

# Photocatalytic activity of nanocrystalline $\text{TiO}_2(\text{B})$ synthesized from titanium glycolate complex by hydrothermal method

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The metastable phase of  $\text{TiO}_2(\text{B})$ , one of the polymorphs of titanium dioxide ( $\text{TiO}_2$ ), was prepared by a hydrothermal treatment of a titanium glycolate complex ( $[\text{Ti}_4(\text{C}_2\text{H}_3\text{O}_3)_4(\text{C}_2\text{H}_3\text{O}_3)_2(\text{O}_2)_4\text{O}_2]^{6-}$ ) at 473 K for 1–72 h in the presence of  $\text{H}_2\text{SO}_4$ . Characterization by X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed that the obtained samples were composed of single phase  $\text{TiO}_2(\text{B})$  and the particles had plate-like morphology. After post-synthetic hydrothermal crystal growth (PHCG) applied to the as-prepared sample, thicker plate-like shaped particles were obtained. The photocatalytic activities of the samples obtained by the hydrothermal treatment and after the subsequent PHCG were evaluated in terms of methanol decomposition.

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## 1. Introduction

Titanium dioxide ( $\text{TiO}_2$ ) has been used as a photocatalyst due to its ability to decompose organic compounds, antifouling and self-cleaning properties. There are eight polymorphs of  $\text{TiO}_2$  that can exist under normal pressure and at room temperature.<sup>1)–7)</sup> However, until now mainly anatase and rutile forms of  $\text{TiO}_2$  have been used as photocatalysts because these two polymorphs can be easily synthesized. Preparation of the other polymorphic forms of  $\text{TiO}_2$  is difficult, and the number of reports about their synthesis and properties is extremely limited. Therefore, photocatalytic activities of the  $\text{TiO}_2$  metastable phases are not well-known, and they may possess superior photocatalytic activity than anatase and rutile.

Synthesis of  $\text{TiO}_2(\text{B})$ , one of the metastable phases of  $\text{TiO}_2$ , by solid-state reaction and solution methods have been reported.<sup>8)–11)</sup> However, these methods employ multi-step procedures, which usually include formation of intermediates such as  $\text{Na}_2\text{Ti}_3\text{O}_7$  and  $\text{H}_2\text{Ti}_3\text{O}_7$ , ion-exchange reaction and deprotonation under mild conditions. As a result, usually the synthesized  $\text{TiO}_2(\text{B})$  has poor crystallinity and includes small amount of anatase as an impurity. We reported direct synthesis of  $\text{TiO}_2(\text{B})$  by a hydrothermal treatment without formation of intermediates such as  $\text{Na}_2\text{Ti}_3\text{O}_7$  and  $\text{H}_2\text{Ti}_3\text{O}_7$ .<sup>12)</sup> In the proposed method titanium complex with glycolic acid was used as a starting reagent. Glycolic acid, which is also known as an easily accessible food product, coordinates  $\text{Ti}^{4+}$  ion together with  $\text{O}^{2-}$  and  $\text{O}_2^{2-}$  ions to form a water-soluble titanium glycolate complex.<sup>13)–16)</sup> The solution of this titanium complex is very stable and does not yield a precipitation for more than several years in the range of temperatures from 0 to 373 K, and at pH ranging from 0 to 12. It is essential that this complex

makes it possible to use water as a solvent for synthesis of titanium-based compounds. Hydrothermal techniques, which rely on using water as a solvent, allow to obtain crystalline materials under low temperatures compared to the conventional solid-state reaction or other solution methods that involve final annealing for crystallization. In this work we report synthesis of the metastable  $\text{TiO}_2(\text{B})$  by the hydrothermal treatment of the titanium glycolate complex and photocatalytic activities of the prepared  $\text{TiO}_2(\text{B})$  in comparison to anatase and rutile.

## 2. Experimental procedure

Titanium metal powder (Toho Titanium Co., Ltd.) was dissolved in cooled solution including 30 mass%  $\text{H}_2\text{O}_2$  (Wako Pure Chemical Industries Ltd.) and 28 mass%  $\text{NH}_3$  aqueous solutions (Wako Pure Chemical Industries Ltd.) yielding after 1.5 h a yellow transparent oxoperoxo titanium complex  $[\text{Ti}(\text{OH})_3\text{O}_2]^-$  solution. Then glycolic acid ( $\text{HOCH}_2\text{COOH}$ , Kanto Chemicals Co., Ltd.) was added as a chelating agent to obtain a titanium glycolate complex ( $[\text{Ti}_4(\text{C}_2\text{H}_3\text{O}_3)_4(\text{C}_2\text{H}_3\text{O}_3)_2(\text{O}_2)_4\text{O}_2]^{6-}$ ). The molar ratio of each chemicals was  $\text{Ti}:\text{glycolic acid}:\text{H}_2\text{O}_2:\text{NH}_3 = 1:1.5:35:16$ . An excess amount of  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$  compared to the stoichiometric ratio is necessary to dissolve metal titanium powder. The solution was dried at 338 K to remove remained  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$  and it transformed into a dry gel-like substance. Distilled water was added to this gel, and it dissolved easily yielding a yellow transparent aqueous solution. The initial pH of the titanium glycolate complex solution was 6. For the next step 4.6 g of  $\text{H}_2\text{SO}_4$  (2.4 ml) (96 mass%, Kanto Chemicals Co., Ltd.) was added to volume of the solution was adjusted to 5 ml by distilled water. The solution of total volume 7.4 ml was sealed in a Teflon-lining stainless steel autoclave of 50 ml volume, and heated at 473 K for 1, 24, 48 and 72 h. Obtained precipitates were separated from the solutions by centrifuging ( $20000 \times g$  for 30 min) and washed with distilled water several times. The pow-

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**Table 1.** Samples Notation and Synthesis Conditions Used in this Work

sample number	reaction time / h	PHCG time / h	PHCG condition	UV( $\lambda_{\max} = 254$ nm) irradiation
i	1	—	—	—
ii	24	—	—	—
iii	48	—	—	—
iv	72	—	—	—
v	72	—	—	1 week
vi	1	72	H <sub>2</sub> O	—
vii	1	72	1M HCl	—
viii	1	72	1M NaOH	—

ders were characterized after drying at 338 K in air. 0.2 g batches of the sample prepared by hydrothermal treatment for 1 h were treated in distilled water, 1 M HCl (Kanto Chemicals Co., Ltd.) or 1 M NaOH (Wako Pure Chemical Industries, Ltd.) solutions using the same autoclave at 473 K for 72 h with stirring at 1000 rpm. This procedure is designated as “post-synthetic hydrothermal crystal growth (PHCG)” further in the text. **Table 1** summarizes synthesis conditions for each sample.

All samples were characterized by powder X-ray diffraction (XRD; Rigaku Co., Geigerflex RAD-C diffractometer) and transmission electron microscopy (Hitachi, Ltd., HF-2200TU, accelerating voltage 200 kV) using scanning mode. The weight losses of TiO<sub>2</sub>(B) samples from room temperature to 1273 K were determined by thermo gravimetric analysis (TG-DTA; Bruker AXS K. K., 2020SA-TU19).

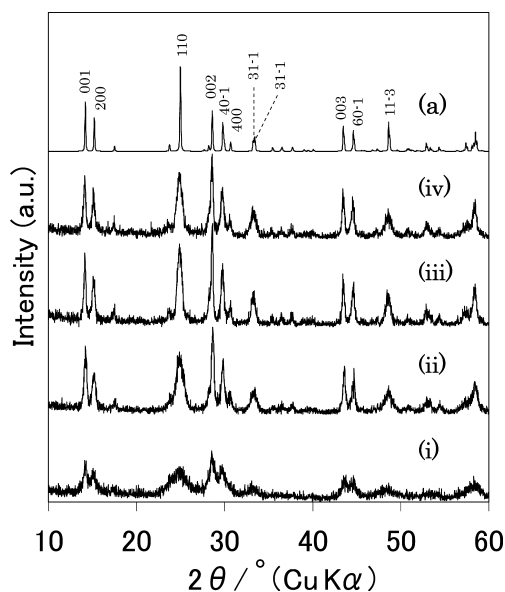
Photocatalytic activities of samples were examined in terms of methanol decomposition. 6  $\mu$ l of methanol was evaporated in a PYREX glass reactor having 176 cm<sup>3</sup> volume. 0.05 g TiO<sub>2</sub> samples were used for the photocatalytic reaction, which were irradiated by UV light ( $\lambda_{\max} = 365$  nm, 20 W  $\times$  2). Concentration of CO<sub>2</sub> formed by decomposition of methanol was determined by a Fourier transform infrared spectrometer (FT-IR; Horiba, Ltd., FT-710). The specific surface areas of samples were measured by the BET method (Shimadzu Co., ASAP2010).

### 3. Results and discussion

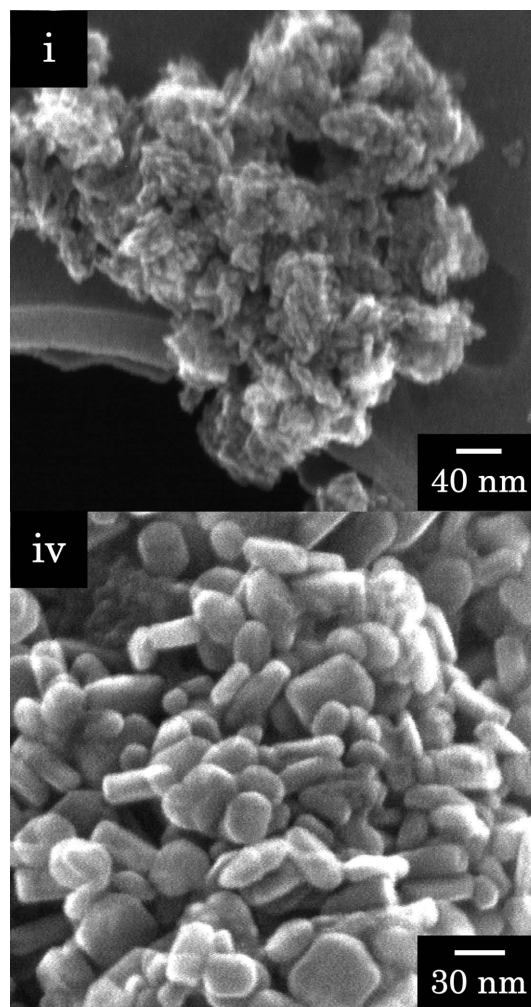
#### 3.1 Synthesis

Samples names and corresponding synthesis conditions are summarized in Table 1. The same samples notation will be used in the discussions below. **Figure 1** shows XRD patterns of the powder samples obtained by hydrothermal treatment of 6 M titanium glycolate complex at 473 K for 1, 24, 48, and 72 h. Single-phase TiO<sub>2</sub>(B) was obtained by adding 4.6 g of H<sub>2</sub>SO<sub>4</sub>. With increase of heating time, crystallinity improved and no transformation of TiO<sub>2</sub>(B) to other phases was observed. On the other hand, rutile was obtained in the case of smaller amount of H<sub>2</sub>SO<sub>4</sub>, and anatase was obtained when large excess of H<sub>2</sub>SO<sub>4</sub> was used. **Figure 2** shows STEM images of Sample i and Sample iv (the same notation as in Table 1). One may notice that after the short reaction time (Sample i) very fine agglomerated particles formed. Prolonged hydrothermal treatment for 72 h (Sample iv in Fig. 2) leads to the growth of plate-like particles of 40  $\times$  40  $\times$  10 nm dimensions. Peak broadening of diffraction lines from 110, 310, 31-1, and 11-3 (*hkl*, *k*  $\neq$  0) planes were observed. This result corresponds to the particle images of Fig. 2.

**Figure 3** shows XRD patterns of another set of samples after



**Fig. 1.** XRD patterns of samples obtained by hydrothermal treatment of titanium glycolate complex aqueous solution. Sample i, ii, iii, iv, (a) Calculated pattern for TiO<sub>2</sub>(B) ICSD #41056.



**Fig. 2.** STEM images of samples obtained by hydrothermal treatment of titanium glycolate complex. Samples i and iv.

PHCG procedure with different additives. Sharper XRD peaks of samples after PHCG indicates that crystallinity of  $\text{TiO}_2(\text{B})$  in all cases increased after additional post-treatment. Sample vi treated in pure water consisted of  $\text{TiO}_2(\text{B})$  as the single-phase, while samples vii and viii were multi-phase containing small amounts of rutile and anatase respectively. To investigate crystal growth during PHCG procedure, the mixtures of sample i and 30 wt% of anatase (ST-01, Ishihara Sangyo Kaisha Ltd.) or 30 wt% of rutile (prepared by hydrothermal treatment of titanium tartarate complex) were treated under the same conditions, and, as a result, single phase anatase or rutile were obtained respectively. These results prove that single-phase  $\text{TiO}_2(\text{B})$  could not be obtained from a multi-phase sample by PHCG due to the transformation from  $\text{TiO}_2(\text{B})$  to another more stable-phase if even small amount of such a phase was formed. Therefore, it is necessary to achieve high purity of  $\text{TiO}_2(\text{B})$  sample in order to prepare highly crystalline  $\text{TiO}_2(\text{B})$  powder by PHCG. Since sample i transformed into rutile and anatase during PHCG in HCl and NaOH solutions respectively, it is an indication that in both cases the seeds of rutile or anatase were present.

The mechanism of PHCG can be described as a variation of recrystallization process. During the first step, all polymorphs of  $\text{TiO}_2$  slightly dissolve in the aqueous solution under the hydrothermal conditions. As one may expect, the dissolution rate should be different for each polymorph. For instance, the dissolution of metastable  $\text{TiO}_2(\text{B})$  phase is easier than dissolution of anatase or rutile because from the thermodynamic view point its crystal lattice is less stable than those of anatase and rutile, but solvation energy of titanium should be the same regardless of the crystalline phase from which it originated. In contrast, deposition rate of dissolved Ti species should be comparable for all polymorphs of  $\text{TiO}_2$  because it is controlled by diffusion of Ti to the surface of the growing crystal and kinetics of Ti-O bonds formation during olation process. Moreover, it seems that composition of the solution during PHCG process can influence transformation into anatase or rutile. For instance, Sample i contained initially seeds of both anatase and rutile, however only

anatase or rutile was found in the final product depending on the nature of additive, indicating that dissolution rates were different in HCl solution (anatase > rutile) and in NaOH solution (anatase < rutile).

**Figure 4** shows STEM image of  $\text{TiO}_2(\text{B})$  sample after PHCG (sample vi). While plate-like crystallites of  $30 \times 30 \times 15$  nm size were observed, the particles were thicker than those in sample iv. Specific diffraction planes ( $hkl$ ,  $k \neq 0$ ) of samples vi and vii were observed sharper than samples obtained by hydrothermal synthesis without PHCG, therefore we conclude thin direction of the particle corresponds to b axis of the crystal. Evidently, this difference of shape can be attributed to the effect of glycolic acid. Most likely -OH and/or -COOH groups adsorb onto crystal facets of  $\text{TiO}_2(\text{B})$ , when synthesis is carried out in the solution containing glycolic acid, and these absorbed molecules retard crystal growth in the specific lattice directions covered by the ligand resulting in the formation of plate-like morphology. At the same time, the solution during PHCG does not contain glycolic acid, and particles continue to grow more isotropically preserving the shape of the seed (sample i).

### 3.2 Photocatalytic properties

**Figure 5** shows photocatalytic activities of the prepared  $\text{TiO}_2(\text{B})$  samples, anatase (Wako Pure Chemical Industries Ltd.) and rutile (Wako Pure Chemical Industries Ltd.) in terms of

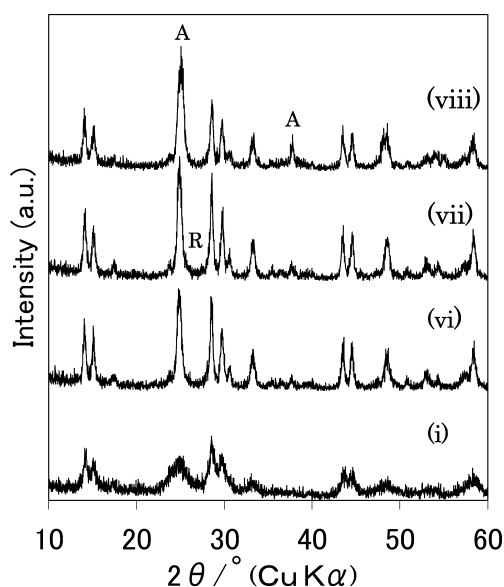


Fig. 3. XRD patterns of samples obtained by hydrothermal treatment of titanium glycolate under the conditions as specified for Samples i, vi, vii, viii, A: peak position of Anatase and R: peak position of rutile.

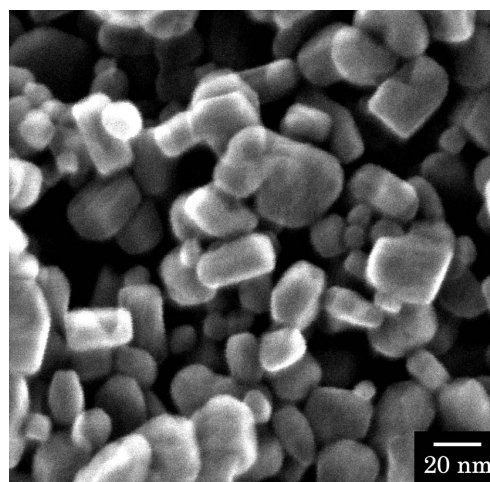


Fig. 4. STEM images of  $\text{TiO}_2(\text{B})$  particles. Sample vi.

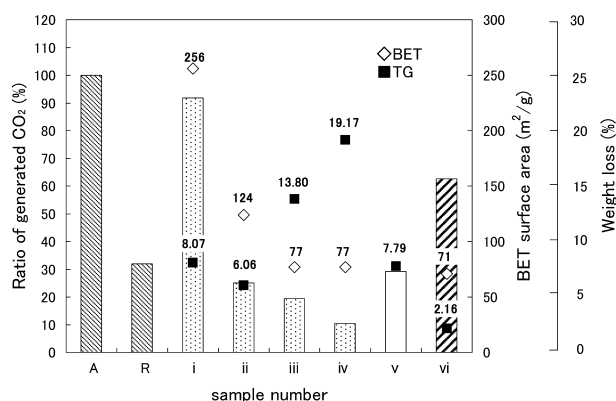


Fig. 5. Photocatalytic activities of  $\text{TiO}_2(\text{B})$  samples prepared in this work compared against. A: Anatase and R: Rutile.

decomposition rate of methanol to produce CO<sub>2</sub>. Anatase demonstrated the highest activity in this reaction. Sample i, which had the smallest size of nanocrystals, had comparably high activity. With increase of heat treatment time, the colors of samples obtained by the hydrothermal treatment changed from white to tan and finally to dark-brown, while their specific surface areas and photocatalytic activities decreased due to decreasing surface area as a result of crystal growth and adsorption of organic compounds. Weight loss due to the oxidation of residual organic compounds in each sample is also presented in Fig. 5. One may notice that with increase of heating time, the amount of adsorbed organics increased. To investigate the influence of adsorbed organic compounds on photocatalytic activity of the prepared samples, Sample iv, which contained the largest amount of adsorbed species was irradiated by UV light for a week in distilled water to remove organic substances by the photocatalytic reaction. After UV irradiation, the sample color changed from dark-brown to light-gray, and weight loss of the sample during heat-treatment became less substantial. As a result of the removal of adsorbed organics, photocatalytic activity also significantly increased (Sample v in Fig. 5). This observation indicated that adsorbed organic species caused degradation of photocatalytic activity. Such a conclusion is also in agreement with the tendency observed for the samples after PHCG. Initially the sample i contained a small amount of adsorbed organic compounds. After PHCG in the pure water the amount of organics decreased (sample vi). At the same time the surface area of this sample became close to those of samples iv and v, however the former one had considerably smaller amount of the adsorbed organics and therefore demonstrated much higher photocatalytic activity. It is worth emphasizing that sample i exhibited still the highest activity among the prepared TiO<sub>2</sub>(B) samples regardless of lower crystallinity and amount of organics on the surface. Nevertheless, if one would take into account very large surface area of this sample, high activity would not be a surprising fact because for the photocatalytic decomposition of methanol in air the effect of large surface outweighs the negative contributions from shadowing the active sites by organic species and lower crystallinity.

#### 4. Conclusion

We synthesized a TiO<sub>2</sub>(B) metastable phase by hydrothermal treatment of a titanium glycolate complex in the presence of H<sub>2</sub>SO<sub>4</sub>. It was established that with increase of heating time, crystallinity of samples improved, but at the same time increase in adsorption of organic compounds by TiO<sub>2</sub>(B) powders was revealed. Such adsorbed organic species caused decrease of photocatalytic activities exhibited by the nanocrystalline samples. Removing of adsorbed organics in the course of PHCG or by UV irradiation resulted in improvement of photocatalytic activity.

The sample with the highest photocatalytic activity was obtained under the following conditions: Ti concentration = 6 M, amount of H<sub>2</sub>SO<sub>4</sub> = 4.6 g, heating temperature = 473 K, heating time = 1 h. It was also found that photocatalytic activity in terms of methanol decomposition in air mainly depended on surface area rather than on amount of adsorbed organics or crystallinity. The prepared TiO<sub>2</sub>(B) samples were strongly agglomerated, therefore it can be expected that further increase of photocatalytic activity of TiO<sub>2</sub>(B) beyond activity of anatase may be achieved by dispersing agglomerated particles.

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