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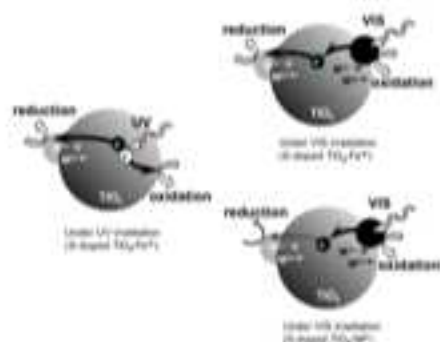
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**Graphical abstract :** Development of metal cation compound-loaded S-doped TiO<sub>2</sub> photocatalysts having a rutile phase under visible light

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Rutile S-doped TiO<sub>2</sub> loaded with metal ion compounds (Fe<sup>5+</sup>, Rh<sup>5+</sup>, Cu<sup>2+</sup>, Co<sup>5+</sup>, Ni<sup>2+</sup>, Cr<sup>5+</sup>) have been prepared (S-doped TiO<sub>2</sub>-M<sup>n+</sup>). The metal ions were adsorbed on the surfaces of S-doped TiO<sub>2</sub> nanoparticles. The photocatalytic activities of S-doped TiO<sub>2</sub> for oxidation of acetaldehyde in gas phase were drastically improved after adsorbing treatment of metal ions under a wide range of incident light wavelengths.



Development of metal cation compound-loaded S-doped  
TiO<sub>2</sub> photocatalysts having a rutile phase under visible light

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## Abstract

We have synthesized S ( $S^{4+}$ )-doped  $TiO_2$  photocatalysts having a rutile phase. Rutile S-doped  $TiO_2$  photocatalysts loaded with metal ion compounds ( $Fe^{3+}$ ,  $Rh^{3+}$ ,  $Cu^{2+}$ ,  $Co^{3+}$ ,  $Ni^{2+}$ ,  $Cr^{3+}$ ) have also been prepared (S-doped  $TiO_2-M^{n+}$ ). The metal ions were adsorbed on the surfaces of S-doped  $TiO_2$  nanoparticles by impregnation methods (IM) or photodeposition methods (PH). The photocatalytic activities of S-doped  $TiO_2$  for oxidation of acetaldehyde in gas phase were drastically improved after adsorbing treatment of metal ions under a wide range of incident light wavelengths. Under photoirradiation at wavelengths longer than 350 nm or 420 nm, S-doped  $TiO_2-Cu^{2+}$ (PH) show the highest level of activity among the metal ions. S-doped  $TiO_2-Fe^{3+}$ (IM) show the highest level of activity for oxidation of acetaldehyde in gas phase compared to the activity levels of S-doped  $TiO_2$  with loading of other metal ions such as  $Rh^{3+}$ ,  $Cu^{2+}$ ,  $Co^{3+}$ ,  $Ni^{2+}$ , and  $Cr^{3+}$  under a wide range of incident light wavelengths. The optimum amount of metal ion compound nanoparticles adsorbed on S-doped  $TiO_2$  was 0.1 wt%. In order to elucidate the role of metal ions adsorbed on the surface of S-doped  $TiO_2$ , we measured

the double beam photoacoustic spectra (DB-PA). The amount of  $Ti^{3+}$  generated as a result of the reaction between  $Ti^{4+}$  and photoexcited electrons was analyzed by this spectroscopy. The relationship between the reaction rate of photocatalytic oxidation of acetaldehyde on S-doped  $TiO_2$  adsorbed with metal ions and the charge separation between photoexcited electrons and holes is discussed.

*Keywords: S-doped  $TiO_2$ ; Loading of metal ions compounds; Degradation of acetaldehyde; Improvement of charge separation*

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## 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. Titanium dioxide ( $\text{TiO}_2$ )-mediated heterogeneous photocatalysis has attracted much attention because of its potential applications to decomposition of pollutants in water and air. [1,2] In these applications, anatase  $\text{TiO}_2$  powders consisting of particles with large surface areas are used as photocatalysts. These powders are useful for absorption of compounds included in the reaction system at low concentrations. In contrast to the case of anatase  $\text{TiO}_2$  photocatalysts, the oxidation of water, which is difficult to oxidize, proceeds efficiently on large rutile  $\text{TiO}_2$  particles. [3] Anatase  $\text{TiO}_2$  photocatalysts do not have photocatalytic activity for oxidation of water.

Since the discovery of photoelectrochemical splitting of water on titanium dioxide ( $\text{TiO}_2$ ) electrodes, [4] semiconductor-based photocatalysis has received much attention. [5-17] Most of these investigations have been carried out under UV light because a  $\text{TiO}_2$  photocatalyst shows relatively high levels of activity and chemical

stability under UV light which exceeds the band-gap energy of 3.0 or 3.2 eV in the rutile or anatase crystalline phase, respectively.

Although  $\text{TiO}_2$ , one of the most promising photocatalysts, is now used in various practical applications, [1, 2] only a small UV fraction of solar light, about 2-3%, can be utilized because of such a large band gap of 3.2 eV. The development of photocatalysts that show a high level of activity under visible light irradiation is needed in order to utilize sunlight or rays from artificial sources more effectively in photocatalytic reactions. In the past, transition metal ions have been used as dopants to red-shift the absorption edge of  $\text{TiO}_2$  and  $\text{SrTiO}_3$  to a visible light region. [18-30] For this purpose, reduced forms of  $\text{TiO}_x$  photocatalysts [31, 32] have also been investigated.

Treatment of  $\text{TiO}_2$  powder with hydrogen peroxide [33] or chelating agents [34] allows some photocatalytic reactions to proceed under visible light. However, most of these catalysts do not show long-term stability or do not have sufficiently high levels of activity for a wide range of applications. Asahi et al. [35] reported that N-doped  $\text{TiO}_2$  shows photoabsorption at wavelengths longer than 400 nm. It has also been reported that N-doped  $\text{TiO}_2$  has photocatalytic activity under visible light. Recently, Umebayashi

et al. have succeeded in synthesizing TiO<sub>2</sub> doped with S anions. [36] Kahn et al. [37] reported that C-doped TiO<sub>2</sub> was obtained as a result of a chemical modification of TiO<sub>2</sub> by controlled combustion of titanium metal in a natural gas flame. These compounds absorb visible light. These findings are supported by the results of theoretical calculations using full-potential linearized augmented plane wave formalism (F-LAPW method). However, the absorption spectra of these compounds in the visible region are relatively small. It should also be noted that dopants such as N and C are incorporated as anions and replaced by oxygen in the lattice of TiO<sub>2</sub>. Other techniques for synthesizing TiO<sub>2</sub> photocatalysts showing relatively high levels of activity under visible light have also been developed recently. [38, 39] We have also developed and reported the synthesis of S-cation-doped TiO<sub>2</sub> having anatase or rutile phase and Fe<sub>2</sub>O<sub>3</sub> nanoparticles loaded on the surfaces of S-doped and N-doped TiO<sub>2</sub>. [40-43]

We have succeeded in preparing S-doped and N-doped TiO<sub>2</sub> loaded with Fe<sub>2</sub>O<sub>3</sub> nanoparticles having an anatase phase in order to enhance the charge separation between electrons and holes, resulting in improvement in photocatalytic activity for oxidation of organic compounds under the condition of visible light irradiation. [44]



In this paper, we report photocatalytic activities of S-doped TiO<sub>2</sub> loaded with several kinds of metal ion compounds having rutile phase for oxidation of acetaldehyde in gas phase. In addition, the relationship between photocatalytic activities of S-doped TiO<sub>2</sub> loaded with metal ion compounds and the kind of metal ions will be discussed in order to elucidate of the role of metal ions under a wide range of photoirradiation by using double beam photoacoustic spectroscopy. [45]

## **2. Experimental**

### *2.1. Materials and Instruments*

TiO<sub>2</sub> powder having a rutile crystal structure was obtained from TAYCA (MT-150A). The content of anatase and the relative surface area of MT-150A particles were 0% and 88.0 m<sup>2</sup>/g, respectively. Thiourea was obtained from Tokyo Chemical Industry Co. Ltd. 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 TiO<sub>2</sub> powders were

determined from X-ray diffraction (XRD) patterns measured with an X-ray diffractometer (Philips, X'Pert-MRD) with Cu target K $\alpha$ -rays ( $\lambda = 1.5405 \text{ \AA}$ ). 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 TiO<sub>2</sub> powders were measured using a JEOL JPS90SX photoelectron spectrometer with an Al K $\alpha$  source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s 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. DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) was used to analyze the nature of the adsorbed species on the photocatalyst. The system consisted of an FTIR spectrometer (Jasco FT/IR-4200) equipped with a DRIFTS cell (Jasco DR-81 Diffuse Reflectance Attachment).

## *2.2. Preparation of rutile S-doped TiO<sub>2</sub> powders loaded with metal ion compound*

*nanoparticles*

The S-doped TiO<sub>2</sub> powders used as starting materials were synthesized by previously reported methods. [40-44, 46]

An appropriate amount of metal chloride salts (FeCl<sub>3</sub>, RhCl<sub>3</sub>, CuCl<sub>2</sub>, CoCl<sub>3</sub>, NiCl<sub>2</sub>, CrCl<sub>3</sub>) was dissolved in deionized water (300 ml). Three g of the doped TiO<sub>2</sub> powder was suspended in an aqueous solution of each metal chloride salt, and each solution was stirred vigorously for 2 h. After filtration of the solution, the amount of metal ion compounds (Fe<sup>3+</sup>, Rh<sup>3+</sup>, Cu<sup>2+</sup>, Co<sup>3+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>) that remained in the solution was determined by UV absorption spectra to estimate the amount of metal oxide compounds loaded on the doped TiO<sub>2</sub> powder. Determination of metal ions in aqueous solution was done by ICP. The residue was washed with deionized water several times until the pH value of the filtrate became neutral. The powders were dried under reduced pressure at 60 °C for 12 h.

*2.3. Photocatalytic degradation of acetaldehyde, formic acid, or acetic acid on doped*

*TiO<sub>2</sub> in gas phase*

The photocatalytic activities of S-doped TiO<sub>2</sub> adsorbed with metal ions were evaluated by measuring the change in concentration of acetaldehyde and evolved CO<sub>2</sub> as a function of irradiation time. A Tedlar bag (AS ONE Co. Ltd.) with a volume of 125 cm<sup>3</sup> was used as the photo-reactor vessel. One hundred mg of the TiO<sub>2</sub> powder was spread evenly on the bottom of a glass dish (area: 9.6 cm<sup>2</sup> = irradiation area), and this was placed in the reaction vessel described above.

Five hundred ppmv of acetaldehyde, formic acid, or acetic acid was prepared in the vessel by injection of saturated gaseous acetaldehyde. The irradiations were conducted at room temperature after equilibrium between the gaseous and adsorbed acetaldehyde had been reached (as ascertained by monitoring the concentration chromatographically about every 30 min). A 500-W Xe lamp (USHIO Co. Ltd., SX-UI501XQ) was used as a light source. To limit the irradiation wavelengths, the light beam was passed through a UV-35, L-42 or Y-47 filter (Kenko Co.) to cut off wavelengths shorter than 350, 420 or 470 nm, respectively. Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity (12.7 mW cm<sup>-2</sup>). After the irradiation was started, the decrease in acetaldehyde concentration was measured

using a gas chromatograph (Shimadzu Model GC-8A, FID detector) equipped with an FEG-20M 20% Celite 545 packed glass column using CR-8A CHROMATOPAC for data processing. At the same time, the amount of gaseous carbon dioxide that evolved was analyzed using a gas chromatograph (Shimadzu Model GC-9A, FID detector) equipped with a TCP 20% Uniport R packed column and a methanizer (GL Sciences, MT-221) operated at a temperature of 375°C. A CR-8A CHROMATOPAC was used for data processing.

#### *2.4. Double-beam photoacoustic (DB-PA) spectroscopic measurement*

In order to elucidate the role of metal ion compounds loaded on S-doped TiO<sub>2</sub>, we measured the DB-PA spectra of S-doped TiO<sub>2</sub> having rutile phase and of metal ions-adsorbed S-doped TiO<sub>2</sub> having rutile phase. A gas-exchangeable photoacoustic (PA) cell equipped with two valves for gas flow was used, and a TiO<sub>2</sub> sample was placed in the cell. The atmosphere was controlled by a flow of artificial air or N<sub>2</sub> containing ethanol vapor (air + EtOH, N<sub>2</sub> + EtOH), and the measurements were conducted after shutting off the valves, i.e., in a closed system at room temperature. Light-emitting

diodes (LED) emitting light at 625 nm (Luxeon LXHL-ND98) were used as probe lights, and their output intensities were modulated by a digital function generator (NF DF1905) at 80 Hz. In addition to the modulated light, a UV-LED (Nichia NCCU033, emitting light at 365 nm,  $2.5 \text{ mW cm}^{-2}$ ) and a blue-LED (Luxeon LXHL-NB98, emitting light at 470 nm,  $8.1 \text{ mW cm}^{-2}$ ) were also used as simultaneous continuous irradiation sources for photoexcitation of  $\text{M}^{n+}/\text{TiO}_2$ . The PA signal acquired by a condenser microphone buried in the cell was amplified and monitored by a digital lock-in amplifier (NF LI5640). Detailed setups for the double-beam photoacoustic (DB-PA) spectroscopic measurements have been reported. [13]

### **3. Results and discussion**

#### *3.1 Characterization of $\text{TiO}_2$ loaded with metal ions*

Figure 1 shows diffuse refraction spectra of bare  $\text{TiO}_2$  and of metal ion-adsorbed S-doped  $\text{TiO}_2$  samples. All of the metal ion-adsorbed S-doped  $\text{TiO}_2$  samples showed a red shift of the absorption edge, but absorption in the visible region depended on the kind of metal ion ( $\text{Rh}^{3+} > \text{Fe}^{3+} > \text{Cr}^{3+} \sim \text{Ni}^{2+} > \text{Cu}^{2+}$  at 430 nm).

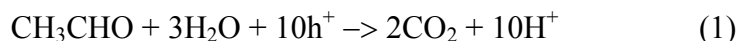
The chemical state of the metal atoms adsorbed on S-doped TiO<sub>2</sub> was assigned as follows by XPS spectra: Rh, Ge, Cr = 3+. Cu, Ni, Co = 2+.

### *3.2 Photocatalytic reaction of metal ion-adsorbed TiO<sub>2</sub> samples under photoirradiation*

Figure 2 shows the time course of CO<sub>2</sub> evolution as a result of acetaldehyde decomposition under photoirradiation at wavelengths longer than 350 nm. S-doped TiO<sub>2</sub> adsorbed with metal ions showed a higher level of photocatalytic activity than that of S-doped TiO<sub>2</sub> without metal loading. Photoexcited electrons were efficiently trapped by metal ions acting as electron acceptors adsorbed on the surfaces of S-doped TiO<sub>2</sub> particles, resulting in charge separation. [43,44] Consequently, isolated holes efficiently oxidized organic compounds adsorbed on the S-doped TiO<sub>2</sub> surface. Moreover, the activity depended on the kind of metal ion (Fe<sup>3+</sup> > Rh<sup>3+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Cr<sup>3+</sup>), and the order of their photocatalytic activity was related to the order of redox potential (Fe<sup>3+</sup>/Fe<sup>2+</sup> = 0.771 V, Rh<sup>3+</sup>/Rh = 0.758 V, Cu<sup>2+</sup>/Cu<sup>+</sup> = 0.159 V, Ni<sup>2+</sup>/Ni = -0.257 V, Co<sup>2+</sup>/Co = -0.272 V, Cr<sup>3+</sup>/Cr<sup>2+</sup> = -0.424 V vs. SHE). These results suggest that metal ions with more positive redox potentials are effective photoexcited electron acceptors for

enhancement of photocatalytic activity.

Complete decomposition of acetaldehyde was observed over S-doped TiO<sub>2</sub>- Fe<sup>3+</sup> after photoirradiation for 25 h, as shown in Fig. 2. The photocatalytic activity level of S-doped TiO<sub>2</sub>- Fe<sup>3+</sup> was 3-times higher than that of S-doped TiO<sub>2</sub> without treatment of Fe<sup>3+</sup>. When the total decomposition of 1-mol acetaldehyde is written as a reaction involving ten holes (eq. 1), this suggests that 26 μmol of excited electrons was consumed by Fe<sup>3+</sup> on the TiO<sub>2</sub> surface, the amount of which was 18 μmol.



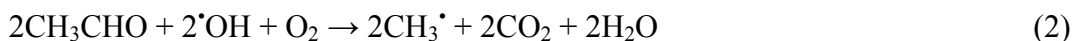
Thus, turnover number of Fe<sup>3+</sup> was more than ca. 1.5. This means that Fe<sup>2+</sup> reduced by excited electrons can be recovered to Fe<sup>3+</sup> by reacting with oxygen species (OS) [43,44]. Therefore, the rate of the recovering process is important for the enhancement of photocatalytic activity in a long reaction.

Figure 3 shows the CO<sub>2</sub> evolution over S-doped TiO<sub>2</sub>-M<sup>n+</sup> as a function of irradiation time under visible light irradiation at wavelengths longer than 440 nm. The photocatalytic activity level of Fe<sup>3+</sup>-adsorbed S-doped TiO<sub>2</sub> was about 7 times higher than that of pure S-doped TiO<sub>2</sub>. However, CO<sub>2</sub> evolution for most of the samples



showed a saturation tendency before reaching 1000-ppm CO<sub>2</sub> under photoirradiation for 25 h.

Nimlos et al. reported a reaction scheme for oxidation of acetaldehyde on TiO<sub>2</sub> photocatalysts. [47] CO<sub>2</sub> was directly evolved by the reaction between acetaldehyde and OH radicals generated photocatalytically. [47] According to a previous report [47], we assumed that reactions by two pathways occur: direct oxidation of acetaldehyde to CO<sub>2</sub> (2) and evolution of CO<sub>2</sub> by oxidation of acetaldehyde via acetic acid (3), (4).



Under visible light irradiation, evolution of CO<sub>2</sub> via route (2) proceeded efficiently over S-doped TiO<sub>2</sub>-M<sup>n+</sup>. At the same time, acetic acid was accumulated on the surface of S-doped TiO<sub>2</sub> according to route (3). As discussed above, acetic acid was thought to be hard to decompose on S-doped TiO<sub>2</sub> even when adsorbed with Fe<sup>3+</sup> ions, especially under visible light irradiation. Therefore, these saturation tendencies are due to accumulation of intermediate species that were not easily decomposed, e.g., acetic acid [44].

### 3.3. DB-PA spectra of S-doped TiO<sub>2</sub> loaded with metal ions under UV irradiation

The behavior of electron migration on TiO<sub>2</sub> particles under UV irradiation was observed using DB-PA spectroscopy. The PA intensity indicates the amount of Ti<sup>3+</sup> ions generated by photoexcited electrons [18,19]. If the photoexcited electrons do not transfer to molecules such as O<sub>2</sub> molecules adsorbed on the surface of TiO<sub>2</sub>, the electrons are trapped at Ti<sup>4+</sup> sites in TiO<sub>2</sub> and reduce Ti<sup>4+</sup> ions to Ti<sup>3+</sup> ions in the bulk of TiO<sub>2</sub> or on the surface of TiO<sub>2</sub>, resulting in an increase in PA intensity. PA measurements were carried out under aerated conditions in order to estimate the reactivity of electrons in S-doped TiO<sub>2</sub>-M<sup>n+</sup> particles. Figure 4 shows the time-course curves of PA signals of S-doped TiO<sub>2</sub> and S-doped TiO<sub>2</sub>-M<sup>n+</sup> particles under UV irradiation in the presence of air + EtOH. The PA intensity of all samples showed an increase under UV irradiation because Ti<sup>3+</sup> species were generated by accumulation of electrons on TiO<sub>2</sub>, as a counterpart of the hole consumption by EtOH (eq. 2)





After prolonged UV irradiation, the PA intensity leveled off because the reduction of  $Ti^{4+}$  by photoexcited electrons and the oxidation of  $Ti^{3+}$  by atmospheric oxygen reached equilibrium. The equilibrium values of the PA intensity of S-doped  $TiO_2$ -  $M^{n+}$  samples were greatly decreased compared to those of S-doped  $TiO_2$  without adsorbing any metal ions. These results suggested that metal ions adsorbed on S-doped  $TiO_2$  played an efficient role as electron acceptors (eq. 3). In addition, the electrons accumulated in metal ions efficiently transfer to atmospheric oxygen. However, only tiny differences in PA signal were observed among Rh, Cu, Cr, and Fe ions in DB-PA measurements (Fig. 4), though an appreciable difference was seen in photocatalytic evaluation (Fig. 3). DB-PA experiments were carried out in the presence of EtOH instead of acetaldehyde under UV irradiation. Therefore, the difference in activity improvements by metal ions for oxidation of EtOH is quite small because EtOH is more easily oxidized compared to acetaldehyde. Acetic acid, which is difficult to oxidize, is accumulated as an intermediate compound during oxidation of acetaldehyde. [44]

These results suggest that the reoxidation rate of  $M^{(n-1)+}$  ions is much faster than the photoexcited electron capturing rate by  $M^{n+}$  ions adsorbed on S-doped  $TiO_2$  ( $k_3 > k_4$ ).

Only small PA intensity differences between pure S-doped  $TiO_2$  and S-doped  $TiO_2$  adsorbed with Co, Cr, or Ni ions were observed as shown in Fig. 4. One possible reason for this is that the rate of electron transfer from  $M^{(n-1)+}$  ions to OS is quite slow. Therefore, most of the metal ions adsorbed on S-doped  $TiO_2$  were reduced very quickly by trapping photoexcited electrons. Under this condition, the behavior of PA intensity is thought to approach the level of bare S-doped  $TiO_2$ .

#### *3.4. DB-PA spectra of S-doped $TiO_2$ loaded with metal ions under VIS irradiation*

Figure 5 shows PA signals of S-doped  $TiO_2$  and S-doped  $TiO_2-M^{n+}$  as a function of irradiation time under visible light irradiation in the presence of  $N_2 + EtOH$ . PA measurements were carried out under deaerated conditions in order to estimate the accumulations of electrons in  $TiO_2$  particles. The PA signal of S-doped  $TiO_2-M^{n+}$  increased even under photoirradiation of ca. 470 nm and was much larger than that of S-doped  $TiO_2$ . These results suggest that metal ions absorbed visible light of ca. 470 nm

to generate excited states. The excited states of metal ions injected electrons into the S-doped TiO<sub>2</sub>, resulting in reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>. In addition, photoexcitation of metal ions adsorbed on the outside surface of S-doped TiO<sub>2</sub> occurred preferentially compared to that of S-doped TiO<sub>2</sub> under visible light irradiation. The mechanism of Ti<sup>3+</sup> generation can be explained in detail as follows: (1) photoexcited metal ions injected electrons into TiO<sub>2</sub> and the metal ions reached an oxidized state (M<sup>(n+1)+</sup>); (2) the injected electrons reduced Ti<sup>4+</sup> to Ti<sup>3+</sup>; and (3) the oxidized state of metal ions (M<sup>(n+1)+</sup>) resulted in oxidation of EtOH to recover the initial state of metal ions (M<sup>n+</sup>).

The amount **s** of injected electrons estimated from DB-PA measurements (Ni<sup>2+</sup> > Rh<sup>3+</sup> > Cu<sup>2+</sup> > Fe<sup>3+</sup> > Cr<sup>3+</sup> > Co<sup>2+</sup>) did not show any relationship with photocatalytic activity as shown in Fig. 3 (Fe<sup>3+</sup> > Rh<sup>3+</sup> > Cu<sup>2+</sup> ≈ Ni<sup>2+</sup> ≈ Co<sup>2+</sup> ≈ Cr<sup>3+</sup>). They also have no relationship with photoabsorption properties as shown in Fig. 1 (Rh<sup>3+</sup> > Fe<sup>3+</sup> Cu<sup>2+</sup> ≈ Ni<sup>2+</sup> ≈ Co<sup>2+</sup> at 470 nm). The excited states of metal ions resulted in injection of electrons into S-doped TiO<sub>2</sub> during visible light irradiation. The oxidized metal ions oxidize acetaldehyde to recover the initial state of metal ions. At the same time, electrons injected by metal ions in the excited state were transferred to the ground state of metal

ions adsorbed on the dark sites of S-doped TiO<sub>2</sub>. In addition, the electrons accumulated in metal ions transferred to OS, resulting in recovery of the initial state of metal ions. However, the efficiency of transfer of accumulated electrons in S-doped TiO<sub>2</sub> to OS via metal ions adsorbed on the surface of S-doped TiO<sub>2</sub> is dependent on the kind of metal ion. When the efficiency is low, the PA intensity, which reflects the electrons accumulated in TiO<sub>2</sub>, remains high. PA intensity is reduced to a rather low level if the electrons in metal ions efficiently transfer to OS. In order to elucidate the behavior of electrons in metal ions, DB-PA measurements were also carried out under aerated conditions. Under these conditions, the efficiency of transfer of accumulated electrons in S-doped TiO<sub>2</sub> to oxygen via metal ions on S-doped TiO<sub>2</sub> was evaluated, and the results are shown in Fig. 6. Among the metal ions, PA intensity values of Fe and Rh drastically decreased because the electrons accumulated in metal ions efficiently transfer to oxygen, while no PA intensity change was observed in the case of Ni ions. This indicates that Fe and Rh ions play two roles, as a photosensitizer and as an electron acceptor; they worked as an electron capturer and an electron releaser to oxygen. On the other hand, Ni ions act only as a photosensitizer, resulting in accumulation of photoexcited electrons in S-doped TiO<sub>2</sub>.

Under this condition, the photocatalytic reaction is gradually slowed down, as shown in Fig. 3.

A typical reaction mechanism for degradation of organic compounds over S-doped TiO<sub>2</sub> adsorbed with metal cations under UV or VIS light irradiation is shown in Scheme 1.

## **Conclusions**

We successfully developed visible light-sensitive rutile S-doped TiO<sub>2</sub> adsorbed with metal ions. Diffuse reflectance spectra showed that the absorption edge of S-doped TiO<sub>2</sub> was shifted to a longer wavelength after doping treatment. Photoabsorption of S-doped TiO<sub>2</sub> in the visible region increased with adsorbing treatment of metal ions on S-doped TiO<sub>2</sub> due to absorption in the visible region of metal ion complexes. S-doped TiO<sub>2</sub> having rutile phase showed a photocatalytic activity for oxidation of acetaldehyde under a wide range of irradiation light including UV and VIS light. The photocatalytic activity of S-doped TiO<sub>2</sub> adsorbed with metal ions was remarkably improved. The

improvement of photocatalytic activity is dependent on the kind of metal ion. Under UV light irradiation at wavelengths longer than 350 nm, Fe-adsorbed S-doped TiO<sub>2</sub> showed the highest level of photocatalytic activity because Fe<sup>3+</sup> ions adsorbed on S-doped TiO<sub>2</sub> efficiently trapped the photoexcited electrons, resulting in an increase in efficiency of charge separation. The order of efficiency of metal ions for photocatalytic activity improvement is as follows: Fe<sup>3+</sup> > Rh<sup>3+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Cr<sup>3+</sup>. The tendency is related to their redox potentials (Fe<sup>3+</sup>/Fe<sup>2+</sup> = 0.771 V, Rh<sup>3+</sup>/Rh = 0.758 V, Cu<sup>2+</sup>/Cu<sup>+</sup> = 0.159 V, Ni<sup>2+</sup>/Ni = -0.257 V, Co<sup>2+</sup>/Co = -0.272 V, Cr<sup>3+</sup>/Cr<sup>2+</sup> = -0.424 V vs. SHE).

On the other hand, under visible light irradiation at wavelengths longer than 420 nm, Fe-adsorbed S-doped TiO<sub>2</sub> also showed the highest level of photocatalytic activity because the excited state of Fe<sup>3+</sup> ions resulted in efficient injection of S-doped TiO<sub>2</sub>. In addition, electrons injected into S-doped TiO<sub>2</sub> were quickly trapped by Fe<sup>3+</sup>, and the trapped electrons efficiently transferred to OS such as oxygen under aerated conditions.

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## Figure captions

Figure 1. Diffuse reflectance spectra of pure TiO<sub>2</sub> having rutile phase, S-doped TiO<sub>2</sub> and S-doped TiO<sub>2</sub> samples adsorbed with metal ions (a); and magnified version of Figure 1 (a) at the range between 0 and 0.4 in absorbance (b).

Figure 2. Amount of CO<sub>2</sub> evolved by oxidation of acetaldehyde over pure S-doped TiO<sub>2</sub> and S-doped TNT samples loaded with metal ions as a function of photoirradiation time under UV light irradiation at wavelengths longer than 350 nm.

Figure 3. Amount of CO<sub>2</sub> evolved by oxidation of acetaldehyde over pure S-doped TiO<sub>2</sub> and S-doped TiO<sub>2</sub> samples adsorbed with metal ions as a function of photoirradiation time under VIS light irradiation at wavelengths longer than 440 nm.

Figure 4. PA spectra of pure S-doped TiO<sub>2</sub> and S-doped TiO<sub>2</sub> samples adsorbed with metal ions at the incident light of center wavelength at 365 nm under aerated conditions.

Figure 5. PA spectra of pure S-doped TiO<sub>2</sub> and S-doped TiO<sub>2</sub> samples adsorbed with metal ions at the incident light of center wavelength at 470 nm under nitrogen atmosphere.

Figure 6. PA spectra of pure S-doped TiO<sub>2</sub> and S-doped TiO<sub>2</sub> samples adsorbed with metal ions at the incident light of center wavelength at 470 nm under aerated conditions.

Scheme 1. Reaction mechanism for degradation of organic compounds over S-doped TiO<sub>2</sub> adsorbed with metal cations under UV or VIS light irradiation.



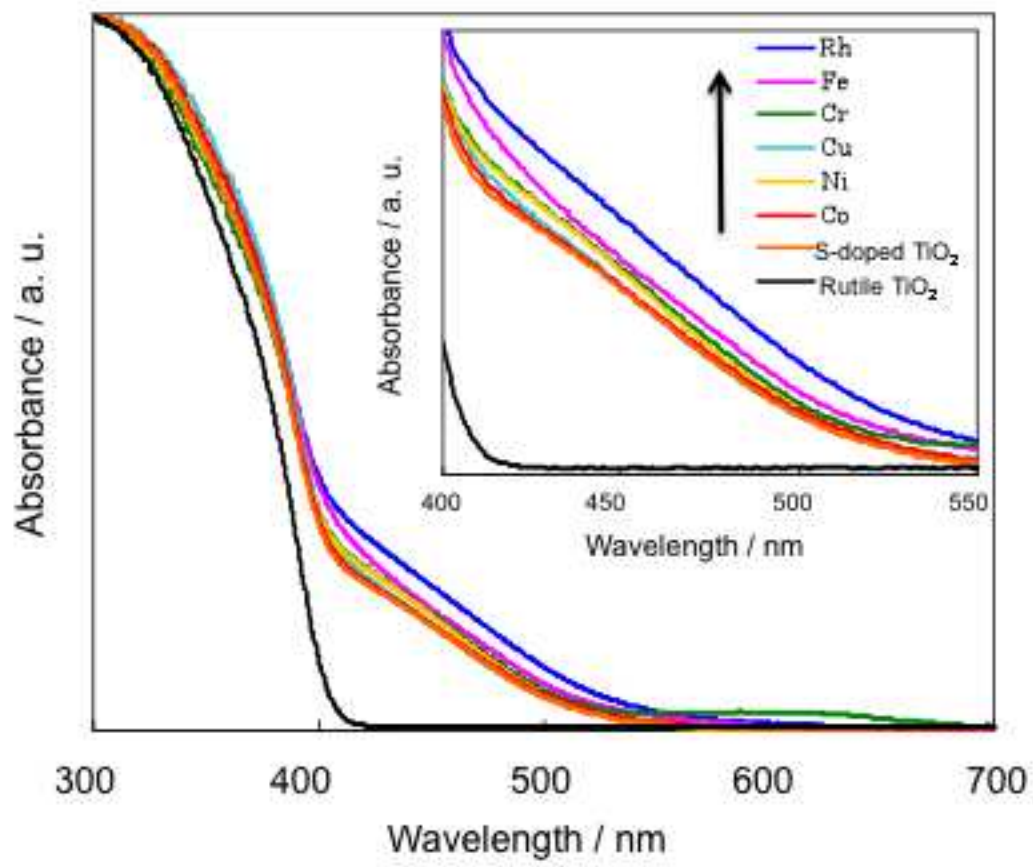


Figure 1. T. Ohno et al.

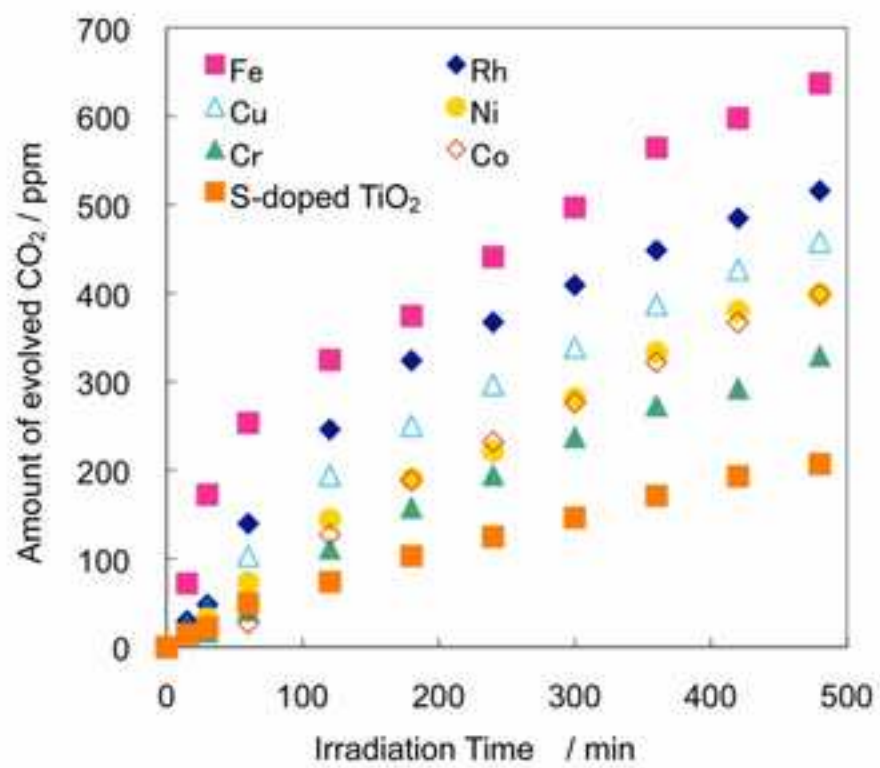


Fig. 2. T. Ohno et al.

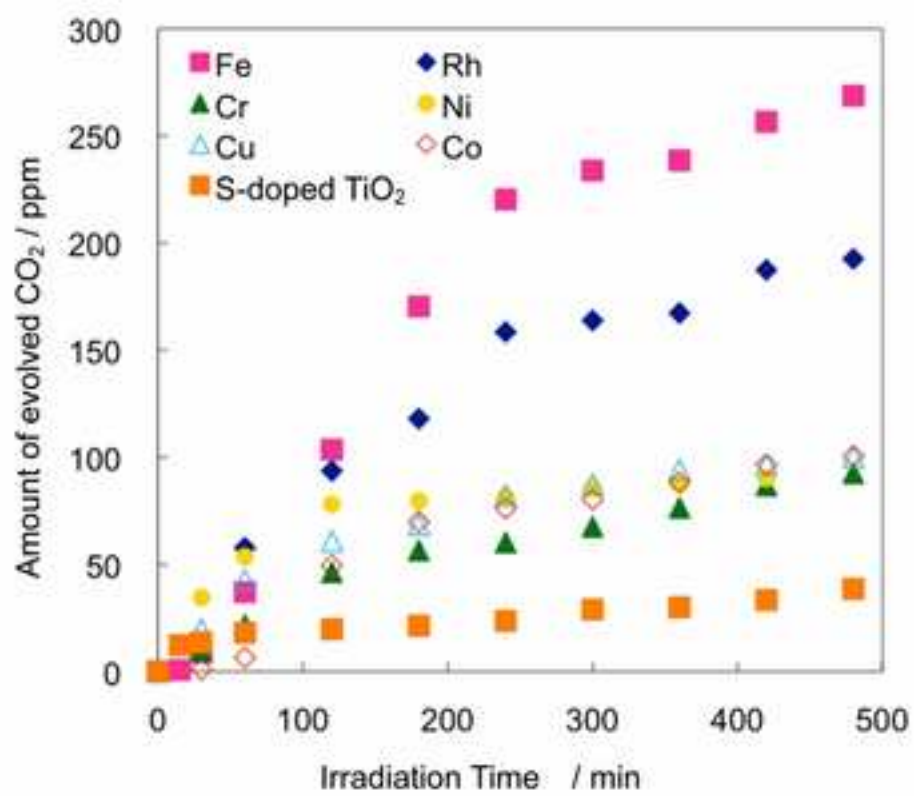


Fig. 3. T. Ohno et al.

Figure(s)

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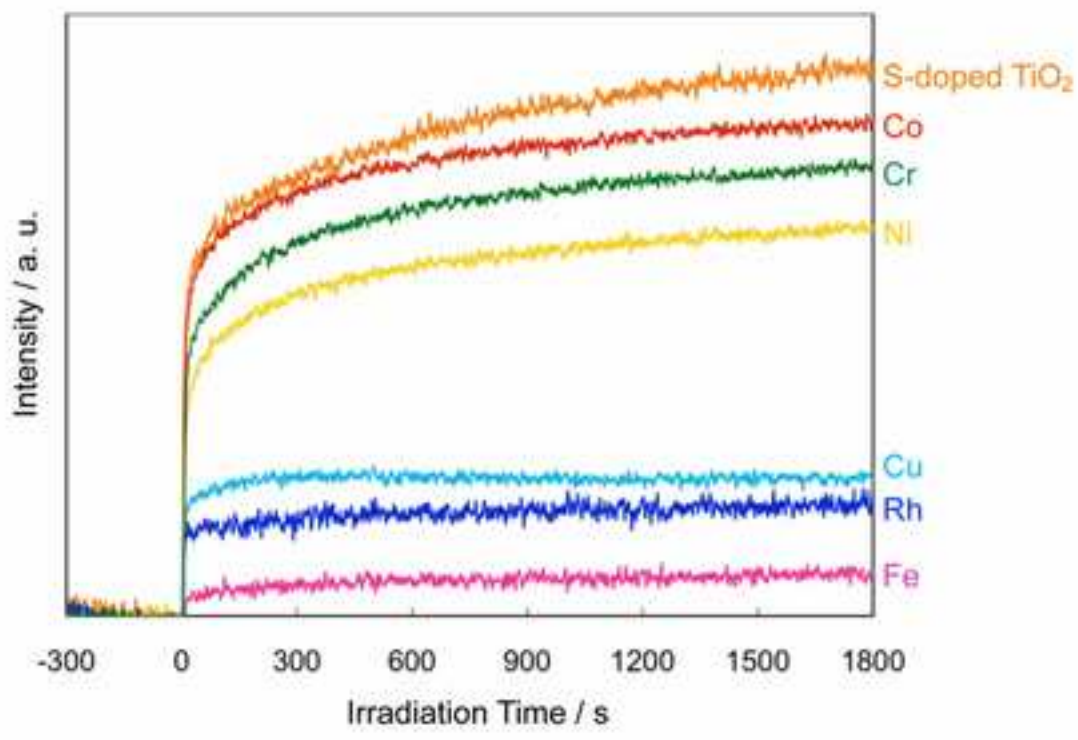


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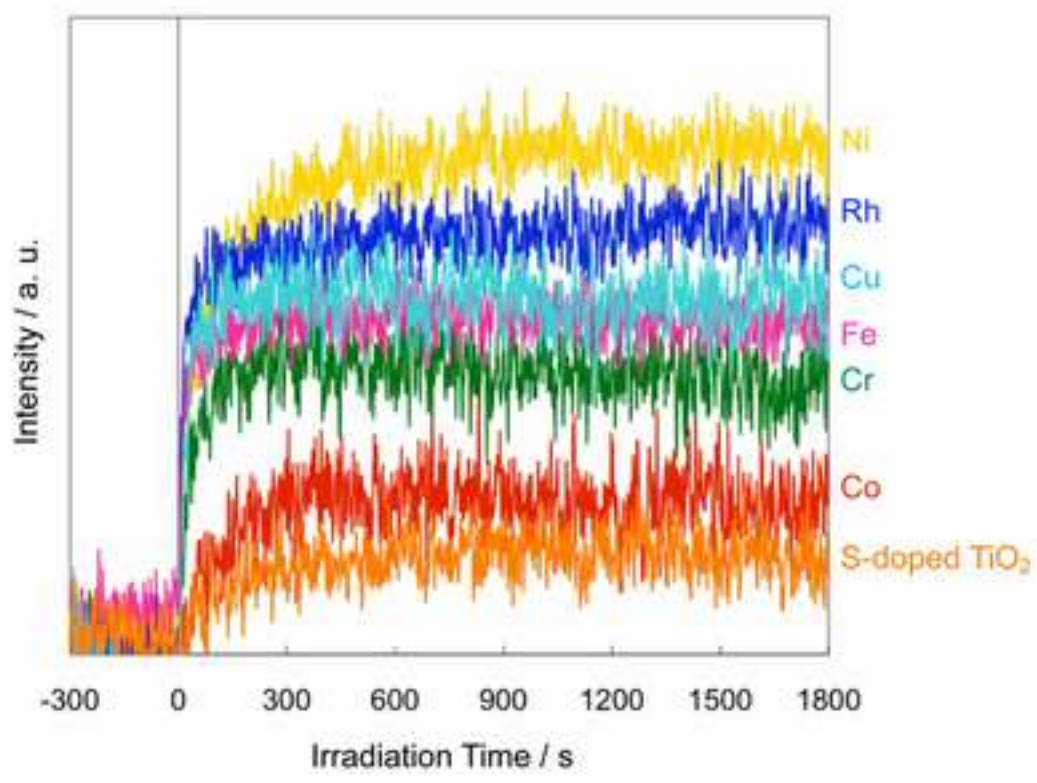


Fig. 5. T. Ohno et al.

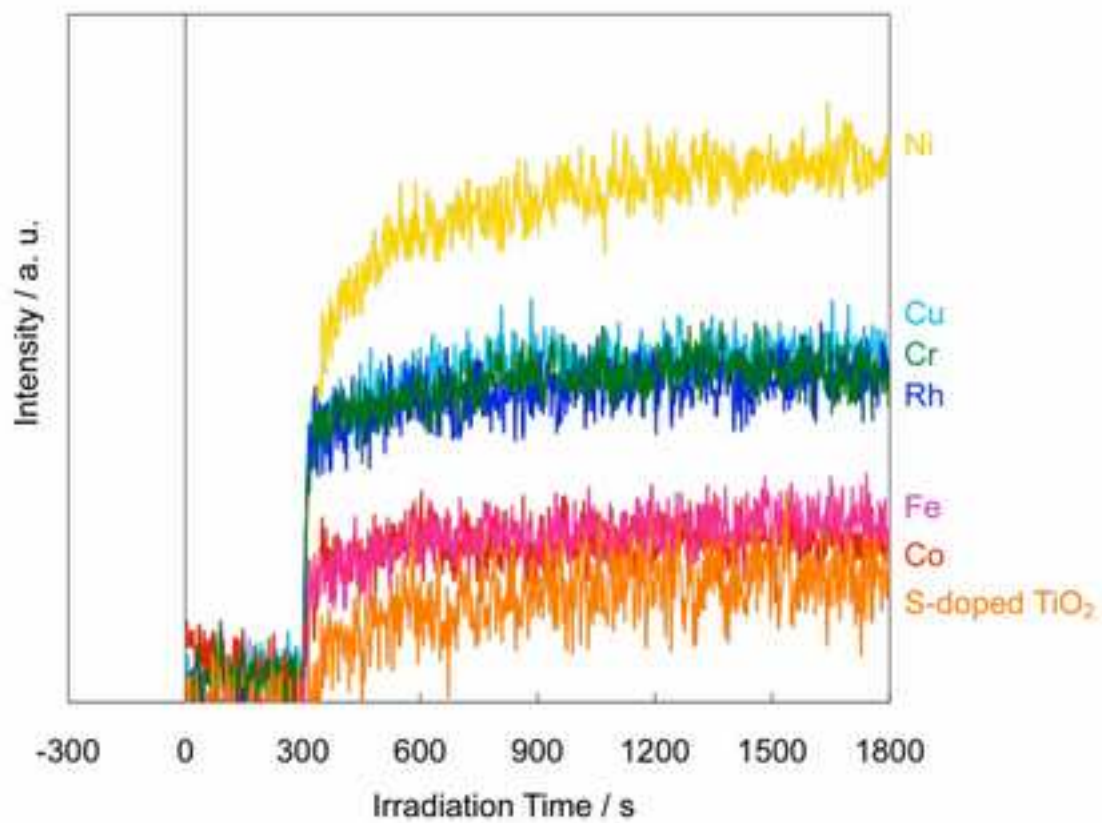


Fig. 6. T. Ohno et al.

