Synthesis of Titanium Oxide Photocatalyst Supported on Spherical Porous Hydroxyapatite

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We report the synthesis of a photocatalytic composite of spherical porous hydroxyapatite (sHAp) and TiO₂. sHAp was prepared by a wet method using simulated body fluid as a slurry and was then mixed with a TiO₂ sol to obtain the sHAp + TiO₂ composite. The TiO₂ content of sHAp + TiO₂ was ~7.8 wt. %. sHAp+TiO₂ showed photocatalytic activity that was more than ten times greater than that of TiO₂ even under irradiation with the low-intensity ultraviolet (UV) light of a fluorescent lamp. Mb decomposition of 58.2% was achieved under UV light with an intensity of $7.60 \times 10^2 \mu\text{W cm}^{-2}$ using the sHAp + TiO₂ composite, which is significantly higher than the 8.05% achieved using only TiO₂. Thus, the composite material showed higher activity than that of unsupported TiO₂. Furthermore, sHAp + TiO₂ could oxidize leucocrystal violet (LCV) to crystal violet (CV) even after being placed in the dark for 120 h. The positively charged holes are suggested to persist on TiO₂ because of the electron withdrawing effects of sHAp and can contribute to LCV oxidation. Thus, the photocatalytic activity of TiO₂ was improved by using sHAp as a support.

Key words: Photocatalyst, titanium, hydroxyapatite, photo-oxidation, composite.

1. INTRODUCTION

The pollution of the environment by harmful chemicals is a serious problem that necessitates the development of new purification technologies and materials. We previously reported the use of composites of TiO₂ photocatalysts and hydroxyapatite (HAp) as environmental purification materials [1-4]. TiO₂ is a chemically stable photocatalyst that can decompose harmful chemicals. It has been used to deodorize air by eliminating NO_x, and as an antibacterial material [5-9]. The band gap energy of anatase TiO₂ (3.2 eV) enables it to absorb ultraviolet (UV) light with wavelengths of < 380 nm.

When electrons in the valence band of TiO₂ are excited to the conductance band, positively charged holes are left behind in the conduction band [10]. The reaction of these holes with water on the crystal surface leads to the formation of hydroxyl radicals ($\cdot\text{OH}$). These radicals are stronger oxidizing agents than ozone and can decompose harmful chemicals [11-13].

Therefore, it is important that the target substance can reach the surface of the catalyst to allow photocatalytic reactions, such as decomposition, to occur. This problem can be solved by using a photocatalyst that has been suitably modified such that the target substance adheres to the catalyst surface. It is desirable to include the ability to both bind and decompose the target substance using light, and this combination of functions can be achieved through the hybridization of adhesive substances, such as activated

carbon or zeolites, with a photocatalyst, such as TiO₂ [11, 14].

If TiO₂ is directly mixed into an organic resin, the resin itself may be oxidized and decomposed. This undesirable photodegradation of the catalyst matrix has hampered efforts to extend the range of applications of photocatalysts. Taoda et al. [15] developed “muskmelon TiO₂ photocatalytic particles” to solve this problem, in which silica covers the TiO₂ surface like the mask of a muskmelon, and Nonami et al. [1-4] developed HAp-covered TiO₂, a composite ceramic in which plate-like crystals of HAp cover the TiO₂ surface.

In these materials, the surface of TiO₂ is covered with non-photoactive silica or HAp, so TiO₂ does not directly encounter the resin, and resin decomposition is prevented. The part of author et al. reported that in HAp-covered TiO₂, the electrons generated at the TiO₂ surface migrate towards HAp, which holds them and helps to suppress electron-hole recombination and may result in improved photocatalytic activity [16].

This composite material was obtained by precipitating fine apatite crystals on the surface of titanium oxide thin films or particles. However, an excessive amount of precipitated apatite could completely cover the titanium oxide surface, causing a loss of photocatalytic activity. Thus, the apatite content of this composite material was as low as 1–5%, which may be insufficient to accommodate the electrons generated in the photocatalytic reaction. Furthermore, the apatite content in the composite material

is small, and the ability of apatite to adsorb the target substance is not sufficient.

HAp is a form of calcium phosphate and a major component of teeth and bones [17]. It has excellent biocompatibility and can absorb various substances by electrostatic attraction [18–20]. It is also an excellent material for ion exchange, and HAp derivatives with different physical properties can be manufactured by the substitution of various elements [21]. Nakane et al. used the fact that the hydroxide groups of HAp can be easily exchanged for fluoride to improve the acid tolerance of HAp, and developed a fluorinated HAp-covered TiO₂ [22].

Kodeira et al. reported the synthesis of spherical porous hydroxyapatite (sHAp) by a wet method using simulated body fluid [23]. sHAp is a form of HAp containing aggregates of plate-shaped crystals that form particles with a diameter of 0.1–0.5 μm and with gaps of a maximum size of $\sim 0.4 \mu\text{m}$ between the aggregated plate-shaped TiO₂. The synthesis of a sHAp + TiO₂ composite material, in which fine TiO₂ particles are supported within the gaps between the plate-shaped crystals of sHAp, was first reported by our group [24]. The HAp content of this composite material can be 90 wt% or more. As the HAp content increases, the possibility of HAp capturing the electrons generated in the photocatalytic reaction increases.

Therefore, more of the electrons generated by the photocatalytic reaction are prevented from recombining with holes, and the photocatalytic activity of the composite material is improved. In addition, the high apatite content of the composite material allows the adsorption abilities of HAp to be demonstrated.

The following three behaviors are expected to occur in sHAp + TiO₂ composites:

(1) TiO₂ is contained between the tabular crystals of apatite and is not exposed. Therefore, even when mixed with paint or other matrices, the photocatalyst does not come into direct contact with the resin binder and the matrix is not decomposed.

(2) Harmful chemicals adhere to sHAp and can then be decomposed by the TiO₂ photocatalyst.

(3) As with HAp-covered TiO₂, electron migration and capture can occur between sHAp and TiO₂, leading to improved photocatalytic ability.

In this study, a sHAp + TiO₂ composite was synthesized, and its photocatalytic properties were evaluated. The discoloration of aqueous solutions of methylene blue (Mb) and changes in the color of leucocrystal violet (LCV) under different intensities of UV illumination were also demonstrated. The part of author et al. [16] have previously reported photocatalytic decomposition using HAp under high-intensity UV irradiation. However, we herein illustrate a significant reduction in the UV irradiation intensity required to achieve high levels of photodegradation using sHAp-supported composites, which do not obstruct the catalytic TiO₂ surface. Our sHAp composite material showed photocatalytic activity even under irradiation with a typical fluorescent lamp, making it suitable for realistic environmental remediation applications.

2. Experimental

2.1 Synthesis of sHAp

The sHAp support was synthesized from simulated body fluid. An aqueous solution of CaCl₂·2H₂O was mixed into phosphate-buffered saline (PBS) ([NaCl] = 54.8 mmol L⁻¹, [KCl] = 1.074 mmol L⁻¹, [KH₂PO₄] = 0.588 mmol L⁻¹, and [Na₂HPO₄] = 3.24 mmol L⁻¹) to obtain a Ca:P mole ratio of 0.300, and the mixture was stirred for 1 h while the temperature was maintained at 40 °C using a water bath (SRS266PA, Advantec). The mixture was left undisturbed for 1 day, after which it was decanted. Desalination was carried out using a centrifugal separator (5420, Kubota) until the conductance using an electroconductivity meter (MPC227, Mettler) was less than 150 $\mu\text{S cm}^{-1}$.

2.2 Preparation of sHAp + TiO₂ composite

A slurry of sHAp (0.2 g) and a TiO₂ sol (TKS-203, Tayca Corporation) were mixed in 1 L of water and stirred for 1 h. The TiO₂ sol was prepared such that its TiO₂ content was 0.2 g per 0.2 g of sHAp. After letting the mixture stand for 1 day, it was decanted and washed with a centrifugal separator until the water contained no further suspended material. Subsequently, the composite was dried for use in further studies. TiO₂ sol (TKS-203, Tayca Corporation) was used as the TiO₂ sample.

2.3 Scanning electron microscopy

The shape and surface of sHAp were studied using scanning electron microscopy (SEM) (S-2600, Hitachi Seisakusho) at an acceleration voltage of 15.0 kV.

2.4 Identification and analysis

sHAp was identified and its crystal structure verified using powder X-ray diffraction (XRD) (Rigaku MiniFlex, Rigaku) with a scan speed of 2.00 ° min⁻¹ and a Cu K α X-ray source. Energy dispersive X-ray spectroscopy (EDXS) was used to identify the elemental composition of the surface of the composites (InTouchScope™ scanning electron microscope JSM-IT100, JEOL - Japan Electro Optical Laboratory).

2.5 Specific surface area

The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method, using nitrogen and helium gas to measure adsorption and desorption isotherms (Monosorb MS-21, Yuasa Ionics).

2.6 Zeta potential

The zeta potential of each sample was measured after 10 min with a surface potential measuring device (Zeta Nanosizer Nano Series Nano-Z; manufactured by Sysmex Corporation). The set temperature was 20 °C, and a He-Ne laser (633 nm) was used as a light source.

2.7 Field-emission scanning electron microscope

We observed high magnification of the surface of the sHAp + TiO₂ composite with field-emission scanning electron microscopy (FE-SEM) (JSM-7800F, Japan Electro Optical Laboratory) at acceleration voltages of 0.500–2.00 kV.

2.8 X-ray fluorescence spectrometry

Quantitative analysis of the containing elements of sHAp-supported TiO₂ was performed using wavelength dispersive X-ray spectrometry using an X-ray fluorescence (XRF) spectrometer (ZSX100e, Rigaku) equipped with a

Rh tube (3 kW) X-ray generator.

2.9 Discoloration of an aqueous Mb solution

TiO₂ (4.0 mg) and HAp + TiO₂ (50 mg) powders were each added to an aqueous solution of Mb (50 mL, 10 ppm). These solutions were stirred in the dark for 30 min and then irradiated with a blacklight (Sankyo Denki, 27W) for 90 min at three levels of UV intensity (3.60×10^3 , 7.50×10^2 , or 2.00×10^2 $\mu\text{W cm}^{-2}$).

The absorbance of Mb at 660 nm was measured using a ratio beam spectrophotometer (U-5100, Hitachi) at 10 min intervals. A similar experiment was also performed using a fluorescent lamp (Panasonic, 32W, ultraviolet light intensity $2.00 \mu\text{W cm}^{-2}$) as the irradiation source.

2.10 Observation of LCV color changes

TiO₂ (10.0 mg) and sHAp + TiO₂ (100 mg) powders were each irradiated by a blacklight (UV intensity of 5.40×10^3 $\mu\text{W cm}^{-2}$) for 6 h. LCV (0.10 g) was then mixed into each of the powders, and the color of the mixtures was observed after leaving them to stand in the dark for either 24 or 120 h.

3. Results and Discussion

3.1 Synthesis of sHAp

Fig. 1 shows SEM images of the synthesized sHAp spheres, which arise from the aggregation of plate-shaped particles of ~ 0.1 – 0.5 μm in size. The particle diameter was averaged over ~ 50 particles and found to be ~ 1 – 5 μm , and gaps exist between the aggregated plate-shaped crystals.

The (002), (211), (112), and (300) reflections of HAp were observed in the powder XRD pattern of sHAp, as shown in Fig. 2. The ratios of the diffraction intensity peaks for each crystal surface in the diffraction pattern were checked. The peaks that appear near $2\theta = 25.7^\circ$ and 33.0° correspond to the *c* (002) and *a* (300) surfaces, respectively. In contrast to the case for regular apatite, the intensity of the (002) reflection of sHAp is greater than that of the (004) reflection. This difference in intensity suggests that the plate-shaped HAp crystals grow in either the *a* or *b* directions, leaving many *c* faces exposed, which matches the results of SEM imaging.

Fig. 1 SEM images of sHAp particles at various magnification levels.

Fig. 2 XRD diffraction pattern of sHAp and peak

intensities of HAp

3.2 Synthesis of sHAp + TiO₂ composites

Fig. 3 shows FE-SEM images of the sHAp + TiO₂ composite. Fine particles of ~ 30 – 50 nm in size are supported on the sHAp surface, which was confirmed to consist of TiO₂ by the detection of Ti in these particles by EDXS analysis. As shown in Fig. 3(b), the TiO₂ particles were mainly supported on the surfaces of the plate-shaped sHAp crystals, and the pores were not completely closed. Therefore, the sHAp surface was not completely covered by TiO₂ and remained available for adsorption.

Table I shows specific surface area and zeta potential values. The surface area of sHAp + TiO₂ was larger than the respective values of sHAp and TiO₂. This is because TiO₂ did not aggregate and was well dispersed and supported in the sHAp pores as shown in Fig 3.

Furthermore, XRF analyses (Table II) showed that the TiO₂ concentration in the sHAp + TiO₂ composite was ~ 7.7 wt %. The calcium-to-phosphorus molar ratio of sHAp was calculated to be 1.78. This is slightly larger than apatite's stoichiometric composition of 1.67.

Fig. 3 FE-SEM Images of sHAp + TiO₂: (a) general view, (b) enlarged view

Table I. The specific surface area and zeta potential

Sample	Specific surface area/ m^2/g	Zeta potential/ mV
sHAp	89.3	-6.66
TiO ₂	97.6	-60.3
sHAp+TiO ₂	105	-21.3
Mb	-	8.82

Table II. Composition weight of sHAp+ TiO₂ analyzed by SQX

Composition	Content /wt%
CaO	59.09
P ₂ O ₅	32.54
TiO ₂	7.77
Na ₂ O	0.45

3.3 Discoloration of methylene blue solutions

The decolorization test results of the Mb aqueous solution are shown in Fig. 4 (a) to (e). When TiO₂ was added to the Mb aqueous solution and stirred in the dark for 30 minutes, the Mb aqueous solution decolorized about 60%. On the other hand, sHAp + TiO₂ and sHAp hardly decolorized the Mb aqueous solution in the dark. As shown in Table 1, since TiO₂ is negatively charged, it was expected to be able to adsorb the positively charged Mb. As shown in Table 1, all the materials are negatively

charged. Among these materials, TiO_2 has the largest difference in zeta potential with methylene blue. Therefore, it can be said that TiO_2 adsorbs most Mb in the dark. A 13.2% reduction in the concentration of an aqueous Mb solution (Fig. 4) after 90 min of irradiation with $3.60 \times 10^3 \mu\text{W cm}^{-2}$ of UV light (approximately the same intensity as that of a clear outdoor sky) was observed for unsupported TiO_2 , while the equivalent irradiation led to a 71.6% reduction in the Mb concentration when sHAp + TiO_2 was used. UV irradiation with an intensity of $7.60 \times 10^2 \mu\text{W cm}^{-2}$ (approximately equivalent to that of sunlight through a window) resulted in Mb concentration reductions of 8.05 and 58.2% for unsupported TiO_2 and sHAp + TiO_2 , respectively. A UV intensity of $2.00 \times 10^2 \mu\text{W cm}^{-2}$ (approximately equivalent to the intensity of a cloudy outdoor sky) led to reductions of 3.07% and 31.2% for unsupported TiO_2 and sHAp + TiO_2 , respectively. Thus, the photocatalytic activity of the sHAp + TiO_2 composite was higher than that of unsupported TiO_2 at each of these UV intensities.

Fig. 4 Changes in the concentration of the Mb aqueous solution when each sample was added and processed (placed in a dark place for 30 minutes and then irradiated with light). Sample legend: sHAp + TiO_2 (●), TiO_2 (○), sHAp (■), without sample (△), sHAp and TiO_2 (Each compound was added without complex treatment) (□). (a)–(e) Relationship between test time and Mb concentration when the sample is added. (a) Irradiate with fluorescent lamp (UV intensity; $2.00 \mu\text{W cm}^{-2}$), (b) Irradiate with UV (UV intensity; $2.00 \times 10^2 \mu\text{W cm}^{-2}$), (c) Irradiate with UV (UV intensity; $7.50 \times 10^2 \mu\text{W cm}^{-2}$), (d), (e) Irradiate with UV (UV intensity; $3.60 \times 10^3 \mu\text{W cm}^{-2}$), (f) Percentage reduction in the concentration of an aqueous Mb solution when irradiated with either UV or fluorescent light in the presence of sHAp + TiO_2 or TiO_2 .

When a typical fluorescent lamp was used to irradiate

aqueous Mb solutions for 90 min, no reduction in the Mb concentration was observed in the presence of unsupported TiO_2 , while a reduction of 6.19% was observed for the sHAp + TiO_2 composite. This result implies that even irradiation with a weak UV source such as a fluorescent lamp activates the catalytic activity of the sHAp + TiO_2 composite.

On the other hand, as shown in Fig. 4 (e), when simply adding sHAp (50 mg) and TiO_2 (4.0 mg) to 50 mL of the Mb aqueous solution to obtain the same sHAp/ TiO_2 ratio as in the sHAp + TiO_2 composite material, the Mb aqueous solution was hardly decolorized. When simply added sHAp and TiO_2 to the Mb, the Mb concentration decreased in the dark. On the other hand, when sHAp was mixed alone, the Mb concentration did not decrease in the dark. Therefore, it is considered that Mb was adsorbed to TiO_2 in the dark. Therefore, no photocatalytic activity improvement occurs if the sHAp and TiO_2 are present separately, and the composite structure with titanium oxide supported in the pores of apatite is necessary to improve the photocatalytic activity.

The part of author et al. [16] reported that although the rate of the photocatalytic oxidation reaction depends on the surface area of the photocatalyst, the reaction rate was higher in the case of HAp-covered TiO_2 , which has a smaller specific surface area than commercial TiO_2 . Therefore, it was proposed that the HAp crystal holds the electrons separate from the holes and suppresses the recombination of the electrons with positive holes, thereby increasing the Mb decomposition rate. The specific surface area of sHAp + TiO_2 synthesized in this study is very large (Table 1). Similarly, in the case of the sHAp + TiO_2 composite material synthesized in this work, it may be concluded that the photocatalytic activity increased due to the electron holding ability of sHAp, which resulted in an improvement of the efficiency of Mb decomposition (Fig. 4).

The part of author et al. [16] reported the Mb decomposition rate when irradiated with UV light was about 2.5 times higher than that of titanium oxide, but no experiments of the decomposition of Mb under weak UV sources were conducted.

The sHAp + TiO_2 composite prepared herein had a sHAp content of > 90 wt.%, which we suggest led to the more than five-fold enhancement in the Mb decomposition rate of sHAp + TiO_2 compared to unsupported TiO_2 . In this composite material, the fine TiO_2 particles in the pores of sHAp are surrounded by sHAp to a greater degree than in the previously reported HAp-coated TiO_2 [16]. When irradiated with a weak UV source, the Mb resolution capability of sHAp + TiO_2 increased to more than ten times that of TiO_2 (Fig. 4). In addition, the increased sHAp content of the sHAp + TiO_2 composite provides improved adsorption. The decomposition rate became very poor when sHAp and TiO_2 were used separately (Fig. 4), so the composite structure is important for improving the photocatalytic ability.

3.4 Changes in leucocrystal violet color

Fig. 5 shows the changes in the color of mixtures of both sHAp + TiO_2 with LCV and unsupported TiO_2 with LCV after irradiation. Whereas the mixture of unsupported TiO_2 and LCV remained almost white after 120 h, the mixture of sHAp + TiO_2 and LCV changed from white to

purple after only 24 h and continued to deepen in color up to 120 h. Since the oxidation of LCV to CV is accompanied by a color change from white to purple [7], we conclude that sHAp + TiO₂ enhances the rate of oxidation of LCV, causing it to change color more rapidly. The irradiation of sHAp + TiO₂ with ultraviolet light causes the photogenerated electrons from TiO₂ to be captured by sHAp, which suppresses electron-hole recombination. The positive holes that remain in TiO₂ contribute to the oxidation of LCV.

Fig. 5 Change in the color of LCV with time. Samples were each irradiated by a blacklight for 6 h. LCV was then mixed into each of the powders the mixture was left to stand in the dark for either 24 or 120 h.

4. Conclusions

In this work, a sHAp + TiO₂ composite was synthesized by mixing sHAp, obtained by a wet method using simulated body fluid, and a TiO₂ sol. The photocatalytic properties of this composite material were evaluated. Irradiating the composite photocatalyst with UV from a blacklight at three intensity levels showed that the percentage reduction in the concentration of an aqueous Mb solution was greater for sHAp + TiO₂ than for unsupported TiO₂, regardless of the UV intensity. We achieved an Mb degradation rate more than 5 times higher than that of unsupported TiO₂.

TiO₂ did not decompose Mb even when irradiated with a fluorescent lamp, but sHAp + TiO₂ decomposed a solution of Mb by 6.19%. Since sHAp + TiO₂ showed a higher photocatalytic activity than unsupported TiO₂ even under the low ultraviolet light intensity of a fluorescent lamp, we conclude that the sHAp support increased the photocatalytic activity of TiO₂.

Furthermore, upon mixing LCV with sHAp + TiO₂ that had been irradiated with light and leaving the mixture in the dark, the mixture of sHAp + TiO₂ oxidized the LCV to form purple-colored CV over time. Based on these results, we suggest that the electrons generated in the photocatalytic reaction move from TiO₂ to sHAp.

This phenomenon helps to suppress the recombination of electrons with holes, and thus the photocatalytic activity is improved. It was predicted that the photocatalytic activity was improved because the electrons generated by the photocatalytic reaction moved from TiO₂ to sHAp and HAp suppressed the recombination of electrons and holes by retaining the electrons. We propose that when the specimen is kept in the dark, the holes of TiO₂ can still contribute to LCV oxidation because of the decreased electron-hole recombination provided by sHAp. This study synthesized a new composite material and showed

that it could be used as a photocatalyst under fluorescent light and darkness. We believe that this new material will contribute to the future applications of TiO₂ photocatalysts.

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