Preparation of Transparent Thin Film of Novel Apatite-based Photocatalyst

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Novel apatite-based photocatalyst (TiHAP) films have been prepared by wet process. The films have high transparency with little infringing color. SEM, XPS, and UV–vis analyses were carried out, and it was revealed that the obtained films were similar to TiHAP powder. The films showed photocatalytic activity against adsorbed Methylene Blue and gaseous isopropyl alcohol and no photoinduced hydrophilicity.

Previously, we have reported a novel apatite-based photocatalyst (TiHAP),[1] which has calcium hydroxyapatite structure partially substituted with Ti ions at calcium sites. This photocatalyst is different from composite systems of TiO_2 and an adsorbent (activated carbon, zeolite, apatite, and so on),[2,3] which are widely studied in terms of an application to water or air purification. Yoneyama et al. have revealed that the stronger adsorbent lowers the photocatalytic activity of TiO_2 composite because it prevents diffusion of adsorbed pollutions on the composite surface.[2] Therefore, it is essential for fabricating a photocatalyst–adsorbent composite system for practical use to choose an adsorbent of appropriate adsorptive ability. The problem of these systems is attributable to a distance between a photocatalytic site and an adsorptive site. However, it seems that our apatite-based photocatalyst does not have such problem, and the strong adsorptive ability of apatite may be effectively available for photocatalytic decomposition.

For a wide application of a photocatalyst, it is essential to develop a coating method. Especially, transparency is often required, e.g., in order to apply to the photocatalytic coating on glass. However, to the best of our knowledge, there have been few reports on transparent thin-film coating of apatite, although the preparation of hydroxy- and fluoroapatite film[4–6] has been reported. In this paper, we report the preparation of transparent thin films of Ti-doped calcium hydroxyapatite (TiHAP) for a photocatalytic coating.

A cleaned glass (Corning 1737 glass 5 × 7 cm, or quartz cover glass 2 × 2 cm) was used as a substrate. To a solution of $Ca(NO_3)_2 \cdot 4H_2O$ (4.246 g, 18.0 mmol) in mixed solvent of ethanol (50 mL) and 2-ethoxyethanol (50 mL), P_2O_5 (0.906 g, 6.0 mmol) was added, and the solution was stirred at room temperature for 2 h. $Ti(OiPr)_4$ (0.568 g, 2.0 mmol) was gradually added to the solution, and the solution was stirred for 1 d. After removing small amount of precipitate by filtration, the clear filtrate ($pH \approx 3$) was used for coating. When phosphoric acid or its ammonium salt was used instead of P_2O_5, calcium ion was quickly precipitated and coating with its filtrate was failed. It is also noteworthy that phase separation was observed at higher concentration of $Ti(OiPr)_4$ (4 mmol against 16 mmol of $Ca(NO_3)_2 \cdot 4H_2O$) and transparent film was not obtained. The solution was coated on a glass substrate by dipping (withdrawing rate 24 cm/min), and it was quickly dried by a heat gun for approximately 10 s. The whole was calcined at 500 °C for 15 min. This process was repeated several times. Additionally, calcium hydroxyapatite (HAP) thin film without Ti was also prepared in the same way without $Ti(OiPr)_4$. Highly homogeneous, transparent, and colorless TiHAP and HAP films were obtained. TiO_2 film was prepared from NDH 510C coating solution (Nippon Soda Co., Ltd.).

It was revealed that the TiHAP film obtained by repeating 10 coating cycles was dense and that its thickness was approximately 700 nm by scanning electron microscopy (SEM, S-5200; Hitachi Co., Tokyo, Japan). Film thickness was also measured by ellipsometric method[7] against films coated on Si wafer in the same way (1 and 3 coating cycles), and it was confirmed that the film thickness per cycle was approximately 70 nm.

Elemental analysis by X-ray photoelectron spectroscopy (XPS; Physical Electronics (PHI) Model 5600 spectrometer equipped with a hemispherical capacitor analyzer) was carried out. XPS spectrum of the obtained film was similar to that of TiHAP powder,[1] as shown in Figure 1. The ratio of Ti against Ca was estimated approximately 10%. Si signals derived from substrate or any other signals from impurities except carbon from surface pollutants were not observed. XRD diffraction was also similar to that of the powder, although it was weak because of thin film. TiO_2 (anatase or rutile) was not detected. Therefore, the obtained films are chemically similar to TiHAP powder.

The obtained films were highly transparent and colorless (Figure 2), owing to low refractive index of hydroxy apatite (refractive index ≈1.5 at 590 nm, calculated from ellipsometric data). Interference color, which depends on refractive index and thickness, was slightly observed with increasing of film thickness; however, TiHAP thin film shows much weaker interference color than TiO_2 of higher refractive index. Absorption of HAP was mainly below ca. 240 nm, and that of TiHAP was be-

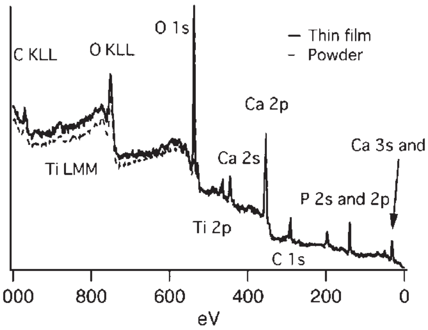

Figure 1. XPS spectra of TiHAP thin film (solid line) and powder (broken line).

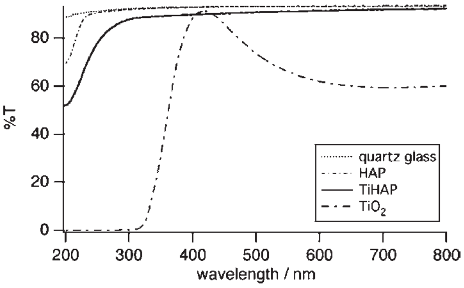

Figure 2. Transmission of quartz glass (substrate), HAP thin film (60 nm), TiHAP thin film (72 nm), and TiO_2 thin film (110 nm).

low ca. 360 nm (absorption over 300 nm is very weak because of thin film and is partially hidden in light scattering). It is obvious that the absorption of TiHAP is changed from that of HAP by introducing Ti^{IV} ion and is restricted to shorter wavelength region than TiO_2.

Photocatalytic activity was evaluated by the decomposition of adsorbed Methylene Blue (MB) decomposition under irradiation of UV light (Hg-Xe lamp, HOYA-SCHOTT UV light source EX250-W without any cut-off filter, 10 mW/cm^2).[8] TiHAP-coated glass (TiHAP thickness 210 nm) was immersed in MB aqueous solution (1 mM) for 2 h and then dried. After UV irradiation, the film was kept under dark for 1 h and then the absorption spectrum was measured by UV–vis spectrometer (Perkin-Elmer Lambda900). Figure 3a shows absorption spectra of MB adsorbed on TiHAP film under UV irradiation. MB was gradually decomposed, while MB adsorbed on a bare glass substrate was not decomposed under these conditions.

Photocatalytic activity was also evaluated by the decomposition of gaseous isopropyl alcohol (IPA) decomposition under irradiation of UV light (black fluorescent light bulb, 1.7 mW/cm^2).[8] The film on a glass substrate was set in a quartz-made vessel, which had a volume of 1000 mL, and then about 500 ppm of the reactant gas was injected. The sample was kept in the dark once the gas concentration remained constant, which implied that the IPA gas finished adsorbing onto the film surface. The component gas concentrations were measured by a gas chromatograph (Shimadzu GC-8A). Figure 3b clearly shows the decrease of IPA and increase of CO_2 by UV irradiation. IPA was decomposed under these conditions, although the observed efficiency was relatively low because of small coated surface area (5×5 cm^2) and small surface roughness. It is noteworthy that acetone, an intermediate of decomposition of IPA, was clearly detected under UV irradiation. This fact is also an evidence of photooxidative ability of TiHAP.

Water contact angle (WCA) change under UV irradiation was also evaluated. WCA on a TiHAP film was ≈45° and not changed even after UV irradiation for 600 h.

In summary, transparent and colorless TiHAP film was prepared, and its photocatalytic activity was evaluated. Both of the adsorbed MB and gaseous IPA decompositions were observed, although UV light absorption of TiHAP is very weak. These oxidative decompositions were not observed under dark; therefore, UV light irradiation was obviously required. This apparent effective photocatalytic decomposition may be derived from the chemical structure of TiHAP, which probably has an adsorptive site as a reaction site, and it was suggested that the reaction mechanism of TiHAP is different from that of TiO_2. Further investigation is now in progress.

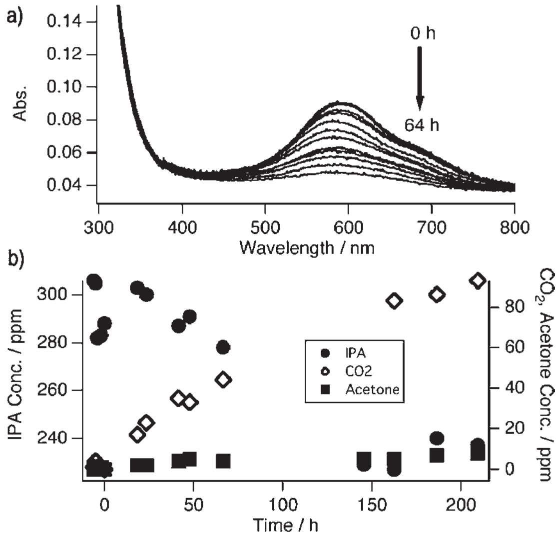

Figure 3. a) Adsorbed methylene blue decomposition and b) gaseous isopropyl alcohol decomposition under UV irradiation.

References and Notes

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7 Thickness was evaluated by using variable-angle spectroscopic ellipsometry and WVASE32 software (VASE system, J. A. Woolam Co., Ltd.). The ellipsometric data were acquired at 70, 75, and 80° angle of incidence over the spectral range 250–1000 nm by 10 nm steps. A four-layer model (Si/SiO_2/thin film/air) 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. Surface roughness was modeled using an effective medium approximation layer consisting of 50% of the material and 50% void.
8 UV light intensity was measured by UVR2 radiometer with UV detector unit UD–36 (TOPCON Corp., Japan). The measuring wavelength of this detector is 310–400 nm (mainly 365 nm).

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