

## Synthesis and Characterization of Colored Titania by Soft Solution Process

Shu Yin, Yohei Aita, Qinglin He, Qing Tang, and Tsugio Sato

IMRAM, Tohoku University, Sendai 980-8577, Japan

Fax: 81-22-217-5599, e-mail: shuyin@tagen.tohoku.ac.jp

In order to utilize solar energy efficiently, it is necessary to develop a visible-light reactive photocatalyst. In the present research, titania nanocrystals which can use visible light were prepared by "Homogeneous Precipitation-Hydrothermal Process" in  $\text{TiCl}_3$ -hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) solution. The phase composition, crystallinity, microstructure and specific surface area of titania powders greatly changed depending on pH and temperature. Yellow titania powders with excellent visible light absorbency and photocatalytic activity were prepared. It is supposed that nitrogen doping and oxygen vacancy lead to the different color in titania crystals. The yellowish titania powders prepared in  $\text{TiCl}_3$ -hexamethylenetetramine solution at pH 7 and  $190^\circ\text{C}$  for 2 h consisted of single phase of brookite and possessed a very high specific surface area of  $167.8 \text{ m}^2/\text{g}$ . The yellowish brookite showed excellent visible light absorbency and photocatalytic ability for nitrogen monoxide destruction under irradiation of the visible light ( $\lambda > 510\text{nm}$ ).

Key words: Brookite, Colored titania, Photocatalytic activities, Visible light absorbency, Soft solution process

### 1. INTRODUCTION

Titania is the principal white pigment in the world and has wide applications in many fields especially in photochemical research [1,2]. Under light irradiation, titania photocatalyst can decompose many pollute substances, such as poisonous nitrogen monoxide in atmosphere and/or organic pollutants in water. Although three polymorphs of titania, rutile, anatase, and brookite are in nature, usually, only anatase and rutile are utilized as photocatalyst. It is reported that anatase possesses higher photocatalytic activity than that of rutile [3], because rutile is usually prepared by calcination of anatase at high temperature and showed harder agglomeration and larger particle size than those of anatase. Few researches have carried out on the photocatalytic activity of brookite. A serious problem in application of anatase as photocatalyst is its large band gap energy of 3.2 eV, i.e. anatase only shows photocatalytic activities under UV light irradiation of  $\lambda < 387 \text{ nm}$ . It is known that sunlight contains about 5 % of UV light and most of it is visible light. In order to utilize the solar energy efficiently, it is necessary to develop a visible-light reactive photocatalyst. Asahi et al. [4] reported that nitrogen doped titania with high visible light photocatalytic activity could be prepared by sputtering  $\text{TiO}_2$  target in an  $\text{N}_2$  (40 %) and Ar gas mixture followed by annealing in  $\text{N}_2$  gas at  $550^\circ\text{C}$  for 4 h. It was observed that nitrogen doped titania was yellow. Ihara et al. [5] also reported that visible-light-active titania could be prepared by RF plasma treatment.

Recently, soft solution process has become a promising method for material synthesis because of the possibility of producing nanosize crystals with soft agglomeration, and controlling the phase composition or morphology by optimizing reaction conditions. In the present study, brookite and/or rutile powder with visible-light activity was prepared by a homogeneous precipitation-hydrothermal process. It is a novel process for the synthesis of nitrogen doped titania photocatalyst.

### 2. EXPERIMENTAL

$\text{TiCl}_3$  (Kanto Chem. Co. Inc. Japan) was used as a starting material. Hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ , Kanto Chem. Co. Inc. Japan) was used as a nitrogen source. The mixed solution of 10 wt%  $\text{TiCl}_3$  and desired amount of HMT was placed into a SUS 314 stainless steel autoclave of internal volume  $200 \text{ cm}^3$  and the chamber of autoclave was replaced by nitrogen gas three times. The autoclave was heated and kept at  $90^\circ\text{C}$  for 1 h to realize homogeneous precipitation and then heated at desired temperature for 2 h. The final pH value of the solution was controlled by changing the amount of HMT. The powder product was separated by centrifugation, washed with distilled water three times, and vacuum dried at  $80^\circ\text{C}$  overnight. The phase constitution of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized  $\text{CuK}\alpha$  radiation. The specific surface areas were determined by the amount of nitrogen adsorption at 77K (BET, Quantachrome NOVA 1000-

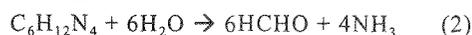
TS). The BET particle size was calculated by the following equation:

$$d = k/(\rho S_w) \quad (1)$$

where,  $d$  is BET particle size;  $k$  is shape constant, in the case of spherical shape,  $k=6$ ;  $\rho$  is density,  $S_w$  is the specific surface area. Microstructures were observed by a transmission electron micrograph (TEM, JEOL JEM-2010). The absorption edges and band gap energies of the products were determined from the onset of diffuse reflectance spectra of the samples measured using an UV-VIS spectrophotometer (Shmadzu UV-2000). The experimental apparatus used for photocatalytic reaction was reported in a previous paper [6]. The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor [373 cm<sup>3</sup> of internal volume] during the photo-irradiation of constant flowed 1 ppm NO-50 vol.% air mixed (balance N<sub>2</sub>) gas [200 cm<sup>3</sup>/min]. The photocatalyst sample was placed in a hollow place of 20×15×0.5 mm<sup>3</sup> on a glass holder plate and set in the center of the reactor. A 450-W high-pressure mercury lamp was used as the light source, where the inner cell had thermostated water flowing through a jacket between the mercury lamp and the reactor. The light wavelength was controlled by selecting various filters, i.e., Pyrex glass for cutting off the light of  $\lambda < 290$  nm, Kenko L41 Super Pro (W) filter < 400 nm and Fuji triacetyl cellulose filter < 510 nm). For comparison, a photocatalytic reaction was also carried out using commercial titania (Degussa P-25).

### 3. RESULTS & DISCUSSION

The hydrolysis of HMT proceeds as follow above 70°C:



In the present experimental conditions, amorphous titania was formed by the homogeneous precipitation at 90°C. Finally, well-crystallized titania was formed by the followed hydrothermal treatment. Figure 1 shows the XRD patterns of the powders prepared by the homogeneous precipitation-hydrothermal process in TiCl<sub>3</sub>-HMT solution at 190°C under different pH values and P-25 titania powder. It was found that P-25 titania consisted of a mixture of 70% anatase and 30% rutile. The powders prepared at pH 2 and 7 in TiCl<sub>3</sub>-HMT solutions were single phase of brookite, while that at pH 9 was single phase of rutile. In previous papers [7,8], it was reported that anatase was usually formed by hydrothermal treatment of amorphous titania, while rutile could be formed in the presence of chloride ion. However no formation of brookite was reported. Present results suggested that existence of NH<sub>3</sub> and HCHO resulted in the formation of brookite, although the detail was not clarified yet.

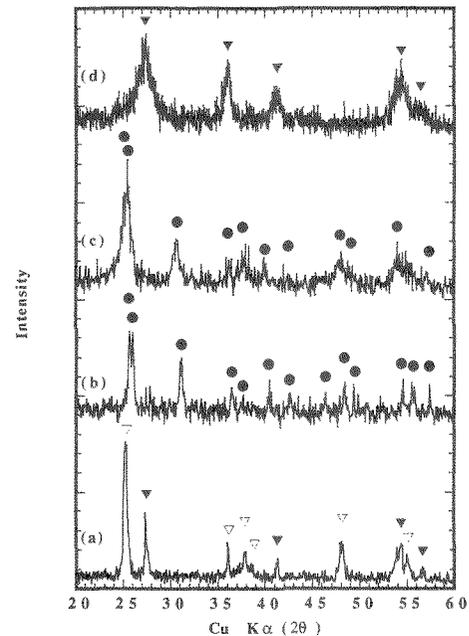


Fig.1 XRD patterns of (a) commercial powder P-25, and the powders prepared by the homogeneous precipitation-hydrothermal process in TiCl<sub>3</sub>-HMT solutions at (b) pH 2 and 190°C; (c) pH 7 and 190°C; and (d) pH 9 and 190°C for 2 h. (▽) anatase; (▼)rutile; (●)brookite.

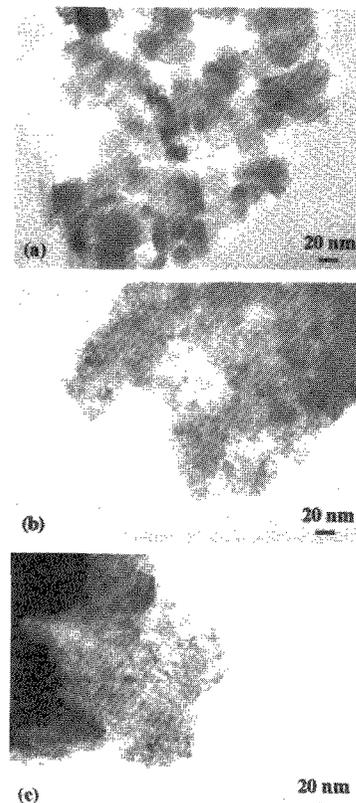


Fig.2 TEM photographs of the powders prepared by the homogeneous precipitation-hydrothermal treatment at (a) pH 2 and 190°C; (b) pH 7 and 190°C; and (c) pH 9 and 190°C for 2 h.

Figure 2 shows the TEM photographs of the powders prepared under various pH values. It was found that rutile obtained at pH 9 showed small particle size and very high specific surface area of 205.3 m<sup>2</sup>/g. The brookite prepared at pH 7 also possessed small particle size and comparatively high specific surface area of 167.8 m<sup>2</sup>/g. On the other hand, the brookite obtained at pH 2 showed large particle size and relatively small specific surface of 41.8 m<sup>2</sup>/g.

Figure 3 shows the diffuse reflection spectra of titania powders prepared under different pH. All powders were light yellow, indicating the formation of nitrogen doped titania during the hydrothermal reaction. The brookite prepared at pH 7 (Fig.3-(b)) possessed good visible light absorbency in wide visible light region over the wavelength of 600 nm. The brookite prepared at pH 2 (Fig.3-(a)) showed less absorbency in visible light area than that prepared at pH 7. It is obvious that rutile (Fig.3-(c)) possesses smaller band gap energy than that of brookite.

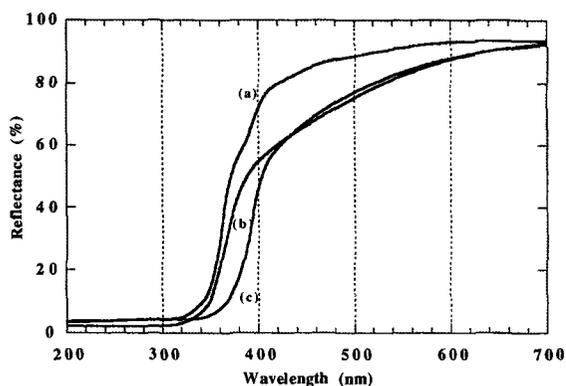


Fig.3 Diffusion reflectance spectra of the powders prepared at (a) pH 2 and 190°C; (b) pH 7 and 190°C; and (c) pH 9 and 190°C for 2 h.

Figure 4 shows the relationship between wavelength of light and photocatalytic ability for the oxidation of nitrogen monoxide. It is accepted that electron/hole pairs are formed by the photo-excitation of titania. In the presence of oxygen, the electrons in the conduction band are immediately trapped by the molecular oxygen to form •O<sub>2</sub><sup>-</sup>, which can then generate active •OOH radicals [6,9]. The nitrogen monoxide reacts with these reactive oxygen radicals, molecular oxygen, and very small amount of water in air to produce HNO<sub>2</sub> or HNO<sub>3</sub>. It is obvious that the yellowish nitrogen doped titania possessed excellent visible-light photocatalytic activity. Under the irradiation of visible light of λ > 510 nm, nearly 34 % of nitrogen monoxide could be continuously destructed by the nitrogen doped titania that prepared by the homogeneous precipitation-hydrothermal treatment in TiCl<sub>3</sub> solution at pH 7 and 190°C for 2 h. The

photocatalytic activity was about 5 times higher than that of commercial titania powder P-25. The photocatalytic activity under λ > 510 nm changed in the following sequence: at pH 7 (brookite, 167.8 m<sup>2</sup>/g) > at pH 9 (rutile, 205.3 m<sup>2</sup>/g) > at pH 2 (brookite, 41.8 m<sup>2</sup>/g) > P-25 (anatase 70%, rutile 30%, 47.0 m<sup>2</sup>/g). On the other hand, no obviously difference was observed under the irradiation of the light of λ > 410 nm and > 290 nm. It is notable that the brookite powders with high specific surface area showed excellent photocatalytic activity, i.e., brookite showed higher photocatalytic activity than that of rutile and anatase with similar specific surface area.

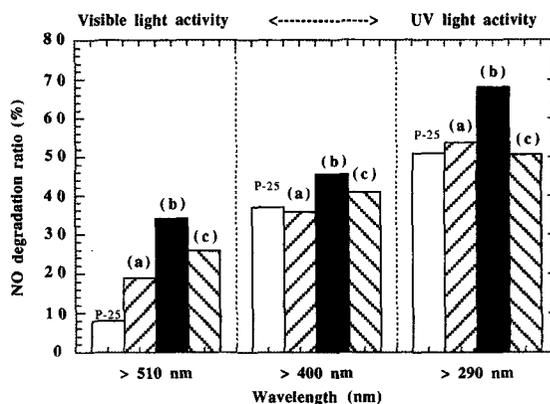


Fig.4 Photocatalytic activity of the commercial powder P-25 and the powders prepared by the homogeneous precipitation-hydrothermal treatment in TiCl<sub>3</sub>-HMT solution at (a) pH 2 and 190°C; (b) pH 7 and 190°C; and (c) pH 9 and 190°C for 2 h.

Table I BET specific surface area and BET particle size of the powders prepared by the homogeneous precipitation-hydrothermal treatment in TiCl<sub>3</sub>-HMT solution at pH 7 and different temperatures.

Temperature (°C)	BET S.S.A. (m <sup>2</sup> /g)	BET particle size (nm)
110	138.5	10.5
130	149.4	9.7
150	171.6	8.5
170	148.3	9.8
190	167.8	8.7
210	43.8	33.2
230	61.8	23.6

The effect of crystallization temperature during hydrothermal treatment was also investigated. In the case of pH 7, all powders consisted of single phase of brookite in the experimental temperature range, although the specific surface area and BET particle size changed depending on crystallization temperature (Table I).

The specific surface area was almost constant until 190°C, then greatly decreased with increasing temperature. It may be due to the crystal growth under high temperature.

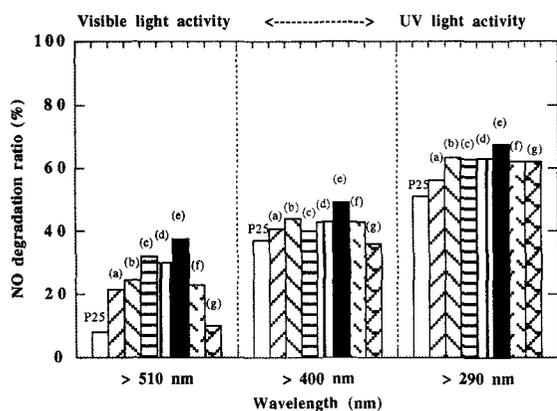


Fig.5 Photocatalytic activity of the commercial powder P-25, and the powders prepared by the homogeneous precipitation-hydrothermal treatment in  $\text{TiCl}_3$ -HMT solution at pH 7 and (a) 110°C, (b) 130°C, (c) 150°C, (d) 170°C, (e) 190°C, (f) 210°C and (g) 230°C for 2 h.

Figure 5 shows the photocatalytic activity of the powders prepared by the homogeneous precipitation-hydrothermal treatment at pH 7 and different temperatures. Under the irradiation of visible light of  $\lambda > 510$  nm, the powders showed quite different photocatalytic activity. The photocatalytic activity strongly related to the specific surface areas, which were well agreed with our previous report [9]. These results indicate that absorption of NO on titania surface is one of the most important steps during the photocatalytic reaction. Similar to the results in Fig.4, there is no obvious difference in their photocatalytic activity under UV light irradiation.

In order to investigate the thermal stability of the brookite prepared, the powders were calcined in air at desired temperatures. The brookite was stable until 400°C, partly transformed to rutile at 500°C and completely transformed to rutile at 600°C. It is notable that the calcined powder retained excellent visible light photocatalytic activity for the destruction of nitrogen monoxide. Even after calcination at such high temperature as 800°C, the yellow color did not disappear, indicating the excellent thermal stability of nitrogen doping titania.

#### 4. CONCLUSIONS

Single phase of nitrogen doped brookite with high specific surface area of 167.8  $\text{m}^2/\text{g}$  was prepared by homogeneous precipitation-hydrothermal process. The brookite was yellow and showed excellent visible light absorbency and photocatalytic activity for nitrogen

monoxide destruction. The nitrogen doped brookite possessed higher photocatalytic activity than those of rutile and anatase phase and excellent thermal stability.

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