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# High visible-light photocatalytic activity of nitrogen-doped titania prepared from layered titania/isostearate nanocomposite

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**Abstract**

A nitrogen-doped titania photocatalyst with a high visible-light activity was synthesized from a layered titania/isostearate nanocomposite which was prepared by the sol–gel technique. Nitrogen doping was conducted by treatment with aqueous ammonia followed by calcination either in an $O_2$ (20%)/$N_2$ mixture or in pure $N_2$ at various temperatures. The visible-light activity of the samples was evaluated on the basis of the decomposition rate of methylene blue (MB) in an aqueous solution with blue-light-emitting diodes (BLED; 470 nm) as the light source. The obtained samples were vivid yellow and absorbed visible light in the region of 380–500 nm. The visible-light absorbance in this region correlated with the doped-nitrogen content in the sample. On the other hand, the visible-light photocatalytic activity did not correlate with it, and was increased by the partial release of the doped nitrogen. High visible-light photocatalytic activity was observed for the 400 °C-calcined samples, which was considerably higher than the activity of the nitrogen-doped anatase titania prepared by the calcination of the hydrolysis product of $Ti(SO_4)_2$ with aqueous ammonia.

*Keywords:* Nitrogen-doped; Titanium oxide; Titania; Anatase; Photocatalysis; Visible-light photocatalyst; Sol–gel process; Layered material

## 1. Introduction

Titania (titanium oxide) has been extensively studied for photocatalytic [1] and photochemical [2] applications because of its good properties such as high photocatalytic activity and chemical stability. Most forms of titania show photocatalytic activity only under UV light irradiation because of its band gap value of around 3.0 eV for rutile and 3.2 eV for anatase. It is known that the UV part of the solar spectrum only accounts for about 5% of the incoming solar energy while the rest is visible light. In order to efficiently utilize the solar energy, it is necessary to develop a visible-light active photocatalyst.

Recently, to extend the optical absorption edge of titania into the visible-light region, nitrogen has been doped into titania [3–11]. To the best of our knowledge, the first study on nitrogen-doped titania including its visible-light photocatalysis was conducted by Sato [3], although the obtained material was described as $NO_x$-doped $TiO_2$. He presumed that nitrogen was incorporated from the $NH_4Cl$ impurity of the commercial titanium hydroxide as the precursor used. After this study, several nitrogen-doping methods into titania have been investigated. These nitrogen-doped titanias were reported to be yellow because of the band gap narrowing.

Various methods of preparing the thin films of nitrogen-doped titania by gas phase growth techniques such as sputtering a $TiO_2$ target in $N_2$ [4], reactive DC magnetron sputtering in $N_2$ [5], and pulsed laser deposition using a TiN target in an $N_2/O_2$ mixture [6] have been widely reported. However, the form of thin film is not suitable for larger-scale photocatalytic use.

Asahi et al. [4] reported that a nitrogen-doped titania powder was prepared by treating commercial anatase $TiO_2$ powder

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(ST-01, Ishihara Sangyo Co.) in $NH_3$ (67%)/Ar atmosphere at 600 °C for 3 h. The visible-light photocatalytic activity was developed in the resulting products (denoted as $TiO_{calNH}$). However, such a high-temperature process would be unfavorable for the photocatalytic performance, because the surface area decreases with temperature through the sintering process. It was actually reported in their study that the specific surface area of the sample decreased from 270 to 67 $m^2 g^{-1}$ by heat treatment. The phase transformation from anatase to rutile developed at higher temperatures also decreased the photocatalytic activity. It is known that anatase has a higher photocatalytic activity than rutile [12,13]. Morikawa et al. [7] also obtained nitrogen-doped rutile titania powder by the oxidative annealing of TiN powder. At room temperature, Yin et al. [8] obtained a powder of nitrogen-doped titania by a mechanochemical reaction with high-energy ball milling. In spite of the low-temperature process, an anatase–rutile phase transformation took place by ball milling with mechanical energy.

Nitrogen-doped anatase titania powder has only been obtained by chemical procedures. Ihara et al. [9] reported that nitrogen-doped anatase titania was prepared by the calcination of the hydrolysis product of $Ti(SO_4)_2$ with aqueous ammonia, and the best sample (denoted as NH-Hy) having a relatively high specific surface area (126 $m^2 g^{-1}$) was obtained by a 400 °C calcination. It was demonstrated that the visible-light photocatalytic activity of NH-Hy was higher than that of $TiO_{calNH}$. Burda et al. [10] also obtaind nitrogen-doped titania by a low-temperature method, which was the direct amination of titania particles by the addition of triethylamine.

In our recent study [11], a nitrogen-doped anatase titania powder was obtained by a novel low-temperature synthetic procedure involving the sol–gel process in a hydrophobic solution to prepare the titania-based inorganic/organic composite, and ion exchange reaction in aqueous ammonia to remove any organic modifiers of the composite. Titania powder with a sheet-like morphology was obtained by this procedure. It was vivid yellow and indicated a good visible-light photocatalysis performance. The use of the titania-based inorganic/organic composite is a key to the low-temperature nitrogen doping.

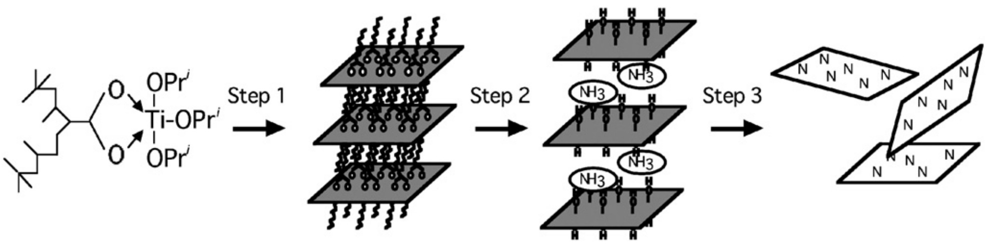
In the present study, the effects of the calcination condition are investigated for the nitrogen-doped titania prepared by our method. The dependences of the amount of doped nitrogen on both the visible-light absorbance and visible-light photocatalytic activity are discussed.

## 2. Experimental

### 2.1. Materials and sample preparation

The synthetic procedure used in this study consists of three steps as illustrated in Scheme 1. Step 1 is the preparation of layered titania/isostearate nanocomposites via a unique sol–gel technique, which was reported in our previous study [14]. This composite has a layered structure constructed by the stacking of titania sheets, to which isostearate modifiers are coordinated. In Step 2, these modifiers were removed and ammonia was simultaneously incorporated into the interlayer by the treatment with aqueous ammonia. This ammonia is the source of the doped nitrogen. The treated samples turned into nitrogen-doped titania by calcination in Step 3. The details of this procedure are as follows:

- Step 1. Preparation of layered titania/isostearate nanocomposites: titanium tetraisopropoxide (Kanto Chemical Co. Inc., >97%), isostearic acid (Tokyo Kasei Kogyo Co. Ltd., >95%), *n*-hexylamine (Tokyo Kasei Kogyo Co. Ltd., >98%), and *o*-xylene (Kanto Chemical Co. Inc., >99%) were used without further purification. Two *o*-xylene solutions were prepared in nitrogen atmosphere. One contained 50 mmol of titanium tetraisopropoxide $Ti(OCH(CH_3)_2)_4$ and 25 mmol of isostearic acid ($CH_3(CH_2)_8$-$CH((CH_2)_6CH_3)$-COOH) in 60 ml of *o*-xylene, and the other contained 5 mmol of isostearic acid and 5 mmol of *n*-hexylamine in 40 ml of *o*-xylene. The sol–gel reaction was started by mixing both solutions. Hydrous nitrogen gas (water was saturated at 10 °C) was used to add the water required for the sol–gel reaction. The mixed solution was kept in the hydrous nitrogen gas with a 10 ml $min^{-1}$ flow rate in order to gradually absorb moisture from the gas. The reaction temperature was 40 °C. After 4 days, a viscous yellowish clear sol containing layered titania/isostearate nanocomposite was formed.
- Step 2. Treatment with aqueous ammonia: the obtained sol was mixed with aqueous ammonia (28%) and stirred for 2 h at 60 °C. The mixed solution was separated into an oil (*o*-xylene) layer and a water layer in a separating funnel. The titania products migrated to the water layer with releasing the isostearate modifiers. Products in the water layer were further sufficiently washed with aqueous ammonia. After drying at 120 °C, a white amorphous powder was obtained.
- Step 3. Calcination: the treated products were calcined in a tube furnace with a gas stream of either a $O_2$(20%)/$N_2$



Scheme 1. Preparation process for nitrogen-doped titania.

mixture or pure $N_2$ at various temperatures (300, 350, 400, 450, 500 °C) for 2 h. Nitrogen-doped titania powder with a sheet-like morphology [11], which reflects the layer structure of the precursor composite, was formed.

### 2.2. Characterization technique

The infrared absorption spectra of the products before and after the treatment with aqueous ammonia were obtained using a Perkin-Elmer 1650FT-IR spectrometer by the transmission method using the KBr pellet technique. The X-ray diffraction (XRD) pattern of calcined samples was measured using an X-ray diffractometer (Rigaku, RINT 2550H). The BET surface areas of the samples were measured by nitrogen gas adsorption using an ASAP-2010 accelerated surface area and porosimetry analyzer from Micromeritics. The ultraviolet–visible (UV–vis) reflectance spectrum of the samples was obtained using a spectrometer (Shimadzu, UV-2400PC). The amount of doped nitrogen was determined using a CHN element analyzer (Perkin-Elmer, 2400 II), in which the sample was thermally decomposed at ca. 1000 °C.

### 2.3. Evaluation of visible-light photocatalytic activity

The photocatalytic activity under visible-light irradiation of the nitrogen-doped titania powders was evaluated on the basis of the degradation rates of methylene blue (MB). A quartz cell with a plug cap was used as the reaction vessel. 2.5 ml of the MB (0.04 mmol $dm^{-1}$) aqueous solution (pH 3, adjusted with HCl) containing 2.5 mg of the sample was placed in the reaction vessel. As the light source, we used 20 blue-light-emitting diodes (BLEDs, E1L53-3B0A6-02, Toyoda Gosei). The emission peak of the BLED is centered at 470 nm. The photocatalytic decomposition of MB was conducted after its adsorption equilibrium was reached. The MB solution was stirred and $O_2$ gas was bubbled by needle piercing the plug cap during the photocatalytic reaction. The concentration of MB in the solution was monitored by its absorbance at 660 nm using UV–vis spectroscopy (UV-2100, Shimadzu).

## 3. Results and discussion

### 3.1. Treatment of layered titania/isostearate nanocomposite with aqueous ammonia

The synthesized layered titania/isostearate nanocomposites as a precursor were treated with aqueous ammonia as the nitrogen source. Fig. 1 shows the FT-IR spectra of the products before and after treatment with aqueous ammonia. The characteristic absorption bands were observed in the spectrum for the product before treatment. Several peaks at 1365, 1428, 1533 and 1590 $cm^{-1}$, and the peak at 2956 $cm^{-1}$ were assigned to the $COO^-$ stretching and CH stretching, respectively. These bands were attributed to the isostearate modifiers hybridized with titania sheets [14–16]. After treatment with aqueous ammonia, the bands of the isostearate modifiers disappeared, and new absorption bands appeared, which were assigned to $NH_4^+$ (3178 $cm^{-1}$: NH stretching, 1401 $cm^{-1}$: NH bending) [17,18] and to OH (3370 $cm^{-1}$: OH stretching, 1632 $cm^{-1}$: OH bending). These results indicate that the isostearate modifiers coodinating on the titania sheet were completely removed and hydroxyl groups and ammonia were instead intercalated. The nitrogen content in the treated product was determined to be 2.9 mass% by elemental analysis. The ammonia-intercalated products would be formed as illustrated in Scheme 1.

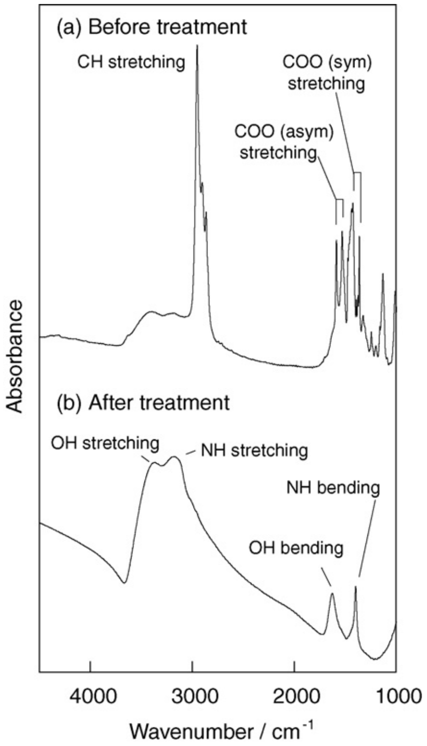


Fig. 1. FT-IR spectra of layered titania/isostearate nanocomposites (a) before and (b) after treatment with aqueous ammonia. The samples were dried at 120 °C.

### 3.2. Calcination of treated products

The nitrogen-doped titania samples were obtained by the calcination of the products treated with aqueous ammonia at 300–500 °C. The ammonia that intercalated into the products acted as the nitrogen source.

Fig. 2 shows the XRD patterns of the samples obtained by the calcination of the treated product in either $O_2/N_2$ (Fig. 2A) or pure $N_2$ (Fig. 2B). No remarkable difference was observed between both cases. It shows that the crystallization behavior with heating of the samples is little affected by firing atmosphere. The diffraction peaks due to anatase were clearly observed in the samples calcined at 350–500 °C without any other peaks. This indicated that a single phase anatase titania was formed. On the other hand, the 300 °C-calcined samples were not well crystallized. The specific surface area decreased with the calcination temperature as shown in Fig. 3.

Fig. 4 shows the doped-nitrogen contents of the samples obtained by the calcination of the treated product in either $O_2/N_2$ or pure $N_2$. A decreasing doped-nitrogen content with

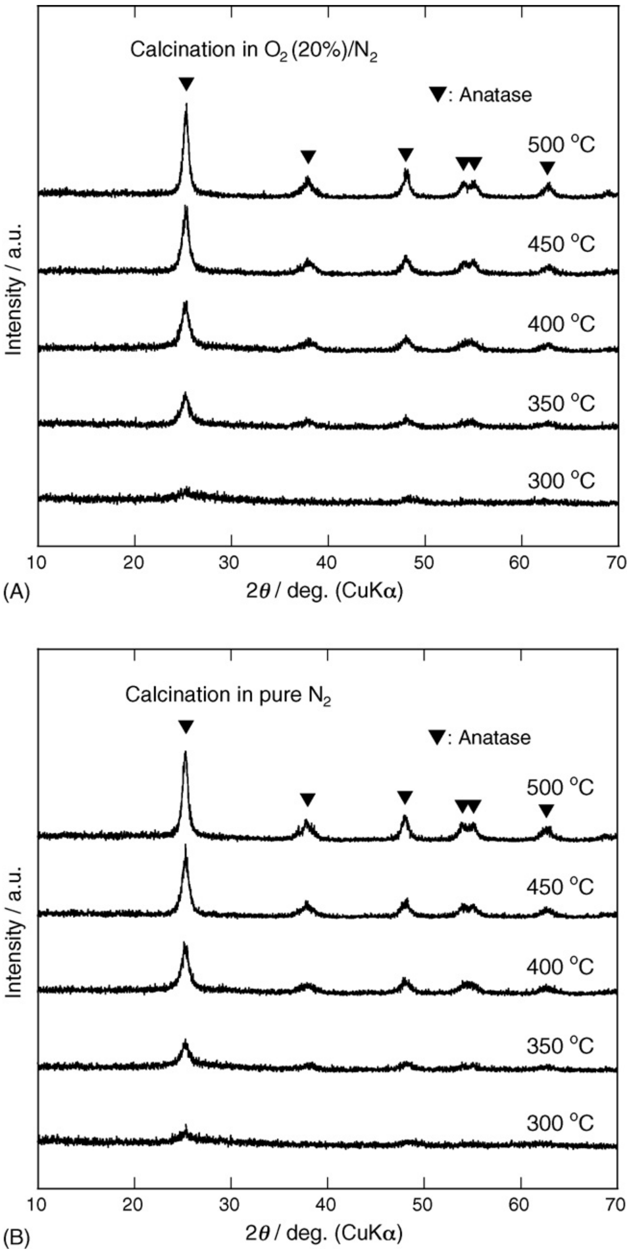


Fig. 2. XRD profiles of resulting nitrogen-doped titania powders. Samples were calcined in (A) $O_2$ (20%)/$N_2$ mixture gas and in (B) pure $N_2$ at the temperatures indicated in the figure.

increasing calcination temperature was observed, and it was particularly significant between 300 and 350 °C. Once doped nitrogen would be released with firing. The decrease of doped nitrogen of the sample calcined in $O_2/N_2$ was more significant than that of the sample calcined in pure $N_2$. It would be due to the oxidation of doped nitrogen by $O_2$ gas in firing atmosphere.

### 3.3. Visible-light absorbance

The typical UV–vis reflectance spectrum of the sample obtained in this study (400 °C-calcined in $O_2/N_2$) is shown in Fig. 5. The spectrum of the commercial anatase titania (ST-01)

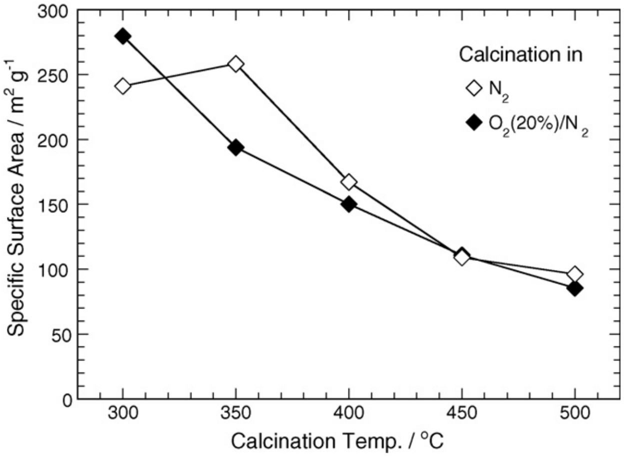


Fig. 3. Specific surface areas of resulting nitrogen-doped titania powders plotted as function of calcination temperature. The calcination atmospheres are indicated in the figure.

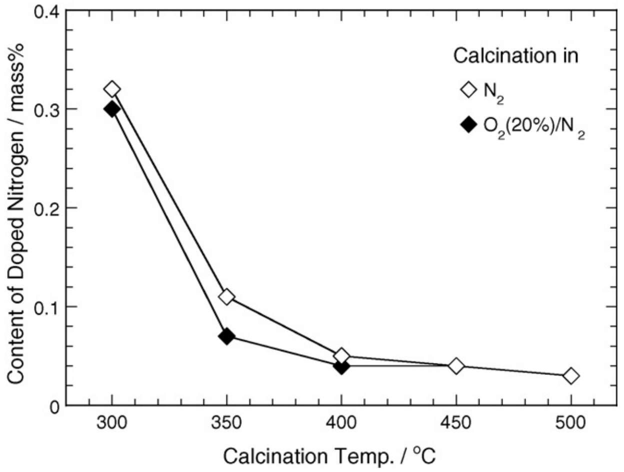


Fig. 4. Content of doped nitrogen in produced nitrogen-doped titania powders plotted as function of calcination temperature. The calcination atmospheres are indicated in the figure.

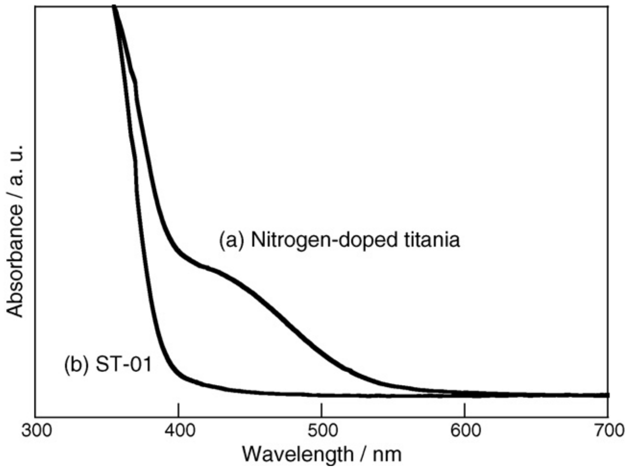


Fig. 5. UV–visible absorption spectra of (a) nitrogen-doped titania powder obtained by 400 °C calcination and (b) commercial anatase powder: ST-01.

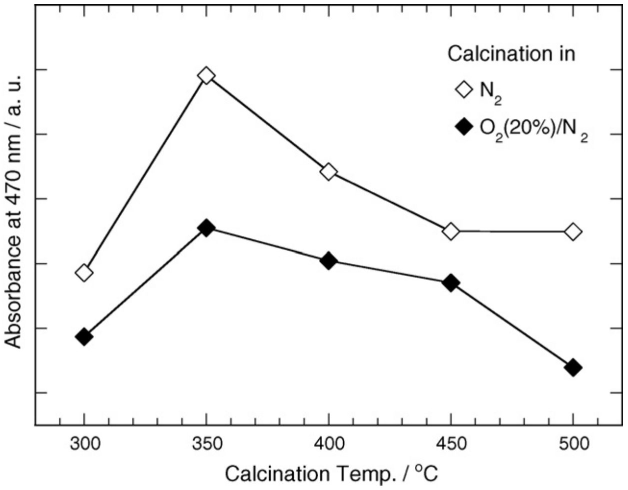


Fig. 6. Absorbance at 470 nm for nitrogen-doped titania as function of calcination temperature. The calcination atmospheres are indicated in the figure.

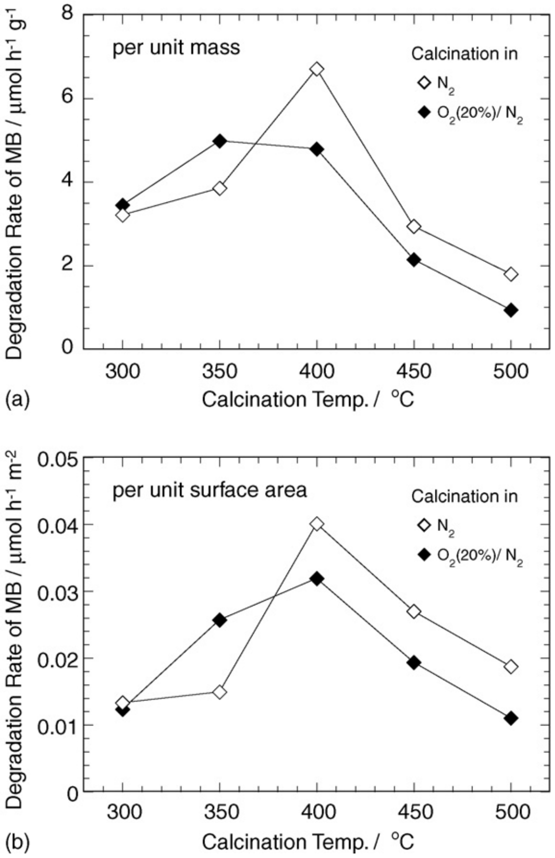


Fig. 7. Photocatalytic degradation rate of methylene blue (MB) on nitrogen-doped titania as function of calcination temperature. The values (A) per unit mass and (B) per unit surface area of the samples are plotted in the each graph, respectively. The calcination atmospheres are indicated in the figures. The samples were dispersed in an MB aqueous solution, and a BLED (470 nm) was used as the light source.

is also represented in the same figure. Photoabsorption was observed in the visible region (380–550 nm) for our calcined sample. The color of the sample was vivid yellow, which indicates that a nitrogen-doped titania was formed.

In Fig. 6, the visible-light absorbance at 470 nm (emission wavelength of BLED) is plotted as a function of the calcination temperature. This value reflects the deepness of the yellow color. The color deepness reached a maximum at 350 °C, and diminished as the temperature was further increased.

Visible-light absorption was slightly observed for the 300 °C-calcined samples, in spite of the large amount of doped nitrogen as shown in Fig. 4. Asahi et al. [4] argued that the visible-light absorption of the nitrogen-doped titania is introduced by band gap narrowing due to mixing of the p states of the doped nitrogen with the O 2p states of the $TiO_2$ crystal. Our 300 °C-calcined samples were poorly crystallized as shown in Fig. 2. The band structure of oxide crystal would be insufficiently constructed for these samples.

For the calcination temperatures above 350 °C, the visible-light absorbance correlated with the doped-nitrogen content. The diminishing visible-light absorbance (discoloration) with increasing calcination temperature would be due to the thermal release of the doped nitrogen.

The visible-light absorbance for the samples calcined in pure $N_2$ was higher than that for the samples calcined in $O_2/N_2$. When the sample was calcined in $O_2/N_2$, release of the doped nitrogen was accelerated by reoxidation of the doped nitrogen.

### 3.4. *Visible-light photocatalytic activity for MB degradation*

Fig. 7 shows the variety of photocatalytic degradation rates of MB during BLED irradiation as a function of the calcination temperature. The values per unit mass and per unit surface area of the samples were plotted in the each graph (Fig. 7A and B), respectively, and a similar tendency was observed in both plots. Low visible-light photocatalytic activity was observed for 300 °C-calcined samples. These samples were poorly crystallized and almost amorphous state as shown in Fig. 2. Low crystallinity of the samples would be cause of low photocatalytic activity because the construction of band structure would be insufficient. In the region above 400 °C, even though the samples were further crystallized, visible-light activity diminished rapidly with increasing calcination temperature. In this region, doped-nitrogen content would be too low to lead to visible-light photocatalysis (see Fig. 4).

The apparent difference in visible-light photocatalytic activity was observed between the both samples calcined in pure $N_2$ and in $O_2/N_2$, in spite of no obvious difference in crystallization behavior as shown in Fig. 2. In the case of the calcination in pure $N_2$, activity at 350 °C was not so high, and it rapidly increased with calcination temperature and reached a maximum at 400 °C. At the same time, nitrogen content diminished with increasing calcination temperature as shown in Fig. 4. On the other hand, in the case of the calcination in $O_2/N_2$, relatively high visible-light photocatalytic activity was appeared even at 350 °C. The change in activity at 350–400 °C was not so significant as that in the case of calcination in pure $N_2$. Visible-light photocatalysis was appeared at lower temperature in the case of calcination in $O_2/N_2$ than that in pure $N_2$.

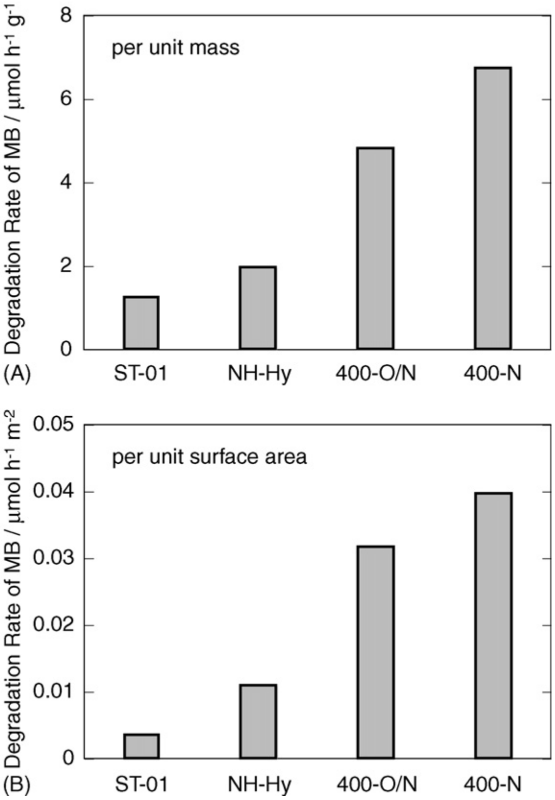


Fig. 8. Comparison of visible-light photocatalytic activities. The activity was evaluated on the basis of the degradation rate of methylene blue (MB) with BLED (470 nm) irradiation. Data were normalized to (A) unit mass and to (B) unit surface area of the samples, respectively.

Comparing the both samples calcined at 350 °C in pure $N_2$ and in $O_2/N_2$ (calcined at same temperature, but in different atmosphere), the activity for the sample calcined in $O_2/N_2$ was higher than that in pure $N_2$. Both samples had almost the same crystallinity (see Fig. 2) but different amount of doped nitrogen. As shown in Fig. 4, the nitrogen content of more active sample (calcined at 350 °C in $O_2/N_2$) was lower than that of less active sample (calcined at 350 °C in pure $N_2$). When $O_2$ gas was included in calcination atmosphere, release of the doped nitrogen would be accelerated by oxidative reaction. These results suggest that the partial release of doped nitrogen would be required for the appearance of the visible-light photocatalysis, although the activity was decreased by further release of nitrogen.

Calcination temperature dependency of visible-light photocatalytic activity was fundamentally dissimilar from that of visible-light absorbance as shown in Fig. 6. For example, in the case of samples calcined in pure $N_2$, the most active sample was obtained at 400 °C while the maximum of visible-light absorbance was observed at 350 °C. The visible-light photocatalytic activity was independent of the visible-light absorbance.

In Fig. 8, the visible-light photocatalytic performances for both samples calcined at 400 °C in $O_2/N_2$ and in pure $N_2$ (denoted as 400-O/N and 400-N, respectively) were compared with those for the other photocatalysts, ST-01 and NH-Hy. ST-01 is a nondoped anatase photocatalyst with a large specific surface area. NH-Hy was a nitrogen-doped titania with relatively high visible-light photocatalytic activity as reported by Ihara et al. [9]. The NH-Hy photocatalyst used in this study was prepared from $Ti(SO_4)_2$ in our laboratory following the instructions in their paper. Residual $SO_4^{2-}$ as an inhibitor of the photocatalytic activity was completely removed by the rinsing process and was not detected by the ICP analysis. The rinsed product was calcined in $O_2/N_2$ at 400 °C. The NH-Hy photocatalyst calcined under this condition exhibited the highest photocatalytic performance in their paper, which is the same condition as that of our 400-O/N. The specific surface areas of the selected samples, namely, ST-01, NH-Hy, 400-N/O and 400-N, are 327, 176, 150 and 167 $m^2\ g^{-1}$, respectively, and the concentrations of the doped nitrogen are 0, 0.08, 0.04 and 0.05 wt.%, respectively.

In spite of the same calcination conditions, the visible-light photocatalytic activity of 400-O/N was over two times higher than that of NH-Hy. The visible-light photocatalytic activity of 400-N, having the highest photocatalytic performance in this study, was grater than three fold that of NH-Hy. Our nitrogen-doped titania showed significantly high visible-light photocatalytic activities.

## 4. Conclusions

A new class of nitrogen-doped titania photocatalysts was prepared by a unique synthetic process at relatively low temperatures. The nitrogen-doped titania with a single anatase phase and a relatively large surface area was obtained.

For the samples obtained in this work, the visible-light photocatalytic activity was independent of the visible-light absorbance. While the visible-light absorbance correlated with doped-nitrogen content, the visible-light activity did not. Partial release of the doped nitrogen is required for appearance of the visible-light photocatalysis. In this work, data for the doped-nitrogen content was only obtained for bulk. Further investigation for the measurement of local-nitrogen content near the surface would be required to clearly understand the mechanism of the improvement in visible-light photocatalytic performance with decrease of nitrogen. An XPS technique with argon sputtering may be useful for this purpose.

Our nitrogen-doped titania showed significantly high visible-light photocatalytic activities. It was higher than that of previously reported nitrogen-doped anatase titania prepared by calcination of the hydrolysis product of $Ti(SO_4)_2$ with aqueous ammonia.

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