

Visible-light-induced photocatalytic activity of $\text{TiO}_{2-x}\text{N}_y$ prepared by solvothermal process in urea–alcohol system

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Abstract

Nitrogen-doped anatase, rutile and brookite titania photocatalyst $\text{TiO}_{2-x}\text{N}_y$ which can be excited by visible light were prepared by mixing aqueous TiCl_3 solutions with urea $(\text{NH}_2)_2\text{CO}$ and various type of alcohols followed by solvothermal treatment at 190°C . The phase composition, crystallinity, microstructure and specific surface area of titania powders greatly changed depending on the pH and type of solvents. Violet, yellowish and grayish $\text{TiO}_{2-x}\text{N}_y$ with excellent visible light absorption and photocatalytic activity were prepared. The $\text{TiO}_{2-x}\text{N}_y$ powders prepared in urea–methanol solution showed excellent photocatalytic ability for the oxidative destruction of nitrogen monoxide under irradiation of visible light $\lambda > 510\text{ nm}$.

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1. Introduction

Titania is the most effective photocatalyst and can be applied in decomposition of some pollute substances, such as nitrogen monoxide in atmosphere and/or organic pollutants in water under light irradiation.^{1,2} However, titania can only be encouraged by UV light because of its large band gap value of ca. 3 eV. In order to utilize the solar energy effectively, it is necessary to develop a visible-light-reactive photocatalyst. In 2001, Asahi et al.^{3,4} reported that nitrogen-doped titanium oxide with high visible-light photocatalytic activities could be prepared by sputtering TiO_2 in an N_2 (40%)/Ar gas mixture followed by annealing in N_2 gas at 550°C or by treating anatase TiO_2 powder in the NH_3 (67%)/Ar atmosphere at 600°C . They also pointed out that nitrogen doping leads to narrowing of band gap by mixing the $\text{N}2p$ and $\text{O}2p$ state and consequently induces the visible-light-responsive photocatalytic activity. It was also forecasted that other kind of anions such as C, S and F would result in the similar effect to

nitrogen. Since then, many researchers paid their much attention on anion-doped photocatalysts.^{5–10} Meanwhile, most methods are high temperature processes, using expensive precursors or preparation instruments. In our previous research, it was found that nitrogen, fluorine or sulfur-doped photocatalyst with high visible-light-induced photocatalytic activity could be prepared by a low-temperature mechanochemical doping process.^{11–14} However, anion-doped titania in only rutile structure can be prepared by this process. In order to realize the phase-compositional and morphological control of anion-doped photocatalysts, a soft solution process is described in this paper, using various alcohol as reaction media. The effects of reaction conditions such as pH and type of solvents on phase composition, microstructure, specific surface area and photocatalytic activity were investigated in detail.

2. Experimental

Desired amount of urea $(\text{NH}_2)_2\text{CO}$ and 21.5 cm^3 of 20 wt.% TiCl_3 solution (Kanto Chem. Co. Inc., Japan) was

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introduced into 25 cm³ of distilled water or alcohols, the mixed solution was placed into a SUS 314 stainless steel autoclave attached with a Teflon tube of internal volume of 200 cm³. After that the chamber of autoclave was flushed by nitrogen gas three times. The autoclave was heated and kept at 90 °C for 1 h to realize the hydrolysis of urea, then heated at 190 °C for 2 h for crystallization. Various types of alcohols such as methanol, ethanol, 1-propanol, and 1-butanol were used as reaction media. The final pH value of the urea solution was controlled to 2, 7 and 9 by using 2, 6 and 10 g of urea. The powder product was separated by centrifugation, washed with distilled water and acetone three times, respectively, then vacuum dried at 80 °C overnight. In order to remove the absorbed nitrogen reagents completely, all the samples were calcined at 400 °C for 1 h before the nitrogen-doped amount analysis.

The phase composition 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). 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 onsets of diffuse reflectance spectra of the samples measured using an 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 nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm³ of internal volume) during the photo-irradiation of a constant flow (200 cm³/min) of a mixture containing 1 ppm NO–50 vol.% air (balance N₂).¹⁵ The photocatalytic sample was placed in a hollow of 20 mm length \times 15 mm width \times 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. The wavelength was controlled by selecting filters, i.e., Pyrex glass for $\lambda > 290$ nm, Kenko L41 Super Pro (W) filter > 400 nm and Fuji triacetyl cellulose filter > 510 nm. The concentration of NO was determined using a NO_x analyzer (Yanaco, ECL-88A). For comparison, a photocatalytic reaction was also carried out using commercial titania (Degussa P25).

3. Results and discussion

3.1. Phase composition and physicochemical characterization

It is well known that the hydrolysis of urea produces CO₂ and NH₃ at above 85 °C. The ammonia react with TiCl₃ to form nitrogen contained TiO_{2-x}N_y·nH₂O precursor. Well-crystallized TiO_{2-x}N_y could be formed by the followed

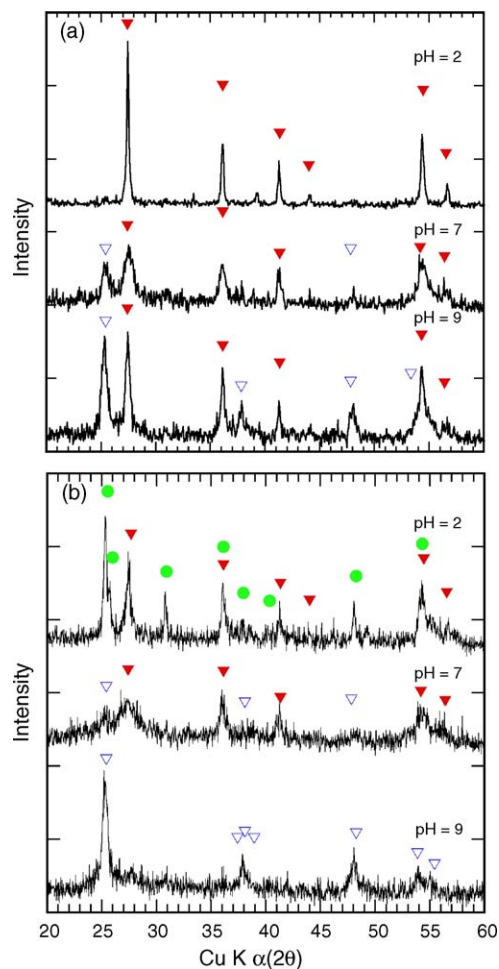


Fig. 1. XRD patterns of the titania prepared by solvothermal treatment of (a) TiCl₃–urea aqueous solution and (b) TiCl₃–urea–methanol solution at pH 2, 7, 9 and 190 °C for 2 h. (▽) Anatase; (▼) rutile; (●) brookite.

solvothermal treatment at 190 °C:

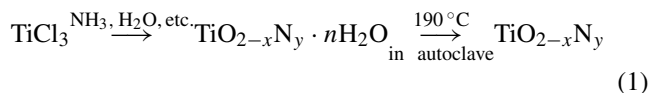


Fig. 1 shows the XRD patterns of the titania powders prepared in TiCl₃–urea aqueous solution and TiCl₃–urea–methanol solution at various pH and 190 °C for 2 h. It was found that the phase composition strongly related to the pH value and type of solvent. The powders prepared at pH 2 in TiCl₃–urea aqueous 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 TiCl₃–urea–methanol solution at 190 °C showed different phase composition. The powder prepared at pH 2 and 7 consisted of brookite/rutile and anatase/rutile mixture, respectively. 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.

Table 1
Effect of treatment solvents on the physical properties of nitrogen-doped titania

Sample no. ^a	Treatment solvent	Final pH	Phase composition ^b	S _{BET} (m ² g ⁻¹)	N-doped amount (wt.%) ^c
P25	As received P25	–	A > R	47.3	0.0
TA2		2	R	25.2	0.130
TA7	Aqueous solution	7	R + A	108.1	0.179
TA9		9	R + A	61.4	0.205
TM2		2	R + B	25.3	0.052
TM7	Methanol aqueous solution	7	A + R	101.9	0.241
TM9		9	A	116.7	0.289
TE2		2	R	36.1	0.058
TE7	Ethanol aqueous solution	7	A > R	64.0	0.110
TE9		9	A > R	52.8	0.164
TE2		2	R	17.4	0.088
TE7	1-Propanol aqueous solution	7	R > A	87.1	0.196
TE9		9	R > A	33.1	0.240
TE2		2	R	15.6	0.073
TE7	1-Butanol aqueous solution	7	R	43.8	0.137
TE9		9	R	33.8	0.310

^a The sample no. TXY denotes “Titania prepared in solvent X (initial letter) at pH Y”.

^b A: anatase; B: brookite; R: rutile.

^c Samples were calcined in air at 400 °C for 1 h before nitrogen-doped amount analysis.

It is accepted that crystal growth in the solution greatly effected by the dielectric constant of the solution.^{16–19} In the present research, several type of alcohols were used for the synthesis of TiO_{2-x}N_y during the solvothermal reaction. Table 1 summarized the treatment conditions on the phase composition, BET specific surface area and nitrogen-doped amount of the prepared TiO_{2-x}N_y samples. The sample number TXY denoted “Titania prepared in X (initial letter of solvent) at pH Y (2, 7, or 9)”. Although five kinds of solvents were applied at different pH values, only the existence of methanol and high concentration of NH₃ preferred to the formation of pure anatase phase. No noticeable difference in XRD patterns could be observed under different solvothermal treatment temperature in the range of 150–230 °C. The phase formation of rutile was promoted by using high-carbon alcohols and by decreasing pH value of the solution. It seemed that the existence of NH₃ also delayed the anatase to rutile phase transformation, although the detail was not clarified yet. Based on the data of Table 1, it is also obvious that nitrogen-doped amount increased with the increment of pH value during the solvothermal treatment.

Fig. 2 shows the diffuse reflectance spectra of titania powders prepared under different pH in TiCl₃–urea–methanol solution (Fig. 2a) together with those after calcination in air at 400 °C for 1 h (Fig. 2b). The powders as-prepared (samples TM) showed violet color with excellent visible light absorption. The violet color might be due to the existence of oxygen vacancy and residual Ti³⁺ in the lattices. It was reported that oxygen vacancies in the lattice lead to the formation of colored titania such as ivory and beige,^{2,20} and the Ti³⁺ produced by UV light or pulsed laser light irradiation lead to violet or dark blue color.^{21,22} It was also demonstrated that the reduction of titania in rutile phase introduces localized oxygen vacancy states at 0.75–1.18 eV bellow the conduction band,⁵ and this will extend the high

reactivity towards radiation in the visible light range.^{5,20–23} The large absorption of sample TM7 might be caused by the existence of residual oxygen vacancy after the solvothermal treatment. Both oxygen vacancy and nitrogen doping should lead to the band-gap narrowing of titania. After calcination in air at 400 °C, the color of samples changed to bright yellow. The visible light absorption of the powders prepared in TiCl₃–urea–methanol solution showed the order in pH 7 > pH 2 > pH 9. At the same time, 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 formation of N–Ti bonding in the TiO_{2-x}N_y. The

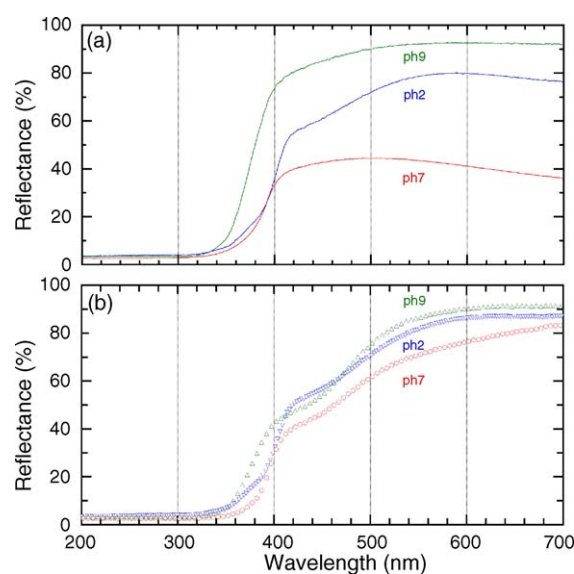
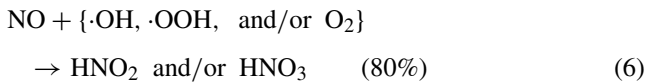


Fig. 2. Diffuse reflectance spectra of the titania powders prepared in TiCl₃–urea methanol solution 190 °C for 2 h. (a) As-prepared powders, (b) after calcination at 400 °C for 1 h.

first absorption edge around 410 nm was related to the original structure of titania. The second absorption edge should be related to the newly formed N1s orbits caused by the nitrogen doping in the molecular structure.^{3,4} In our previous paper, it was also confirmed that N–Ti bonding could be formed by a solvothermal process in hexamethylenetetramine aqueous solution system.^{24,25} Based on above results, it was suggested that not only pH value, but also treatment solvent type greatly affected the phase composition, nitrogen-doped amount and absorption in visible area of the titania powders. To the best of our knowledge, no similar result was reported by other researchers.

3.2. Photocatalytic activity of $\text{TiO}_{2-x}\text{N}_y$ prepared in various alcohol solvents

It is accepted that electron/hole pairs are formed by the photo-excitation of titania (Eq. (2)). In the presence of oxygen, the electrons in the conduction band are immediately trapped by the molecular oxygen to form $\cdot\text{O}_2^-$ (Eq. (3)), which can then generate active $\cdot\text{OOH}$ radicals (Eq. (4)).^{19,26,27} At the same time, the holes are trapped by water in air to produce hydroxyl radical (Eq. (5))^{19,26,27}



The nitrogen monoxide reacts with these reactive radicals, molecular oxygen, and very small amount of water in air (humidity was about 25% in the present research) to produce HNO_2 or HNO_3 (Eq. (6)). It was reported that about 20% of nitrogen monoxide was decomposed to nitrogen and oxygen directly (Eq. (7)).^{1,28} Fig. 3 shows the photocatalytic activities under UV and visible light irradiation and the BET specific surface area plotted with the dielectric constant of the treatment media. The photocatalytic activity of the sample greatly changed with the treatment solvents and showed a similar profiles with those of BET specific surface area (Fig. 3b). However, at pH 2 and $\lambda > 510$ nm, the maximum in the specific surface area was observed for a dielectric constant of 23.8, while the maximum of NO elimination was situated at a dielectric constant of 33.1. This result might be explained by the different phase composition, remember that large amount of brookite phase was existed in the sample TM2. In our recent research,²⁵ it was also found that pure brookite phase showed higher photocatalytic activity than that of pure

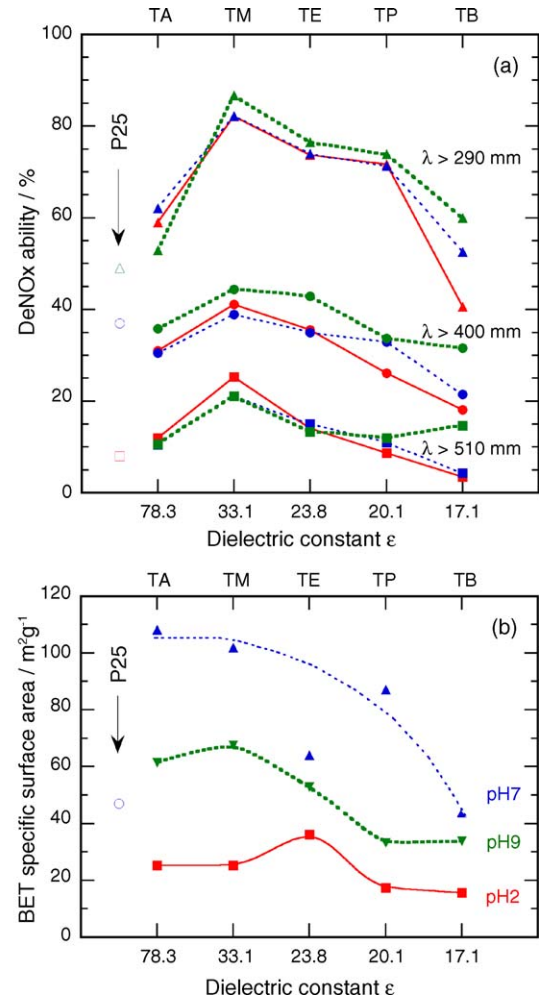


Fig. 3. (a) Photocatalytic activities under irradiation of light wavelength $\lambda > 510$ nm (■), $\lambda > 400$ nm (●), and $\lambda > 290$ nm (▲); (b) BET specific surface area plotted with the dielectric constant of the treatment solvent. The $\text{TiO}_{2-x}\text{N}_y$ powders were prepared in aqueous solution (TA), methanol solution (TM), ethanol solution (TE), 1-butanol solution (TB) and 1-propanol solution (TP) at pH 2 (solid lines), pH 7 (thick dotted lines), pH 9 (thin dotted lines) and 190 °C for 2 h. The open symbols (□, ○, and △) show those of standard P25 powders.

rutile phase if they possessed the same BET specific surface areas. The powders prepared in TiCl_3 -urea-methanol solution (sample TM) showed higher visible-light and UV-light photocatalytic activity than those in TiCl_3 -urea aqueous solutions (sample TA) or those in other solvents (samples TE, TP and TB). It is accepted that crystal growth can be enhanced by increasing the dielectric constant, ϵ , i.e., increasing the solubility of the sample in the solvent. Methanol ($\epsilon = 33.1$) and ethanol ($\epsilon = 23.8$) possessed higher ϵ than those of 1-propanol ($\epsilon = 20.1$) and 1-butanol ($\epsilon = 17.1$), and lower ϵ than that of water ($\epsilon = 78.3$); as a result, the powders obtained possessed fine crystalline and high crystallinity, and those in 1-propanol and 1-butanol possessed low crystallinity. On the other hand, since water has such high dielectric constant as 78.3, the powders prepared in aqueous solution possessed high crystallinity but large crystalline size and hard agglomer-

ation caused by the existence of the hydrogen bonding.^{29,30} It was known that well-crystallized fine particles with high specific surface areas and soft agglomeration possessed excellent photocatalytic activity.^{18,19} In the present research, The BET specific surface area of the samples strongly changed with pH and showed the sequence of TX7 > TX9 > TX2 (Fig. 3b), however, the crystallinity (Fig. 1, peak intensity of XRD patterns) showed quite different sequence of TX7 < TX9 < TX2. In addition, the nitrogen-doped amount and phase composition of titania also greatly changed with treatment pH of the solution. In photocatalysis research, different crystalline phase of titania usually shows different photocatalytic activity.^{31,32} It is ascribable to the differences of the Fermi level and the extents of surface hydroxylation of the solid.³² As mentioned above, many factors affected the photocatalytic activity of the samples at the same time, and led to the complexity in the photocatalytic activity of the prepared powders. As a comprehensive result, the photocatalytic activity was greatly affected by the solvent but slightly affected by the pH value of the solution. The most excellent photocatalytic activity under visible-light irradiation was obtained by the solvothermal treatment in TiCl₃–urea–methanol solution, continuously destructing nearly 25 and 87% of nitrogen monoxide under the irradiation of visible-light of $\lambda > 510$ nm and UV-light of $\lambda > 290$ nm. The photocatalytic activity was much higher than that of commercial standard titania powder P25 (Fig. 3, open symbols). Commercial P25 consisted of 70% anatase and 30% rutile. It was found that about 8% of NO could be destructed under irradiation of light wavelength > 510 nm. This might be related to the impurity in the powders, although the detail was not understood yet.

3.3. Thermal stability of TiO_{2-x}N_y

Fig. 4 shows the phase composition, rutile fraction and BET specific surface area of the TiO_{2-x}N_y powders prepared by calcination of the as-prepared TM7 sample at various temperatures in air for 1 h. With increasing calcination temperature, the anatase fraction decreased and rutile fraction increased. The BET specific surface area decreased also. A little part of anatase transformed to rutile phase after calcination at 400 °C, and almost all of the anatase transformed to rutile after calcination above 800 °C. Fig. 5 shows TEM photographs of the titania powders calcined in air at different temperatures. The powders obtained in urea–aqueous solution at pH7 showed fine fibrous structure and high specific surface area of 108 m² g⁻¹. It could be seen that the fine fibrous particles grew to large rod-like particles after high temperature calcination, and the specific surface area also decreased to below 10 m² g⁻¹. Fig. 6 shows the color and the DRS spectra of the samples before and after calcination at various temperatures. Compared with white Ti commercial titania P25, the as-prepared TiO_{2-x}N_y sample showed violet color. After calcination in air at 200–800 °C for 1 h, it changed to weak violet, bright-yellow, weak yellow and gray, respectively. However,

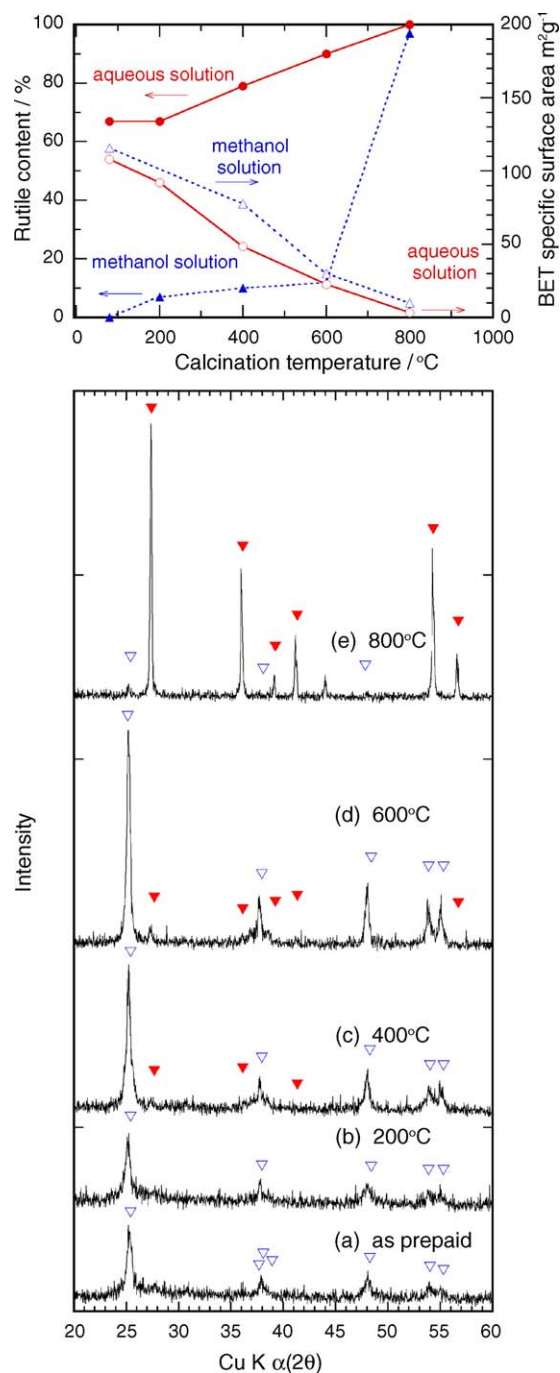


Fig. 4. XRD patterns of the TiO_{2-x}N_y powders prepared by: (a) solvothermal treatment of TiCl₃–urea–methanol solution at 190 °C and pH 7, followed by calcination in air at (b) 200 °C, (c) 400 °C, (d) 600 °C, and (e) 800 °C; together with the rutile content fraction (solid symbols) and BET specific surface area (open symbols) of the prepared powders. (∇) Anatase; (♥) rutile; samples TM: dotted lines; samples TA: solid lines.

it is obvious that even if the TiO_{2-x}N_y sample was calcined at such high temperature as 800–1000 °C, it did not changed to white color, indicating the thermal stability of the Ti–N bonding in TiO_{2-x}N_y powders prepared by the present solution route. It is obvious that the yellowish sample (c) and (d) possessed clear two-step absorption edges around 400 nm

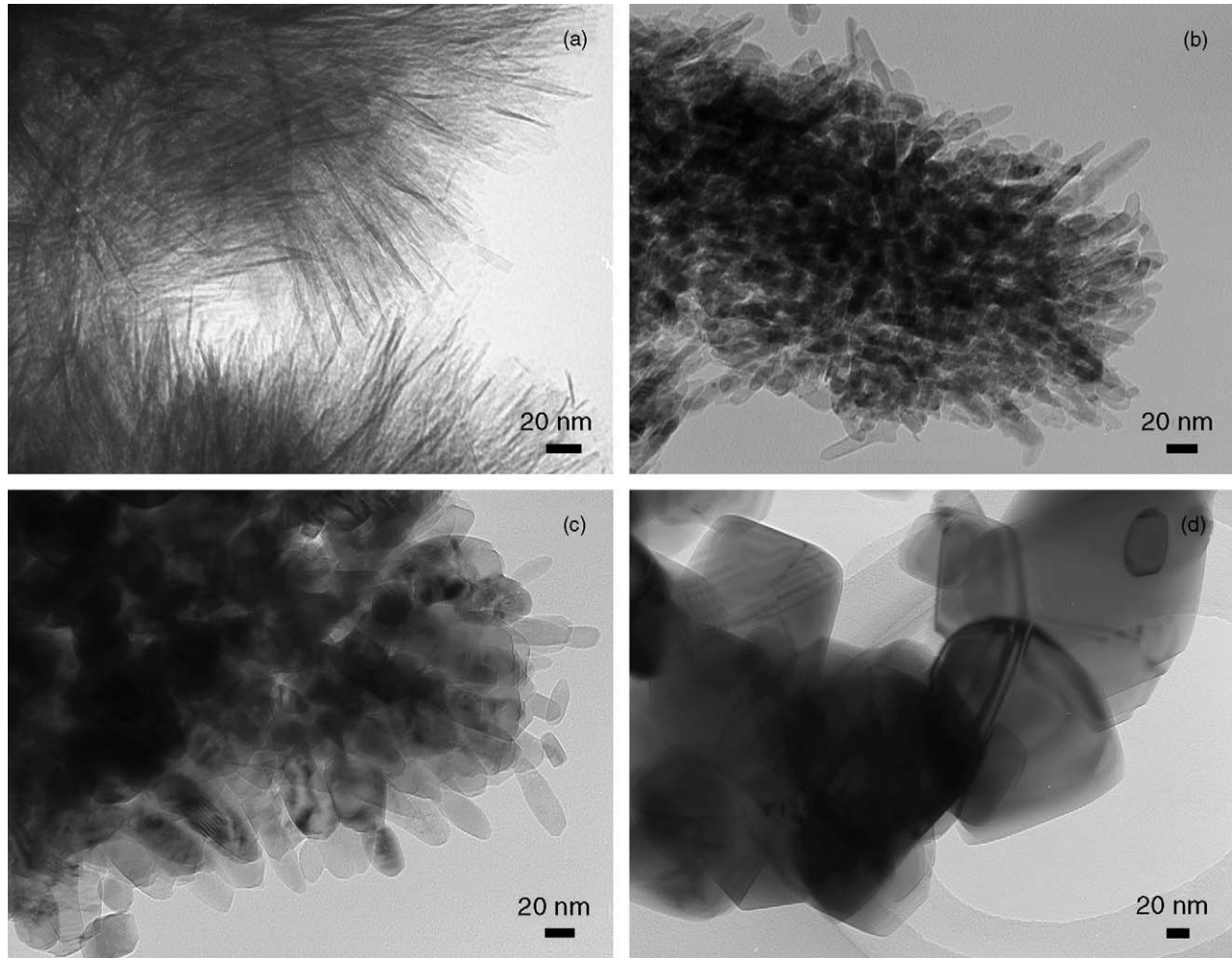


Fig. 5. TEM photographs of the $\text{TiO}_{2-x}\text{N}_y$ powders prepared by calcination in air at: (a) 200 °C, (b) 400 °C, (c) 600 °C, and (d) 800 °C.

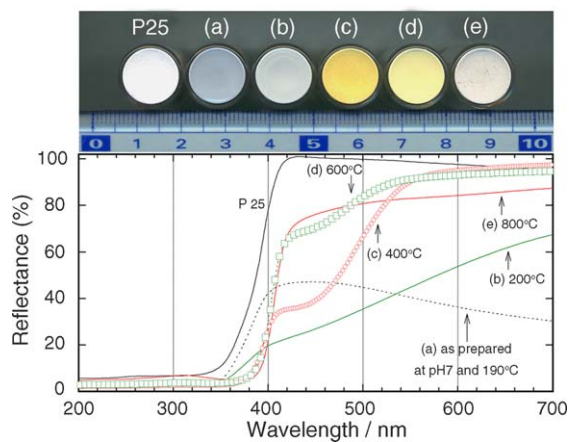


Fig. 6. Diffuse reflectance spectra and color of titania powders prepared by: (a) heat treatment of TiCl_3 -urea solution at 190 °C and pH 7 followed by calcination in air at (b) 200 °C, (c) 400 °C, (d) 600 °C, and (e) 800 °C, together with that of commercial P25. The color image was illustrated by scanning the powder samples in transparent glass bottles with an Epson scanner.

and 520–540 nm, indicating the existence of Ti–N bonding in the lattice. The two-step absorption was clearly existed until 600 °C. Fig. 7 shows the effect of calcination temperature on the nitrogen-doped amount and the photocatalytic activity under irradiation of different wavelength light. Although the nitrogen-doped amount decreased with calcination temperature, however, it was found that even if the powders was calcined at such high temperature as 800–1000 °C, small amount of residual nitrogen was still existed. Usually, the photocatalytic activity strongly related with the crystallinity, agglomerate state and the specific surface area.^{18,19} However, although the specific surface area decreased in about half after calcination at 400 °C, the photocatalytic activity did not decrease. The most excellent photocatalytic activity under visible light (>510 nm) was observed in the $\text{TiO}_{2-x}\text{N}_y$ prepared from TiCl_3 -urea-methanol solution, continuously destructing nearly 21–25% of nitrogen monoxide. The photocatalytic activity was several times higher than that of commercial standard titania powder P25. The $\text{TiO}_{2-x}\text{N}_y$ calcined at 400 °C showed higher visible light photocatalytic activity than that before calcination. This might be due to the

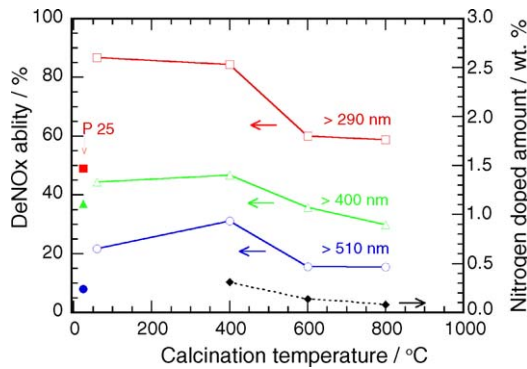


Fig. 7. The effect of calcination temperature on the nitrogen-doped amount (\blacklozenge) and photocatalytic activity ((\square) , $\lambda > 290$, (Δ) , $\lambda > 400$ and (\circ) , $\lambda > 500$ nm) of $\text{TiO}_{2-x}\text{N}_y$ powders prepared by heat treatment in TiCl_3 -urea-methanol solution at pH 7. The solid symbols (\blacksquare), (\blacktriangle), (\bullet) showed the photocatalytic activities of standard commercial powder Degussa P25.

removal of the absorbed by-products in the samples and the increase in crystallinity by calcination.

4. Conclusions

Based on the above experimental results, the following conclusions might be drawn:

Nitrogen-doped titania photocatalyst $\text{TiO}_{2-x}\text{N}_y$ with various phase composition was successfully prepared by solvothermal treatment of TiCl_3 solutions with urea and various alcohols at 190°C . The $\text{TiO}_{2-x}\text{N}_y$ powders showed various color and excellent visible light absorption and photocatalytic ability for the oxidative destruction of nitrogen monoxide under irradiation of visible light. In addition, visible-light-responsive photocatalyst $\text{TiO}_{2-x}\text{N}_y$ powders possessed excellent thermal stability. Nearly 25 and 86% of nitrogen monoxide could be continuously destructed under visible-light ($\lambda > 510$ nm) and UV-light irradiation ($\lambda > 290$ nm).

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