

## Photochemical Properties of Titania Nanocrystals Prepared by Hydrothermal Process in Urea Solution

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Well-crystallized titania nanocrystals with different colors were prepared by Homogeneous Precipitation-Hydrothermal Process in  $\text{TiCl}_3$ -urea ( $\text{N}_2\text{H}_4\text{CO}$ ) aqueous solution and  $\text{TiCl}_3$ -urea methanol solution. At first, titanium ion was precipitated as amorphous hydroxide by ammonia that formed by the hydrolysis of urea at  $90^\circ\text{C}$ , then the crystallization of titania was realized at higher temperatures. The phase composition, crystallinity, microstructure, specific surface area and photochemical properties of titania powders were greatly changed depending on pH, solvent, and calcination temperature. Blue or yellow titania powders with excellent visible light absorption were prepared. It was supposed that nitrogen doping and oxygen vacancy lead to the different color of titania. Single phase anatase, single phase rutile, anatase-rutile mixture and brookite-rutile mixture with various morphologies were prepared under different conditions. The yellowish titania prepared by post-hydrothermal calcination below  $600^\circ\text{C}$  possessed two absorption edges around 406 and 520-540 nm. The photocatalytic activity for nitrogen monoxide destruction was characterized.

Key words: Colored titania, Photocatalytic activities, Visible light absorption, Urea solution, Hydrothermal process

### 1. INTRODUCTION

Titania photocatalyst can decompose many pollute substances, such as poisonous nitrogen monoxide in atmosphere and/or organic pollutants in water under light irradiation [1]. It is reported that anatase possesses higher photocatalytic activity than that of rutile [2], 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 been carried out on the photocatalytic activity of brookite. In order to utilize the solar energy efficiently, it is necessary to develop a visible-light reactive photocatalyst. Asahi et al. [3] 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. [4] also reported that visible-light-active titania could be prepared by RF plasma treatment. Hydrothermal process is 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 a previous paper [5], it was reported that both rutile and brookite titania with visible-light activity could be prepared as single phase by Homogeneous Precipitation-Hydrothermal Process

in  $\text{TiCl}_3$ -hexamethylenetetramine solution. However, anatase phase could not be obtained as single phase. In the present study different phases of titania powder were prepared by the homogeneous precipitation-hydrothermal processes in  $\text{TiCl}_3$ -urea aqueous solutions and  $\text{TiCl}_3$ -urea methanol solutions. The photocatalytic activity for nitrogen monoxide destruction of prepared powders was also characterized.

### 2. EXPERIMENTAL

$\text{TiCl}_3$  (Kanto Chem. Co. Inc. Japan) was used as a starting material. Urea ( $\text{N}_2\text{H}_4\text{CO}$ , Kanto Chem. Co. Inc. Japan) was used as a nitrogen source. A desired amount of urea and 21.5 ml of 20 wt.%  $\text{TiCl}_3$  solution were mixed with 25 ml of distilled water or pure methanol. The mixture 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 urea. The powder product was separated by centrifugation, washed with distilled water and acetone three times respectively, then 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). 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  $\text{cm}^3$  of internal volume] during the photo-irradiation of constant flowed 1 ppm NO-50 vol.% air mixed (balance  $\text{N}_2$ ) gas [200  $\text{cm}^3/\text{min}$ ]. The photocatalyst sample was placed in a hollow place of  $20 \times 15 \times 0.5 \text{ mm}^3$  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  $\lambda < 290 \text{ nm}$ , Kenko L41 Super Pro (W) filter  $< 400 \text{ nm}$  and Fuji triacetyl cellulose filter  $< 510 \text{ nm}$ . For comparison, a photocatalytic reaction was also carried out using commercial titania (Degussa P-25).

### 3. RESULTS & DISCUSSION

The hydrolysis of urea produces  $\text{CO}_2$  and  $\text{NH}_3$  at about  $85^\circ\text{C}$ . In the present experimental conditions, amorphous hydrous titania was formed by the homogeneous precipitation at  $90^\circ\text{C}$ . 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  $\text{TiCl}_3$ -urea aqueous solutions and  $\text{TiCl}_3$ -urea-MeOH solutions at  $190^\circ\text{C}$  and different pH. It was found that the powders prepared at pH 2 in  $\text{TiCl}_3$ -urea aqueous solutions consisted of single phase rutile, while those at pH 7 and 9 were anatase and rutile mixture. On the other hand, the powders prepared in  $\text{TiCl}_3$ -urea methanol solution at  $190^\circ\text{C}$  showed different phase composition. The powder prepared at pH 2 and 7 consisted of brookite and rutile mixture. Single phase anatase could be obtained at pH 9. These results suggested that methanol depressed the anatase to rutile phase transformation and promoted the formation of brookite. In addition, it seemed that phase transformation from anatase to rutile was promoted by decreasing pH, indicating the existence

of  $\text{NH}_3$  also delayed the anatase to rutile phase transformation, although the detail was not clarified yet. No noticeable difference in XRD patterns could be observed under different hydrothermal treatment temperature in the range of  $150$ - $230^\circ\text{C}$ .

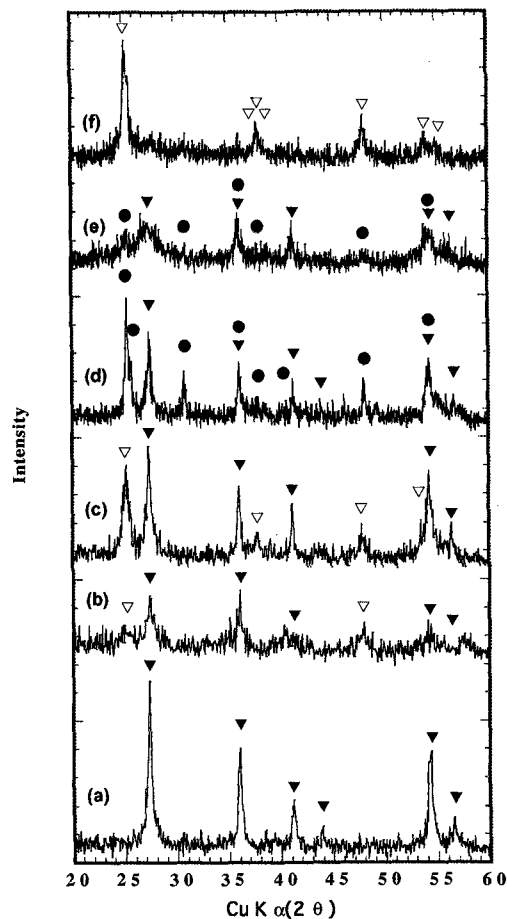


Fig.1 XRD patterns of the samples prepared by hydrothermal treatment of  $\text{TiCl}_3$ -urea aqueous solutions at pH (a) 2, (b) 7, (c) 9; and  $\text{TiCl}_3$ -urea methanol solution at (d) pH 2, (e) 7, (f) 9 and  $190^\circ\text{C}$  for 2h. ( $\nabla$ ) anatase; ( $\blacktriangledown$ ) rutile; ( $\bullet$ ) brookite.

Figure 2 shows the TEM photographs of the powders prepared in  $\text{TiCl}_3$ -urea aqueous solutions and  $\text{TiCl}_3$ -urea methanol solutions under various pH values. Rutile obtained at pH 2 in  $\text{TiCl}_3$ -urea aqueous solution consisted of rod-like particles with large aspect ratio (Fig.2-(a)). The powder prepared at pH 7 showed agglomerated particles consisted of fine needle-like particles (Fig.2-(b)), while the powders prepared at pH 9 showed small rod-like particles with small aspect ratio (Fig.2-(c)). In  $\text{TiCl}_3$ -urea methanol solution, the powders obtained at pH 2 and 7 consisted of the mixture of rod-like and spherical particles. On the other hand, the anatase prepared as single phase at pH 9 in  $\text{TiCl}_3$ -urea methanol solution was spherical. The specific surface areas and crystalline phases of the prepared

powders are summarized in Table I. It is clear that the powders prepared at pH 7 possessed higher specific surface areas than those at pH 9 and 2 in aqueous solution, although the crystallinity was not so good. No noticeable difference in BET specific surface area was observed between  $\text{TiCl}_3$ -urea aqueous solution and  $\text{TiCl}_3$ -urea methanol solution system except for pH 9.

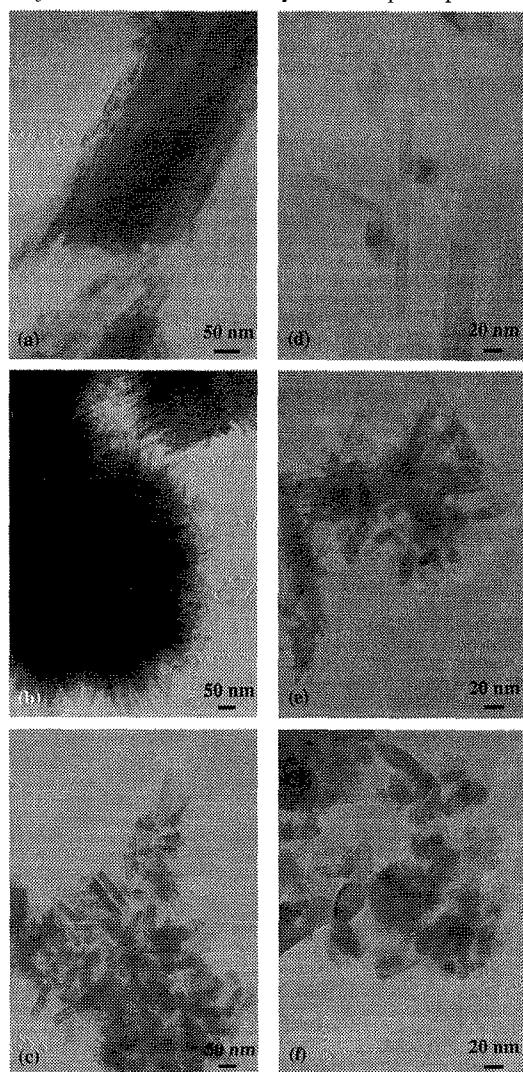


Fig.2 TEM photographs of the powders prepared by hydrothermal treatment of  $\text{TiCl}_3$ -urea aqueous solutions at pH (a) 2, (b) 7, (c) 9; and  $\text{TiCl}_3$ -urea methanol solution at (d) pH 2, (e) 7, (f) 9 and 190°C for 2h.

Table I Specific surface areas of the samples

Solution	Aqueous solution			Methanol solution		
pH	2	7	9	2	7	9
BET ( $\text{m}^2\text{g}^{-1}$ )	25.8	108.1	61.4	25.3	101.9	115.8
Phase	R	R+A	R+A	B+R	B+R	A

Figure 3 shows the diffuse reflectance spectra of titania powders prepared under different pH in  $\text{TiCl}_3$ -urea aqueous solution and  $\text{TiCl}_3$ -urea methanol solution together with those calcined in air at 400°C for 1h.

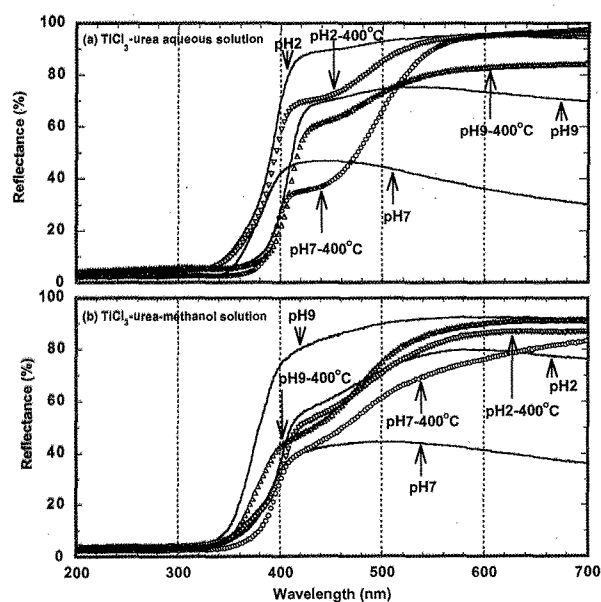


Fig.3 Diffusion reflectance spectra of the powders as-prepared by hydrothermal reactions of (a)  $\text{TiCl}_3$ -urea aqueous solutions and (b)  $\text{TiCl}_3$ -urea methanol solutions at 190°C and various pH for 2 h and calcined in air at 400°C for 1h.

Preparation conditions

Solution	Aqueous			Methanol			P-25
PH	2	7	9	2	7	9	-
as-precipitated	(a)	(c)	(e)	(g)	(i)	(k)	(m)
calcined	(b)	(d)	(f)	(h)	(j)	(l)	

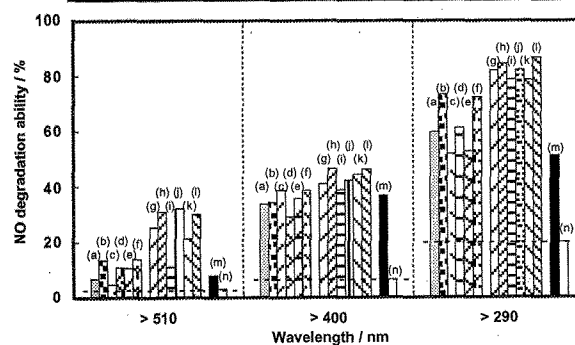


Fig.4 Photocatalytic activity of the powders as-precipitated by hydrothermal reactions of  $\text{TiCl}_3$ -urea aqueous solution and  $\text{TiCl}_3$ -urea methanol solutions at 190°C for 2 h and calcined at 400°C for 1 h. (n) Blank without catalyst.

The powders as-precipitated at pH 7 in both systems showed blue color with excellent visible light absorption. The blue color might be due to the existence of oxygen vacancy. After calcination in air at 400°C the color changed to bright yellow. On the other hand, the powders prepared at pH 2 and 9 were light yellow after calcination at 400°C. After calcination at 400°C the absorption in the range of 400-500 nm increased and the samples clearly showed two absorption edges

around 400 nm and 520-540 nm, indicating the increase in the amount of nitrogen doped in the lattice. The visible light absorption of the powders prepared in  $\text{TiCl}_3$ -urea aqueous solution were in the order  $\text{pH } 7 > \text{pH } 9 > \text{pH } 2$ , while that prepared in  $\text{TiCl}_3$ -urea methanol solution were in the order  $\text{pH } 7 > \text{pH } 2 > \text{pH } 9$ . After calcination of both samples the visible light absorption in the range of 400-500 nm were in the order  $\text{pH } 7 > \text{pH } 9 > \text{pH } 2$ .

Figure 4 shows the photocatalytic activity of the powders as-prepared by hydrothermal treatment at  $190^\circ\text{C}$  for 2 h and calcined in air at  $400^\circ\text{C}$  for 1 h for the oxidative decomposition of nitrogen monoxide under various light irradiation. It is obvious that the yellowish nitrogen doped titania possessed excellent photocatalytic activity under the irradiation of visible light of  $\lambda > 510$  nm. The photocatalytic activity of the sample before calcination changed a little depending on the pH, but no noticeable effect of pH was observed after calcination in each system. It is notable that although the photocatalytic activity of titania P-25 decreased after calcination, that of nitrogen doped titania in the present study greatly increased. The photocatalytic activities of the nitrogen doped titania prepared in  $\text{TiCl}_3$ -urea methanol solutions were higher than those in  $\text{TiCl}_3$ -urea aqueous solutions. These results suggested that nitrogen doped brookite and anatase prepared in methanol solution possessed high photocatalytic activity in visible light range. The most excellent photocatalytic activity under visible light ( $>510$  nm) was obtained by the homogeneous precipitation-hydrothermal reaction in  $\text{TiCl}_3$ -urea methanol solution at pH 7 followed by calcination at  $400^\circ\text{C}$ , continuously destructing nearly 32 % of nitrogen monoxide. The photocatalytic activity was about 5 times higher than that of commercial standard titania powder P-25.

Figure 5 shows the effect of calcination temperature on the rutile phase fraction and BET specific surface area of the powders prepared by hydrothermal treatment. With increasing calcination temperature, the rutile fraction increased and BET specific surface area decreased. Usually, the photocatalytic activity strongly related with the specific surface area [7,8]. Although the specific surface area decreased in about half after calcination at  $400^\circ\text{C}$ , the photocatalytic activity increased. This might be due to the increase in the amount of nitrogen doped in the lattice and crystallinity by calcination. The phase of the powders prepared by hydrothermal process was stable until about  $600^\circ\text{C}$ . Almost 100% rutile was formed after calcination at  $800^\circ\text{C}$  for 1 h, but the yellow color was not disappeared, indicating the excellent thermal stability of nitrogen doped titania.

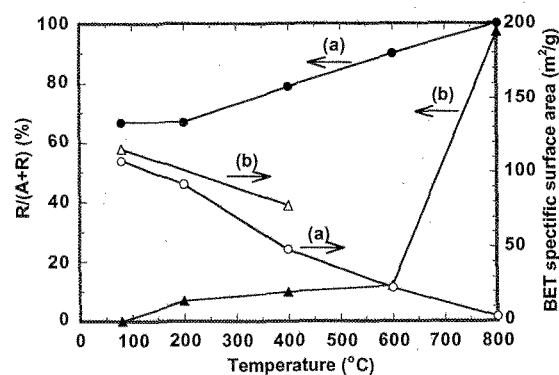


Fig.5 Rutile phase fractions and BET specific surface areas of the powders prepared by the hydrothermal reaction of (a)  $\text{TiCl}_3$ -urea aqueous solution at pH 7 and (b)  $\text{TiCl}_3$ -urea methanol solution at pH 9 and  $190^\circ\text{C}$  for 2 h and followed by calcination in air at different temperatures for 1h.

#### 4. CONCLUSIONS

Nitrogen doped titania consisted of anatase, rutile, brookite-rutile mixture or anatase-rutile mixture were prepared by homogeneous precipitation-hydrothermal process. All powders showed excellent visible light absorption. The powders prepared in  $\text{TiCl}_3$ -urea methanol solution showed better photocatalytic activity for nitrogen monoxide destruction than those obtained in  $\text{TiCl}_3$ -urea aqueous solution.

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