

Sensitization of photocatalytic activity of S- or N-doped TiO₂ particles by adsorbing Fe³⁺ cations

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Abstract

A new method to dope Fe³⁺ ions only onto the surface of S- or N-doped TiO₂ is proposed. The photocatalytic activities of Fe³⁺ ions adsorbed on S- or N-doped TiO₂ photocatalysts for oxidation of 2-propanol are markedly improved compared to those of S- or N-doped TiO₂ without treatment of Fe³⁺ ions under a wide range of incident light wavelengths, including UV light and visible light. When the amount of Fe³⁺ ions adsorbed on S- doped TiO₂ particles was 0.90 wt.%, photocatalytic activity reached maximum. In the case of N-doped TiO₂ with Fe³⁺ ions, the optimum amount of Fe³⁺ ions was 0.36 wt.%. The photocatalytic activities of Fe³⁺ ions adsorbed on S- or N-doped TiO₂ photocatalysts decreased gradually when the amount of Fe³⁺ ions was greater than 1.0 wt.%. In addition, when S- or N-doped TiO₂ photocatalysts adsorbed with Fe³⁺ ions was observed after reduction by NaBH₄ followed by air oxidation, further improvement in their photocatalytic activities were observed. In this case, the optimum amounts of Fe³⁺ adsorbed on the surfaces of S- and N-doped TiO₂ photocatalysts were 2.81 and 0.88 wt.%, respectively. During the treatment, Fe³⁺ ions adsorbed on S- or N-doped TiO₂ were reduced to generate metal Fe, and Fe was reoxidized again to form Fe³⁺ ions under an aerated condition. After the treatment, the crystal structure of Fe³⁺ ions adsorbed on S-doped TiO₂ and adsorbitivity of 2-propanol on the photocatalyst were changed.

Keywords: Photocatalysts; Titanium dioxide; Visible light; S-doped TiO₂; N-doped TiO₂; Fe³⁺ ions; Reduction and oxidation

1. Introduction

Environmental pollution and destruction on a global scale are issues of increasing concern in today's society. There is a need for effective catalysts for degradation of pollutants. In recent years, there has been an extensive interest in the use of semiconductors as photocatalysts to initiate photocatalytic reactions at their interfaces [1]. Metal oxide semiconductor powders that show activity under UV light irradiation have been used as photocatalysts for degradation of pollutants. TiO₂ has been widely used a catalyst because of its merits, including optical and electronic properties, low cost, high level of photocatalytic activity, chemical stability and non-toxicity [2]. Although TiO₂, which is one of the most promising photocatalysts, is now used in various practical applications [1,3] only a small UV fraction of solar light, about 2–3%, can be utilized because of its large band gap of 3.2 eV. Therefore, the development of a TiO₂ photocatalyst that shows a high level of activity under visible light is needed. In the past, transition metal cations have been used as dopants to red-shift the absorption edge of TiO₂ and SrTiO₃ to a visible light region [4– 13].

N, S or C anion-doped TiO₂ photocatalysts having an anatase form that show a relatively high level of activity when irradiated by visible light have been reported [14–19]. Recently, we have also reported the preparation of S or C cation-doped TiO₂ having an anatase phase and S, C cation-codoped TiO₂ having a rutile phase and their photocatalytic activities [20–23]. However, their photocatalytic activities under the condition of visible light irradiation are not sufficient for practical application. Therefore, we have modified S- and N-doped TiO₂ photocatalysts to improve their photocatalytic activities. We have succeeded in preparing S- and N-doped TiO₂ photocatalysts adsorbed with Fe³⁺ having an anatase phase in order to enhance the charge separation between electrons and holes, resulting in improvement in photocatalytic activity under the condition of visible light irradiation. These activity enhancements were improved by reduction and air oxidation of the doped TiO₂ powders with Fe³⁺ ions. There has been no report on doping metal ions only onto S- or N-doped TiO₂ having an anatase phase and its photocatalytic activity under the condition of visible light irradiation.

In this paper, we describe the procedure for preparation of S- and N-doped TiO₂ photocatalysts adsorbed with Fe³⁺ ions having an anatase phase and their photocatalytic activities for oxidation of 2-propanol under the condition of visible light irradiation.

2. Experimental

2.1. Materials and instruments

Titanium dioxide (TiO₂) powder having an anatase phase was obtained from Ishihara Sangyo (ST-01). The relative

surface area of ST-01 was 285.3 m²/g. 2-Propanol, FeCl₃ and acetone were obtained from Wako Pure Chemical Industry. Thiourea and urea were obtained from Tokyo Chemical Industry Co., Ltd. Other chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification. The crystal structures of TiO₂ powders were determined from X-ray diffraction (XRD)

patterns measured by using an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target K α -ray ($\lambda = 1.5405 \text{ \AA}$). The relative surface areas of the powders were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). The absorption and diffuse reflection spectra were measured using a Shimadzu UV-2500PC spectrophotometer. X-ray photoelectron spectra (XPS) of the TiO₂ powders were measured using a JEOL JPS90SX photoelectron spectrometer with an Al K α source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C1s level at 285 eV as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a non-linear least-squares procedure after proper subtraction of the baseline. ESR spectra were obtained on a JEOL JES-ME3 X-band spectrometer equipped with a 100-kHz field modulation unit; a standard MgO/Mn²⁺ sample calibrated with NMR magnetometer was employed for calibration of the magnetic field.

2.1. Preparation of S- or N-doped TiO₂ powders adsorbed with Fe³⁺ ions

S- or N-doped TiO₂ powders as starting materials were synthesized by previously reported methods [20–24]. An appropriate amount of FeCl₃ was dissolved in deionized water (300 ml). Three g of the doped TiO₂ powder was suspended in an FeCl₃ aqueous solution, and the solution was stirred vigorously for 2 h. After filtration of the solution, the amount of Fe³⁺ ions that remained in the solution was determined by UV absorption spectra to estimate the amount of Fe ions adsorbed on the doped TiO₂ powder. The residue was washed with deionized water several times until pH of the filtrate was neutralized. The powders were dried under reduced pressure at 60 °C for 12 h.

2.3. Reduction and air oxidation treatments of S- or N-doped TiO₂ powders adsorbed with Fe³⁺ ions

One g of S- or N-doped TiO₂ powder adsorbed with Fe³⁺ ions was suspended in deionized water (30 ml). NaBH₄ whose amount is 10 times its mol of Fe³⁺ ions was added to the solution. The solution was stirred for 2 h under aerated conditions. After filtration, the residue was washed with deionized water several times until pH of the filtrate was neutralized. The powders were dried under reduced pressure at 60 °C for 12 h.

2.4. Oxidation states of Fe ions during photoirradiation under anaerobic or aerobic conditions

ESR spectra of Fe³⁺ ions adsorbed on the surfaces of the doped TiO₂ particles were obtained under reduced pressure and an aerated condition at 77 K. A 250-W high-pressure mercury lamp was used as an irradiation light source. The oxidation condition of Fe ions on doped TiO₂ was followed during photoirradiation under reduced pressure. After photoirradiation, the powder was exposed to air and analyzed by ESR spectroscopy again. ESR observations of the powders that had been subjected to photoirradiation were also performed under aerated conditions. For photoirradiation during ESR measurements, a 350-W high-pressure mercury lamp (WACOM Co. Ltd., BMI-350DI) was used as a light source.

2.5. Photocatalytic oxidation of 2-propanol on photoirradiation of TiO₂ powder

Photocatalytic reactions were carried out in a Pyrex tube containing doped TiO₂ particles (100 mg) and 5 ml of an acetonitrile solution of 2-propanol (50 mM). The solution was bubbled with oxygen at a rate of 2.0 ml/min for 15 min, and the glass tube was sealed with a septum. The flasks containing the solution and TiO₂ powder were sonicated before the photocatalytic reaction and rotated at a rate of about 100 rpm during the reaction to suspend the TiO₂ particles in solution. S- or N-doped TiO₂ photocatalysts adsorbed with or without Fe³⁺ ions or pure TiO₂ powder (ST-01) were used as photocatalysts. The suspension was photoirradiated using a 500-W Xe lamp (USHIO Co. Ltd., SXUI-501XQ), which emits both UV and VIS light over a wide wavelength with an integrated photon flux of $1.1 \times 10^{-2} \text{ Einsteins (E) s}^{-1} \text{ cm}^{-2}$ between 350 and 540 nm. To limit the irradiation wavelength, the light beam was passed through a UV-34, L-42, Y-44 Y-50 or Y-54 filter (Kenko Co.) to cutoff wavelengths shorter than 340, 420, 440 or 500 nm, respectively. Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity. The amounts of acetone produced by photocatalytic reactions were determined using a capillary gas chromatograph (Hitachi G3500, FID detector) equipped with a DB-WAX capillary column and using a Shimadzu C-R6A-FFC chromatopac for data processing.

3. Results and discussion

3.1. Absorption spectra of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions

Fig. 1A shows absorption spectra of N-doped TiO₂ adsorbed with Fe³⁺ ions. The absorption spectra of the doped TiO₂ were not changed when the amount of Fe³⁺ ions adsorbed on the doped TiO₂ was lower than 0.36 wt.%. The absorbance of N-doped TiO₂ with an amount of Fe³⁺ ions greater than 0.88 wt.% in the visible light region increased because Fe compounds on N-doped TiO₂ are thought to show absorbance in the visible light region. After treatment with NaBH₄, absorbance of N-doped TiO₂ with Fe ions in the visible light region increased slightly as shown in Fig. 1B. The main factor for the change of spectra is under investigation.

Fig. 2A also shows absorption spectra of S-doped TiO₂ with Fe³⁺ ions. Absorbance of S-doped TiO₂ with adsorbed Fe³⁺ ions in the visible light region also changed with change in the amount of Fe³⁺ ions as shown in Fig. 1B. When the amount of Fe³⁺ ions adsorbed on S-doped TiO₂ powder was less than 0.37 wt.%, no absorption change was observed. An increase in absorbance of S-doped TiO₂ in the visible light region was observed when the amount of Fe³⁺ ions adsorbed on S-doped TiO₂ was greater than 0.90 wt.%. After treatment with NaBH₄, change in the absorbance of S-doped TiO₂ with Fe ions in the visible light region was similar to that in the case of N-doped TiO₂ with Fe ions.

3.2. ESR spectra of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions under the condition of photoirradiation

Fig. 3A shows ESR spectra of N-doped TiO₂ adsorbed with Fe³⁺ ions (0.36 wt.%) under reduced pressure. A broad peak at 4.4 assigned to Fe³⁺ species was observed. Under the condition of photoirradiation using a high-pressure mercury lamp (350 W; 18.5 mW/cm²) for 5 min, the peak assigned to Fe³⁺ was reduced by half as shown in Fig. 3A. The peak disappeared completely under the condition of photoirradiation for more than 20 min. These results suggested that Fe³⁺ ions were efficiently reduced to generate Fe²⁺ ions that are not detected by ESR measurement, by trapping electrons generated during photoirradiation under reduced pressure. When air was introduced into the sample tube containing the doped TiO₂ with Fe²⁺ ions, the peak assigned to Fe³⁺ ions was recovered after 5 min because Fe²⁺ ions were oxidized to generate Fe³⁺ ions as a result of the reaction between oxygen and Fe²⁺ ions (Fig. 3A). In addition, the peak assigned to Fe³⁺ ions was not changed during photoirradiation under an aerated condition as shown in Fig. 3B. This result suggested that the rate of generation of Fe²⁺ ions during photoirradiation is much slower than that of oxidation of Fe²⁺ ions by oxygen.

In the case of S-doped TiO₂ adsorbed with Fe³⁺ ions, the results of ESR measurements were similar to those in the case of N-doped TiO₂ with Fe³⁺ ions. Under reduced pressure, the peak attributed to Fe³⁺ ions decreased because photogenerated electrons were trapped by Fe³⁺ ions on the surface of S-doped TiO₂. On the other hand, no change was observed during photoirradiation under aerated conditions.

These results suggested that charge separation between electrons and holes generated photocatalytically is improved because photoexcited electrons were efficiently trapped by oxygen through Fe³⁺ ions adsorbed on the surface of the doped TiO₂ photocatalysts.

We have reported the photoelectrochemical properties of a TiO₂ single crystal electrode in 0.1 M H₂SO₄ containing 2-propanol in the presence of Fe³⁺ ions [25–27]. The results of these studies ruled out the possibility that reoxidation of Fe²⁺ ions by photogenerated holes at the TiO₂ electrode since water is effectively oxidized on photoirradiated TiO₂ in a solution containing both Fe²⁺ and Fe³⁺ ions. We proposed the reaction mechanism of photocatalytic oxidation of water using TiO₂ and Fe³⁺ ions for oxidation of 2-propanol in the paper. The results of our previous studies are consistent with the results reported in this paper.

Changes in ESR spectra of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions treated with NaBH₄ and air oxidation were similar to those of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions without treatment.

3.3. XRD spectra of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions under the condition of photoirradiation

Fig. 4 shows XRD spectra of N-doped TiO₂ adsorbed with Fe³⁺ (4.17 wt.%) ions before and after redox treatment (reduction by NaBH₄ and oxidation by air). Before the redox treatment, a small peak at 35.88, which was assigned to *g*-Fe₂O₃, was observed. A peak assigned to *g*-FeO(OH) (18.38) appeared, while the phase of *g*-Fe₂O₃ completely disappeared as shown in Fig. 4 [28–30]. A change in crystal structure of Fe compounds loaded on the surface of S-doped TiO₂ particles was also observed in the case of S-doped TiO₂ adsorbed with Fe³⁺ cations before and after redox treatment. As discussed in a later Section 3.4.2, the photocatalytic activities of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions are related to the crystal structure of Fe compounds on the doped TiO₂. That is, the crystal structure of Fe compounds on the surfaces of doped TiO₂ particles is an important factor for determining the enhancement of photocatalytic activity of doped TiO₂ adsorbed with Fe³⁺ ions.

3.4. Photocatalytic oxidation of 2-propanol using S- or N-doped TiO₂ adsorbed with Fe³⁺ ions

3.4.1. Photocatalytic activities of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions

Fig. 5A shows the photocatalytic oxidation of 2-propanol using N-doped TiO₂ that was adsorbed with various amounts of Fe³⁺ ions. ST-01 having anatase fine particles was used as a reference. Photocatalytic activities of N-doped TiO₂ with Fe³⁺ ions increased with increase in Fe ions. N-doped TiO₂ powders adsorbed with Fe³⁺ ions of which the amount was 0.36 wt.% showed the highest level of activity for oxidation of 2-propanol. As described in Section 3.2, Fe³⁺ ions adsorbed on N-doped TiO₂ were efficiently trapped by photoexcited electrons, resulting in improvement of the charge separation between electrons and holes. Above the amount of 0.36 wt.%, the activity of N-doped TiO₂ with Fe³⁺ ions gradually decreased with increase in Fe³⁺ ions because the large excess amount of Fe³⁺ ions was thought to occupy active sites on the surface of N-doped TiO₂ and to function as a recombination center between electrons and holes [26].

Fig. 5B also shows the results of photocatalytic activities of Fe³⁺ ions adsorbed on S-doped TiO₂ photocatalysts for oxidation of 2-propanol. The dependence of changes in photocatalytic activities of S-doped TiO₂ powders with change in the amount of Fe³⁺ ions is similar to that of N-doped TiO₂ adsorbed with Fe³⁺ ions. The photocatalytic activity of S-doped TiO₂ with Fe³⁺ ions showed a maximum when 0.90 wt.% of Fe³⁺ ions was adsorbed on the surface of an S-doped TiO₂ photocatalyst. The quantum efficiency for oxidation of 2-propanol using S-doped TiO₂ adsorbed with Fe³⁺ cations (0.90 wt.%) was roughly estimated to be 2.1%. Compared to N-doped TiO₂ with Fe³⁺ ions, S-doped TiO₂ photocatalysts are slightly different from N-doped TiO₂ catalysts in the optimum amount of Fe³⁺ cations. These results indicated that the doping atoms, and the density of defects located on the surface of the doped TiO₂ particles are thought to be one of important factor to determine an optimum amount of Fe³⁺ ions.

Fig. 6 shows the rate of decomposition of 2-propanol as a function of the cutoff wavelengths of glass filters with an Xe lamp using S-doped TiO₂ with and without Fe³⁺ ions as a catalyst. Although absorption spectra of S-doped TiO₂ adsorbed with Fe³⁺ ions are not different from those of S-doped TiO₂ without Fe³⁺ cations, the photocatalytic activity levels of S-doped TiO₂ adsorbed with Fe³⁺ cations as a catalyst were about 2.5-times higher than those of S-doped TiO₂ without Fe³⁺ cations under a wide range of irradiation wavelengths, including UV light and VIS light. Similar improvement in the properties of photocatalytic activity of N-doped TiO₂ adsorbed with Fe³⁺ cations was also observed when its activity was compared to that of N-doped TiO₂ without Fe³⁺ ions (data not shown). These results suggest that the improvement in photocatalytic activities of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions under a wide range of irradiation light originates from electron trapping by Fe³⁺ compounds on S- or N-doped TiO₂ particles that results in efficient charge separation between photoexcited electrons and holes.

3.4.2. Photocatalytic activities of S- or N-doped TiO₂ photocatalysts adsorbed with Fe³⁺ ions that were treated with NaBH₄ and air oxidation (redox treatment)

The photocatalytic activities of N-doped TiO₂ adsorbed with Fe³⁺ ions that was treated with NaBH₄ and air oxidation for oxidation of 2-propanol were estimated. The photocatalytic activity levels of the photocatalysts were higher than those of N-doped TiO₂ photocatalysts with Fe³⁺ ions without redox treatment when 0.88 wt.% of Fe³⁺ ions was adsorbed only on the surface of N-doped TiO₂ as shown in Fig. 7A. The optimum amount of Fe³⁺ on N-doped TiO₂ adsorbed with Fe³⁺ ions treated with NaBH₄ and air oxidation for oxidation of 2-propanol was slightly larger than that of N-doped TiO₂ with Fe³⁺ ions without NaBH₄ treatment. S-doped TiO₂ adsorbed with Fe³⁺ ions treated with NaBH₄ and air oxidation showed tendencies similar to those of N-doped TiO₂ with Fe³⁺ ions as shown in Fig. 7B. The maximum quantum efficiency of S-doped TiO₂ adsorbed with Fe³⁺ ions (2.81 wt.%) after treatment with NaBH₄ was roughly estimated to be 3.0%.

As described in Section 3.3, the crystal structure of Fe compounds on S- or N-doped TiO₂ changed from *g*-Fe₂O₃ to *g*-FeO(OH) after treatment with NaBH₄ and air oxidation. Although the main factor responsible for improving photocatalytic activity of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions after treatment with NaBH₄ and air oxidation is not clear yet, the change in crystal structure of Fe compounds on S- or N-doped TiO₂ photocatalysts is thought to be an important factor for improvement of photocatalytic activity for oxidation of 2-propanol by doped TiO₂ with Fe³⁺ ions.

4. Conclusions

We have succeeded in preparing S- or N-doped TiO₂ adsorbed with Fe³⁺ cations. The photocatalytic activity levels of these photocatalysts were two to four times higher than those of S- or N-doped TiO₂ without adsorption of Fe³⁺ ions. Improvement in the photocatalytic activities by Fe³⁺ treatment was observed under a wide range of irradiation light, including UV light and VIS light. Fe³⁺ ions adsorbed on the surface of S- or N-doped TiO₂ particles were efficiently trapped by photoexcited electrons generated in the photocatalysts, resulting in improvement in charge separation between electrons and holes. In addition, the photocatalytic activities of S- or N-doped TiO₂ adsorbed with Fe³⁺ ions increased markedly after treatment with NaBH₄ and air oxidation.

S- or N-doped TiO₂ powder adsorbed with Fe³⁺ ions, which shows a high level of photocatalytic activity under a wide range of irradiation light, may have a wide variety of practical applications. We expect that the activity will be further

improved by optimizing conditions for preparing S- or N-doped TiO₂ powders with Fe³⁺ ions.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Science, and Technology (MEXT), Japan and Nissan Science Foundation.

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