

Preparation of Nitrogen-doped Anatase Titania by Treatment of Layered Titania/Isostearate Nanocomposite with Aqueous Ammonia

Taki Matsumoto,^{*,†,††} Nobuo Iyi,[†] Yoshiro Kaneko,[†] Kenji Kitamura,[†] Yoshio Takasu,^{††} and Yasushi Murakami^{††}

[†]Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044

^{††}Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, 386-8567

^{†††}Research Fellow of the Japan Society for the Promotion of Science

(Received September 1, 2004; CL-041030)

A layered titania/isostearate nanocomposite was prepared via the sol-gel process in a hydrophobic solvent with a salt catalyst. The isostearate modifiers hybridized with titania sheets were completely removed by treatment with aqueous ammonia. A vivid yellow powder of plate anatase was obtained by firing the treated sample at 450 °C, and it showed a strong photoabsorption in the visible light region. Rapid degradation of methylene blue was observed in an aqueous solution during irradiation with 470-nm light.

Most titania photocatalysts only show photocatalytic activity under UV (ultraviolet) light irradiation. Recently, trials to extend the optical absorption edge of titania into the visible light region have been made and visible light reactivity was reported for the titania doped with nitrogen.^{1-7,10,11} To the best of our knowledge, the first study on nitrogen-doped titania including its visible-light reactivity was that of Sato,¹ although the obtained material was described as NO_x-doped TiO₂. He presumed that the impurity NH₄Cl contained in commercial titanium hydroxide used as a precursor was the cause of the incorporated nitrogen. After this study, several methods to intentionally introduce the nitrogen into titania as a dopant have been investigated. Such nitrogen-doped titanias were reported to be yellow.

For obtaining the thin films of nitrogen-doped titania, various techniques, such as sputtering a TiO₂ target in N₂,² reactive DC magnetron sputtering in N₂,³ annealing anatase TiO₂ films in gaseous NH₃,⁴ and pulsed laser deposition using a TiN target in N₂/O₂ mixture⁵ have been used. For larger scale use, a powder nitrogen-doped titania is more practical. Yin et al. reported that a powder of nitrogen-doped titania was prepared by a mechanochemical reaction, though crystallization into rutile took place by ball milling.⁶ Morikawa et al. also obtained nitrogen-doped rutile titania powder by the oxidative annealing of TiN powder.⁷ Anatase titania is more preferable because it is known to have a higher photocatalytic activity than the rutile.^{8,9} So far, nitrogen-doped anatase titania powder has been obtained only by chemical procedures such as the hydrolysis of Ti(SO₄)₂ by aqueous ammonia¹⁰ and the direct amination of titania particles by the addition of triethylamine.¹¹

In the present study, we prepared a nitrogen-doped plate anatase titania powder with visible-light activity by treating a layered titania/isostearate nanocomposite with aqueous ammonia. It is a novel process for the synthesis of the nitrogen-doped anatase titania.

A viscous sol containing layered titania/isostearate nanocomposites was prepared via the sol-gel process of isostearate-modified titanium tetraisopropoxide in *o*-xylene solvent with *n*-

hexylammonium isostearate as the salt catalyst, which was described in our previous report in detail.¹² The C and H contents in the obtained composite measured by CHN analysis were 52.5 and 9.2 wt %, respectively. These values were consistent with the calculated ones (51.6 and 8.6 wt %) derived from the starting composition (TiO₂ + 3/5 isostearic acid). The obtained composite has a layered structure constructed by the stacking of titania sheets, to which isostearate modifiers are coordinating. The obtained sol was mixed with aqueous ammonia (28%) and stirred for 2 h at 60 °C. In a separating funnel, the mixture separated into two phases and the titania products migrated to the water phase by releasing the isostearate modifiers. Products in water phase were further washed with aqueous ammonia followed by several centrifugal separations. After drying at 120 °C, a white amorphous powder was obtained. FTIR spectra of the products before and after treatment in aqueous ammonia indicated that isostearate modifiers were completely removed and new absorption bands assigned to NH₄⁺ (3178 cm⁻¹: stretching, 1401 cm⁻¹: bending)^{13,14} and to -OH (3370 cm⁻¹: stretching, 1632 cm⁻¹: bending) appeared due to the treatment. The treated products were fired in air at various temperatures (350, 450, 550, 650 °C) for 2 h. A sheet-like morphology, which reflects the layer structure of the precursor composite, was observed for the fired samples (at 450 °C) in the SEM photograph as shown in the graphical abstract.

Figure 1 shows the XRD patterns of the fired samples. The specific surface areas for these samples determined by the BET

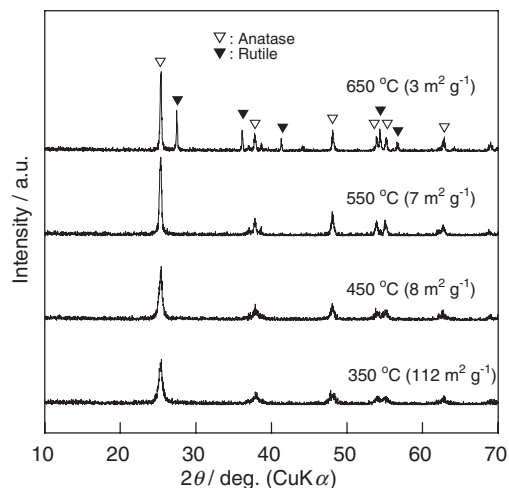


Figure 1. XRD patterns of plate titanium oxides prepared at various calcination temperatures.

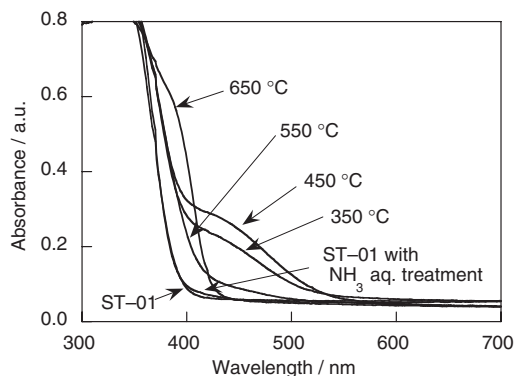


Figure 2. UV-vis absorption spectra of plate titanium oxides prepared at various calcination temperatures.

method are also shown in parenthesis. A single-phase anatase was observed in the samples fired at 350, 450, and 550 °C, while peaks due to rutile additionally appeared for the 650 °C-sample. The specific surface area decreased with degree of crystallization.

The UV-vis reflectance spectra of the fired samples and commercial anatase powder (ST-01, Ishihara Sangyo Co., $327 \text{ m}^2 \text{ g}^{-1}$) are shown in Figure 2. Photoabsorption in the visible region (vis-absorption) was observed only for the samples fired at 350 and 450 °C, while that at 450 °C was more intense. The color of the powder turned to vivid yellow by the firing, which indicates that a nitrogen-doped titania was formed at these temperatures. A small amount of nitrogen (ca. 0.08 wt %) was detected in the 450 °C-sample using a nitrogen/oxygen analyzer (TC-436AR, LECO), in which the sample was decomposed at ca. 3000 °C. For the samples fired at 550 and 650 °C, the vis-absorption bands disappeared. The doped nitrogen was probably released by oxidation in the air at these higher temperatures.

For comparison, ST-01 was treated with aqueous ammonia and fired at 450 °C. The powder hardly changed color and no vis-absorption bands appeared. Adequate nitrogen doping would not have occurred for ST-01. Layered composites have a large number of coordination sites to which isostearate modifiers are coordinating, and NH_4^+ ions were incorporated by ligand exchange in aqueous ammonia. On the other hand, ST-01 probably has a few coordination sites because it is a well-crystallized anatase. Coordination sites remaining in the precursor would have played an important role in nitrogen doping process.

The photocatalytic activity under visible-light irradiation of the nitrogen-doped titania powders was evaluated by the decomposition rates of methylene blue (MB; $0.05 \text{ mmol dm}^{-3}$) in aqueous solution (3 ml, $\text{pH} = 3$) containing 3 mg of samples with O_2 bubbling. As the light source, we used 20 blue-light-emitting diodes (E1L53-3B0A6-02, Toyoda Gosei) with a 470-nm-emission. The concentration of MB in the solution was monitored by its absorbance at 660 nm using UV-vis spectroscopy (V570, JASCO). The activity of the sample fired at 450 °C, which showed the most intense vis-absorption, was extremely higher than the other samples and the commercial anatase photocatalyst (ST-01) as shown in Figure 3. And also, its decomposition rate was ca. 2.1 times higher than that of the nitrogen-doped anatase titania prepared from $\text{Ti}(\text{SO}_4)_2$ following the reported procedure.¹⁰ In spite of relatively intense vis-absorption, the ac-

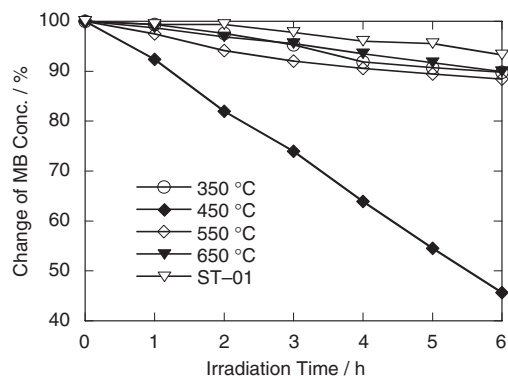


Figure 3. Photodecomposition of methylene blue on plate titanium oxides prepared at various calcination temperatures.

tivity for the sample fired at 350 °C was very low. The reason is now under investigation. MB showed no degradation in the aqueous solution containing only MB under the same irradiation conditions.

In conclusion, a new class of nitrogen-doped plate anatase titania powder was obtained from titania-based composites by a unique process which consists of the preparation of titania/isostearate nanocomposites and successive treatment with aqueous ammonia for the incorporation of nitrogen into the titania. The activity will be further improved by controlling the size and morphology of the nanocomposites and also by optimizing the treatment process.

References

- 1 S. Sato, *Chem. Phys. Lett.*, **123**, 1267 (1986).
- 2 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science*, **293**, 269 (2001).
- 3 T. Lindgren, J. M. Mwabora, E. Avendano, J. Jonsson, A. Hoel, C.-G. Granqvist, and S.-E. Lindquist, *J. Phys. Chem. B*, **107**, 5709 (2003).
- 4 M. Miyauchi, A. Ikezawa, H. Tobimatsu, H. Irie, and K. Hashimoto, *Phys. Chem. Chem. Phys.*, **6**, 865 (2004).
- 5 Y. Suda, H. Kawasaki, T. Ueda, and T. Ohshima, *Thin Solid Films*, **453–454**, 162 (2004).
- 6 S. Yin, Q. Zhang, F. Saito, and T. Sato, *Chem. Lett.*, **32**, 358 (2003).
- 7 T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, and Y. Taga, *Jpn. J. Appl. Phys.*, **40**, L561 (2001).
- 8 J. Augustynski, *Electrochim. Acta*, **38**, 43 (1993).
- 9 R. I. Bickley, T. Gonzalez-Carreno, J. S. Lees, L. Palmisano, and R. J. Tilley, *J. Solid State Chem.*, **92**, 178 (1991).
- 10 T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara, *Appl. Catal., B*, **42**, 403 (2003).
- 11 C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, *Nano Lett.*, **3**, 8 (2003).
- 12 T. Matsumoto, Y. Murakami, S. Masaki, T. Imai, N. Iyi, Y. Kaneko, W. Sugimoto, and Y. Takasu, *Catalysts & Catalysis*, **45**, 457 (2003).
- 13 G. Ramis, G. Busca, V. Lorenzelli, and P. Forzatti, *Appl. Catal.*, **64**, 243 (1990).
- 14 A. A. Tsyganenko, D. V. Pozdnyakov, and V. N. Filimonov, *J. Mol. Struct.*, **92**, 299 (1975).