A)-C after soaking for 6 h in SBF	20.6	17.5	14.3	47.6

Table 2
Percentage areas of the TiO_2, TiOH, Ti–OH, and calcium carbonate (vaterite) peaks obtained by deconvoluting the XPS O_{1s} spectra of the surface of the T(R) and T(R)-C compacts before and after soaking in SBF

Sample	Percentage area of the deconvoluted peaks			
	TiO_2	TiOH	Ti-OH	Vaterite
T(R) before soaking	88.3	9.7	2.0	
T(R) after soaking for 6 h in SBF	89.2	8.1	2.7	
T(R)-C before soaking	17.2	5.5	3.4	73.9
T(R)-C after soaking for 6 h in SBF	12.4	15.9	13.8	57.9

increases after the dissolution of vaterite, resulting in an increase in the amount of the adsorbed water around the surface. At an early stage in the formation of hydroxyapatite in SBF, Ca^{2+} ion was suggested to make a bond with the functional groups to induce apatite nucleation.[17] The negatively charged units on titania would be postulated to interact selectively with the positively charged calcium ions in the fluid. An excellent apatite-forming ability on the titania–calcium carbonates compacts is suggested to originate from rapid formation of a bond between Ti–OH and Ca^{2+} ion, which is released into SBF due to the dissolution of the vaterite in the compacts, and from the associated increase in the supersaturation of apatite in SBF.

3.2. *Apatite formation on powder-compacts consisting of titania (rutile) and calcium carbonate containing vaterite*

Titania (rutile) also has photocatalytic activities. In comparison with the anatase phase, the rutile phase has much lower activities.[18] In the present work the apatite-forming ability of a powder mixture containing titania (rutile) was also examined.

Fig. 3 shows TF–XRD and FT-IRRS spectra, and SEM micrographs of T(R)-C powder-compacts before and after soaking in SBF. Although no significant changes are seen in the TF–XRD and FT-IRRS spectra after 2 days of soaking, the SEM micrograph shows some newly formed particles. The TF-XRD and FT-IRRS spectra show that the apatite forms after soaking for 7 days. On the T(A)-C compacts, apatite formed after soaking for 1 day. The apatite-forming ability on T(A)-C is higher than that on T(R)-C.

Changes in the amounts of titanium hydroxide groups on the surface of the T(R) and T(R)-C compacts were also examined using XPS of the O_{1s} levels before and after the soaking in SBF. The relative ratios of their peak areas are shown in Table 2. Changes in the ratios on the surface of T(R) and T(R)-C are similar to those on the surface of T(A) and T(A)-C, respectively. After 6 h of soaking, the ratios of titanium hydroxide groups on the compacts increase independently of the crystal structure (anatase or rutile).

These results indicate that the apatite-forming ability of the anatase phase is higher than that of the rutile phase. It has been suggested that the apatite-forming abilities of chemically treated titanium metals and of a sol-gel-derived titania are closely related to the structure of crystalline titania (anatase), which is included in them;[11,19] the present results are consistent with that finding.

4. Conclusion

Apatite formed on compacts of powder mixtures consisting of titania and calcium carbonate in SBF at 37 °C within 2 days. The apatite-forming ability was much higher than that of powder-compacts of titania crystals (anatase or rutile) without calcium carbonates. It is suggested that plentiful Ti–OH groups at the titania surface induce the apatite nucleation and a large amount of Ca^{2+} ion due to dissolution of vaterite increases the supersaturation of the apatite in SBF, resulting in rapid deposition of the apatite. Anatase is more effective than rutile. The present method utilizing titania (anatase phase) and calcium carbonates containing vaterite is promising for the preparation of titania–apatite composites as environmental materials. Experiments for finding the optimum ratio of titania to calcium carbonate in the mixtures and the evaluation of the environmental activity are in progress.

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