PREPARATION OF PHOTOCATALYTIC THIN FILMS OF TRICALCIUM PHOSPHATE BY DOPING TITANIUM(IV) ION

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Abstract: Thin films of tricalcium phosphate (TCP) with doping Ti(IV) ion were prepared. These prepared films were characterized by XRD, UV-vis transmission, FT-IT (RAS), and wettability. These characterization indicated that phase separation such as TiO₂ did not occur and that substitution with Ti(IV) occurred at Ca site. Photocatalytic activity was evaluated by methylene blue decomposition, and the results suggested that the activity was enhanced by doping Ti(IV).

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INTRODUCTION

Previously we have reported preparation of photocatalytic thin film based on a novel apatite Ti-doped calcium hydroxyapatite (TiHAP), which have calcium hydroxyapatite (HAP) structure partially substituted with Ti⁴⁺ ions at calcium sites. This photocatalyst is found to be different from composite systems of TiO₂ and an adsorbent (apatite, activated carbon, zeolite, and so on). Yoneyama et al. have revealed that stronger adsorbents lowered the photocatalytic activity of the composite because it prevents migration of adsorbed pollutants on the composite surface. The problem of this composite system is attributable to a distance between photocatalytic site and adsorptive site. However, this apatite-based photocatalyst is not thought to have such problem, and the strong adsorptive ability of apatite may be effectively available.

Several groups reported catalytic activities of calcium phosphates such as thermal oxidation reaction of alcohols, trichloroethylene, and so on. Nishikawa suggested a possibility of OH radical reactions, that is, OH radical forms thermally at the surface of CP and attacks adsorbed substrates. In the event of TiHAP, it may form photochemically.

Doping of metal ion was reported by Suzuki et al. and Wakamura et al. for HAP with many divalent and trivalent metal ions such as Pb²⁺, Sn²⁺, Cu²⁺, Mn²⁺, Ni²⁺, Co³⁺, Al³⁺, La³⁺, Fe³⁺, and Cr³⁺, and Hashimoto et al. for β-TCP for Li⁺, Na⁺, K⁺, Mg²⁺, Sr²⁺, and Al³⁺, for example. In many cases, limits of the concentration for solid solutions are not so high, and especially for TiHAP, it was suggested that the substitution with Ti⁴⁺ was occurred at columnar site probably with a certain amount of Ca-deficiency. For β-TCP, the substitution site may depend on radius of doped metal ion. Anyway, doping of metal ion causes changes in lattice constants and perturbation of electronic states, so that it is plausibly expected that doping of metal ions promote photochemical generation of OH radical.

As a photocatalytic coating, self-cleaning property is also important. TiO₂ photocatalytic coating has been developed as a self-cleaning material, in terms of its photocatalytic activity and photo-induced superhydrophilicity. Small amount of water can spread over its surface due to photo-induced superhydrophilicity, which can easily sweep surface stains away. The photocatalytic activity contributes to the self-cleaning property by decomposition of the residual stains. In this way, the superhydrophilicity of the surface plays an important role of self-cleaning property of the practical TiO₂ coating. However, a fatal problem of the hydrophilic self-cleaning material is an inherent higher affinity to stains due to the high surface energy. Another approach for self-cleaning material is preparing a composite of a photocatalyst and hydrophobic material. Low affinity of the hydrophobic surface to stains would prevent adhesion of those, and a large amount of stains would be easily swept away from the surface. From this point of view, the combination of hydrophobicity and photocatalyst may be more preferable as a self-cleaning material, although any composites with TiO₂ have not shown enough properties for practical usage because of strong photocatalytic activity (photocatalytic decomposition of hydrophobic...
materials) and photo-induced superhydrophilicity of TiO$_2$. Therefore, photocatalytic calcium phosphates may be attractive as a candidate for self-cleaning materials; photocatalytic activity for decomposition of pollutant and no photo-induced hydrophobicity.

Here, we report preparation of thin films of Ti-doped tricalcium phosphates (TiTCP) toward a novel photocatalytic material.

**MATERIALS AND METHOD**

*Substrate*

TCP, TiTCP, and anatase TiO$_2$ thin films were prepared on a cleaned glass substrate (Corning EAGLE XG glass, 5 × 5 cm) or Au-coated glass substrate for FT-IR RAS analysis (Au 100 nm / Cr 20 nm / Corning 1737 glass, prepared by vapor deposition). After washing by ultrasonication in CH$_2$Cl$_2$, acetone and water, successively, a Si (100) wafer (Aki Corp., Miyagi, Japan) was cleaned by vacuum ultraviolet illumination with a Xe excimer lamp (172 nm wavelength, UER-20; Ushio Inc., Tokyo, Japan) for 10 min in air at room temperature. The resultant surface was highly hydrophilic, and was used immediately after this process. The preparation procedure has been reported previously. All reagents were used as received without further purification.

General Synthesis of Precursor Solutions for TCP and TiTCP thin films

To a solution of Ca(NO$_3$)$_2$·4H$_2$O (10.0-x mmol) in 2-ethoxyethanol (25 mL) and ethanol (25 mL) was added P$_2$O$_5$ (3.3 mmol). The solution was stirred for 2h at room temperature. TiOiPr$_4$ (x mmol) was gradually added to the solution, and after stirring for 1d, the resultant solution was filtered under vacuo.

General Preparation Procedure of TiTCP thin Films

The prepared precursor solutions were spin-coated (1500rpm for 10 sec.) onto the freshly cleaned glass substrates. Just after spin-coating, the obtained substrates were dried at 120°C for 10 min, and then, were calcined at 500°C for 30 min. As a control, a TiO$_2$ thin film was also prepared from a precursor solution (NDH-510C, Nihon Soda) in the same manner.

Surface Characteristics

X-ray diffraction patterns were obtained for 20 diffraction angles between 10 and 50° using MXP3VHF22 (MAC Science Co. Ltd.) with CuKα operated at 40 kV-30 mA.

UV-vis transmission spectra were recorded with a UV-3600 UV-vis spectrometer with an integration sphere ISIR-3100 (Shimadzu).

FT-IR-RAS spectra were recorded with JASCO FTIR4700 and RAS (RAS PRO410-H) system. For FT-IR-RAS measurements, these thin films were coated on Au (100 nm)/Cr (20 nm)/ Corning 1737 glass prepared by vapor deposition. Accumulation times were 512 for both background and sample measurements, and the resolution was 4 cm$^{-1}$.

AFM surface roughness (Ra) was evaluated using an atomic force microscope (AFM, KEYENCE, Tokyo, Japan) with a Si cantilever. Thickness was determined by using variable-angle spectroscopic ellipsometry and WVASE32 software (VASE system, J. A. Woollam Co. Ltd.) for the thin films on Si wafer. The ellipsometric data were acquired at 70°, 75°, and 80° angles of incidence over the spectral range 250–1000 nm by 10 nm steps. A three-layer model (thin film /SiO$_2$/Si) was used for determining the thickness. Native oxide thickness (2 nm) was separately determined for a cleaned substrate, and this value was used for evaluation of all samples.

The contact angle measurements were carried out with a 3 μL droplet of ion exchanged water at room temperature by a contact angle meter (sessile drop method, Drop master 500, Kyowa Interface Science Co.). A contact angle was evaluated as an average of 5 points. Wettability change under UV-irradiation was evaluated with a UV light source (EX250, HOYA-SCHOTT, 6 mW/cm$^2$).

Methylene blue (MB) decomposition tests were carried out as follows. An MB solution was coated on the sample films by spin-coating method (1500rpm). MB degradation under UV-irradiation (black light bulb, 1 mW/cm$^2$) was evaluated using UV-vis spectra of MB measured by a UV–vis spectrometer.

**RESULTS and DISCUSSION**

Colorless and transparent thin films of TCP (thickness: 78 nm), TiTCP5 (66 nm), and TiTCP10 (64nm) were obtained. UV-vis transmission spectra were shown in Figure 1. TCP and TiTCPs showed almost similar spectra although slight decrease in visible region was observed for TiTCP5 probably due to decrease in reflection. TiTCP seemed to absorb more UV-vis light than TCP and TiTCP. As previously reported, TiHAP showed only slight increase in UV region. If it was considered that calcium phosphate (CP) is not a photo-semiconductor but insulator, plausibly metal-doped CPs do not have strong absorption bands in UV-vis region.

XRD suggested that all samples were amorphous as shown in Figure 2. Under these preparation conditions, crystallization and its growth may be difficult.

Figure 3 shows FT-IR-RAS spectra. The thin film of TCP without doping showed strong absorption peak of P-O-P stretching and weak peak
of P-OH. In the case of HAP, relatively strong peak of P-OH was usually observed probably due to its composition (Ca_{10}(PO_4)_{6}(OH)_2). By doping Ti(IV) ion, blue shift of P-O-P peak from 1121 to 1135 cm\(^{-1}\) was observed, and it would be derived from formation of P-O-Ti bond. P-OH peak around 950 cm\(^{-1}\) seemed to be broadened by doping, this fact suggested that the bond was perturbed by doped Ti. It is also noteworthy that these measurements revealed that TiTCPs contained no TiO\(_2\).

Wettability change under UV-irradiation was evaluated as shown in Figure 4. Before UV irradiation (as-prepared), TiTCP10 was more hydrophobic than TiTCP5. Both surfaces showed similar surface roughness (1.7-2.1 nm for areas of 50 \(\mu\)m \(\times\) 50 \(\mu\)m) by AFM, therefore, the difference may be due to intrinsic change in surface energy, that is, surface chemical structure and/or composition. Water contact angles of TiTCPs were not significantly changed during UV irradiation, although the prepared TiO\(_2\) thin film showed the photo-induced superhydrophilicity. This results also suggested that TiTCPs contained no photocatalytic TiO\(_2\).
Photocatalytic activity was also evaluated by MB decomposition as shown in Figure 5. TCP showed almost no activity, and only slight decrease in absorption of MB was observed even after 300 h. For the TiTCP5 and TiTCP10, MB decomposition rate was almost similar (Figure 6), although TiO$_2$ decomposes quickly (< 100 h) under the same conditions. Although photocatalytic activity of these TiTCPs may be weaker than that of TiO$_2$, furthermore, generally CPs are soluble in water under acidic or basic conditions, improvement of self-cleaning ability as an composite with low energy materials are expected.

CONCLUSION

Transparent thin films of amorphous Ti-doped TCP were successfully prepared. FT-IR-RAS spectra suggested the formation of P-O-Ti bond and absence of photocatalytic TiO$_2$. The prepared TiTCPs showed no photo-induced hydrophilicity, different from TiO$_2$. TiTCPs showed photocatalytic activity on MB decomposition.

REFERENCES

10. K. Yoshida, H. Hyuga, N. Kondo, H. Kita, M.


