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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Synthesis of N-doped titanium oxide by hydrothermal treatment

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Abstract N-doped TiO_2 nanoparticles have been prepared by continuous or batch treatment of the colloidal TiO_2 nanoparticles under hydrothermal conditions with formamide, nitric acid, ammonia or triethylamine. The optical absorption tail of the obtained photocatalysts near the band gap extended to the visible region around $\lambda = 500$ nm. The efficiency of nitrogen doping was strongly dependent on the kind of nitrogen compounds, treatment method as well as treatment temperature. The most effective N-doping could be accomplished by the batch treatment with a small amount of triethylamine, which showed the efficient photocatalytic activity for both the reduction of Ag^+ ions and the degradation of methylene blue under visible light irradiation.

Introduction

Among various photocatalysts, TiO_2 has been most widely used because of the chemical stability as well as the high photocatalytic activity [1–3]. However, due to the wide band gap, it shows efficient photocatalytic activity only under UV light irradiation which consists of about 5% of the solar energy. To utilize a wider range of wavelengths, narrowing the band gap of TiO_2 is substantially important. The several methods have been attempted to narrow the band gap of TiO_2 by doping with transition metal cations [4, 5], by sensitizing with dye molecules [6] or by generating oxygen vacancies in the lattice [7]. Asahi et al. have recently revealed that substitutional doping with nitrogen is particularly effective to narrow the band gap of TiO_2 and yield the high photocatalytic activity under visible light irradiation [8]. They prepared N-doped TiO_2 films and powders by sputtering the TiO_2 target in N_2/Ar gas mixture and then annealing in N_2 gas at 440 °C and by treating anatase TiO_2 powder in NH_3/Ar atmosphere at 600 °C for 3 h, respectively. Those N-doped TiO_2 exhibited high photocatalytic activity under visible light irradiation such as photodegradations of methylene blue (MB) and gaseous acetaldehyde and hydrophilicity of the film surface [8]. Many other groups have also prepared N-doped TiO_2 by treating TiO_2 powders or crystals with NH_3 at very high temperatures [9–11]. In contrast with previous studies, Gole et al. synthesized N-doped TiO_2 by the direct nitridation of the colloidal TiO_2 nanoparticles with an excess amount of alkylammonium salts at room temperature [12]. More recently, a solvothermal approach to nitrogen doping has been devised by treating TiO_2 gel in NH_3/ethanol fluid under supercritical conditions [13].

In this study, we developed a hydrothermal method to prepare N-doped TiO_2 by treating the colloidal TiO_2 nanoparticles with a small amount of nitrogen compounds such as formamide, ammonia, nitric acid, and triethylamine (TEA). The activity of prepared N-doped TiO_2 nanoparticles was tested by examining the photocatalytic reduction of Ag^+ ions or the photocatalytic degradation of MB in an aqueous solution under visible or UV light irradiation. The colloidal TiO_2 nanoparticles treated with TEA by a batch system was found to show particularly efficient photocatalytic activity under visible illumination.

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Experimental method

Materials

Ti(IV) tetraisopropoxide, formamide, ammonia, TEA, silver perchlorate, and MB were purchased from Kishida Chemical Co. Nitric acid was obtained from Matsunoen Chemicals Ltd. All materials were used without further purification. The aqueous solution of the colloidal TiO_2 nanoparticles was synthesized by hydrolysis of Ti(IV) tetraisopropoxide under an acidic condition according to the method described in ref. [14] and used as a precursor to nitrogen doping. The size of as-prepared colloidal TiO_2 nanoparticles was about 5–10 nm according to the observation by a transmission electron microscope (TEM). The crystalline structure determined by an X-ray diffraction pattern was of anatase-type.

Preparation and characterization of N-doped TiO_2 nanoparticles

N-doped TiO_2 nanoparticles were prepared by the hydrothermal treatment of the colloidal TiO_2 nanoparticles with four kinds of nitrogen compounds. For the hydrothermal treatment, two different methods were tested; continuous and batch treatment methods. In the continuous treatment, the aqueous solution containing 1.6×10^{-4} M colloidal TiO_2 nanoparticles and 2.5×10^{-2} M formamide or 1.3×10^{-2} M ammonia or 0.29×10^{-2} M nitric acid was consecutively injected into the high-temperature high-pressure reactor by a HPLC pump. The detail of the reactor has been already described elsewhere [15]. During treatment, pressure and temperature of the reactor were kept at $P = 40$ MPa and at $T = 25$–400 °C by using a backup pressure regulator and an electric furnace, respectively. The treated solution was collected from the outlet of the backup regulator. The average treatment time was about 2 min as the inner volume of the reactor was 1 cm^3 and the flow rate was 0.5 cm^3 min^{-1}. Hereafter, we represent the colloidal TiO_2 nanoparticles after the hydrothermal treatment as TiO_2-X-T, where X and T denote the nitrogen compound used in the treatment and temperature, respectively.

The batch treatment was carried out for the prolonged treatment of the colloidal TiO_2 nanoparticles with a small amount of TEA. A 5.6 cm^3 of the aqueous solution containing 1.6×10^{-2} M colloidal TiO_2 nanoparticles and a 0.123 cm^3 of TEA was transferred into a small autoclave made of Hastelloy (8 cm^3 in inner volume) and heated up to $T = 300$ °C. During heating, pressure inside the reactor was kept less than $P = 40$ MPa by a backup pressure regulator. After treatment at $T = 300$ °C for 2 h, the reactor was allowed to cool down slowly at room temperature. The yellow suspension was finally obtained from the reactor.

The UV-Vis absorption spectra of the obtained N-doped TiO_2 nanoparticles were recorded on a V-560 spectrophotometer (JASCO Co).

Activity test

The activity of the prepared photocatalyst under UV or visible illumination was tested by examining the photocatalytic reduction of Ag^+ ions or the photocatalytic degradation of MB in an aqueous solution.

For the reduction of Ag^+ ions, a 1.5 cm^3 of the aqueous solution containing 1.6×10^{-4} M colloidal TiO_2 nanoparticles and a 3.0 cm^3 of 2 mM $AgClO_4$ aqueous solution were mixed in a quartz cuvette ($1 \times 1 \times 4$ cm) and illuminated in air by near-UV ($\lambda_{uv} = 300$–400 nm) or visible light ($\lambda_{vis} = 420$–550 nm) from a 500 W high-pressure mercury lamp combined with adequate color filters. The degree of Ag^+ reduction was evaluated from the variation in the absorption spectrum of the solution. In a similar manner, a 2.0 cm^3 of the aqueous solution containing 1.6×10^{-4} M colloidal TiO_2 nanoparticles and a 0.04 cm^3 of 1.34×10^{-4} M MB aqueous solution were mixed in the quartz cuvette and illuminated by the visible light ($\lambda_{vis} = 420$–550 nm) in air without bubbling. The degradation of MB was estimated by the decrease in the absorbance at $\lambda = 665$ nm characteristic of MB.

Results and discussion

Temperature effect on N-doping efficiency

We began with examining the efficiency of nitrogen doping when the TiO_2 colloidal solution was subjected to the continuous hydrothermal treatment with formamide at different temperatures (TiO_2-CH_3NO-T). Figure 1 shows the absorption spectra of the solutions containing untreated colloidal TiO_2 nanoparticles or TiO_2-CH_3NO-T for $T = 100$–300 °C. The absorption near the band gap energy extended to the visible region after hydrothermal treatments with formamide. The correlation between temperature and the optical absorption in the visible region was not so straightforward but TiO_2-CH_3NO-300 showed the highest absorbance at $\lambda = 400$–500 nm. It has been well known that the hydrothermal water around $T = 300$ °C is highly corrosive [16, 17] and shows the largest value of the ionic product [18]. Under such conditions, even stable TiO_2 surface may be partially dissolved in water and thus the nitrogen doping is enhanced in the course of reprecipitation of TiO_2 nanoparticles.

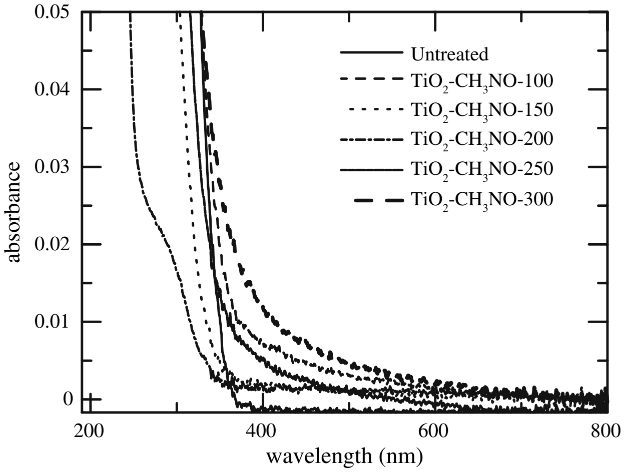


Fig. 1 Absorption spectra of the solutions containing the colloidal TiO_2 nanoparticles before and after continuous hydrothermal treatments with formamide at different temperatures. The concentration of TiO_2 was 1.6×10^{-4} M for all samples

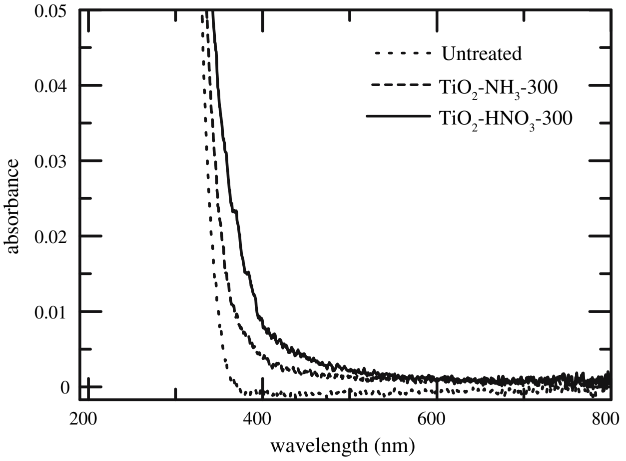


Fig. 2 Absorption spectra of the solutions containing the TiO_2 colloidal nanoparticles before (dotted line) and after continuous hydrothermal treatments with NH_3 (broken line) and HNO_3 (solid line) at $T = 300$ °C. The concentration of TiO_2 was 1.6×10^{-4} M for all samples

One can notice that the optical density corresponding to the band gap of TiO_2 remarkably decreased after the treatment at $T = 200$ °C. This behavior was not realized when the hydrothermal treatment of the colloidal TiO_2 nanoparticles was carried out without formamide at the same temperature [19]. Formamide is known to partially decompose into carbon monoxide and certain nitrides such as ammonia above $T = 180$ °C [20]. Those by-products from formamide may shift the pH of the solution to be close to the isoelectric point of TiO_2 at $T = 200$ °C, which results in the coagulation of colloidal TiO_2 nanoparticles leading to the drop-off in absorbance. The pH at other temperatures was away from the isoelectric point and thus the precipitation of TiO_2 nanoparticles did not occur.

Comparison between different nitrogen compounds

In the continuous treatment with formamide, the most effective N-doping has been accomplished at $T = 300$ °C. We next carried out the hydrothermal treatment of the colloidal TiO_2 nanoparticles with nitric acid or ammonia at a fixed temperature, $T = 300$ °C, and compared the results with those with formamide. Figure 2 shows the absorption spectra of the solutions containing the colloidal TiO_2 nanoparticles before and after treatments with nitric acid (TiO_2-HNO_3-300) and ammonia (TiO_2-NH_3-300) at $T = 300$ °C. In both spectra, the absorption tail extended to the visible region around about $\lambda = 500$ nm. For comparison, the absorbance at $\lambda = 400$ nm for the different colloidal TiO_2 nanoparticles was summarized in Table 1. It is increased in order of formamide > nitric acid > ammonia when compared between TiO_2-X-300 treated by the continuous method. The difference in the doping efficiency can be correlated with the bond dissociation energy for nitrogen compounds to generate N atom. These values were roughly calculated to be about 860 kJmol^{-1} for nitric acid ($E_{N-H} + 3 \times E_{N-O}$), about 1,170 kJmol^{-1} for ammonia ($3 \times E_{N-H}$) and about 930 kJmol^{-1} for formamide ($E_{C-N} + 2 \times E_{N-H}$), respectively. The highest dissociation energy for ammonia will lead to the lowest efficiency of nitrogen doping, which is consistent with the present observation. In any case, thermal energy required to generate N atom is considerably large, which resulted in the low efficiency of nitrogen doping.

The highest efficiency of nitrogen doping was achieved by the batch treatment of the colloidal TiO_2 nanoparticles with TEA at $T = 300$ °C for 2 h (TiO_2-TEA-300). The absorption spectrum of the solution containing TiO_2-TEA-300 is shown in Fig. 3. The intense absorption band extended to the visible region around $\lambda = 500$ nm. The solution displayed a yellow color typical of N-doped TiO_2. This result may be justified in view of the small bond dissociation energy of about 231 kJmol^{-1} for TEA ($3 \times E_{C-N}$) and the long treatment time for 2 h.

Photocatalytic reactions

The photocatalytic reduction of Ag^+ ions by the prepared TiO_2 nanoparticles under near-UV light was first examined. Figure 4 shows the variations in the absorption spectra of the solutions consisting of TiO_2-CH_3NO-T and 1.3×10^{-3} M $AgClO_4$ under near-UV light irradiation ($\lambda_{uv} = 300$–400 nm). The distinct absorption band attributed to the surface plasmon (SP) resonance of the colloidal

Table 1 Properties of the colloidal TiO_2 nanoparticles before and after hydrothermal treatments with different nitrogen compounds

Photocatalyst	Nitrogen compound	Temperature (°C)	Treatment method	Abs. at 400 nm	Conversion (%)[a]
As prepared TiO_2	Untreated	–	–	0.000	–
TiO_2-CH_3NO-100	Formamide	100	Flow	0.007	–
TiO_2-CH_3NO-150	Formamide	150	Flow	0.002	–
TiO_2-CH_3NO-200	Formamide	200	Flow	0.002	–
TiO_2-CH_3NO-250	Formamide	250	Flow	0.005	–
TiO_2-CH_3NO-300	Formamide	300	Flow	0.012	15
TiO_2-HNO_3-300	Nitric acid	300	Flow	0.009	6
TiO_2-NH_3-300	Ammonia	300	Flow	0.004	20
TiO_2-TEA-300	TEA	300	Batch	0.140	26

[a] Conversions of MB after visible light irradiation for 120 min

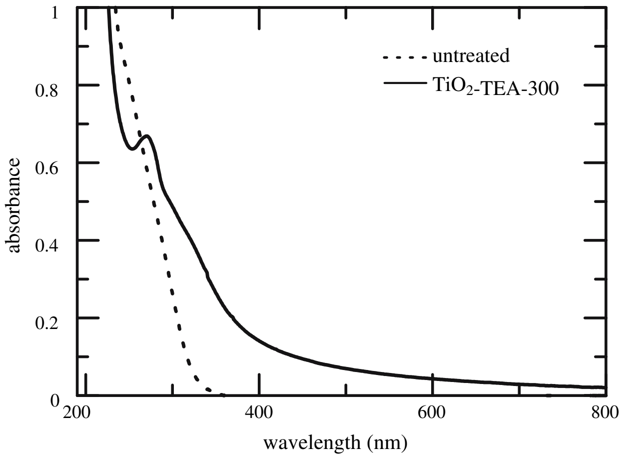


Fig. 3 Absorption spectra of the solutions containing the colloidal TiO_2 nanoparticles before (broken line) and after (solid line) batch hydrothermal treatment with TEA at $T = 300$ °C. The concentration of TiO_2 was 1.6×10^{-4} M

Ag nanoparticles developed around $\lambda = 400$ nm with irradiation, indicating that Ag^+ ions were reduced by the conduction-band electrons of TiO_2 nanoparticles [14]. The rate of the growth of the SP band was initially decreased with rising treatment temperature up to $T = 100$ °C and restored to some extent at $T = 200$–250 °C, but depressed again at $T = 300$ °C. This behavior is almost the same as that observed for the colloidal TiO_2 nanoparticles treated in the absence of nitrogen compound [19]. The TEM observations revealed the growth of TiO_2 nanoparticles after hydrothermal treatment. It is therefore suggested that the photocatalytic activity under near-UV irradiation was mainly affected by the structural changes in the TiO_2 nanoparticles caused by the hydrothermal treatment irrespective of nitrogen doping.

Figure 5 displays the variations in the absorption spectra of the solutions containing the untreated TiO_2 or various TiO_2-X-300 and 1.3×10^{-3} M $AgClO_4$ under visible light irradiation ($\lambda_{vis} = 420$–550 nm). For the untreated TiO_2, no significant change in the absorption spectrum was observed upon irradiation, which is consistent with the fact that TiO_2 has no spectral sensitivity to visible light. On the other hand, the broad SP band around $\lambda = 400$ nm developed upon visible illumination for the TiO_2 treated with formamide, ammonia, and TEA. This observation clearly indicates that these N-doped TiO_2 nanoparticles exhibited the photocatalytic activity responsive to visible light. The broadening of the SP band suggests the formation of somewhat larger Ag nanoparticles. The growth of the SP band was found to slow down at the irradiation time longer than 30 min. This may be explained by considering the electron-hole recombination as well as a "filter effect" due to Ag nanoparticles covering the TiO_2 surface.

The highest activity was realized for TiO_2-TEA-300, which is in good agreement with the intense absorption in the visible region. The peak intensity of the SP band after visible illumination for 120 min in Fig. 5(e) is almost comparable to that of the untreated TiO_2 under near-UV light irradiation, indicative of quite high activity of TiO_2-TEA-300 under visible light. It is noted that the absorbance around $\lambda = 300$–400 nm was decreased upon initial irradiation between 0 and 30 min, which may be related to the precipitation of a part of TiO_2-TEA-300 by agglomeration with colloidal Ag nanoparticles. In fact, a small amount of the thread-like precipitation was seen suspended in the solution after 120 min irradiation.

It is curious that no appreciable activity was found for TiO_2-HNO_3-300 under visible light irradiation although it has higher absorbance in the visible region than TiO_2-NH_3-300. According to the first-principle calculations by Asahi et al. nitrogen doped into substitutional sites of TiO_2 is indispensable for efficient photocatalytic activity under visible light and band-gap narrowing. However, that would not be the case with TiO_2-HNO_3-300. Among nitrogen compounds used in this study, only nitric acid is a strong oxidizing reagent, which can produce NO_x by decomposition during hydrothermal treatment.

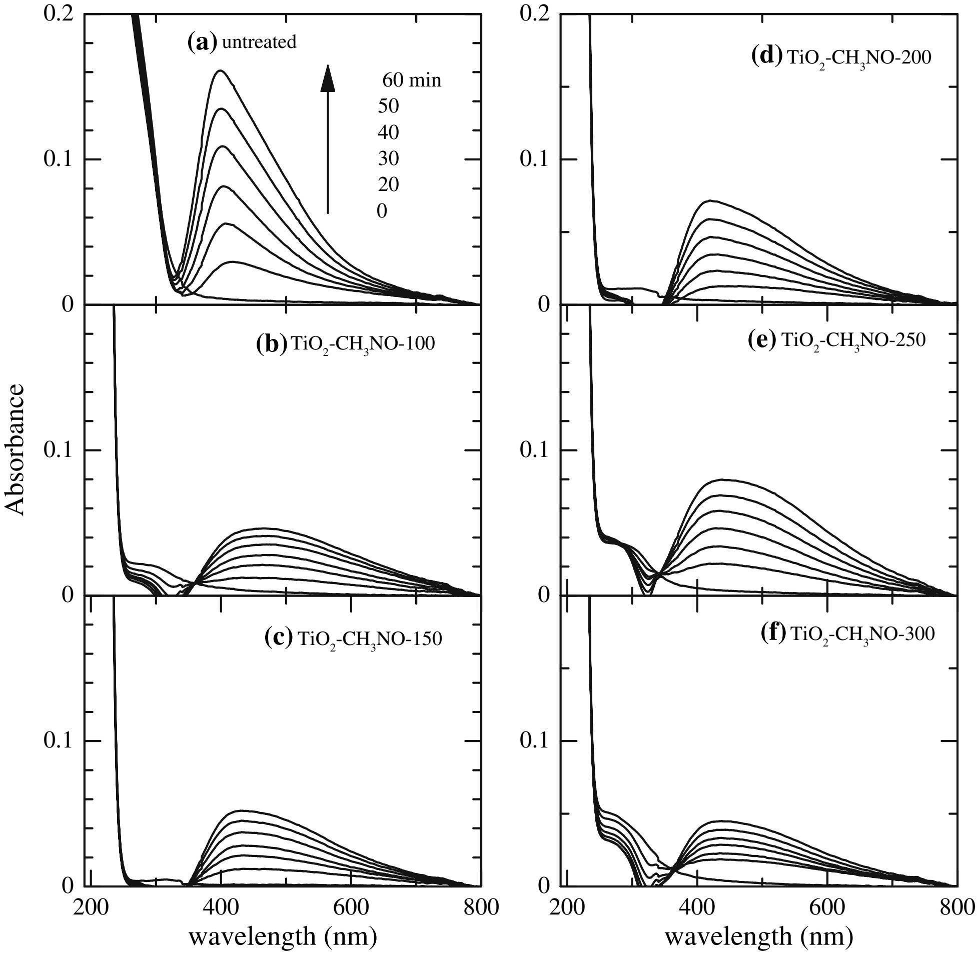


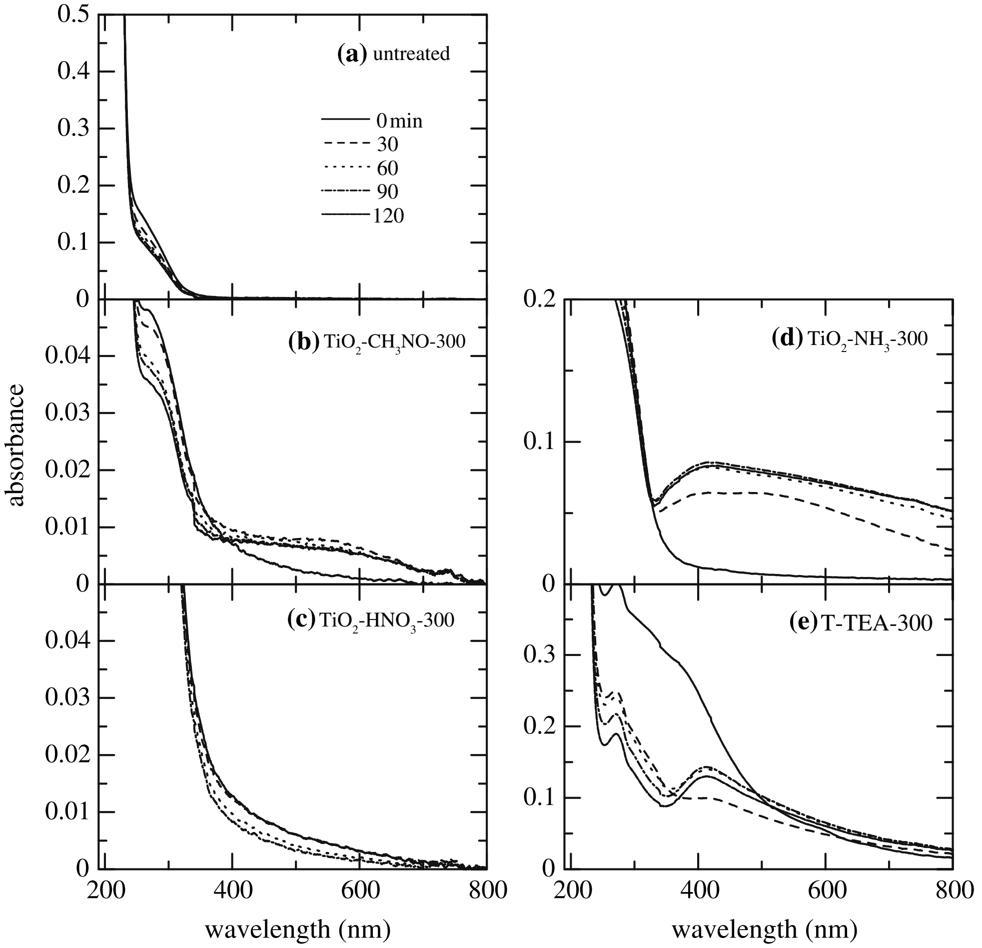
Fig. 4 The variations in absorption spectra of the solutions containing the untreated TiO_2 or TiO_2-CH_3NO-*T* and 1.3×10^{-3} M $AgClO_4$ under near-UV light irradiation ($\lambda_{uv} = 300$–400 nm) for 0, 20, 30, 40, 50, and 60 min

The photocatalytic degradation of MB by the colloidal TiO_2 nanoparticles was also examined in an aqueous solution under visible light irradiation ($\lambda_{vis} = 420$–550 nm). The results were shown in Fig. 6. The photobleaching of MB was almost negligible under visible illumination without photocatalysts. The conversions of MB at 120 min irradiation are summarized in Table 1, which is increased in order of TiO_2-TEA-300 > TiO_2-NH_3-300 > TiO_2-CH_3NO-300 > TiO_2-HNO_3-300. This order well agrees with that for the photocatalytic reduction of Ag^+ ions. This observation indicates that the holes of TiO_2-X-300 are also highly active under visible light irradiation. It is noticed that the degradation rate slowed down at the irradiation time longer than 30 min especially for TiO_2-TEA-300, which may reflect the consumption of holes with by-products of decomposed MB or the filter effect caused by MB adsorbed on the TiO_2 surface. The photocatalytic activity of TiO_2-HNO_3-300 for visible light was the lowest among the catalysts examined in this study in spite of the increased absorption in the visible region. It is reasonable to assume that the presence of NO_x is harmful for the preparation of efficient N-doped TiO_2 catalyst.

Conclusions

N-doped TiO_2 nanoparticles have been prepared by continuous or batch treatment of the colloidal TiO_2 nanoparticles under hydrothermal conditions with four kinds of nitrogen compounds, formamide, nitric acid, ammonia, and TEA. The obtained photocatalysts exhibited the optical absorption extending to the visible region around $\lambda = 500$ nm. The efficiency of nitrogen doping was strongly dependent on the kind of nitrogen compounds, treatment method as well as treatment temperature. Among nitrogen compounds used in this study, nitric acid was not suitable to yield the photocatalytic activity responsive to visible light. The most efficient N-doping could be accomplished by the batch treatment with a small amount

Fig. 5 The variations in absorption spectra of the solutions containing the untreated TiO_2 or various TiO_2-X-300 and 1.3×10^{-3} M $AgClO_4$ under visible light irradiation (λ_{vis} = 420–550 nm) for 0, 30, 60, 90, and 120 min



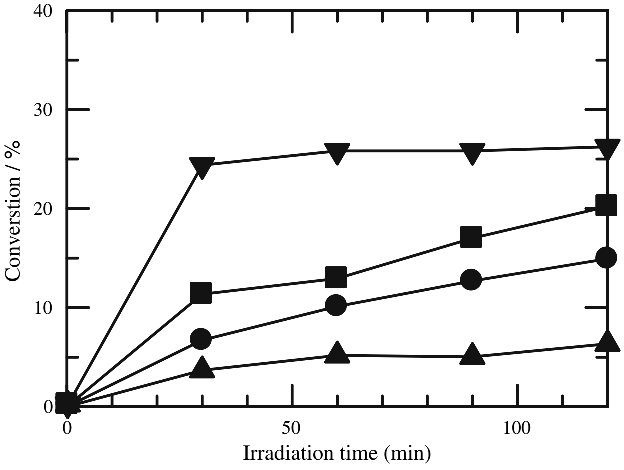


Fig. 6 Photocatalytic degradation of MB by different N-doped TiO_2 nanoparticles under visible light irradiation. ▼: TiO_2-TEA-300; ■: TiO_2-NH_3-300; ●: TiO_2-CH_3NO-300; ▲: TiO_2-HNO_3-300

of TEA, which exhibited the efficient photocatalytic activity for both the reduction of Ag^+ ions and the degradation of MB under visible light irradiation.

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