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Rapid Communication

Phase-compositional control and visible light photocatalytic activity of nitrogen-doped titania via solvothermal process

Yohei Aita, Masakazu Komatsu, Shu Yin,* and Tsugio Sato

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

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Abstract

Nitrogen-doped titania nanoparticles consisted of pure anatase, rutile and brookite phases were successfully prepared by a solvothermal process in $TiCl_3$–HMT (hexamethylenetetramine, $C_6H_{12}N_4$)-alcohol mixed solution. The powders were yellow or beige and showed excellent visible light absorption and photocatalytic ability for the oxidative destruction of nitrogen monoxide under irradiation of visible light of wavelength >510 nm.

Keywords: Solvothermal process; Nitrogen-doped titania; Visible light induced; Photocatalyst; deNO$_x$; Phase-compositional control

1. Introduction

Titania has received much attention with respect to the degradation of various environmental pollutants [1–3]. TiO_2 is, however, active only in the ultraviolet (UV) region because of its wide band gap (3.0–3.2 eV). Therefore, a material capable of visible-light photocatalysis is required with regard to solar energy and interior lighting applications. Recent researches concerning TiO_2-doped with nonmetal elements such as nitrogen [4–6], fluorine [7], sulfur [8] and carbon [9] have been reported. Asahi et al. [5] reported that nitrogen-doped TiO_2 prepared by sputtering TiO_2 target in an N_2 (40%) and Ar gas mixture followed by annealing in N_2 gas at 550°C for 4 h showed excellent visible light photocatalytic activity for the decomposition of methylene blue and the degradation of acetaldehyde. Uma et al. [10] reported that transition metal incorporated microporous titanium silicate showed efficient photocatalytic activity for the decomposition of acetaldehyde using visible and UV light irradiation. Usually, anatase phase possesses higher photocatalytic activity than that of rutile. In our previous research, it was found that nitrogen-doped rutile titania with excellent visible light photocatalytic activity could be prepared by a low-temperature mechanochemical process [11,12]. Recently, the solvothermal reaction is becoming a promising method to produce nanosize crystals with soft agglomeration. In this communication, different phases of nitrogen-doped titania such as anatase, rutile and brookite were successfully prepared by the solvothermal process in $TiCl_3$–hexamethylenetetramine (HMT)–alcohol solution and their photocatalytic activities for the oxidative destruction of nitrogen monoxide under visible-light irradiation were also characterized.

2. Experimental section

$TiCl_3$ and HMT (Kanto Chem. Co.) were used as starting materials. A desired amount of HMT and 21.5 mL of 20 wt% $TiCl_3$ aqueous solution were mixed with 25 mL of distilled water or pure alcohol such as methanol or ethanol. The mixture was placed into a SUS 314 stainless-steel autoclave of internal volume 200 cm^3 and the chamber of autoclave was replaced by nitrogen gas three times. The autoclave was heated and kept at 90°C for 1 h to realize homogeneous precipitation and then heated at 190°C for 2 h. Usually, HMT hydrolyzes to form ammonia and formaldehyde above 70°C [13]. The final pH value of the solution was

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*Corresponding author. Fax: +81222175599.
E-mail address: shuyin@tagen.tohoku.ac.jp (S. Yin).

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controlled to 1, 7 and 9 by using 2, 6, and 10 g of HMT. The powder product was separated by centrifugation, washed with distilled water and acetone three times, respectively, then vacuum dried at 80°C overnight. The phase constitution of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized Cu*K*α radiation. The specific surface areas were determined by the amount of nitrogen adsorption at 77 K (BET, Quantachrome NOVA 1000-TS). 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 binding energy of N 1*s* was measured by a X-ray electron spectrometer (Perkin Elmer PHI 5600). The amount of nitrogen-doped in titania was determined by an oxygen–nitrogen analyzer (HORIBA, EMGA-2800). The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor during the photo-irradiation of 1 ppm NO-50 vol% air mixed (balance N_2) gas. The light wavelength was controlled by selecting various cut filters. The details of the photocatalytic characterization and the experimental apparatus were reported in a previous paper [14]. For comparison, a photocatalytic reaction was also carried out using commercial titania powders (Degussa *P*-25).

3. Results and discussion

Fig. 1 shows the XRD patterns of the powders prepared by the solvothermal process in $TiCl_3$–HMT–methanol and $TiCl_3$–HMT–ethanol solutions at 190°C and different pH values. The powders prepared in $TiCl_3$–HMT–ethanol solution at pH 1 and 9 consisted of single phase of brookite and rutile, respectively, while that at pH 7 consisted of a mixture of rutile and brookite. Similar results were observed in $TiCl_3$–HMT–aqueous solution, but single brookite phase was observed at pH 7. On the other hand, the powders prepared in $TiCl_3$–HMT–methanol solution at pH 9 showed anatase single phase. Other alcohols such as *i*-propanol and butanol were also used as reaction solvents. The phase compositions were same with those in ethanol solution. The present results suggested that existence of methanol resulted in the formation of anatase, although the detail was not clarified yet. All the prepared powders possessed well-crystallized nanocrystals with yellowish or beige color, certifying the formation of nitrogen doping. The phase compositional control of nitrogen-doped titania could be realized by the solvothermal reactions using different solvents. The powders homogeneously precipitated at 90°C consisted of amorphous structure and yellow color, indicating the formation of nitrogen doping at such low temperature. It was accepted that amorphous precursor crystallized to crystalline by dissolution–reprecipitation mechanism during hydrothermal reaction [15]. However, the detail mechanism for different titania phases formation was not completely understood yet. More experimental investigations are underway to understand some of the results discussed in this report.

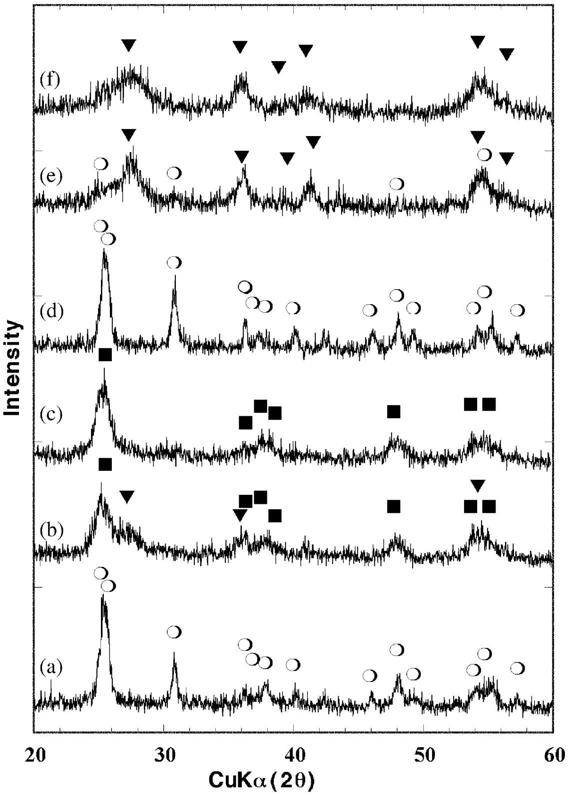

Fig. 1. XRD patterns of the nitrogen-doped titania prepared at 190°C in $TiCl_3$–HMT–methanol solution at final pH (a) 1, (b) 7and (c) 9 and in $TiCl_3$–HMT–ethanol solution at final pH (d) 1, (e) 7 and (f) 9. (○) Brookite; (▼) Rutile; (■) Anatase.

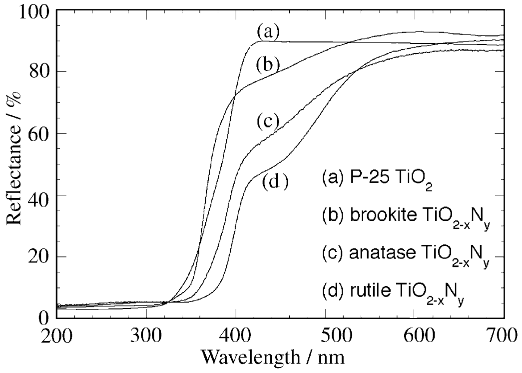

Fig. 2. Diffuse reflectance spectra of: (a) *P*-25 titania powder, and N-doped TiO_2 powders prepared at 190°C in (b) $TiCl_3$–HMT–methanol solution at final pH 1, (c) $TiCl_3$–HMT–methanol solution at final pH 9, and (d) $TiCl_3$–HMT–ethanol solution at final pH 9.

Fig. 2 shows the diffusion reflectance spectra of the N-doped TiO_2 powders prepared by the solvothermal reactions together with that of commercial titania powder *P*-25. It was obvious that nitrogen-doped brookite, anatase and rutile powders showed two step absorption edges and excellent visible-light absorption. The two-step absorption became clear after calcination at 400°C. The first edge is thought to be related to the band structure of original titania, and the second one around 520–535 nm is caused by the formation of $N2_p$ band which locates above $O2_p$ valence band in $TiO_{2-x}N_y$ [5,6].

Fig. 3 shows the N 1*s* spectrum of titania powders prepared in $TiCl_3$–HMT aqueous solution at pH 7 and 190°C. It was obvious that binding energy around 396 eV which related to the existence of N–Ti binding could be observed, although the peak intensity was not so strong.

Table 1 summarizes the phase compositions, specific surface areas, band gap values, nitrogen-doped amounts and photocatalytic activities under irradiating 450 W high pressure mercury arc filtered with various cut filters of the samples prepared under different conditions. Commercial titania *P*-25 was also listed for comparison. All samples prepared at pH 9 possessed high specific surface above 200 m^2/g. The sample prepared in $TiCl_3$–HMT–ethanol solution showed the largest specific surface area of 264.2 m^2/g. On the other hand, single phase of brookite was formed at lower pH values. It was obvious that particle size increased with decreasing pH value of solution. Except for the commercial *P*-25, all the powders showed two step absorption around 400–410 nm (c.a. 3.0–3.1 eV) and 520–535 nm (c.a. 2.2–2.3 eV). The amount of nitrogen in the samples after calcination at 400°C were 0.12–0.20 wt%. These results confirmed that nitrogen element was successfully doped in titania by the solvothermal reaction and nitrogen-doped titania was stable even after calcination in air at 400°C.

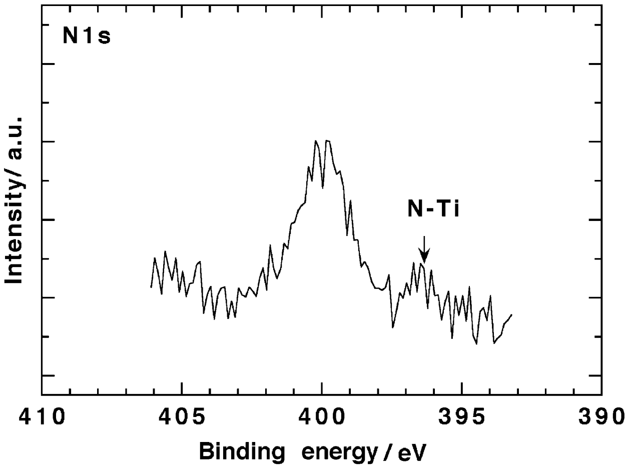

Fig. 3. N 1*s* XPS spectrum of titania powder prepared in $TiCl_3$–HMT–aqueous solution at final pH 7 and 190°C.

The nitrogen-doped anatase with high S.S.A. of 201 m^2/g could continuously destruct 39% and 83% of nitrogen monoxide under irradiation of light of wavelength >510 nm and >290 nm, respectively. The visible light photocatalytic ability was more than 5 times higher than that of commercial titania powder *P*-25. Moreover, under the irradiation of the lights of $\lambda > 400$ and >290 nm all the prepared powders showed higher photocatalytic activities than those of *P*-25.

Table 1
Effect of treatment solvents on the physico-chemical properties and photocatalytic activity of nitrogen doped titania

Treatment solvent	Final pH	Phase composition[a]	S.S.A. (m^2 g^{-1})	Band gap (eV)		N-doped amount (wt%)[b]	NO destruction ability (%)		
				1st	2nd		>510 nm	>400 nm	>290 nm
As received *P*-25	—	A>R	47.3	3.04	—	0.0	8.0	37.0	51.2
Aqueous solution	1	B	41.8	3.35	2.48	0.099	12.6	33.7	52.6
	7	B	168	3.26	2.34	0.149	34.0	45.7	68.1
	9	R	205	3.02	2.38	0.138	25.8	40.9	50.5
Methanol aqueous solution	1	B	86.4	3.26	2.38	0.172	23.9	28.3	47.8
	7	A>R	213	3.10	2.34	0.176	36.7	55.6	83.3
	9	A	201	3.10	2.34	0.197	38.9	51.1	83.3
Ethanol aqueous solution	1	B	70.0	3.26	2.29	0.134	29.0	38.7	78.5
	7	R>B	175	3.02	2.45	0.164	31.2	40.2	80.6
	9	R	264	3.02	2.32	0.175	35.6	44.4	77.8

[a] A: Anatase; B: Brookite; R: Rutile.

[b] Samples were calcined in air at 400°C for 1 h.

4. Conclusions

In summary, nitrogen-doped titania photocatalyst consisted of various single phases were successfully synthesized by the solvothermal reaction in $TiCl_3$–HMT–alcohol solution. The nitrogen-doped anatase, rutile and brookite possessed excellent visible light absorption and photocatalytic ability for nitrogen monoxide destruction under irradiation of visible light ($\lambda > 510$ nm). The photocatalytic activity strongly related to the S.S.A. and phase compositions. These results suggested that the solvothermal reaction is an effective method for nitrogen doping to inorganic materials.

Acknowledgments

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