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Solvothermal Synthesis of Visible-light Reactive Titania Nanocrystals

Masakazu Komatsu[1)] Yohei Aita[1)], Shu Yin[1)], Koyu Aoki[2)], Yasunori Taga[2)], and Tsugio Sato[1),]
1) IMRAM, Tohoku University, Sendai 980-8577, Japan, 2) Toyota Central R & D Lab., Nagakute, Aichi 480-1192, Japn
Fax: 81-22-217-5599, e-mail: komatsu@kuroppe.tagen.tohoku.ac.jp

Nitrogen doped titania and nitrogen and fluorine co-doped titania nanocrystals were prepared by "Homogeneous Precipitation-Hydrothermal Process" in $TiCl_3$-Hexamethylenetetramine ($C_6H_{12}N_4$) solutions. The nitrogen doped titania powders prepared at pH 1 and 190°C for 2 h consisted of single phase of brookite and that prepared at pH 9 was single phase of rutile. The nitrogen and fluorine co-doped titania powers prepared at pH 1, 7 and 9 consisted of single phase of brookite, anatase and rutile, respectively. The titania powers prepared above pH 2.5 possessed very high specific surface areas of more than 100 m^2/g. The nitrogen and fluorine co-doped titania contained more nitrogen than the nitrogen doped titania. All powders were yellow and showed excellent visible light absorption and photocatalytic ability for nitrogen monoxide destruction under irradiation of the visible light (λ>510nm).
Key words: Nitrogen and fluorine co-doped titania nanocrystals, Photocatalytic activity, Visible light absorption, Hexamethylenetetramine, Homogeneous Precipitation-Hydrothermal Process.

1. INTRODUCTION

Since Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes in the beginning of 1970s [1], various researches have been performed about semiconductor-based photocatalysts [2]. Titanium oxide (titania) is the most promising photocatalyst and widely applied [1-4]. The disadvantage of the titania is, however, the relatively large bandgap energy about 3 eV which does not cover the main part of the solar energy. In order to use visible light of the sun light or indoor lamp, the photocatalyst should possess small bandgap energy less than 3 eV. Nitrogen doped titania prepared by calcination of titania in ammonia gas atmosphere at 500-600°C possessed photocatalytic activity under visible light irradiation because of decreasing band gap energy by the generation of the new valence bands consist of N2p orbital above the O2p orbital [5]. It is also reported that fluorine doped titania films prepared by sol-gel method with a small amount of ammonium fluoride showed excellent photocatalytic activity [6]. It is considered when N^{3-} are substituted for O^{2-}, the anion defect which causes recombination of electron/hole pairs is generated due to the charge compensation. Since nitrogen and fluorine co-doping potentiates the substitution of nitrogen without generation of any defect as follow, photocatalytic activity is expected to be improved.

$$2O^{2-} \rightarrow N^{3-} + F^{-}$$

In addition the solvothermal synthesis is a promising method to fabricate fine particles of high crystallinity. In our previous papers, it was reported that fine crystals of titania prepared by the solvothermal reactions showed much better photocatalytic activity than those fabricated by calcination [7-9]. The excellent photocatalytic properties of titania may have been a result of their consistency of fine powders with good crystallinity. In the present study, both nitrogen doped titania and nitrogen and fluorine co-doped titania nanoparticles were prepared by the solvothermal reactions and their photocatalytic activities for the oxidative decomposition of nitrogen monoxide and acetaldehyde under visible light irradiation were evaluated.

2. EXPERIMENTAL

2.1 Synthesis

Titanium trichloride solution ($TiCl_3$, Kanto Chem. Co. Inc. Japan) was used as a starting material. Hexamethylenetetramine ($C_6H_{12}N_4$, Kanto Chem. Co. Inc. Japan) was used as a nitrogen source. Sodium fluoride (NaF, Kanto Chem. Co. Inc. Japan) and titanium fluoride (TiF_4, Acros Organics USA) were used as a fluorine source. Nitrogen doped titania nanoparticles were obtained as follows. After dissolving the desired amount of hexamethylenetetramine in 50 cm^3 of 0.38 M titanium trichloride aqueous solution, the solution was heated at 90°C for 1 h to precipitate nitrogen doped amorphous hydrous titania nanoparticles by the homogeneous precipitation reaction, and then heated at 190°C for crystallization. In the case of nitrogen and fluorine co-doped titania, sodium fluoride or titanium fluoride was dissolved in the titanium trichloride aqueous solution together with hexamethylenetetramine. The final pH of the reaction solution was adjusted by changing the amount of hexamethylenetetramine. The products were separated by centrifugation, washed with distilled water and acetone, respectively, three times, and vacuum dried at 60°C overnight.

2.2 Analysis

The phase compositions of the samples were identified by X-ray diffraction analysis (Shimadzu XD-D1) using graphite-monochromatised CuK α

radiation. The specific surface areas of the samples were determined by 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 samples were determined from the onset of reflectance spectrum measured by UV-VIS spectrophotometer (Shimadzu UV-2000). The binding energy of F1s orbital was measured by XPS (PERKIN ELMER PHI5600 ESCA System)

2.3 Photocatalytic activity.

The photocatalytic activity for the oxidative decomposition of nitrogen monoxide was determined by measuring the concentration of NO gas at the outlet of the reactor (373cm^3 of internal volume) during the photo-irradiation of constant flowed 1ppm NO and 50 vol.% air (balance N_2) mixed gas (200 cm^3 min^{-1}). The photocatalyst sample was placed in a hollow place of 20 mm length x 15 mm width x 0.5 mm depth on a glass holder plate and set in the bottom center of the reactor. A 450 W high pressure mercury arc was used as the light source, where the light wavelength was controlled by selecting filters, i.e., Pyrex glass for cutting off the light of $\lambda < 290$ nm and Kenko L41 Super Pro (W) filter < 410 nm and Fuji triacetyl cellulose filter < 510 nm. The concentration of NO was determined using a NO_x analyzer (Yanako, ECL-88A). For comparison, a photocatalytic reaction was also carried out using commercial titania (Degussa P-25).

The photocatalytic activity for the oxidative decomposition of gaseous acetaldehyde was determined by measuring the concentration of acetaldehyde and CO_2 in the reactor (1000 cm^3 of internal volume) filled 600 ppm acetaldehyde during the photo-irradiation. The photocatalyst sample (0.1 g) was placed in the bottom center of the reactor. A 10 W fluorescent lamp was used as the light source, where the light wavelength was controlled by Fujifilm SC42 filter for the cutting off the light of $\lambda < 410$ nm.

3. RESULTS AND DISCUSSION

It is well known that the hydrolysis of HMT proceeds above 70°C as follow.

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

In the present experimental conditions, amorphous titania was formed by homogeneous precipitation at 90°C and then crystallization of titania proceeded during followed solvothermal treatment at higher temperature. Crystalline phases of the nitrogen doped titania and nitrogen and fluorine co-doped titania prepared at 190°C under different final pHs are summarized in Table I. Nitrogen doped titania prepared at pH 1 consisted of single phase of brookite and that prepared at pH 9 was single phase of rutile. On the other hand, the main phase of the powder prepared at pH 2-8 changed with the increase in pH as : Brookite → Anatase → Rutile. In previous papers [8, 10], it was reported that anatase was usually formed by the hydrothermal treatment of amorphous titania, while rutile was formed in the presence of chloride ion. However, no formation of brookite was reported. Present results suggested that existence of hexamethylenetetramine resulted in the formation of brookite, although the detail was not clarified yet. On the other hand, the nitrogen and fluorine co-doped titania powers prepared at pH 1, 7 and 9 consisted of single phase of brookite, anatase and rutile, respectively, indicating that fluoride ion tended to promote the generation of anatase. The specific surface area tended to increase with increasing solution pH and all samples prepared above pH 2.5 showed quite high specific surface area above 100 m^2•g^{-1}.

Table I Crystalline phases and BET surface areas of the nitrogen doped titania and nitrogen and fluorine co-doped titania prepared at 190°C.

Added /M HMT*	Added /M NaF	Final pH	Phase	BET surface area /m^2•g^{-1}
0.29	0	1.0	B	45.9
0.76	0	2.5	B>A	114
0.79	0	3.0	B>A	115
0.83	0	6.0	B=A	117
0.91	0	7.5	A=R	117
1.45	0	9.0	R	137
0.55	0.08	2.0	B	42.4
0.91	0.24	7.0	A	138
1.45	0.41	9.0	R	160

*HMT: hexamethylenetetramine, A: anatase, B: brookite, R: rutile, $TiCl_3$ concentration: 0.38 M

The XPS spectra of F1S orbital of the nitrogen and fluorine co-doped titania powders prepared using different fluorine sources (NaF, TiF_4) are shown in Figure 2. The binding energies of the samples prepared using both NaF and TiF_4 were the same, i.e. 684.4 eV, which was different with that of NaF, i.e. 683.9 eV. These results suggested the doing of fluorine in titania.

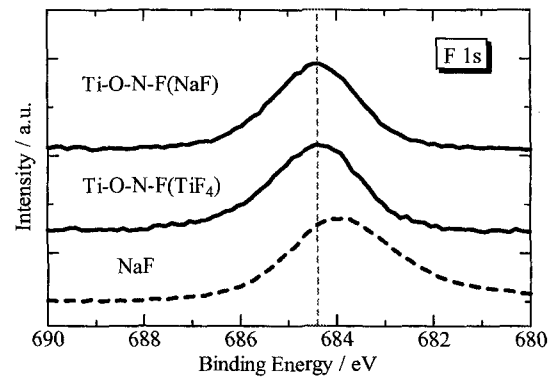

Figure 2 XPS spectra of the nitrogen and fluorine codoped titania powders prepared using NaF or TiF_4 as fluorine source at 190°C and final pH 7 and NaF.

Figure 3 shows the TEM photographs of the nitrogen doped and the nitrogen and fluorine co-doped titania powders prepared at 190°C under different final pHs. All samples consisted of nanoparticles. The particle size decreased with increasing solution pH. It may be due to the decrease in the solubility of titania with increasing the concentration of HCHO formed by the solvothermal reaction of HMT. Brookite observed in Figure 3 (a) consisted of rod-like particles with 20-50 nm in length and 3.0~3.2 of aspect ratio. Anatase observed in Figure 3 (b) and (d) consisted of spherical particles ca. 10 nm in diameter. Rutile observed in

Figure 3 (c) consisted of rod-like ca. 20 nm in length and 7.8 of aspect ratio.

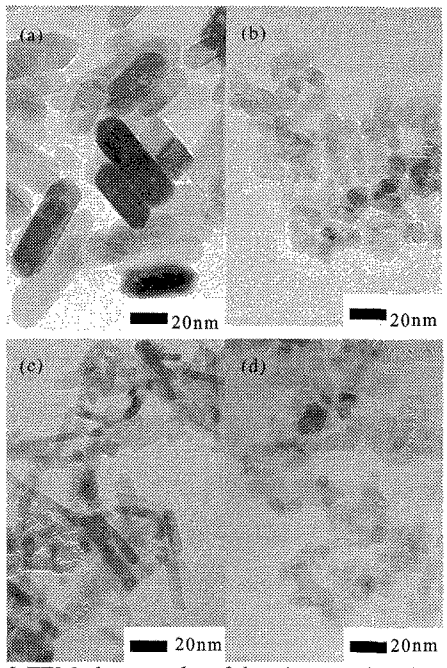

Figure 3 TEM photographs of the nitrogen doped titania powders prepared at 190°C and final pH (a) 1, (b) 6, (c) 9 and (d) nitrogen and fluorine co-doped titania powder prepared using NaF at 190°C and final pH 7.

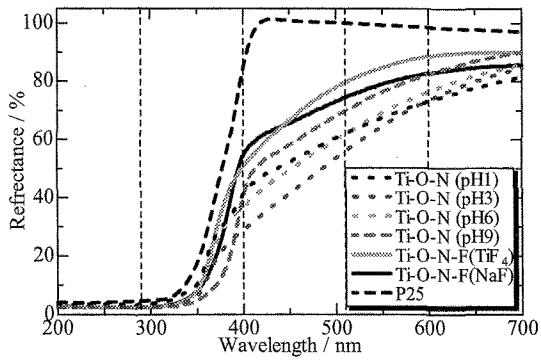

Figure 4 Diffuse reflectance spectra of the nitrogen doped titania powders prepared at 190°C and different pHs, the nitrogen and fluorine codoped titania powders prepared using different fluorine sources and commercial titania (P-25).

All nitrogen doped titania and nitrogen and fluorine co-doped titania were light yellow, while pure titania is white. Figure 4 shows the diffuse reflectance spectra of the nitrogen doped titania powders prepared at 190°C and different pHs, nitrogen and fluorine co-doped titania powders prepared using different fluorine sources and commercial titania (Degussa P-25). Commercial titania (P-25) showed absorption edge of 420 nm which is equivalent to the band gap energy of 2.95 eV and showed no absorption in the visible light regions. On the other hand, all nitrogen doped titania and nitrogen and fluorine co-doped titania showed absorption in the visible light regions. The absorption of the visible light was in the order Ti-O-N (pH3) > Ti-O-N (pH 1, 6) > Ti-O-N (pH 9)> Ti-O-N-F (NaF) >Ti-O-N-F (TiF_4) >> P-25.

Figure 5 shows the nitrogen content in the powders prepared at 190°C and different final pHs. The nitrogen contained in the commercial titania (P-25) was 0.02 wt.% probably due to the absorption of air. Since all samples obtained in the present reactions contained 0.10-0.45 wt.% of nitrogen, nitrogen doping was confirmed. The nitrogen contents in the nitrogen and fluorine co-doped titania powders were about three times higher than those of the nitrogen doped ones, indicating that the nitrogen and fluorine co-doping is very effective to increase the amount of nitrogen doping.

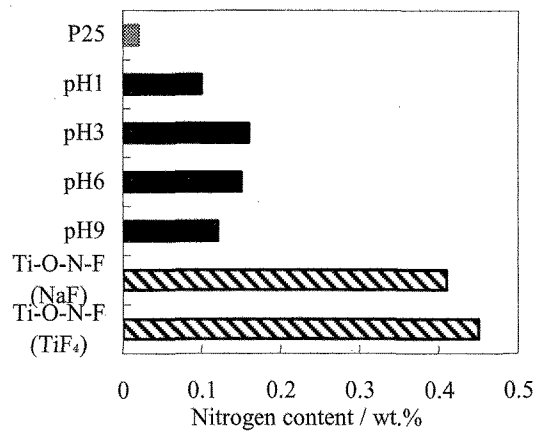

Figure 5 Nitrogen content of the nitrogen doped titania powders prepared at 190°C and different final pHs and the nitrogen and fluorine codoped titania powders prepared using different fluorine sources.

The photocatalytic activities of nitrogen doped titania and the nitrogen and fluorine co-doped titania powders were measured for the oxidative decomposition of nitrogen monoxide and gaseous acetaldehyde. Figure 6 shows the photocatalytic activity for the oxidative decomposition of nitrogen monoxide under irradiation of high pressure mercury arc filtered with various cut filters. After checking no decomposition of nitrogen monoxide under dark, the photocatalytic ability was measured under irradiation of high pressure mercury arc with the wavelength of >510nm for 10 min., >400nm for 10 min. and >290nm for 10 min., in order. The nitrogen doped and the nitrogen and fluorine co-doped titania powders showed excellent photocatalytic activity under visible light irradiation (λ > 510 nm), while the photocatalytic activity of the commercial titania (P-25) was poor because of its relatively large band gap energy of ca. 3 eV. The photocatalytic activity of the nitrogen and fluorine co-doped samples agreed with the absorption of the visible regions (530~580 nm) shown in Figure 4, except for Ti-O-N (pH 1) because of its specific surface area was smaller than other samples as shown in Table Ⅰ. Under UV irradiation, the photocatalytic ability of the nitrogen doped titania and the nitrogen and fluorine co-doped titania powders were as same as that of the commercial titania (P-25).

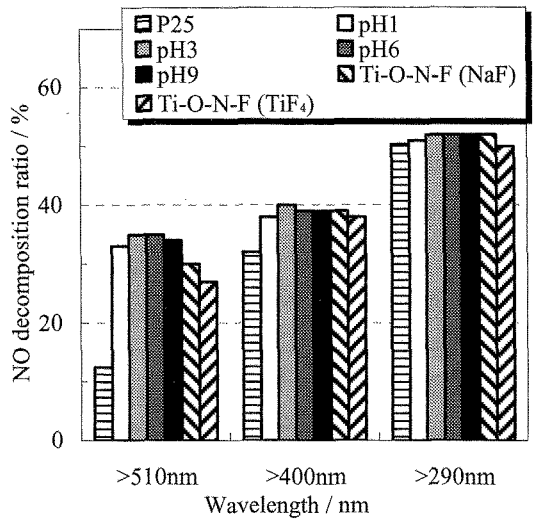

Figure 6 Oxidative decomposition of nitrogen monoxide under irradiation of high pressure mercury arc filtered with various cut filters in the presence of the nitrogen doped titania powders prepared at 190°C and different final pHs, the nitrogen and fluorine co-doped titania powders prepared at pH 7 using different fluorine sources and commercial titania (P-25).

Figure 7 shows CO_2 generation capacities of various samples during the photodecomposition of acetaldehyde under irradiation of fluorescent lamp cut off under 410 nm. The photocatalytic activity of the nitrogen doped titania and the nitrogen and fluorine co-doped titania powders were higher than that of the commercial titania (P-25). It is notable that the photocatalytic ability of the nitrogen and fluorine co-doped titania powder was more than two times higher than that of the nitrogen doped samples. It may be due to the decrease in anion defects by the nitrogen and fluorine co-doping.

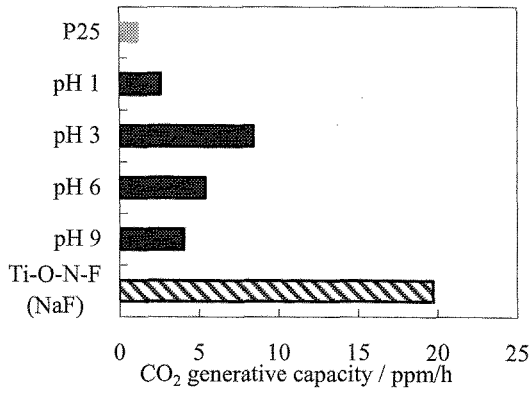

Figure 7 Photocatalytic activity of various samples for the oxidative decomposition of acetaldehyde under irradiation of fluorescent lamp cut off under 410 nm.

4. CONCLUSIONS

The nitrogen doped titania and the nitrogen and fluorine co-doped titania nanocrystals colored light yellow with high specific surface area were prepared by "Homogeneous Precipitation-Hydrothermal Process" in $TiCl_3$-hexamethylenetetramine solutions. Three kinds of crystalline phases, i.e. brookite, anatase and rutile, were obtained depending on the final pH of the reaction solution. The nitrogen doped titania and the nitrogen and fluorine co-doped titania powders showed absorption in the visible light regions and continuously photo-decomposed nitrogen monoxide and acetaldehyde under irradiation of visible light. The photocatalytic activity for the oxidative decomposition of gaseous acetaldehyde was remarkably improved by co-doping with nitrogen and fluorine.

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