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FULL PAPER

Photo-induced hydrophilicity of brookite TiO_2 prepared by hydrothermal conversion from Mg_2TiO_4

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Super-hydrophilic titanium dioxide (TiO_2) photocatalysts with some *mild* oxidizing ability are favorable for the self-cleaning applications on plastic films. In this study, we have focused on brookite TiO_2 for such purposes. Brookite TiO_2 powders were synthesized by the hydrothermal conversion method using Mg_2TiO_4 as a precursor. Mg_2TiO_4 (1 g) and 1 M HCl (30 mL) were put into a polytetrafluoroethylene (PTFE)-lined autoclave. The hydrothermal conversion was conducted at 110–150°C for 24 h. The photocatalytic oxidizing properties of brookite TiO_2/silicone films on glass substrates, prepared by the flow-coating method, were measured by methylene blue decomposition, and the photo-induced hydrophilicizing properties were evaluated using the contact angle of water under UV irradiation. The brookite TiO_2/silicone film prepared from the sample treated at 150°C exhibited well-balanced properties for self-cleaning applications.

Key-words : Titanium dioxide, Brookite, Hydrothermal conversion, Mg_2TiO_4, Photocatalytic activity, Oxidizing property, Photo-induced hydrophilicity

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1. Introduction

Titanium dioxide (TiO_2) has three naturally occurring polymorphs, i.e., anatase, rutile and brookite.[1)–3)] Another very rare polymorph, bronze-type TiO_2 [TiO_2 (B)], is also naturally yielded.[4)] Among these TiO_2 polymorphs, rutile and anatase TiO_2 are widely used for practical applications since they are easily synthesized and cost-effective. Thermally stable rutile TiO_2 is applied for white pigments, whereas thermally metastable anatase TiO_2 is applied for photocatalysts as well as for ingredients of various titanates. TiO_2 photocatalysts, particularly the anatase phase, have useful functions as for hydrogen production,[5)–7)] oxidizing decomposition of organic compounds,[8)–10)] antibacteria,[11)–13)] photo-induced hydrophilicity (self-cleaning) and others.[14)–17)]

In 1998–1999, Machida et al. focused on the self-cleaning functions of anatase TiO_2 and developed an anatase TiO_2/SiO_2 composite system with excellent hydrophilicity, even under dark conditions.[18)] More recently, Machida et al.[19)] have also reported on a long-term field testing of self-cleaning functions using anatase TiO_2/SiO_2 composite film; silicone resin with the hardening temperature of ~120°C was used as the SiO_2 precursor since a polyethylene-terephthalate (PET) film covering on a window-glass panel was used as the substrate. Despite the excellent hydrophilicity of the anatase TiO_2/SiO_2 composite film, the strong oxidizing ability of anatase TiO_2 also accelerated the formation of $CaSO_4$ from Ca^{2+} ions and SO_x gas in air, resulting in undesirable white precipitates on the PET-film-coated window glass.[19)]

Here, we propose that TiO_2 with somewhat *milder* oxidizing ability maintaining hydrophilicity, perhaps brookite, is more suitable for the self-cleaning applications on plastic films. Brookite TiO_2 has a band-gap of ~3.0 eV, which is comparable to that of rutile TiO_2. Brookite TiO_2 is metastable, much like anatase TiO_2, but it is more difficult to synthesize than anatase.[20)] The literature on the synthesis of brookite TiO_2 is relatively limited. Ohtani et al.[21)] reported the preparation of brookite and brookite/rutile TiO_2 mixture by air oxidation of $TiCl_3$ in an aqueous HCl solution. Pottier et al.[22)] reported the synthesis of brookite and brookite/rutile TiO_2 by pyrolysis of $TiCl_4$ in concentrated HCl solutions. Zheng et al.[23)] reported the preparation of brookite TiO_2 from $Ti(SO_4)_2$ and $TiCl_4$ as precursors under hydrothermal conditions. The hydrothermal temperatures of brookite formation from $Ti(SO_4)_2$ and $TiCl_4$ were ≥250 and ≥200°C, respectively. Tomita et al.[24)] successfully prepared single-phase brookite TiO_2 by hydrothermal treatment of $(NH_4)_6[Ti_4(C_2H_2O_3)_4(C_2H_3O_3)_2(O_2)_4O_2]\cdot 4H_2O$ complex. This precursor is particularly effective for obtaining single-phase brookite TiO_2, but synthesis of the precursor requires torturous multi-step reactions.

Recently, Kozawa et al.[25)] have developed an alternative

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route to preparation of brookite TiO_2 involving hydrothermal conversion method from Mg_2TiO_4. Hydrothermal conversion of Mg_2TiO_4 to brookite TiO_2 proceeded in 1 M HCl solution as low as at 100°C.[25] A simple solid state reaction at 1250°C was used to synthesize the Mg_2TiO_4 precursor. The authors evaluated some photocatalytic activities of the synthesized brookite (i.e., the oxidizing ability of benzyl alcohol), but the photo-induced hydrophilicity (self-cleaning) has not yet been reported.

The purpose of the present study is to achieve a balance between oxidizing and hydrophilicizing abilities of TiO_2 photocatalyst. Super-hydrophilic photocatalysts with a *mild* oxidizing ability have been achieved by brookite TiO_2. Brookite TiO_2 powders were synthesized by hydrothermal conversion of Mg_2TiO_4 and their photocatalytic activities, especially their photo-induced hydrophilicity, were investigated.

2. Experimental procedures

2.1 Synthesis of brookite TiO_2 by hydrothermal conversion

Brookite TiO_2 powders were synthesized by hydrothermal conversion using Mg_2TiO_4 as a precursor (i.e. Kozawa method),[25] as shown in **Fig. 1**. At first, Mg_2TiO_4 powder was synthesized by a solid-state reaction between $MgCO_3$ (basic) [or more precisely, hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] and anatase TiO_2 powders (both 99.9% purity, Kojundo Chemical Laboratory Co., Ltd.). Prior to weighing, TG–DTA analysis (up to 1000°C, DTA-50, Shimadzu) was conducted on the $MgCO_3$ (basic) powder to determine the weight-loss during the heating.

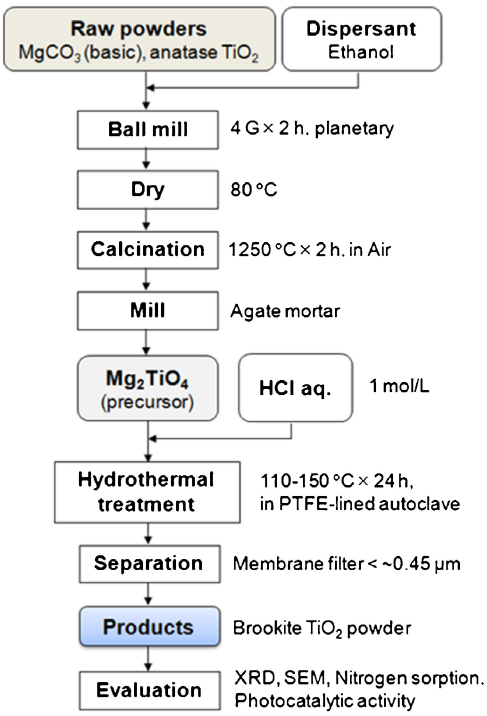

Fig. 1. Schematic flow of the synthetic procedure of brookite TiO_2.

With compositional calibration using the TG–DTA results, $MgCO_3$ (basic) and TiO_2 powders (Mg:Ti = 2:1 in molar ratio) were planetary ball-milled (acceleration: 4 G, Pulversette 6, Fritsch) with ZrO_2 balls in ethanol for 2 h. The mixed slurries were vacuum dried, and the dried powders were placed in an oven at 80°C for 1 h. The mixed powder was calcined in an alumina crucible at 1250°C for 2 h in air.

The synthesized Mg_2TiO_4 powder (1 g) and 1 mol/L HCl (30 mL) were put into an autoclave with a polytetrafluoroethylene inner container (50 mL of inner volume, HU-50, San-Ai Kagaku Co. Ltd.). Hydrothermal conversion was conducted at 110–150°C for 24 h in a static condition. The resulting products (i.e., brookite TiO_2 powders) were collected using membrane filters (opening: ~0.45 µm), washed with distilled water and then dried at 80°C.

2.2 Materials characterization

The constituent phases of the samples were analyzed by X-ray diffraction (XRD, Multiflex, Cu-K_α, 40 kV and 40 mA, Rigaku) at a scanning rate of 4°/min in the 2θ range of 10–70°. The microstructure of the Mg_2TiO_4 and brookite TiO_2 powders was observed by scanning electron microscopy (SEM, SU-70, Hitachi High-Technologies). The nitrogen adsorption/desorption isotherms at 77 K of brookite TiO_2 powders were measured using a gas sorption analyzer (Autosorb-3-AG, Quantachrome).

2.3 Thin film preparation

Coating suspensions were prepared with brookite powders and silicone binder (N-103X, Colcoat Co. Ltd.) with the weight ratio of TiO_2:silicone = 1:1. The solid contents of the coating suspensions were adjusted to 2.5 wt% by adding ethanol. The brookite/silicone suspensions were coated on slide glass (S1214, Matsunami Glass Ind., Ltd.) using the flow-coating method. The coated glass samples were cured at 80°C to obtain hard thin films. As references, P25 TiO_2 (Nippon Aerosil)/silicone film and silicone-only film were also prepared by the flow-coating method.

2.4 Measurement of photocatalytic activities

Photocatalytic methylene blue (MB) decomposition was evaluated as an oxidizing ability test. Thin film samples were soaked in 20 µmol/L MB aqueous solution for 16 h and dried for 1 h at room temperature. The starting absorbance at 664 nm (Abs_0) was measured using a UV–Vis spectrophotometer (UV-1280, Shimadzu) before UV irradiation. The surface of the thin film was UV irradiated with 20-W BLB fluorescent light (FL20SBL-B, NEC Corp) until the UV intensity (300–410 nm) reached 0.95 mW/cm^2 (measured by C9536-01/H9958-01, Hamamatsu Photonics K. K.). The intermediate and ending absorbances (Abs_t) were measured in the same way after 24 h. The decomposition rate (ΔAbs) was calculated by the following equation:

$$\Delta Abs = Abs_t - Abs_0 \quad (1)$$

As concerns the hydrophilic properties, the contact angle of water on the surface of the thin film was measured using a contact angle meter (CA-X150, Kyowa Interface Science Co., Ltd.) 30 s after the water-dropping with a microsyringe to the surface, while irradiating the surface of the thin film with UV rays for 48 h with a 20-W BLB fluorescent light until the UV intensity (300–410 nm) reached 0.95 mW/cm^2.

3. Results and discussion

3.1 Phase analysis

Figure 2 shows the XRD patterns of the powders before and after hydrothermal treatment. The powder before hydrothermal treatment consisted of single-phase Mg_2TiO_4, as shown in Fig. 2(a). After hydrothermal treatment, the products became brookite TiO_2 with a minor rutile component of TiO_2, as shown in Figs. 2(b)–2(d), which is in good agreement with the literature.[25] The shapes of the XRD profiles suggest that the crystallinity of the obtained brookite phase increased with increases in the hydrothermal temperature.

The weight fractions of brookite and rutile TiO_2 can be estimated from the following empirical equation proposed by Zhang and Banfield:[26),27]

$$W_B = \frac{2.721 A_B}{A_R + 2.721 A_B} \quad (2)$$

where W_B represents the weight fraction of brookite, and A_B and A_R represent the integrated intensities of the peaks of brookite 121 and rutile 110, respectively. **Table 1** summarizes the weight fractions of the brookite and rutile TiO_2 phases estimated from the XRD integrated intensities. Although we should note the possibility of remnant amorphous TiO_2 and anatase TiO_2, based on the current XRD analyses, the hydrothermal conversion method yielded ~94 and ~97% brookite at 110 and 150°C, respectively. Considering the ease of processing, these values are sufficiently high for potential applications.

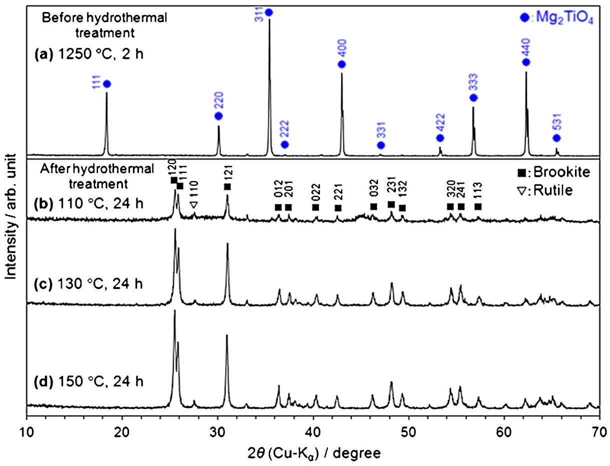

Fig. 2. XRD patterns of the samples (a) before hydrothermal treatment and (b)–(d) after hydrothermal treatment: (b) at 110°C for 24 h, (c) at 130°C for 24 h, and (d) at 150°C for 24 h.

Table 1. Weights fraction of brookite and rutile TiO_2 estimated from XRD integrated intensities

Hydrothermal conditions	Brookite (wt %)	Rutile (wt %)
110°C, 24 h	94.2	5.8
130°C, 24 h	96.8	3.2
150°C, 24 h	97.2	2.8

3.2 Microstructure

Figures 3(a) and 3(b) show the microstructure of the Mg_2TiO_4 powder, i.e., before hydrothermal treatment. Due to the solid-state synthesis, the Mg_2TiO_4 powder consisted of angular particles (ca. 1–3 µm in diameter) with irregular shapes and smooth surfaces, similar to those observed in the previous report.[25] After hydrothermal treatment at 110°C for 24 h, the macroscopic shapes of the product were nearly unchanged from those of the initial Mg_2TiO_4 [Fig. 3(c)]. Judging from the broad XRD pattern, however, these micrometer-sized particles were thought to be composed of aggregates of much finer brookite TiO_2 nanoparticles. A large number of minute particles (ca. 50–100 nm) was deposited on the micrometer-sized particles, moreover, and some pores were observed on a part of these [Fig. 3(d)]. As is explained by Kozawa et al.,[25] these pores were likely formed by the serious lattice shrinkage (57%) from Mg_2TiO_4 (601 Å^3) into brookite TiO_2 (257 Å^3) during the following reaction under hydrothermal conditions:

$$Mg_2TiO_4 + 4HCl \rightarrow TiO_2 + 2MgCl_2 \text{ (soluble in water)} + 2H_2O$$

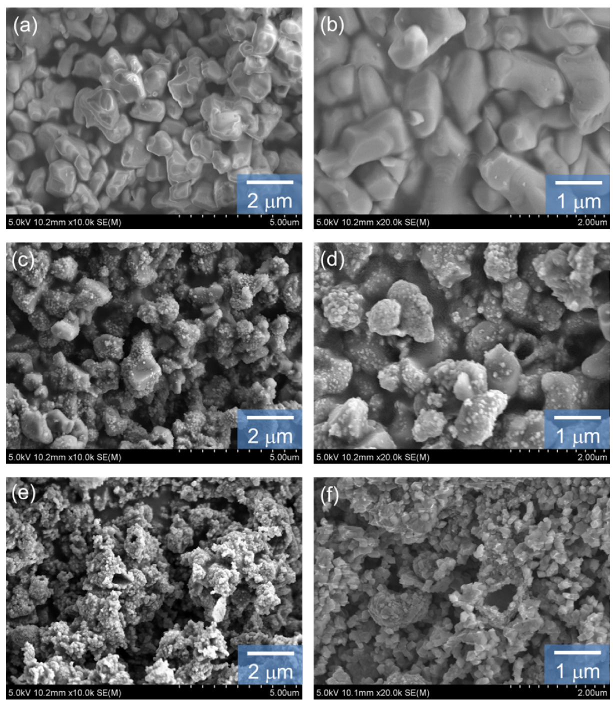

Fig. 3. SEM photographs of the samples (a), (b) before hydrothermal treatment, and (c), (d) after hydrothermal treatment: (c), (d) at 110°C for 24 h, and (e), (f) at 150°C for 24 h.

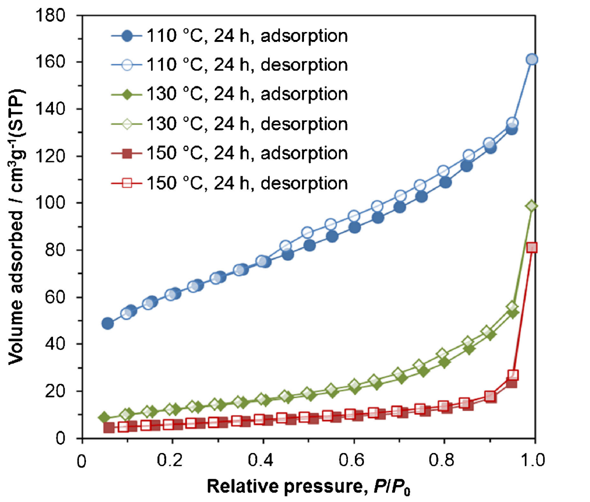

Fig. 4. Nitrogen adsorption/desorption isotherms of brookite TiO_2 powders obtained by hydrothermal conversion.

After hydrothermal treatment at 150°C for 24 h, the initial macroscopic shapes of Mg_2TiO_4 tended to collapse [Fig. 3(e)], and brookite TiO_2 particles typically became 50–200 nm in diameter [Fig. 3(f)], and started to become facetted (also see in Fig. S1).

3.3 Nitrogen sorption analyses

Figure 4 presents the N_2 adsorption/desorption isotherms for the brookite TiO_2 powders. Judging from the IUPAC type-IV hysteresis loop, the powder obtained from the treatment at 110°C contained mesopores. The specific surface area calculated by the BET method using the adsorption isotherm was relatively large, 207 m^2/g. From the BJH analysis of the desorption curve, the diameter of the mesopores was estimated at 3.5 nm in diameter. The powder obtained from the treatment at 150°C contained almost no mesopores, and its surface area was relatively small, 20.6 m^2/g.

3.4 Photocatalytic methylene blue (MB) decomposition

Figure 5 shows the MB decomposition rates as a function of UV irradiation time for the thin film samples composed of TiO_2/silicone. As expected, P25 TiO_2 (anatase:rutile ~ 4:1)/silicone film showed the highest oxidizing ability. The brookite TiO_2/silicone film prepared from the powder treated at 150°C showed the second highest oxidizing ability (nearly half of that of P25 TiO_2). The oxidizing ability of the brookite TiO_2/silicone film prepared from the powder treated at 110°C decreased to nearly half of that of prepared from the powder treated at 150°C. Although the 110°C sample had higher specific surface area than 150°C sample, its lower crystallinity as well as the inaccessibility in its inner surfaces though mesopore channels presumably led to the lower photocatalytic activity.

3.5 Photo-induced hydrophilicity

Figure 6 presents the water contact angle as a function

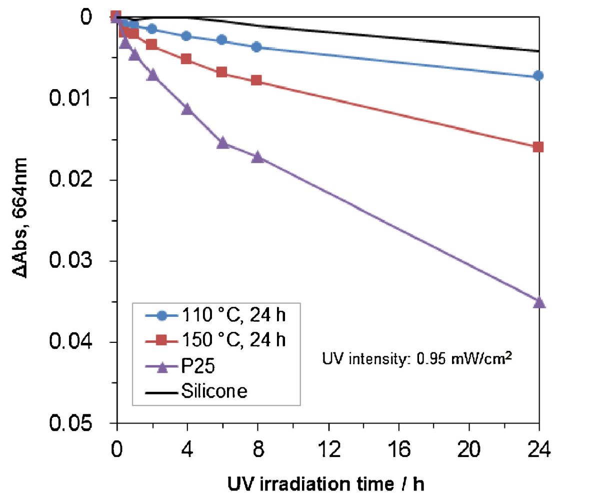

Fig. 5. Methylene blue (solid-state) decomposition under UV irradiation of brookite TiO_2 thin films prepared from synthesized brookite TiO_2 powders. P25 TiO_2 film and silicone-only film were also measured as references.

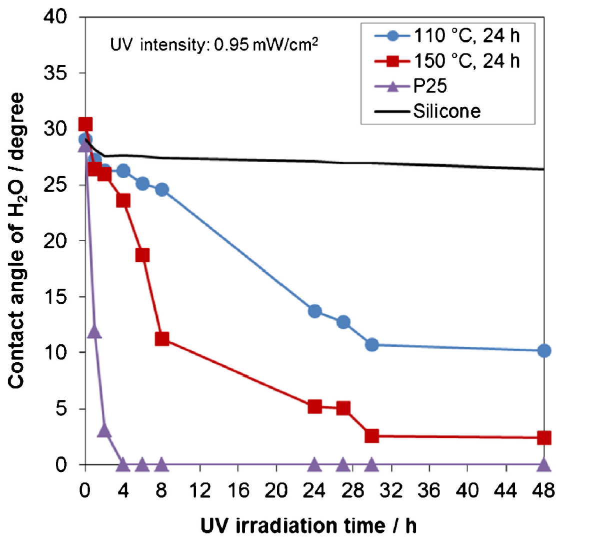

Fig. 6. Contact angles of water under UV irradiation of brookite TiO_2 thin films prepared from brookite TiO_2 powders obtained by hydrothermal treatment. P25 TiO_2 film and silicone-only film were also measured as references.

of UV irradiation time for the thin film samples composed of TiO_2/silicone. The thin film sample with silicone-only (as a controlled sample) showed almost no change in the water contact angle under UV irradiation. The contact angle of water for the film composed of TiO_2 treated at 150°C became super-hydrophilic, with a contact angle such as <5°, with about 24 h UV irradiation. In the film containing TiO_2 treated at 110°C, on the other hand the contact angle of water decreased to ~10°, even when the film was irradiated with UV rays for 48 h.

The XRD results suggest that the crystallinity of brookite hydrothermally treated at 150°C is higher than that treated at 110°C. In general, photocatalytic activity increases with increases in the crystallinity of TiO_2. Hence, it is considered that the contact angle of water with the film composed of brookite TiO_2 treated at 150°C decreased more quickly than that at 110°C, and the final contact angle also became lower.

The contact angle of water for the film composed of Aerosil P25 became <5° within 2 h of UV irradiation. This result indicates that the photocatalytic activity of anatase/rutile TiO_2 is remarkably higher than that of the brookite TiO_2 prepared in this study. As proposed in the introduction, we consider the repression of photocatalytic oxidizing ability and preservation of photo-induced hydrophilic ability to be key factors for self-cleaning applications. These results suggest that the oxidizing ability can be controlled by using brookite TiO_2 while maintaining the hydrophilic ability.

4. Conclusions

Here brookite TiO_2 powders were synthesized from Mg_2TiO_4 by hydrothermal conversion. The photocatalytic oxidizing ability and the photo-induced hydrophilicity were evaluated under UV irradiation. These evaluations led to the following conclusions:

(1) About 94% brookite TiO_2 powders with a minor rutile TiO_2 component were obtained by hydrothermal conversion at 110°C, and 97% at 150°C. SEM observation indicated that hydrothermal conversion proceeded with little change of the macroscopic morphology of precursor grains at a lower temperature, but the morphology tended to collapse at a higher temperature. The brookite TiO_2 powder obtained with the treatment at 110°C was composed of aggregated nanoparticles with a mesoporous structure (pore size: 3.5 nm in diameter) and had a relatively large specific surface area of 207 m^2/g. The powder obtained with the treatment at 150°C was composed of facetted (well-crystalized) submicron-sized particles without mesopores and with a small specific surface area of 20.6 m^2/g.

(2) As expected, brookite TiO_2 showed a *mild* oxidizing ability while maintaining hydrophilicity. For the photocatalytic oxidization (methylene blue decomposition under UV irradiation), the decomposition rates of the brookite TiO_2 films prepared from powders treated at 110°C and 150°C were about 1/4 and 1/2 those of P-25 TiO_2 film. In the measurement of photo-induced hydrophilicity, the contact angle of water for the film composed of TiO_2 treated at 150°C became super-hydrophilic with about 24 h UV irradiation. Super-hydrophilic brookite TiO_2 films with a mild oxidizing ability can be considered favorable for use in plastic-film-coated window glass for a self-cleaning function.

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