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Nitrogen-doped titanium dioxide photocatalysts for visible response prepared by using organic compounds

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Abstract

In order to utilize visible light in photocatalytic reactions, nitrogen atoms were doped in commercially available photocatalytic TiO₂ powders by using an organic compound such as urea and guanidine. Analysis by X-ray photoelectron spectroscopy (XPS) indicated that N atoms were incorporated into two different sites of the bulk phase of TiO₂. A significant shift of the absorption edge to a lower energy and a higher absorption in the visible light region were observed. These N-doped TiO₂ powders exhibited photocatalytic activity for the decomposition of 2-propanol in aqueous solution under visible light irradiation. The photocatalytic activity increased with the decrease of doped N atoms in O site, while decreased with decrease of the other sites. Degradation of photocatalytic activity based on the release of nitrogen atoms was observed for the reaction in the aqueous suspension system.

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Keywords: Photocatalyst; Titanium dioxide; Nitrogen doping; Guanidine; Visible light

1. Introduction

Photocatalytic reactions at the surface of titanium dioxide (TiO₂) have been attracting much attention in view of their practical applications to environmental cleaning such as self cleaning of tiles, glasses, and windows [1–4]. TiO₂ has the advantages of its high chemical stability, nontoxicity, and relatively low-price, but a serious disadvantage would be that only UV light can be used for photocatalytic reactions. Therefore, it is of great interest to find ways to extend the absorption wavelength range of TiO₂ to visible region without the decrease of photocatalytic activity [5–10]. Several groups have been succeeded in doping transition metals into TiO₂ photocatalyst to obtain photo-response at visible light [6–8]. Recently, TiO₂ doped with S atom [9,10] and F atom [11] have been reported. Two decades ago, Sato reported that a kind of NO_x-doped TiO₂ prepared from a commercial titanium hydroxide by calcination [5]. He concluded that the spectral sensitization of NO_x-doped TiO₂ was due to NO_x impurity which was

formed from NH₄OH used in the preparation of titanium hydroxide. Asahi et al. reported that N-doped TiO₂ shows a significant shift of the absorption edge to a lower energy in the visible light region [12]. They calculated densities of states of the substitutional doping of C, N, F, or S for O in the anatase TiO₂ crystal, by the full-potential linearized augmented plane wave (FLAPW) formalism in the framework of the local density approximation [12]. The substitutional doping of N atom was the most effective because its p states contribute to the band-gap narrowing by mixing with O 2p [13]. Irie et al. suggested that the isolated N 2p narrow band formed above the O 2p valence band was responsible for the visible light but the oxygen vacancy state was not visible light sensitive [14].

Guanidine is a tri-amine of low molecular weight and know to form hydrogen bond and consequently to brake second structures of biological molecules. Since urea has been reported as a N source for mechanical N-doping [15], in the previous paper we reported briefly the application of guanidine hydrochloride as a nitrogen source for N-doping [16]. In the present work, we tried several nitrogen-source compounds for comparison. The properties of the prepared N-doped TiO₂ powders are characterized by X-ray

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diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS). The relationship between the properties such as the nitrogen content measured with XPS and the photocatalytic activity with visible light was discussed for N-doped TiO₂ powders.

2. Experimental

Organic nitrogen compounds employed for N-doping were urea, guanidine hydrochloride (Gua-HCl), and guanidine carbonate (Gua-Carbonate), whose chemical structures are shown in Fig. 1. Fig. 2 shows a flow chart for the preparation of N-doped TiO₂ powder. For the preparation, 8 g of commercially available TiO₂ powder was mixed with aqueous solution (20 mL) of the organic nitrogen compound and stirred at room temperature for 1 h. The mixture was kept in dark for one day and then dried completely under reduced pressure to obtain white powder. N-doped TiO₂ powder was obtained after the calcinations at various temperatures for various periods under aerated conditions. The calcination temperature was usually 350, 450, and 550 °C, and the calcination period was usually 0.5, 1, and 5 h. The calcined powder was washed with diluted sulfuric acid and then with pure water. Finally the N-doped TiO₂ sample was obtained after vacuum drying. The commercially available TiO₂ powders tested were ST-01, ST-21, PT-101 (Ishihara Sangyo Ltd.), AMT-100, AMT-600, MT-500B, MT-600B (TAYCA Ltd.), Degussa P-25 (Japan Aerosil), and Hombikat UV-100 (Sachtleben Chemie). Among them ST-01 was mainly investigated due to its superior properties for N-doping. The structural and optical properties of the prepared TiO₂ powders were investigated by X-ray diffraction (MAC science M03XHF22) analysis, X-ray photoelectron spectroscopy (JEOL JPS-100SX), and diffuse reflection spectroscopy (SHIMADZU UV-3150 with ISR-3100).

The photocatalytic activity was evaluated by measuring the decomposition of 10 mM 2-propanol in 0.5 cm³ aqueous suspension of 1 mg of N-doped TiO₂ powder. The visible light was obtained by a 500 W super high pressure Hg lamp (Ushio, USH-500D) with a glass filter (Toshiba Glass, L-42) and used to irradiate the suspension in a rotating NMR sample tube for typically 10 h. The concentrations of 2-propanol and acetone were estimated using a proton NMR spectrometer (JEOL GX-270).

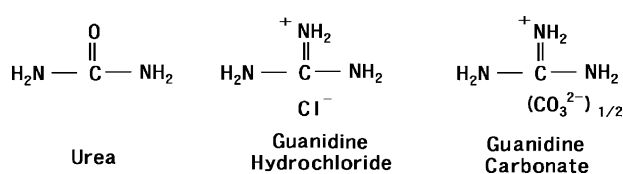


Fig. 1. Molecular structure of organic nitrogen compounds used in the present study.

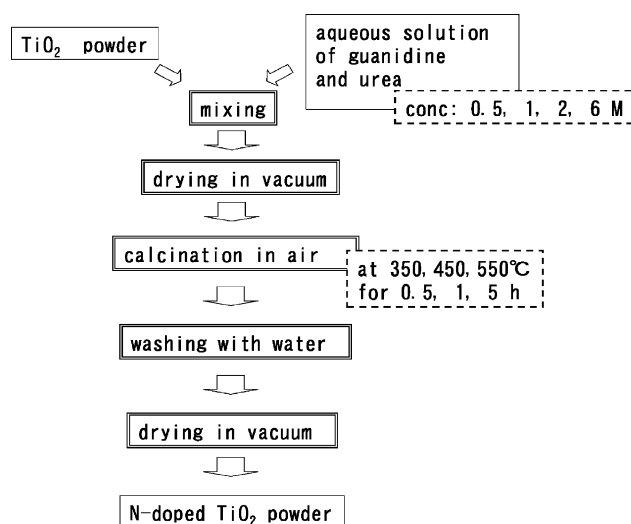


Fig. 2. Flow chart for the preparation of nitrogen doped TiO₂ by calcination with organic nitrogen compounds.

3. Results and discussion

At first the most efficient TiO₂ powder for N-doping was selected from nine kinds of commercially available TiO₂ powder of different particle size and different crystalline component. The primary particle size of each TiO₂ was evaluated from XRD line width measurements. TiO₂ powders of smaller particles consist of anatase and those of larger one consists of rutile. For comparison, the N-doping of nine TiO₂ powders was performed with urea and calcination for 1 h at 350 °C. The visible light photocatalytic activity was evaluated by measuring the photocatalytic oxidation of 2-propanol in aqueous solution using proton NMR spectroscopy. It is reported that 2-propanol is a good model system for evaluating photocatalytic activity because the initial reaction pathway involves almost exclusively a partial oxidation to acetone [17]. Fig. 3 shows the amount of the photocatalytic

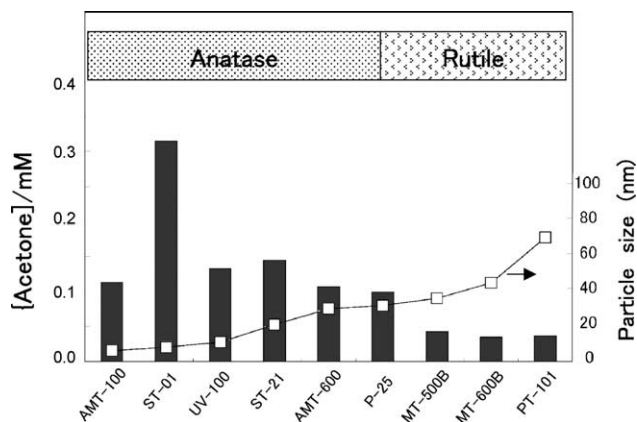


Fig. 3. Amount of the photocatalytic product, acetone, with various N-doped TiO₂ powders prepared from commercial TiO₂ powders. Crystalline modification and primary particle size of the original powder are also shown.

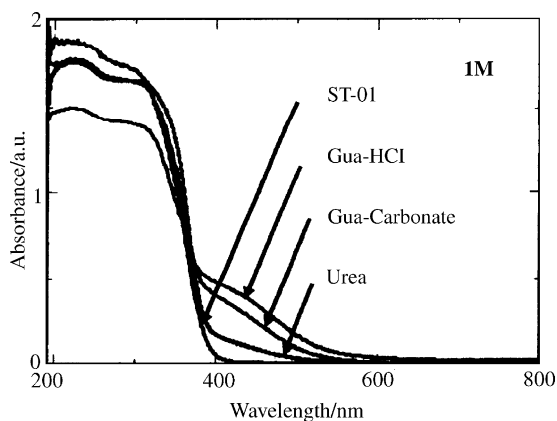


Fig. 4. Diffuse reflectance spectra of standard TiO_2 powder (ST-01), and N-doped TiO_2 powder prepared with guanidine hydrochloride (Gua-HCl), guanidine carbonate, and urea. Nitrogen doping was performed with 1 M organic compound and calcination at 450°C for 1 h.

product, acetone, on decomposition of 2-propanol with visible light of wavelength of longer than 420 nm. Generally TiO_2 with the smaller particle size became N-doped photocatalysts with higher visible activity. Among them, ST-01 provides N-doped TiO_2 with the highest visible activity. In the doping process, calcination increased the crystallite size as proved previously by XRD measurement [16], then small particle containing amorphous titanate could include a large amount of nitrogen in the growing process. In the following experiments ST-01 TiO_2 was used for preparing N-doped photocatalysts.

To compare the source materials, urea, guanidine hydrochloride, and guanidine carbonate, were used at the same concentration to prepare N-doped TiO_2 . The UV–Vis diffuse reflectance spectra of the obtained powder are shown in Fig. 4. A higher absorbance was obtained with guanidine than urea, indicating a higher amount of nitrogen was doped with guanidine. This absorption in visible region was caused by N-doping as has been reported in literature. Fig. 5 shows the visible light activity of acetone production from 2-propanol. The N-doped TiO_2 prepared with urea shows higher activity than that prepared with guanidine hydrochloride. Comparing the difference in activity with the absorption spectra, the increase in the visible-light absorption does not correlate with that in the photocatalytic activity. This fact suggests that there should be at least two origins in the absorbance. One is active for visible light photocatalytic reaction and another is not participate to the photocatalytic activity.

Fig. 6 shows X-ray photoelectron (XPS) spectra (with Mg $K\alpha$ line of $h\nu = 1253.6$ eV) of the N1 s profiles for these N-doped photocatalysts. Two peaks were observed in the spectrum around 396 eV and 400 eV. Several research groups investigated the N 1 s peak in XPS spectra during the oxidation of TiN, and assigned the peaks as atomic β -N (396 eV) and molecularly chemisorbed γ - N_2

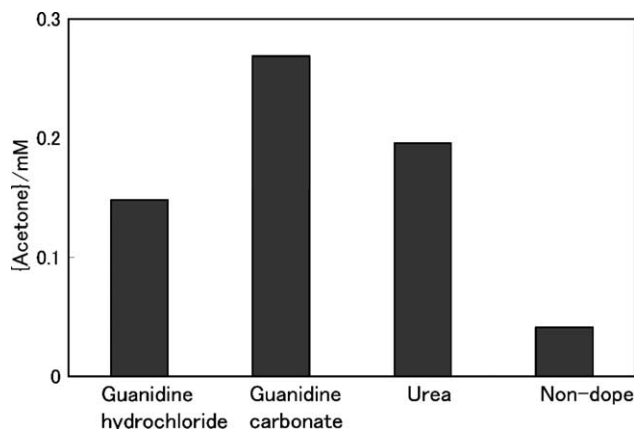


Fig. 5. Amount of the photocatalytic product, acetone, for various N-doped TiO_2 powders prepared with various nitrogen-containing organic compound by calcination at 450°C for 1 h. Non-doped sample is ST-01 TiO_2 calcined at the same condition.

(400 and 402 eV) [18–21]. Based on these reports, Asahi et al. described that the peak at 396 eV corresponds to N atoms in Ti–N bonds, while the peak around 400 eV corresponds to N_2 molecules incorporated into the TiO_2 lattice [12]. It has been analyzed that the peak at 396 eV is attributed to N bound to Ti atoms, and the signal around 400 eV is to N bound to O, C, or N atoms. In the present study, the peaks at 396 and 400 eV change depending on the solution concentration and the calcination conditions. No peak attributable to C atoms was observed in XPS spectra. Since the XRD pattern did not indicate the formation of Ti–N crystallite, the substitution occurs randomly or Ti–O–N bonds formed. Then, observed peak at 396 eV shows the substitution of N for lattice O, while the peak at 400 eV indicates the formation of doping of the other type. It is notable that, comparing Fig. 6 with Figs. 4 and 5, the intensity of optical absorbance correlates with the peak

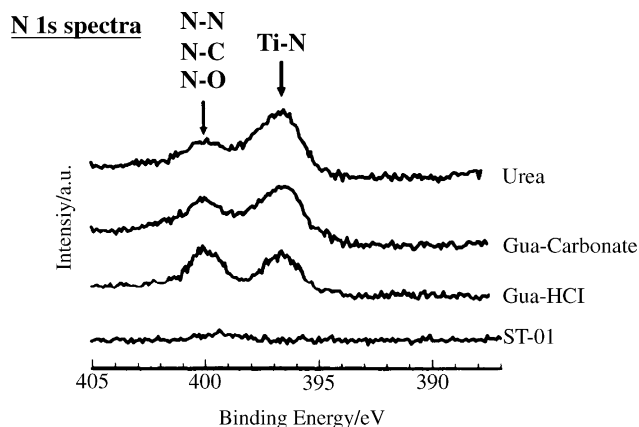


Fig. 6. X-ray photoelectron spectra of the N1 s profiles for N-doped TiO_2 prepared with urea, guanidine carbonate, and guanidine hydrochloride after the Ar^+ ion etching. Nitrogen doping was performed with 1 M organic compound and calcination at 450°C for 1 h. The spectra were measured after the surface of powder was etched with Ar^+ to remove the adsorbed contaminants.

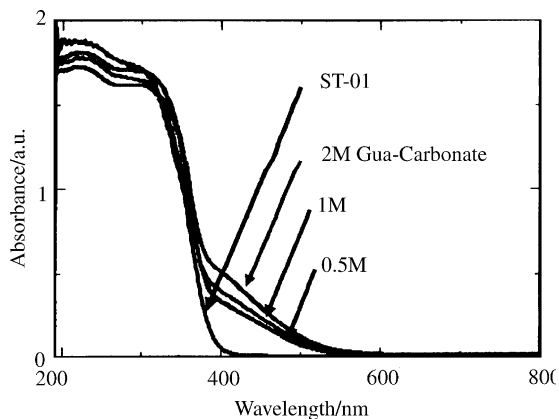


Fig. 7. Diffuse reflectance spectra of standard TiO_2 powder (ST-01), and N-doped TiO_2 powder prepared with various concentration of guanidine carbonate and by calcination at 450°C for 1 h.

intensity at 400 eV, while the visible light activity correlates with the peak intensity at 396 eV.

Fig. 7 show diffuse reflectance spectra of standard TiO_2 powder (ST-01), and N-doped TiO_2 powders prepared with various concentrations of guanidine carbonate. The absorbance does not increase significantly with the increase of the concentration of guanidine carbonate up to the maximum soluble concentration was 2 M. On the other hand, a higher visible absorbance was observed for N-doped TiO_2 powder prepared with 6 M urea and 6 M guanidine hydrochloride (not shown in the figure). However, the photocatalytic activity for these deep yellow powders was decreased to half and one fifth, respectively.

Fig. 8 shows photocatalytic activity by the formation of acetone for various N-doped TiO_2 powders which were prepared at various calcination temperatures and periods, and various nitrogen source concentrations of guanidine carbonate, and 1 M urea. Common feature is that the visible photocatalytic activity was decreased with the higher calcination temperature while the calcination period ranging from 30 min to 5 h likely causes no effect on the activity. When we compare the concentration of guanidine carbonate as source solution, the photocatalytic activity increased drastically with the decrease of the concentration, though the absorbance of these powders does not change significantly as shown in Fig. 7. This observation also suggests that one of the some components of the visible light absorption causes an effective photocatalytic reaction.

Fig. 9 shows the correlation of the photocatalytic activity with the amount of two kinds of doped N atoms for samples calcined for 1 h at various temperatures from 300 to 600°C by 50°C step. The N content in atom % was analyzed by comparing the signal intensity of Ti 2p with a TiN standard. The N-doped TiO_2 powder with the highest photocatalytic activity was obtained by the calcination at 400°C . At this temperature the amount of N of Ti–N observed at 396 eV in XPS spectra shows the maximum, while the amount of N

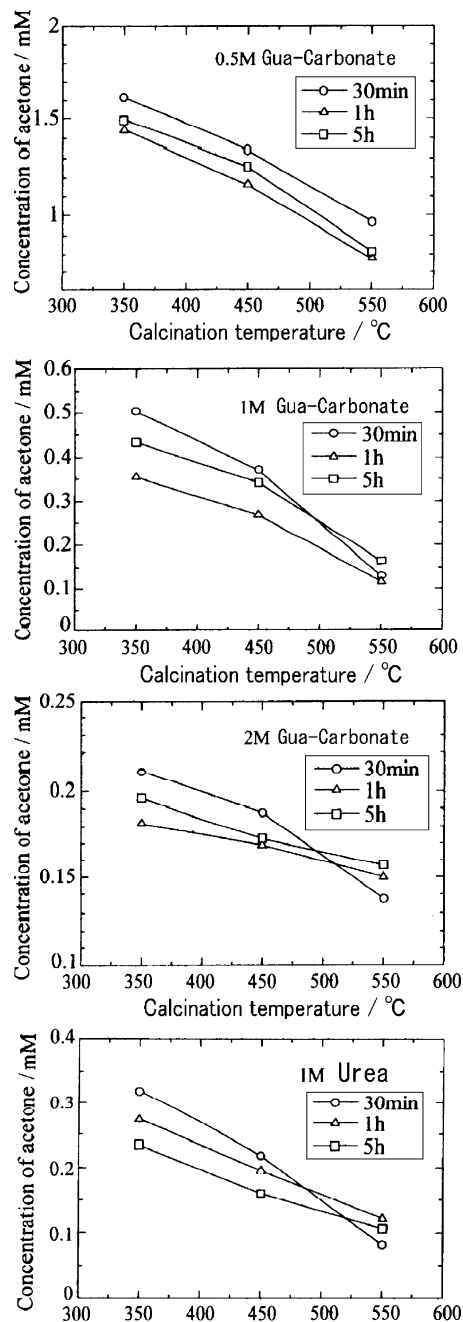


Fig. 8. Photocatalytic formation of acetone for various N-doped TiO_2 powders prepared with 0.5, 1 and 2 M guanidine carbonate and 1 M urea solutions and calcination at 350 , 450 , and 550°C and for 30 min, 1, and 5 h.

observed at around 400 eV showed the maximum when it was calcined at 500°C . This experimental results indicate that doped N atoms observed at 396 eV act as a visible responsive semiconductor, while those observed at around 400 eV decrease the photocatalytic activity.

Fig. 10 shows durability of N-doped TiO_2 powders prepared with 0.5 M guanidine carbonate and the calcination at 350°C for 30 min. After the irradiation for 100 h, the production of acetone decreased to one half of

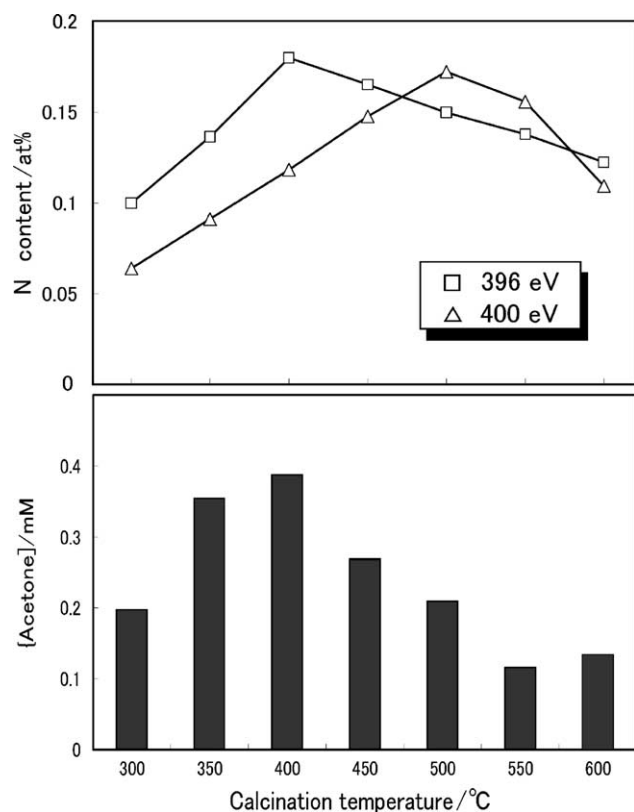


Fig. 9. Photocatalytic formation of acetone for various N-doped TiO₂ powders prepared with 1 M guanidine carbonate and calcination at various temperatures for 1 h (lower part), and atomic % of doped nitrogen calculated from XPS intensity at 396 eV peak (○) and 400 eV peak (△).

the initial production rate. This observation indicates that the surface of the N-doped photocatalysts was covered with some byproducts or the doped nitrogen atom was released from TiO₂ lattice. To understand the origin of the deactivation of the photocatalyst, the state of N was checked by XPS measurements. As shown in Fig. 11, N atoms of Ti–N state observed at 396 eV decreased by

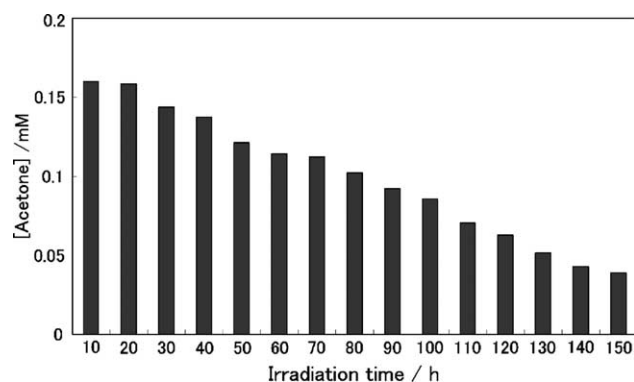


Fig. 10. Photocatalytic formation of acetone as a function of successive irradiation time. The amount of acetone was measured by Increment of 10 h irradiation to 0.1 M 2-propanol aqueous solution in NMR sample tube. N-doped TiO₂ powders used was prepared with 0.5 M guanidine carbonate and calcination at 350 °C for 30 min.

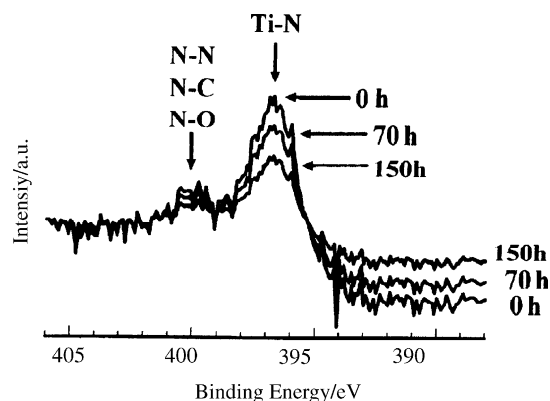


Fig. 11. X-ray photoelectron spectra of the N1 s profiles for N-doped TiO₂ prepared with 0.5 M guanidine carbonate and calcined at 350 °C for 30 min after the Ar⁺ ion etching.

the photocatalytic reaction for 70 and 150 h. This observation clearly shows that the oxidation of 2-propanol in aqueous solution is related to the liberation of doped N atoms.

4. Conclusion

In the present investigation of the preparation of photocatalysts of visible light response, the following conclusions have been obtained.

- (1) Guanidine carbonate is more efficient than guanidine hydrochloride and urea to prepare N-doped TiO₂ powders.
- (2) Photocatalytic activity does not correlate with the visible light absorbance at wavelength longer than 420 nm.
- (3) XPS observations showed that there are two kind of N signals in N-doped TiO₂ and the both contribute the visible light absorbance. The intensity of XPS signal at 396 eV assigned to Ti–N, which is substituted N atom for the O site in TiO₂ lattice, correlates with the photocatalytic activity with visible light. On the other hand, the intensity of another XPS peak at about 400 eV assigned to N–O have a negative correlation with the visible light photocatalytic activity.

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