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Preparation and properties of titania–apatite hybrid films

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Abstract

TiO_2–hydroxyapatite (HAp) hybrid films were prepared by laminating TiO_2 films with holes on the HAp film. We prepared transparent porous HAp film through spray pyrolysis deposition (SPD) method. The HAp possessed affinity against proteins. TiO_2 films were prepared using phase separation of alkoxide. The holes provided from this process serve as an adsorption field and photocatalytic reaction field for reactants. This work demonstrated that the TiO_2–HAp hybrid films produced by this process are candidates for photocatalytic decomposition of germs, viruses, and other biohazardous substances in the environment.

Keywords: TiO_2; Photocatalyst; Apatite; Phase separation; Albumin

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1. Introduction

Titanium dioxide (TiO_2) is a well-known photocatalyst material [1]. When ultraviolet (UV) is illuminated onto TiO_2, electron and hole pairs are generated, which reduce and oxidize adsorbates on the surface, respectively, thereby producing radical species, such as OH radicals and O_2^-. These radicals can decompose most organic compounds or bacteria [2–6]. Many studies have been conducted on the application of TiO_2 to water and air purification [7].

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, denoted as HAp, has attracted great interest for applications in the orthopedic and dental fields because of its excellent biocompatibility and tissue bioactivity properties [8]. Because HAp has a good affinity to proteins and lipids, TiO_2 combined with HAp has been developed to improve photocatalytic decomposition activity against bacteria, virus, pollen, and other biohazardous substances and chemicals. Nonami et al. prepared TiO_2–HAp composite films in which a porous HAp layer is formed on the surface of a dense TiO_2 layer [9]. This film is transparent and exhibits higher photocatalytic decomposition activity on the bacteria in air than pure TiO_2. Nevertheless, because of the porous structure of HAp layer, abrasion resistance of the coating surface is not so high. Recently, Wakamura et al. [10] modified HAp by substituting Ti(IV) for Ca ion. Their material also exhibits excellent antibacterial performance. It is a new photocatalyst material with a different adsorption capability from TiO_2. However, this material does not always exhibit higher photocatalytic decomposition activity than pure TiO_2 under some experimental conditions.

The present study prepared TiO_2–HAp hybrid films. For HAp film formation, we chose spray pyrolysis deposition (SPD) process. This method is attractive because of its simplicity, low cost, and myriad available types and contents of participating ions. Several studies have been published regarding the powder synthesis of HAp by spray pyrolysis

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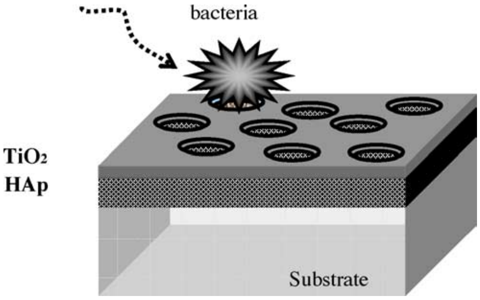

Fig. 1. Schematic illustration of TiO_2–HAp hybrid films.

[11–13], but few studies have reported film processing by SPD. Encouraged by successful preparation of other oxide films, SPD was employed for fabrication of HAp thin films in this study. Moreover, Kajihara and Yao revealed that dense TiO_2 films with holes can be prepared by controlling phase separation conditions of Ti-alkoxide [14–16]. We tried to laminate this film by referring to their research work on HAp films. In this film, holes become the field for both adsorption and photocatalytic reactions because their bottom is the HAp surface (Fig. 1). We evaluated photocatalytic activity of the films.

2. Experimental procedure

2.1. Film preparation

This study uses only water-based inorganic starting materials for HAp film preparation because of their low cost, nonflammability, and lack of carbon contamination. Reagent-grade phosphoric acid (H_3PO_4; Wako Pure Chemical Industries Ltd., Tokyo, Japan) and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, Wako Pure Chemical Industries Ltd.) were dissolved into distilled water. The Ca/P molar ratio in the solution was the stoichiometric amount for HAp (=1.67). Calcium phosphate was not precipitated and a clear solution was obtained because of acidic condition of the solution resulting from the existence of nitrate group from calcium source and phosphoric acid. Solution concentrations were fixed as 3.3×10^{-3} mol HAp/L. The solution was sprayed using argon gas through the double-fluid nozzle. It was decomposed thermally on a Pyrex glass plate that was heated to 500 °C. Cleaning and etching of the glass plate were carried out immediately before deposition according to vacuum ultraviolet (VUV) illumination for 30 min using a Xe excimer lamp (172 nm wavelength, UER-20; Ushio Inc., Tokyo, Japan) in air at room temperature. The distance separating the top of the nozzle and the glass plate was about 40 cm. Argon was supplied at 2.5 kgf/cm^2. The rate of spray of the solution was about 11 g/min, and the SPD period was 3 min.

Reagent grade titanium isopropoxide ($Ti(OC_3H_7)_4$, denoted as TTIP; Wako) was mixed with ethanol (TTIP:ethanol = 17 g:23 g; Wako). After stirring for a few minutes in air, the mixed solution was hydrolyzed by adding a nitric acid solution (HNO_3 (70%):H_2O:ethanol = 0.65 g:0.9 g:23 g; Wako) with stirring under cooling by ice. Polyethylene glycol (PEG2000; Wako) flake was then added (2.5 g) and dissolved to the hydrolyzed sol by heating at 40 °C for 1 h. After cooling to room temperature, a coating liquid for TiO_2 film was prepared. We then coated the liquid on a Pyrex glass plate with the HAp film using dip coating with constant pulling rates (7.5–30 mm/min) under various relative humidity atmospheres (30–60%) at 25 °C. The films were exposed to the conditions for drying and then fired at 500 °C for 10 min in air.

2.2. Evaluation

2.2.1. Characterization of films

Crystalline phases of the films were evaluated using X-ray diffraction (XRD: PW-3050; Philips Co., Amsterdam, Netherlands) with Cu Kα radiation. The microstructure and film thickness were observed using a scanning electron microscope (SEM: S4200; Hitachi Ltd., Tokyo Japan). Transmittance of the visible wavelength range was evaluated from the spectra using a UV–vis–NIR scanning spectrophotometer (V-570; Jasco Inc., Tokyo, Japan). Film surface composition was evaluated by X-ray photoelectron spectroscopy (XPS, ESCA-3400; Shimadzu Corp., Tokyo Japan).

In this study, we have chosen albumin as a model decomposition reactant because this substance adsorbs well to HAp and not well to TiO_2 [10]. The HAp film without TiO_2 lamination were soaked into an albumin (Wako) solution (5 g/l) for 30 min to confirm the absorption capability of protein. After soaking, the film was dried in an oven at 60 °C, then cooled again to room temperature. Then, a ninhydrine solution (Wako) was sprayed to the film surface and the film was dried again at 110 °C. Finally, we observed the film coloring.

The microstructures in the hole of TiO_2–HAp hybrid film after soaking in 250 ppm albumin solution and drying, and after subsequent UV illumination (80 mW/cm^2, 30 min) were also evaluated using the non-contact mode of scanning probe microscopy (SPM, JSPM-5200; JEOL, Tokyo, Japan) with a Si cantilever, and a Hg–Xe lamp. The size of albumin gel in water was evaluated by dynamic light-scattering method (ELS-8000; Otsuka Electronics Co. Ltd., Tokyo, Japan).

2.2.2. Evaluation of photocatalytic activity

The obtained film (2 cm × 3 cm) was set in the bottom of a Pyrex glass vessel (film surface facing up) containing 25 g of the aqueous albumin solution (50 ppm) after holding 21 h at room temperature. Preliminary experiments revealed that holding 21 h before UV illumination is sufficient for adsorption saturation. Total organic carbon (TOC) concentration in the solution was measured using a TOC meter (TOC-5050A; Shimadzu Corp., Tokyo, Japan). Albumin concentration in water was fixed as 50 ppm before starting UV illumination. Then, UV light was illuminated from the bottom side of the

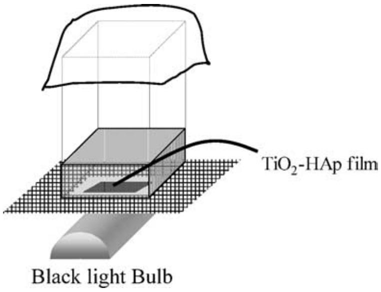

Fig. 2. Schematic illustration of experimental procedure for the evaluation of photocatalytic decomposition activity on albumin in water.

vessel using a black-light bulb. A schematic illustration of the experimental condition is shown in Fig. 2. The illumination intensity at the inner front surface of the vessel was 1 mW/cm^2 at 365 nm. The effect of dissolved CO_2 from the atmosphere was eliminated by subtracting this value after TOC measurement. For comparison, photocatalytic decomposition performance of a dense TiO_2 film with no holes was also evaluated under identical conditions.

Photocatalytic degradation behavior of albumin adsorbed on the hybrid film was also evaluated using the sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) method. Before and after UV illumination (1 mW/cm^2), the albumin adsorbed on the hybrid film was removed by 0.5 M KH_2PO_4 buffer solution (pH 7.2). Preliminary experiments revealed that all adsorbed albumin on HAp could be removed by this procedure. The molecular weight distribution was then evaluated using SDS-PAGE method and detected by Sypro® ruby staining.

3. Results and discussion

Figs. 3–7 show XRD patterns, transparency and microstructure of prepared films. The XRD patterns revealed that the film obtained by SPD was crystalline HAp (Fig. 3); no other crystalline phase exists in the film. The HAp film was transparent (Fig. 4); its thickness was around 70 nm (Fig. 6(b)). The obtained HAp film was porous and no peeling part was observed at the interface between the glass substrate and films. Viguie and Spitz investigated the condition dependence of film characteristics by SPD. Their study indicates that the best film is obtained when metal salt volatizes and the vapor deposits directly on the substrate [17]. We tried to prepare HAp film by changing the substrate–nozzle distance from 30 to 47 cm, and spray rate from 5 to 15 g/min. However, only the condition described in the experimental section provided transparent HAp film. This SPD condition will be close to optimum as was indicated by Viguie and Spitz. For shorter distances than 40 cm or higher spray rates than 11 g/min, the obtained films were heterogeneous and not transparent (Fig. 5). Optical microscopic observation revealed that numerous droplet marks or cracks were observed in the coating. This cracking will be caused by local cooling during vaporization of the droplets of aqueous solution on the film surface. The film was not formed at longer distances than 40 cm or with a smaller spray rates than 11 g/min: a white powder was scattered on the substrate surface suggesting droplet drying before reaching substrate.

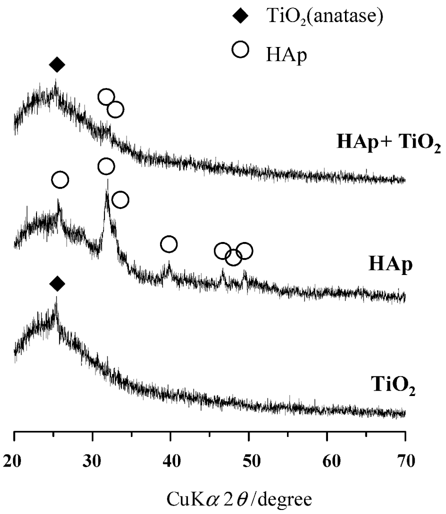

Fig. 3. XRD patterns of films.

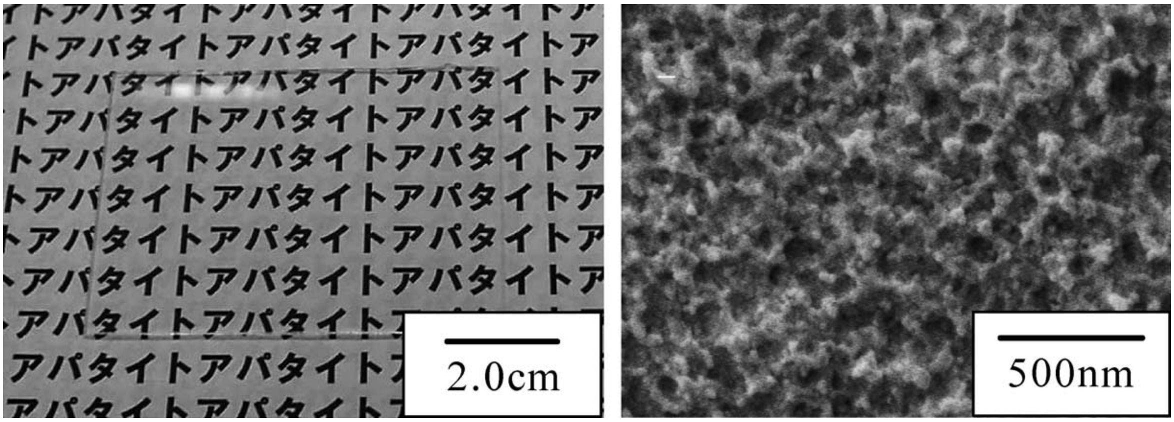

Fig. 4. Prepared HAp film (a) and its SEM micrograph (b) under SPD condition described in the experimental section.

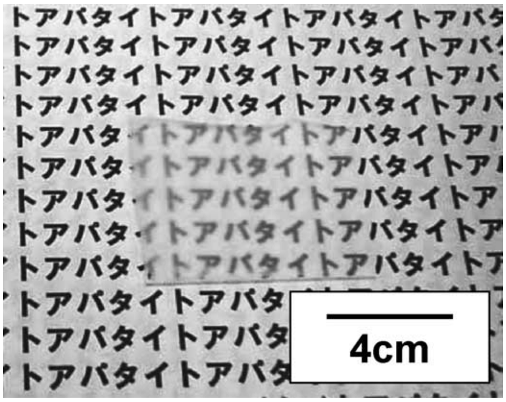

Fig. 5. Prepared HAp film when substrate–nozzle distance is 30 cm (spray rate: 11 g/min.).

These results imply that the substrate–nozzle distance and spray rate are one of the critical conditions for transparent film processing by SPD.

The molar ratios of Ca/P on the film were 1.62, indicating that the surface composition was almost identical to that of ideal HAp. Remaining nitrogen identified from the film surface was less than 1 at.%, suggesting that the nitrate group of the Ca source was vaporized as NO_x gases with water. In the starting reagent for the solution, no materials, such as organic substances, are thermally decomposed. This fact represents a merit for high-purity film processing. We confirmed the blue-purple coloration of films using the ninhydrine reaction. Results suggested that the HAp film obtained from this process possesses protein-absorption capability in aqueous solutions.

Fig. 6(a) shows a SEM micrograph of the TiO_2 film with holes prepared on the transparent HAp film under a pulling rate of 22.5 mm/min in 60% relative humidity. Although the hole size is distributed, the average size is about 1 μm. SEM observation of a crosscut section revealed that average film thickness is around 60 nm (Fig. 6(b)). The area ratio of TiO_2/HAp measured from the SEM micrograph was about two. This structure was formed by phase separation of TTIP-solvent–PEG system; the hole was the place where PEG existed before heat treatment. The film microstructure depends strongly on the pulling rate, humidity, and the concentration of the coating liquid. It was determined by chemical composition (thermodynamics) and the viscosity increase resulting from solvent evaporation or gelation (kinetics), as reported by Kajihara and Yao [14–16]. Surface roughness and the affinity of PEG against film surface are increased when HAp film is formed on the glass surface. These phenomena affect the coating condition that the TiO_2 film with holes is obtainable. Therefore, the optimal condition is different from pure glass substrate. The detailed relationship between film preparation condition and film structure will be reported elsewhere. The following photocatalytic activity evaluation was performed using the film with the same structure shown in Fig. 6.

Fig. 7 shows transmittance for the visible light on the film shown in Fig. 6. The HAp film exhibited greater than 90% transmittance in the visible wavelength range. However, the

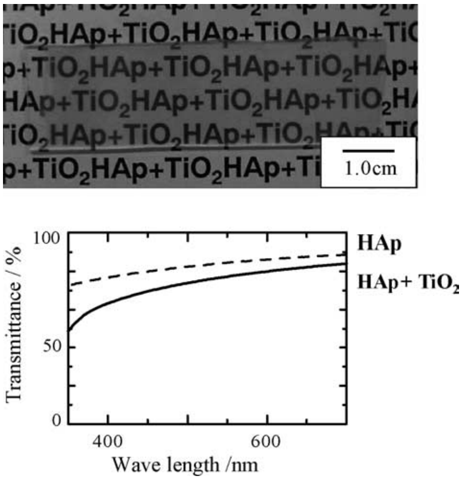

Fig. 7. Transmittance for the visible light on the hybrid film shown in Fig. 5.

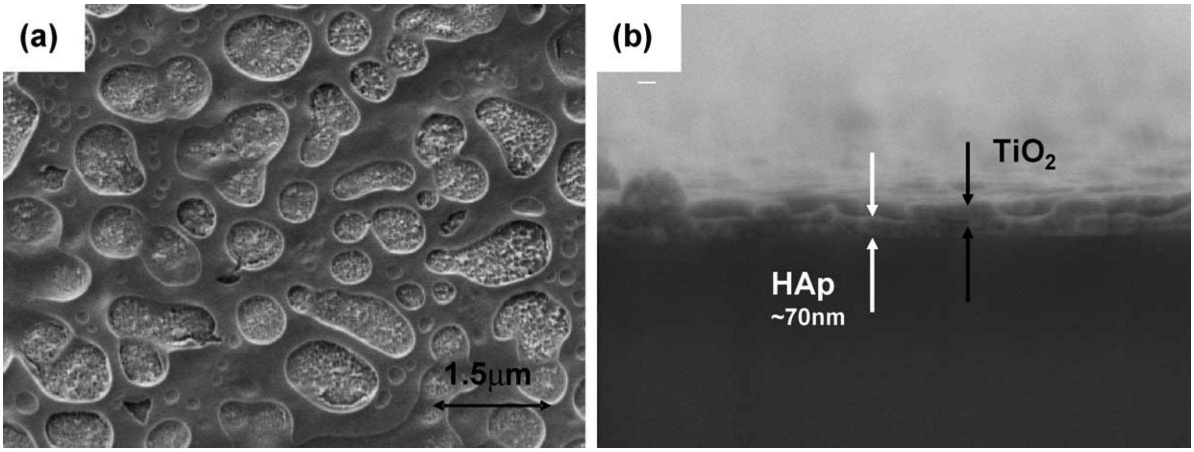

Fig. 6. SEM micrograph of the TiO_2 film prepared on the transparent HAp film under a pulling rate of 22.5 mm/min in 60% relative humidity; (a) surface and (b) crosscut section.

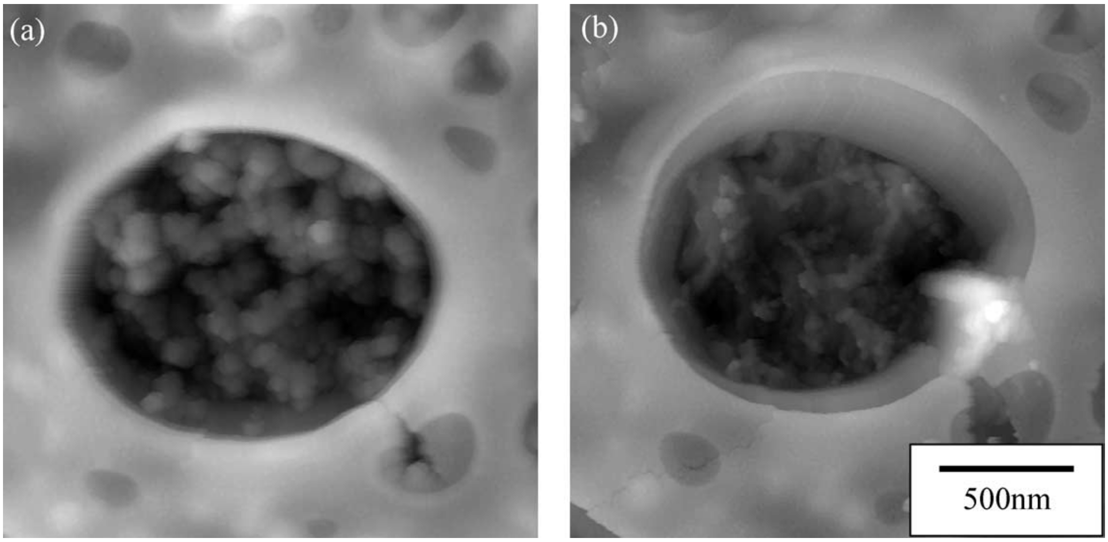

Fig. 8. SPM micrographs of structure around holes (a) after soaking albumin solution, and (b) after UV illumination (80 mW, 30 min).

transmittance value of the HAp–TiO_2 hybrid film is 70–80% in almost all wavelength ranges, suggesting that the film is not completely transparent, but instead slightly hazy because of the scattering of light attributable to the hole structure of laminated TiO_2 film. Hole size control is necessary to improve transparency.

Fig. 8 shows SPM micrographs of the structure around holes after soaking in albumin solution (a) and after UV illumination (b). After soaking, a small particulate-like structure can be observed in the hole. This structure disappears after UV illumination. Hence, this structure is albumin gel adsorbed on the HAp film surface. The size of this structure was almost the same as that measured on albumin gel in the solution by dynamic light-scattering method. This structure is not observed on the TiO_2 film surface, suggesting that albumin adsorbs preferably to the inside of the hole: the HAp surface. This fact agrees with results of Wakamura et al. [10] and implies that the hole of this hybrid film provides the field for adsorption.

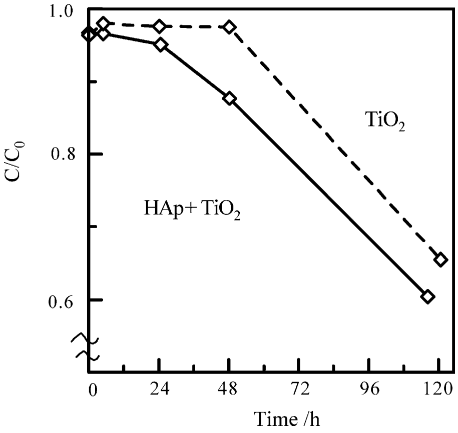

Fig. 9. Change of albumin concentration before and during UV illumination.

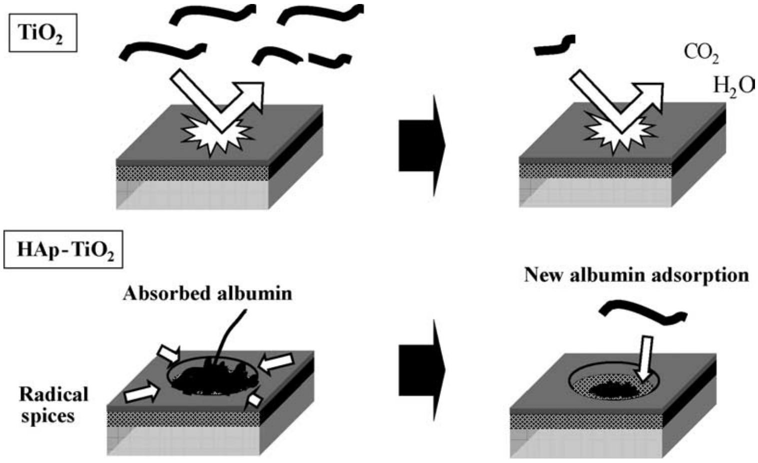

Fig. 10. Schematic illustration of the decomposition behavior difference between pure TiO_2 film and TiO_2–HAp hybrid film.

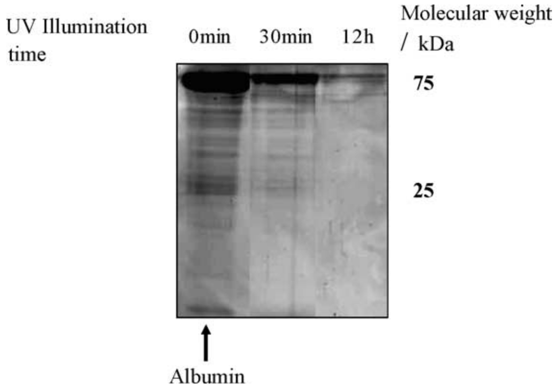

Fig. 11. Degradation of the molecular weight chromatogram of albumin before and after 1 mW/cm^2 UV illumination by SDS-PAGE method.

Fig. 9 shows the change of albumin concentration during UV illumination. Film thickness evaluated by direct observation of crosscut section by SEM of the no-hole TiO_2 film was around 200 nm; thus, this film is thicker than the hybrid film's TiO_2 layer. Albumin concentration of the solution did not decrease until about 48 h, when the no-hole TiO_2 film was set in the solution. However, when the hybrid film was set in the solution, albumin concentration decreased gradually from the beginning of UV illumination. After 120 h, the total decomposition amount was greater than for the no-hole TiO_2 film. This result means that albumin is decomposed effectively by this hybrid film. TiO_2 does not have good affinity with albumin. Therefore, only molecular cutting advances in the early stage (first 48 h) of UV illumination, following the accidental contact rate of albumin molecule to the no-hole TiO_2 film surface in the system. Therefore, TOC does not decrease remarkably (Fig. 10). After 48 h, TOC decreases because average molecular weight is decreased in the solution. However, for the hybrid film, albumin molecules adsorbed on the HAp site can be decomposed into CO_2 effectively by diffused radical species from TiO_2 because of the small desorption possibility during photocatalytic decomposition. Therefore, once a new adsorbent site becomes available, a different albumin molecule adsorbs and the TOC value in the solution decreases gradually from the early stage of UV illumination. Fig. 11 shows a chromatogram of albumin by SDS-PAGE method with Sypro$^{®}$ ruby staining. Initial molecular weight before UV illumination was revealed as around 75 KDa. Albumin gradually diluted with increasing UV illumination time. This result implies that molecular albumin adsorbed to HAp was gradually decomposed by UV illumination.

4. Conclusion

The present study prepared transparent porous HAp film using SPD method. The HAp possessed affinity against proteins. TiO_2–HAp hybrid films were prepared by laminating dense TiO_2 films with holes on the HAp film by controlling Ti-alkoxide phase separation. The holes provided from this process serve as an adsorption field and photocatalytic reaction field for reactants. This work demonstrated that the TiO_2–HAp hybrid films from this process are candidates for photocatalytic decomposition of germs, viruses, and other biohazardous substances in the environment.

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