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 ×10^2 μW 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 NOx, 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 (·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 ~0.4 μm between the aggregated plate-shaped HAp. 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 activity.

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 leucocystal 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 (SR266PA, Advantec). The mixture was left undisturbed for 1 day, after which it was decanted. Desalination was carried out using a centrifugal separator (S420, Kubota) until the conductance using an electroconductivity meter (MP227, Mettler) was less than 150 μS cm−1.

2.2 Preparation of sHAp + TiO2 composite

A slurry of sHAp (0.2 g) and a TiO2 sol (TKS-203, Taeya 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, Taeya 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 Kα X-ray source. Energy dispersive X-ray spectroscopy (EDXS) was used to identify the elemental composition of the surface of the composites (InTouchScopeTM 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 for 30 min and then irradiated with a blacklight (Sankyo Denki, 27W) for 90 min at three levels of UV intensity (3.60 × 10², 7.50 × 10², or 2.00 × 10³ µW 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 µW 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 × 10³ µW 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 2θ = 25.7° 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.](image)

![Fig. 2 XRD diffraction pattern of sHAp and peak intensities of HAp](image)

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.

![Table I. The specific surface area and zeta potential](image)

<table>
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<tr>
<th>Sample</th>
<th>Specific surface area/m²/g</th>
<th>Zeta potential/mV</th>
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<tbody>
<tr>
<td>sHAp</td>
<td>89.3</td>
<td>-6.66</td>
</tr>
<tr>
<td>TiO₂</td>
<td>97.6</td>
<td>-60.3</td>
</tr>
<tr>
<td>sHAp+TiO₂</td>
<td>105</td>
<td>-21.3</td>
</tr>
<tr>
<td>Mb</td>
<td>-</td>
<td>8.82</td>
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Table II. Composition weight of sHAp + TiO₂ analyzed by SQX

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content /wt%</th>
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<tbody>
<tr>
<td>CaO</td>
<td>59.09</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>32.54</td>
</tr>
<tr>
<td>TiO₂</td>
<td>7.77</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.45</td>
</tr>
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</table>

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, TiO2 has the largest difference in zeta potential with methylene blue. Therefore, it can be said that TiO2 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 × 10^3 μW cm^-2 of UV light (approximately the same intensity as that of a clear outdoor sky) was observed for unsupported TiO2, while the equivalent irradiation led to a 71.6% reduction in the Mb concentration when sHAp + TiO2 was used. UV irradiation with an intensity of 7.60 × 10^2 μW cm^-2 (approximately equivalent to that of sunlight through a window) resulted in Mb concentration reductions of 8.05 and 58.2% for unsupported TiO2 and sHAp + TiO2, respectively. A UV intensity of 2.00 × 10^2 μW cm^-2 (approximately equivalent to the intensity of a cloudy outdoor sky) led to reductions of 3.07% and 31.2% for unsupported TiO2 and sHAp + TiO2, respectively. Thus, the photocatalytic activity of the sHAp + TiO2 composite was higher than that of unsupported TiO2 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 + TiO2 (●), TiO2 (○), sHAp (■), without sample (△), sHAp and TiO2 (◎) (each compound was added without complex treatment) (□). (a) Irradiate with fluorescent lamp (UV intensity; 2.00 × 10^2 μW cm^-2), (b) Irradiate with UV (UV intensity; 2.00 × 10^2 μW cm^-2), (c) Irradiate with UV (UV intensity; 3.60 × 10^2 μW cm^-2), (d) Irradiate with UV (UV intensity; 7.50 × 10^2 μW cm^-2), (e) Irradiate with UV (UV intensity; 3.60 × 10^2 μW 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 + TiO2 or TiO2.

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 TiO2, while a reduction of 6.19% was observed for the sHAp + TiO2 composite. This result implies that even irradiation with a weak UV source such as a fluorescent lamp activates the catalytic activity of the sHAp + TiO2 composite.

On the other hand, as shown in Fig. 4 (e), when simply adding sHAp (50 mg) and TiO2 (4.0 mg) to 50 mL of the Mb aqueous solution to obtain the same sHAp/TiO2 ratio as in the sHAp + TiO2 composite material, the Mb aqueous solution was hardly decolorized. When simply added sHAp and TiO2 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 TiO2 in the dark. Therefore, no photocatalytic activity improvement occurs if the sHAp and TiO2 are present separately, and the composite structure with titanium oxide supported in the pores ofapatite 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 TiO2, which has a smaller specific surface area than commercial TiO2. 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 + TiO2 synthesized in this study is very large (Table 1). Similarly, in the case of the sHAp + TiO2 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 in 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 + TiO2 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 + TiO2 compared to unsupported TiO2. In this composite material, the fine TiO2 particles in the pores of sHAp are surrounded by sHAp to a greater degree than in the previously reported HAp-coated TiO2 [16]. When irradiated with a weak UV source, the Mb resolution capability of sHAp + TiO2 increased to more than ten times that of TiO2 (Fig. 4). In addition, the increased sHAp content of the sHAp + TiO2 composite provides improved adsorption. The decomposition rate became very poor when sHAp and TiO2 were used separately (Fig. 4), so the composite structure is important for improving the photocatalytic activity.

3.4 Changes in leucocrystal violet color

Fig. 5 shows the changes in the color of mixtures of both sHAp + TiO2 with LCV and unsupported TiO2 with LCV after irradiation. Whereas the mixture of unsupported TiO2 and LCV remained almost white after 120 h, the mixture of sHAp + TiO2 and LCV changed from white to
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.

References

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