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Solvothermal synthesis of visible light responsive nitrogen-doped titania nanocrystals

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Nitrogen ion-doped titania nanoparticles were obtained by the homogeneous precipitation in hexamethylenetetramine-titanium trichloride mixed solution followed by heat treatment in the solution at desired temperatures. After that the sample powders obtained were calcined in air at desired temperatures. Various phases of titania such as anatase, rutile and brookite were obtained depending on the reaction condition. Crystallite size, specific surface area and color also greatly changed as 5-50 nm, 20–200 $m^2 \cdot g^{-1}$ and light gray-yellow, respectively, depending on the solvent, pH, etc. The products after calcination around 400°C were yellow indicating doping with nitrogen ion. Photocatalytic activity for the oxidative decomposition of NO in air atmosphere was also evaluated by using a continuous flow system with 1 ppm NO gas, where the high pressure mercury arcs filtered using various filters were irradiated. All colored titania nanoparticles showed photocatalytic activity under visible light irradiation for the oxidative decomposition of nitrogen monoxide in air. Especially, the nanoparticles of anatase type nitrogen-doped titania obtained by the homogeneous precipitation using hexamethylenetetramine-methanol aqueous solution around 200°C showed excellent photocatalytic activity under visible light irradiation.

1. Introduction

Photoelectrochemical processes at semiconductor colloid-electrolyte interfaces have been received special attention because of their possible application to conversion of solar energy into chemical energy and pollution control [1, 2]. Now, photocatalytic reaction systems have been commercially supplied to conduct self-cleaning, deodorant, anti-bacteria, etc., and are expected to be applied to the pollution control to decompose toxic materials in air and waste water using sun light and indoor light. Until now so many photocatalysts have been developed, however, only titania has been commercially used because of the excellent photocatalytic activity and chemical stability. The disadvantage of titania is the relatively large band gap energy about 3 eV that does not cover the main part of solar spectrum. From the point of view of solar energy use, the photocatalysts should possess small band gap energy less than 3 eV covering the main part of solar spectrum. Recently, it was reported that the band gap of titania could be narrowed by doping with anions such as nitrogen ion [3]. Nitrogen ion-doped titania particles possessing photocatalytic activity under visible light irradiation have been successfully prepared by calcining titania powder in ammonia gas atmosphere at 500–600°C [3] or treating amorphous hydrous titania with ammonia solution followed by calcination around 400°C [4]. It is well known that the electron and hole recombination can be depressed by increasing the crystallinity of semiconductor to decrease the crystal defects which act as recombination centers [5]. In addition the efficiency of photocatalytic reaction can be also improved by increasing the specific surface area of semiconductor because of the enhancement of adsorption of substrates. Consequently, the preparation of fine particles of small band gap semiconductor with high crystallinity is desired to obtain visible light active photocatalysts.

Solvothermal synthesis is a promising method to fabricate fine particles with high crystallinity. In our previous papers, it was reported that fine crystals of

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titania prepared by the heat treatment of amorphous titania gel and protonic layered tetratitanate precursors in water and alcohols showed much better photocatalytic performance than those fabricated by calcinations [6–9]. The excellent photocatalytic properties of titania seems to be a result of their consistency of fine powders with good crystallinity. Therefore, in the present study, nitrogen ion-doped titania nanoparticles were prepared by the solvothermal reactions to investigate their photocatalytic activity for the oxidative decomposition of nitrogen monoxide under visible light irradiation.

2. Experimental methods

All chemicals were reagent grade and used without further purification. Nitrogen ion-doped titania nanoparticles were obtained by the homogeneous precipitation followed by heat treatment in solution as follows. After dissolving 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 amorphous titania nanoparticles by the homogeneous precipitation reaction, and then heated in the solution at desired temperatures. The final pH of the reaction solution was adjusted by changing the amount of hexamethylenetetramine. The effect of the solvent on the microstructure of the sample was also investigated by adding alcohols in titanium trichloride aqueous solution. The products were separated by centrifugation, washed with distilled water and acetone three times, respectively, and vacuum dried at 60°C overnight.

The phase compositions of the samples were identified by X-ray diffraction analysis (Shimadzu XD-D1) using graphite-monochromatised CuKα radiation. The specific surface areas of the samples were determined by nitrogen adsorption at 77 K (Quantachrome NOVA 1000-TS). Crystallite sizes were estimated by line-broadening analysis according to the formula $d_{XRD} = 0.9\lambda/(\beta \cos \Theta)$, where d_{XRD} is the crystallite size, λ is the wave length of X-rays, Θ is the diffraction angle, β is the half-width of the diffraction peaks. The absorption edge of the sample was determined from the onset of reflectance spectrum measured by UV-VIS spectrophotometer (Shimadzu UV-2000). The amount of nitrogen doped in titania was determined by an oxygen-nitrogen analyzer (Horiba, EMGA-2800).

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 (373 cm^3) during the photoirradiation of constant flowed 1 ppm NO and 50 vol% air (balance N_2) mixed gas at the flow rate of 200 cm^3 min^{-1}. The photocatalyst sample was placed in a hollow place of 20 mm length × 15 mm width × 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, 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 (Yanaco, ECL-88A).

3. Results and discussion

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

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

Under present experimental conditions, amorphous titania was formed at first by the homogeneous precipitation at 90°C by the reaction with ammonia released by the hydrolysis of hexamethylenetetramine and then crystallization of titania proceeded during followed solvothermal treatment at higher temperature. The XRD patterns and Raman spectra of the powders prepared by the homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH (a) 9 and (b) 7, (c) $TiCl_3$-hexamethylenetetramine mixed 50 vol% methanol solutions at pH 9 and 190°C for 2 h are shown in Figs. 1 and 2.

It is seen that the crystalline phase of the sample changed significantly depending on the solution pH and solvent, i.e., the XRD patterns of (a), (b) and (c) were identified as rutile, brookite and anatase, respectively. Ranman bands at 449 and 610 cm^{-1} of sample (a) and 397, 516 and 639 cm^{-1} of sample (c) agreed with the reported values for rutile and anatase [10], respectively. Since XRD peaks shown in Fig. 1 was not clear, it was not able to

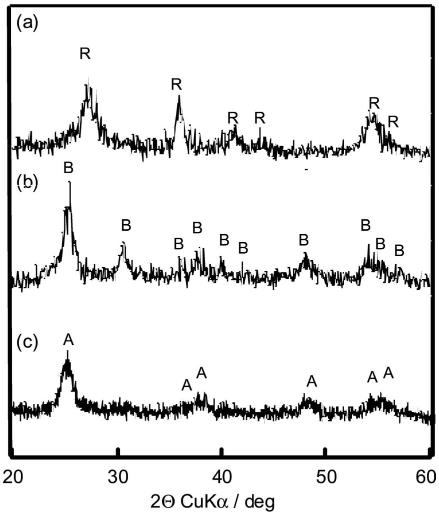

Figure 1 X-ray diffraction patterns of the powders prepared by the homogeneous precipitation-solvothermal reaction in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH (a) 9, (b) 7 and (c) 50 vol% methanol solutions at pH 9 and 190°C for 2 h. A: Anatase, B: Brookite, R: Rutile.

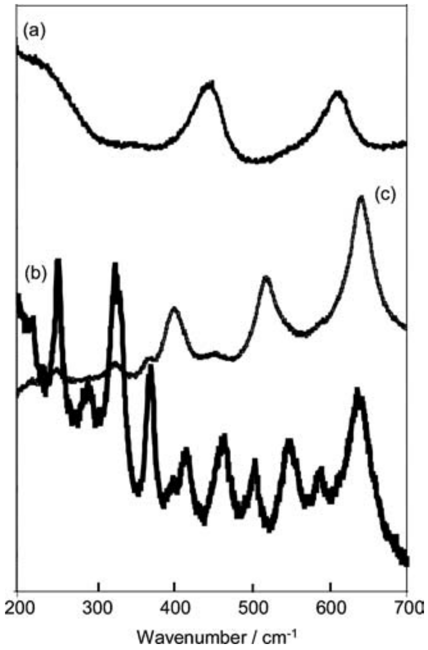

Figure 2 Raman spectra of the powders prepared by the homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH (a) 9, (b) 7 and (c) 50 vol% methanol solutions at pH 9 and 190°C for 2 h.

be cleared whether anatase coexisted in sample (b). However, the sample (b) showed Raman band at 214, 247, 288, 322, 396, 412, 502, 545, 585 and 636 cm^{-1}, but no band corresponding to anatase, indicating sample (b) consisted of single phase brookite. In previous papers [7–9] , 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 hexamethylenetetramine played an important role for the formation of brookite, although the details were not clarified yet.

Fig. 3 shows the TEM photographs of the powders prepared in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH (a) 9 and (b) 7 and (c) $TiCl_3$-hexamethylenetetramine mixed 50 vol% methanol solutions at pH 9 and 190°C for 2 h. All samples consisted of nanoparticles less than 10 nm in diameter. Rutile and anatase prepared in aqueous solution and methanol solution at pH 9 showed similar crystallite size, but brookite prepared in water at pH 7 showed larger crystallite size.

The amount of nitrogen doped, crystalline phases, BET surfaces areas and crystallite sizes of the samples prepared in various solvents are listed in Table I. Since all samples contained 0.06–0.20 wt.% nitrogen, nitrogen-doping in titania was confirmed. All samples consisted of nanoparticles less than 20 nm in diameter. The specific surface area increased and crystallite 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 hexamethylenetetramine, since the initial amount of hexamethylenetetramine increased with increasing solution pH. The samples prepared at pH 7 and 9 possessed large specific surface areas above 155 m^2 g^{-1}. Only brookite was formed at pH 1, but brookite, rutile and anatase were formed at 7 and 9 depending on the reaction solvent. It was notable that anatase was formed only in the methanol solution at pH 9. Rutile and anatase obtained in aqueous solution and aqueous methanol solution at pH 9 showed very high specific surface area ca. 200 m^2 g^{-1}. The brookite prepared at pH 7 also showed high specific surface area of 168 m^2 g^{-1}. Therefore, these three samples were used for the further experiment.

Although pure titania is white, the samples obtained in the present study were light yellow, indicating the formation of nitrogen-doped titania during the solvothermal reactions. The diffuse reflectance spectra of brookite, rutile and anatase type nitrogen-doped titania powders prepared in aqueous solution at pH 7, 9 and aqueous methanol solution at pH 9, respectively, are shown in Fig. 4 together with that of commercial titania (Degussa P-25). Commercial titania showed absorption edge at 420 nm which is

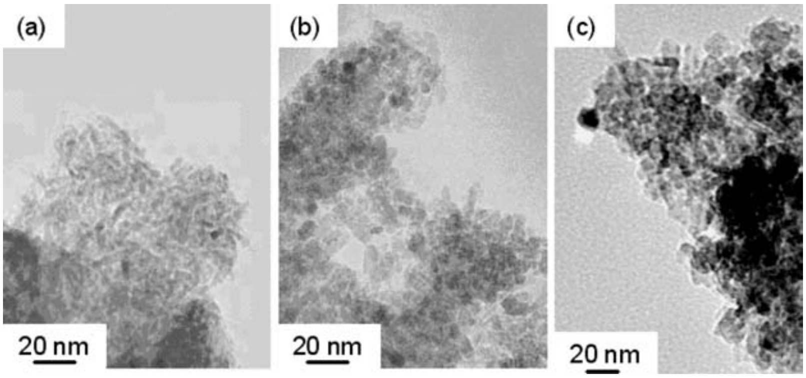

Figure 3 Transmission electron micrographs of the powders prepared by the homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH (a) 9, (b) 7 and (c) 50 vol% methanol solutions at pH 9 and 190°C for 2 h.

TABLE I Crystalline phases, BET surfaces areas and crsytallite sizes of the samples prepared by the homogeneous precipitation-solvothermal treatment of $TiCl_3$-hexamethylenetetramine*solutions at 190°C and various final pHs for 2 h.

Solvent	pH	HMT*/M	N/wt%	Phase	SSA/m^2 g^{-1}	$d_{XRD/nm}$
Water	1	0.29	0.06	B	41.8	19.5
Water	7	0.86	0.14	B	168	7.9
Water	9	1.43	0.14	R	205	3.6
Methanol	1	0.29	0.17	B	86.4	13.4
Methanol	7	0.86	0.18	B+A	213	5.6
Methanol	9	1.43	0.20	A	201	3.6
Ethanol	9	0.86	0.18	R	264	1.6
1-Propanol	9	0.86	0.17	R	224	4.5
1-Buthanol	9	0.86	0.12	R	157	4.0

SSA: Specific surface area, d_{XRD}: crystallite size, A: Anatase. B: Brookite, R: Rutile

equivalent to the band gap energy of 2.95 eV. On the other hand, all samples prepared in the present study showed absorption in the visible light regions up to 600 nm. It was reported that the doping of nitrogen is effective to obtain visible light responsive TiO_2 because N 2p states contribute to the band gap narrowing by mixing with O 2p state [3]. The results shown in Fig. 4 also suggested that the doping of nitrogen was accomplished under present solvothermal reaction conditions.

Specific surface areas and photocatalytic activity for the oxidative decomposition of NO under irradiating visible light ($\lambda > 510$ nm) of brookite type nitrogen doped titania are shown in Fig. 5 as a function of the solvothermal reaction temperature at pH 7. 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 $.O_2^-$, which can then generate active .OOH radicals, while holes in the valence band react with water to form .OH radical [11]. Nitrogen monoxide reacts with these reactive oxygen radicals, molecular oxygen and water to produce HNO_3. The overall chemical reaction can be described as follow.

$$NO + 1/2H_2O + 3/2O_2 \rightarrow HNO_3$$

It is seen that the specific surface area did not change so much (137-168 m^2 g^{-1}) until 190°C, and then greatly decreased with increasing temperature probably because of the crystal growth at high temperature. The photocatalytic activity showed similar trend with the specific surface area, i.e., the photocatalytic activity increased a little at first with increasing solvothermal temperature up to 190°C, after that greatly decreased. Generally, the photocatalytic activity depends on both the specific surface area and crystallinity. The increase in the photocatalytic activity up to 190°C may be due to the increase in the crystallinity of the sample to decrease the crystal defects which act as the recombination center of photoinduced

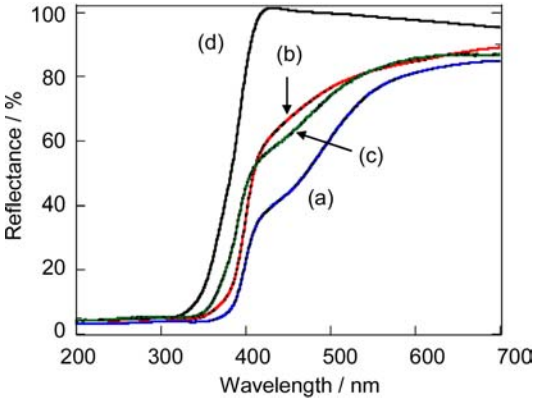

Figure 4 Diffuse reflectance spectra of the powders prepared by the homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH (a) 9, (b) 7 and (c) 50 vol% methanol solutions at pH 9 and 190°C for 2 h together with that of (d) commercial titania (Degussa P-25).

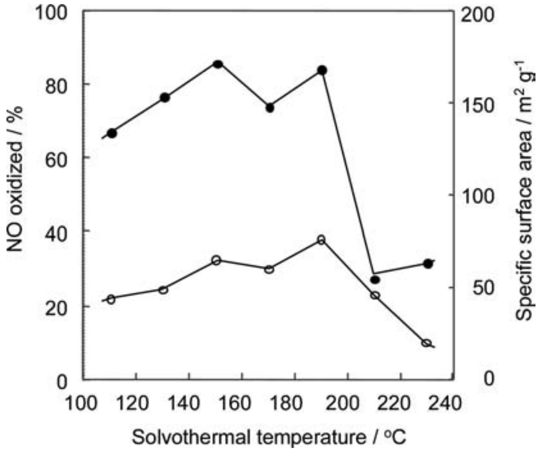

Figure 5 (a) Specific surface area and photocatalytic activity of nitrogen-doped titania prepared by the homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethylenetetramine mixed aqueous solutions at pH 9 and various temperatures for 2 h. Initial NO concentration: 1 ppm, Irradiation light: 450 W High pressure mercury light ($\lambda > 510$ nm).

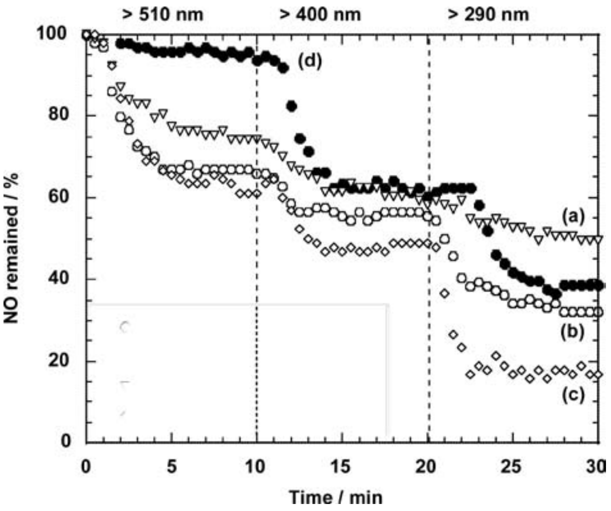

Figure 6 Photocatalytic activity of nitrogen-doped (a) brookite, (b) rutile and (c) anatase and (d) commercial titania (P-25) for the oxidative decomposition of NO. Initial NO concentration: 1 ppm, Irradiation light: 450 W high pressure mercury light.

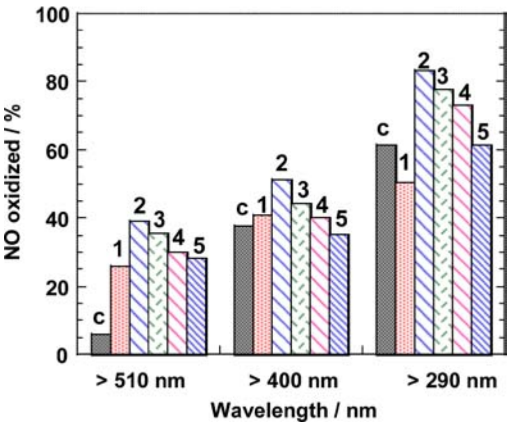

Figure 7 Photocatalytic activity of nitrogen doped titania prepared in (1) water, (2) methanol, (3) ethanol, (4) 1-propanol, (5) 1-buthanol for the oxidative decomposition of nitrogen monoxide under irradiating 450 W high pressure mercury arc filtered with various cut filters. (c): commercial TiO_2 (P-25). Initial NO concentration: 1 ppm.

electrons and holes, since the specific surface area was almost constant. On the other hand, the decrease in the photocatalytic activity above 190°C may be due to the decrease in the specific surface area of the sample.

Fig. 6 shows the photocatalytic activity of nitrogen-doped brookite, rutile and anatase, and commercial titania (P-25) for the oxidative decomposition of NO under irradiating high pressure mercury arc filtered with various cut filters. The samples prepared in the present study showed excellent photocatalytic activity under visible light irradiation ($\lambda > 510$ nm), although the photocatalytic activity of commercial titania (P-25) was poor because of its relatively large band gap energy of ca. 3 eV. The photocatalytic activity of nitrogen-doped titania under visible light irradiation was in the order anatase > brookite > rutile. It is notable that nearly 40 % of nitrogen monoxide could be continuously destructed by the nitrogen-doped anatase nanoparticles prepared in methanol solution at pH 9. Both anatase and brookite type nitrogen-doped titania shower more excellent photocatalytic activity than P-25 even under UV-light ($\lambda > 290$ nm) irradiation.

Fig. 7 shows the photocatalytic activity of nitrogen-doped titania prepared in (1) water, (2) methanol, (3) ethanol, (4) 1-propanol and (5) 1-buthanol for the oxidative decomposition of nitrogen monoxide under irradiating 450 W high pressure mercury arc filtered with various cut filters together with that of (c) commercial TiO_2 (P-25). All samples prepared in the present study showed excellent photocatalytic activity under visible light irradiation ($\lambda > 510$ nm). The photocatalytic activity of nitrogen-doped titania under visible light irradiation ($\lambda > 510$ nm) changed depending on the reaction solvent as methanol > ethanol > 1-propanol > 1-buthanol > water. It is also notable that both anatase and rutile type nitrogen-doped titania prepared in methanol, ethanol and 1-propanol showed higher activity than P-25 even under UV light irradiation ($\lambda > 290$ nm).

X-ray diffraction patterns of the samples as-prepared by the homogeneous precipitation-solvothermal reaction in $TiCl_3$-hexamethylenetetramine mixed 50 vol% methanol solutions at pH 9 and 190°C for 2 h followed by calcination at various temperatures in air for 1 h are shown in Fig. 7. The anatase was stable up to 400°C, but began to transform to rutile at 500°C and completely transformed to rutile at 700°C.

The specific surface areas and photocatalytic activities for the oxidative decomposition of NO are shown in Fig. 8 as a function of calcination temperature. The specific surface area decreased with increasing calcination temperature, but the sample retained high specific surface

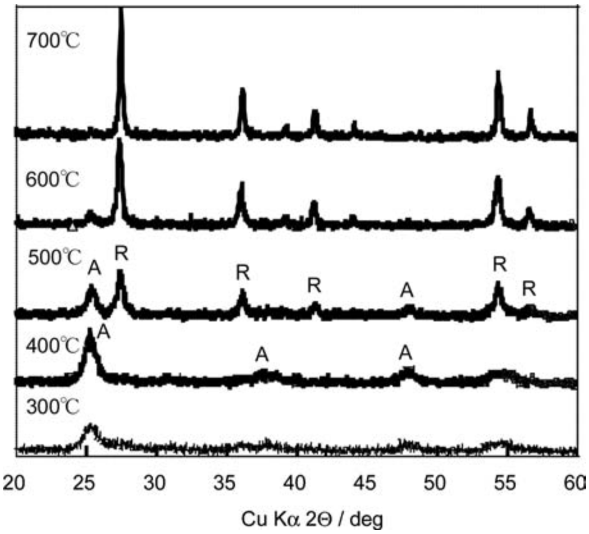

Figure 8 XRD patterns of TiO_2 powders prepared in $TiCl_3$-HMT-methanol solution at pH 9 and 190°C for 2 h followed by calcination at various temperatures.

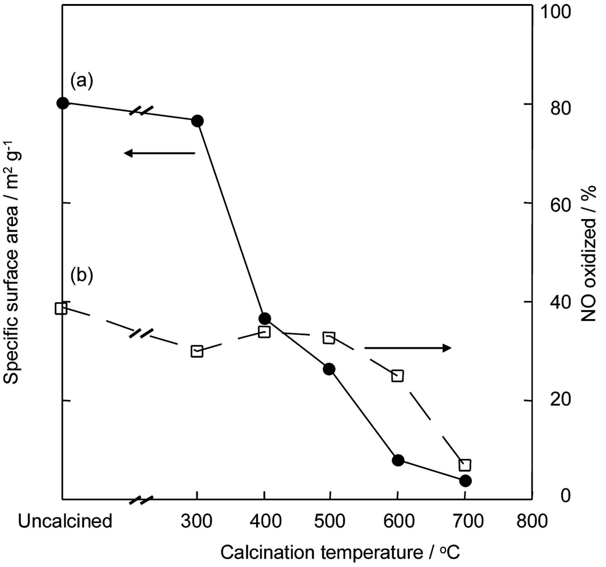

Figure 9 (a) Specific surface areas and photocatalytic activities of nitrogen doped titania calcined at various temperatures. Initial NO concentration: 1 ppm, Irradiation light: 450 W High pressure mercury light ($\lambda > 510$ nm).

area above 70 m^2 g^{-1} until 500°C. Even after calcination at such high temperature as 700°C, the yellow color did not disappear, indicating the excellent thermal stability of nitrogen-doped titania. The photocatalytic activity under irradiation of visible light ($\lambda > 510$ nm) slightly decreased with increasing calcination temperature up to 600°C and then greatly decreased at 700°C. By calcination the specific surface area decreases whereas the crystallinity increases. This may be the reason why the sample retained excellent visible light responsive photocatalytic activity until 600°C although the specific surface area decreased.

The nitrogen content and photocatalytic activity of nitrogen-doped titania prepared in the present study are summarized in Fig. 10. The photocatalytic activity under visible light ($\lambda > 510$ nm) and UV light ($\lambda > 290$ nm) irradiation increased at first with increasing nitrogen content up to 0.2 wt%, thereafter decreased. The increase in the initial stage may be due to the band gap narrowing by doping nitrogen. On the other hand, the decrease by doping excess nitrogen may be due to the promotion of electron and hole recombination, since the substitution of O^{2-} by N^{3-} would result in the formation of oxygen vacancy which acts as an electron-hole recombination center for charge compensation.

4. Conclusions

From the present results, following conclusions may be drawn. 1) Nitrogen-doped titania nanoparticles can be obtained by the homogeneous precipitation in hexamethylenetetramine-$TiCl_3$ alcohol aqueous solutions at 90°C followed by heating at 190°C. 2) The crystalline phase of nitrogen-doped titania changed as anatase, rutile and brookite depending on the solvent and pH. 3) Nitrogen-doped titania was yellow and showed photocatalytic activity under visible light irradiation for the oxidative decomposition of nitrogen monoxide in air. 4) The photocatalytic activity of nitrogen-doped titania was in the order anatase > brookite > rutile.

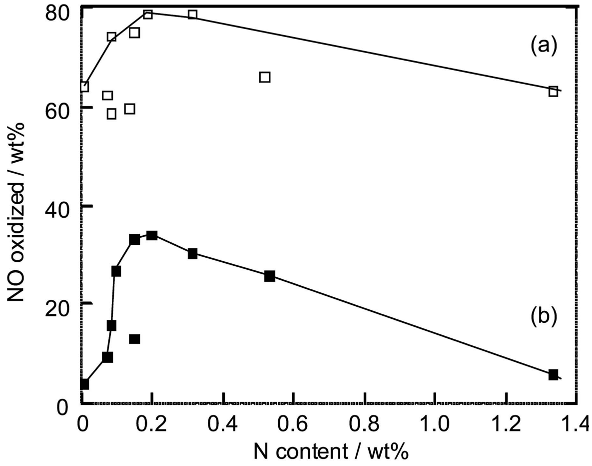

Figure 10 Relationship between the nitrogen content and photocatalytic activity of nitrogen-doped titania prepared by the solvothermal reaction of $TiCl_3$ and hexamethylenetetramine or urea in various solvents. Initial NO concentration: 1 ppm, Irradiation light: 450 W high pressure mercury arc filtered with (a) 290 and (b) 510 nm cut filters.

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