

## Research Article

# Photocatalytic Hydrogen or Oxygen Evolution from Water over S- or N-Doped TiO<sub>2</sub> under Visible Light

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S- or N-doping of TiO<sub>2</sub> powder having an anatase or rutile phase extended the photocatalytic activity for water oxidation and reduction under UV light and visible light irradiation. For the reduction of water, anatase-doped TiO<sub>2</sub> showed higher level of activity than that of doped TiO<sub>2</sub> having a rutile phase using ethanol as an electron donor. Furthermore, the activity level of S-doped TiO<sub>2</sub> for hydrogen evolution was higher than that of N-doped TiO<sub>2</sub> photocatalysts under visible light. Photocatalytic oxidation of water on doped TiO<sub>2</sub> having a rutile phase proceeded with fairly high efficiency when Fe<sup>3+</sup> ions were used as electron acceptors compared to that on doped TiO<sub>2</sub> having an anatase phase. In addition, water splitting under visible light irradiation was achieved by construction of a Z-scheme photocatalysis system employing the doped TiO<sub>2</sub> having anatase and rutile phases for H<sub>2</sub> and O<sub>2</sub> evolution and the I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> redox couple as an electron relay.

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## 1. INTRODUCTION

Photocatalytic reactions on the surfaces of TiO<sub>2</sub> particles have been attracting much attention because of their possible application to the conversion of solar energy into chemical energy (water splitting) [1, 2] and to water purification from pollutants [3–5]. TiO<sub>2</sub> is chemically stable and nontoxic and it has a high oxidation power under photoirradiation. However, a high oxidation power of TiO<sub>2</sub> is only shown under UV light, which is a great disadvantage for practical application. Therefore, the development of a TiO<sub>2</sub> photocatalyst that shows a high level of activity under visible light is needed.

N, S, or C anion-doped TiO<sub>2</sub> photocatalysts having an anatase phase that shows a relatively high level of activity under visible light irradiation have been reported [6–9]. Sakthivel and Kisch succeeded in preparing TiO<sub>2</sub> photocatalysts containing some carbon species that show photocatalytic activity under visible light [10]. We have also reported the preparation of S cation-doped TiO<sub>2</sub> having anatase and rutile phases and its photocatalytic activity for oxidation of organic compounds [11, 12]. The absorbance of S cation-doped TiO<sub>2</sub> in the visible region is larger than that of N, C, or S anion-

doped TiO<sub>2</sub>, and the photocatalytic activity level of S cation-doped TiO<sub>2</sub> for oxidation of organic compounds is relatively high under visible light compared to that of N, C, or S anion-doped TiO<sub>2</sub>. It should be noted that S atoms were incorporated into the lattice of TiO<sub>2</sub> as cations and were thought to be replaced by Ti ions in the case of S cation-doped TiO<sub>2</sub>.

Among the chemical reactions suitable for energy conversion is the decomposition of water, because the change in Gibbs energy is large. Hence, there have been many attempts to achieve photodecomposition of water using semiconductor particles such as TiO<sub>2</sub> [13], SrTiO<sub>3</sub> [14], and K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> [15].

Abe et al. developed a water-splitting system by combining two photocatalytic systems including oxidation of water and reduction of water systems under visible light [16]. However, the efficiency of each system (hydrogen-evolving and oxygen-evolving systems) is not sufficient for application to a practical system. The aim of our study was to establish effective oxygen- and hydrogen-evolving systems. In this paper, we report the photocatalytic activities of S-doped or N-doped TiO<sub>2</sub> for reduction of water into molecular hydrogen and oxidation of water into molecular oxygen under visible

light using ethanol and  $\text{Fe}^{3+}$  ions as electron donors and electron acceptors, respectively.

## 2. EXPERIMENTAL

### 2.1. Materials and instruments

Various kinds of  $\text{TiO}_2$  powders having anatase and rutile crystal structures were obtained from the Catalysis Society of Japan (TIO-3), Ishihara Sangyo (ST-01), TAYCA Corporation (MT-150A), and Toho Titanium Co. (NS-51). The contents of anatase and the surface areas of these powders were as follows: ST-01: 100%,  $320.5 \text{ m}^2/\text{g}$ ; MT-150A: 0%,  $81.5 \text{ m}^2/\text{g}$ ; TIO-3: 0%,  $48.1 \text{ m}^2/\text{g}$ ; NS-51: 1.0%,  $6.5 \text{ m}^2/\text{g}$ . Ethanol,  $\text{FeCl}_3$ , thiourea, and urea were obtained from Wako Pure Chemical Industry. Other chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification. The crystal structures of  $\text{TiO}_2$  powders were determined from X-ray diffraction (XRD) patterns measured with an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target  $\text{K}\alpha$ -ray ( $\lambda = 1.5405 \text{ \AA}$ ). The relative surface areas of the powders were determined by  $\text{N}_2$  adsorption/desorption isotherm analysis (BET method). The measurements were performed using 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  $\text{TiO}_2$  powders were measured using a JEOL JPS90SX photoelectron spectrometer with an Mg  $\text{K}\alpha$  source ( $1253.6 \text{ eV}$ ). The shift of binding energy due to relative surface charging was corrected using the C 1s level at  $284.6 \text{ eV}$  as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a nonlinear least-squares procedure after proper subtraction of the baseline.

### 2.2. Preparation of S- or N-doped $\text{TiO}_2$ powders

S- or N-doped  $\text{TiO}_2$  powders were synthesized by previously reported methods [11, 12, 17–19].

S- or N-doped  $\text{TiO}_2$  powders having a rutile or anatase phase were prepared as follows. Thiourea (for S doping) or urea (for N doping) was mixed with various kinds of  $\text{TiO}_2$  powders having an anatase or rutile phase in an agate mortar. The mixed powder was packed in an alumina crucible and calcined at  $400\text{--}600^\circ\text{C}$  under air atmosphere for 3 hours. After calcination, the powder was washed with distilled water. The resulting samples were yellow in color and were found to have a homogenous anatase or rutile phase from XRD analysis. For  $\text{TiO}_2$  powder calcined at a temperature higher than  $600^\circ\text{C}$ , no absorbance in the visible region was observed. The surface areas of S-doped and N-doped  $\text{TiO}_2$  powders having an anatase phase (ST-01) calcined at  $400^\circ\text{C}$  were  $120 \text{ m}^2/\text{g}$  and  $90 \text{ m}^2/\text{g}$ , respectively. The surface areas of S-doped  $\text{TiO}_2$  powders having a rutile phase (MT-150A, TIO-3, and NS-51) calcined at  $500^\circ\text{C}$  were  $52.5 \text{ m}^2/\text{g}$ ,  $32.2 \text{ m}^2/\text{g}$ , and  $5.4 \text{ m}^2/\text{g}$ , respectively. The surface areas of N-doped  $\text{TiO}_2$  powders having a rutile phase (TIO-3 and NS-51) calcined at  $600^\circ\text{C}$  were  $26.3 \text{ m}^2/\text{g}$  and  $4.9 \text{ m}^2/\text{g}$ , respectively. The relative sur-

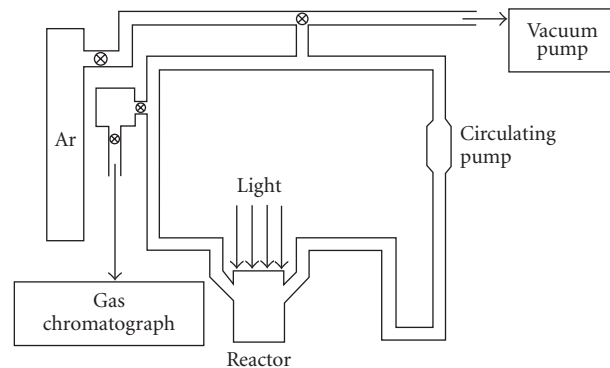


FIGURE 1: Schematic diagram of the closed gas circulating system.

face area decreased with increase in the calcination temperature.

### 2.3. Preparation of Pt-loaded $\text{TiO}_2$ photocatalysts for hydrogen evolution

Pt-loaded  $\text{TiO}_2$  powders were prepared by a photochemical deposition method. The doped  $\text{TiO}_2$  photocatalyst was stirred in a 5% ethanol aqueous solution containing  $\text{H}_2\text{PtCl}_6$  and irradiated by a 500 W high-pressure Hg lamp ( $2 \text{ mW}/\text{cm}^2$ ) for 12 hours. Photoreduction of  $\text{H}_2\text{PtCl}_6$  took place, and highly dispersed Pt metal particles were deposited on the surface of the photocatalyst. After filtrating and washing by deionized water, the powder was dried at  $100^\circ\text{C}$  for 2 hours under reduced pressure to remove the ethanol adsorbed on the surface of the photocatalyst.

### 2.4. Photocatalytic reaction

The photocatalytic reactions were carried out using a closed gas-circulating system (Figure 1). The reaction under a wide range of incident light including UV and visible light was performed using a quartz glass-made outer irradiation type reactor. Irradiation to the aqueous suspension of a catalyst was carried out from outside the reactor using a 500 W xenon lamp (USHIO Co. Ltd., SXUI-501XQ) for  $\text{H}_2$  evolution and  $\text{O}_2$  evolution. To limit the irradiation wavelength, the light beam was passed through a UV-35, L-39, or L-42 filter (Kenko Co.) to cut off wavelengths shorter than 350, 390, or 420 nm, respectively. The irradiance of irradiation light was adjusted to  $340 \text{ mW}/\text{cm}^2$ . The photocatalyst powder ( $0.3 \text{ g}$ ) was suspended in distilled water using a magnetic stirrer. S- or N-doped  $\text{TiO}_2$  having anatase phase (ST-01) was used for hydrogen evolution, and S- or N-doped  $\text{TiO}_2$  having rutile phase (NS-51) was used for oxygen evolution. The required amount of sacrificial reagent ethanol for hydrogen evolution and  $\text{Fe}^{3+}$  for oxygen evolution was added to the suspension. The pH of the solution containing  $\text{Fe}^{3+}$  ions was adjusted to 2.4 using 1 M HCl aqueous solution in order to prevent formation of  $\text{Fe}(\text{OH})_3$ .

In the case of water splitting in the two-step redox system, a 500 W high-pressure mercury lamp (USHIO Co. Ltd., SX-U1501HQ) was used as a light source. The Hg lamp has

emission line spectrum with peaks at 314, 365, 405, and 436 nm. To limit the irradiation wavelength, the light beam was passed through a UV-35 or L-39 filter (Kenko Co.) to cut off wavelengths shorter than 350 or 390 nm, respectively. A mixture (0.3 g) of S-doped TiO<sub>2</sub> powder having anatase phase (ST-01) and S-doped TiO<sub>2</sub> powder rutile phase (NS-51) which weight ratio was 1 : 1 was suspended in distilled water. The required amount of solute, such as NaI, was added to the suspension. I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> ions were used as a redox couple [16]. The pH of the solutions was adjusted to 9 using 1 M NaOH aqueous solution in order to prevent generation of I<sub>3</sub><sup>-</sup> ions [16].

Finally, the suspension was thoroughly degassed and then argon gas (35 Torr) was introduced into the system and the system was exposed to irradiation. Evolved H<sub>2</sub> or O<sub>2</sub> gases were analyzed by online gas chromatography (TCD, molecular sieve 5 A).

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Physical properties of S-doped and N-doped TiO<sub>2</sub>

Diffuse reflectance spectra for the obtained S-doped TiO<sub>2</sub> and N-doped TiO<sub>2</sub> are shown in Figure 2. All doped TiO<sub>2</sub> powders showed absorption in the visible region. Photoabsorption in the visible region of the doped TiO<sub>2</sub> having an anatase phase was stronger than that of the doped TiO<sub>2</sub> having a rutile phase. The TiO<sub>2</sub> having a rutile phase was hardly doped by S atoms or N atoms because the rutile phase has a smaller surface area and more stable crystal structure than those of the anatase phase. The absorption band edge of S-doped TiO<sub>2</sub> shifted to a longer wavelength than that of N-doped TiO<sub>2</sub>. The band gap energies of S-doped TiO<sub>2</sub> and N-doped TiO<sub>2</sub> can be estimated from the tangent lines in the plot of the square root of the Kubelka-Munk functions against the photon energy [20], as shown in the insert to Figure 2. The band gap energies were estimated to be 2.28 eV (S-doped TiO<sub>2</sub> having an anatase phase), 2.58 eV (N-doped TiO<sub>2</sub> having an anatase phase), 2.34 eV (S-doped TiO<sub>2</sub> having a rutile phase), and 2.94 eV (N-doped TiO<sub>2</sub> having a rutile phase).

The chemical states of S atoms or N atoms incorporated into TiO<sub>2</sub> were studied by measuring the XPS spectra of the S-doped TiO<sub>2</sub> or N-doped TiO<sub>2</sub>. Figure 3(a) shows the S2p<sub>3/2</sub> spectrum of S-doped TiO<sub>2</sub>. As shown in Figure 3(a), a strong peak around 168 eV was observed. This peak is thought to consist of several oxidation states of S atoms such as S<sup>6+</sup> and S<sup>4+</sup> states [11, 12]. Figure 3(b) shows the N 1s spectrum of N-doped TiO<sub>2</sub>. Two peaks around 396 eV and 399 eV were observed. The peak around 396 eV was assigned to N atoms forming Ti–N bonds, and the peak around 399 eV was assigned to N<sub>2</sub> molecules adsorbed on the TiO<sub>2</sub> surface [17].

#### 3.2. Selective water oxidation over doped TiO<sub>2</sub> photocatalysts in an aqueous solution containing Fe<sup>3+</sup> ions

We investigated photocatalytic reduction of water into H<sub>2</sub> or oxidation of water into O<sub>2</sub> over various semiconductor

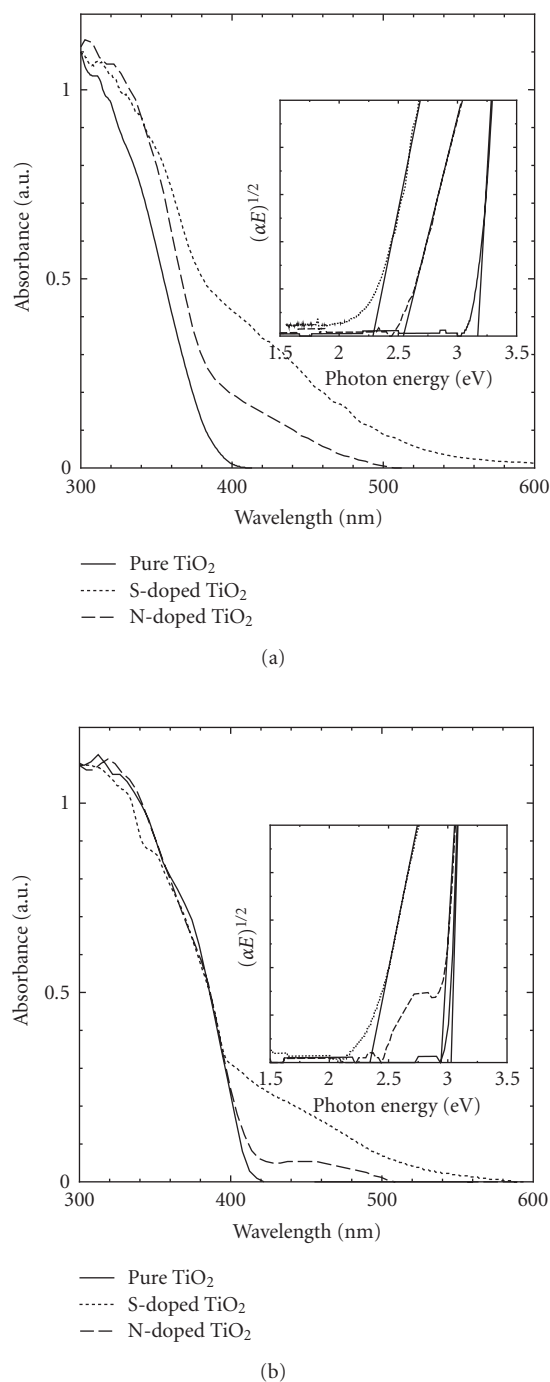
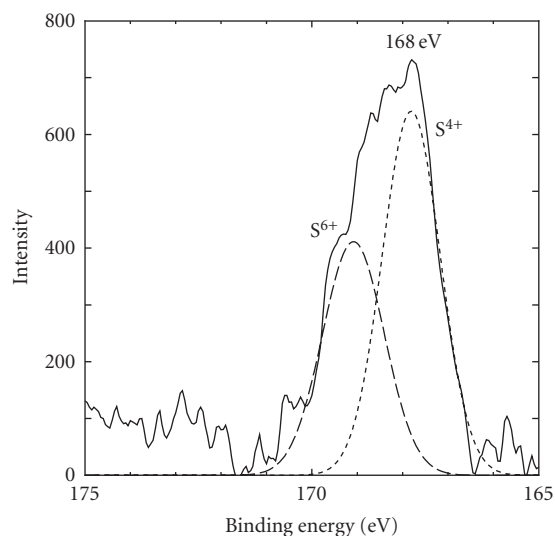
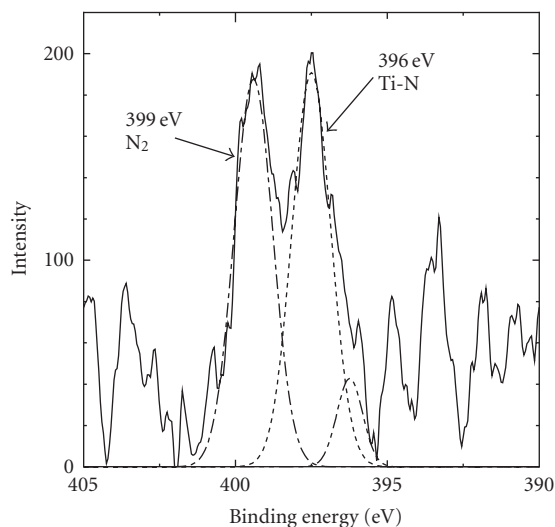


FIGURE 2: Diffuse reflectance spectra for the obtained S-doped TiO<sub>2</sub> and N-doped TiO<sub>2</sub> having an anatase or rutile phase. (a) TiO<sub>2</sub> having an anatase phase (ST-01), (b) TiO<sub>2</sub> having a rutile phase (NS-51).

photocatalysts in an aqueous solution containing an electron donor or an electron acceptor. In most cases, the reactions readily terminated when the concentration of the product in the solution reached a certain level because of the backward reactions. However, we found that efficient and selective O<sub>2</sub> evolution proceeded over TiO<sub>2</sub> photocatalysts having a rutile



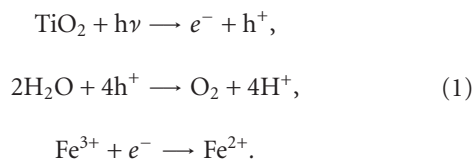
(a)



(b)

FIGURE 3: XPS spectra of S-doped TiO<sub>2</sub> and N-doped TiO<sub>2</sub>. (a) S-doped TiO<sub>2</sub>, (b) N-doped TiO<sub>2</sub>.

phase in the aqueous solution (pH < 3) containing Fe<sup>3+</sup> ions as electron acceptors with the following reactions [21]:



The optimized concentration of Fe<sup>3+</sup> ions was 2 mmol/L. The rate of oxygen evolution was lowered by raising the concentrations of Fe<sup>3+</sup> ions owing to a filter effect of the solution

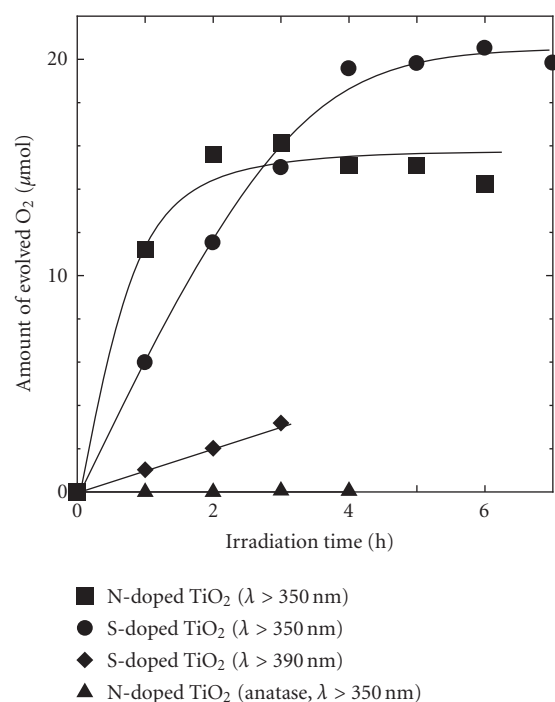


FIGURE 4: Amount of evolved O<sub>2</sub> from water containing Fe<sup>3+</sup> ions as electron acceptors on S-doped TiO<sub>2</sub> having rutile phase (NS-51), N-doped TiO<sub>2</sub> having rutile phase (NS-51), and N-doped TiO<sub>2</sub> having anatase phase (ST-01).

at a high concentration [21]. Excess Fe<sup>3+</sup> ions decreased rate of evolved oxygen because Fe<sup>3+</sup> aqueous solution has absorption in visible light region. Figure 4 shows the amounts of evolved O<sub>2</sub> over S- or N-doped TiO<sub>2</sub> having rutile phase (NS-51) and N-doped TiO<sub>2</sub> having anatase phase (ST-01) from water containing Fe<sup>3+</sup> ions as electron acceptors. The photocatalytic activity level of S-doped TiO<sub>2</sub> for water oxidation was higher than that of N-doped TiO<sub>2</sub>. However, the amounts of evolved O<sub>2</sub> on S- or N-doped TiO<sub>2</sub> did not agree with concentration of Fe<sup>3+</sup> ions. The backward reaction, oxidation of Fe<sup>2+</sup> ions with holes, was thought to proceed. S-doped TiO<sub>2</sub> showed photoinduced oxidation of water under visible light irradiation at wavelengths longer than 390 nm. Photocatalytic oxidation of water on doped TiO<sub>2</sub> having a rutile phase proceeded with a fairly high efficiency compared to that on doped TiO<sub>2</sub> having an anatase phase as shown in Figure 4. This result suggested that the activity for the evolution of O<sub>2</sub> from H<sub>2</sub>O is dependent on the particle size of doped TiO<sub>2</sub> powders. On anatase particles with a large surface area, decomposition of pollutants in air and water proceeds efficiently [4, 5]. In these reactions, the large surface area is especially important, because the concentrations of the pollutants are usually very low. On the other hand, for splitting water, which is an important reaction to convert light energy into chemical energy, rutile particles with a small surface area are efficient [21–23]. In this case, a band bending should be developed in each particle to oxidize water, and hence large particles are advantageous.

### 3.3. Selective water reduction over doped TiO<sub>2</sub> photocatalysts deposited with Pt in an aqueous solution containing ethanol

H<sub>2</sub> evolution from water containing ethanol as a sacrificial reagent proceeded over platinized TiO<sub>2</sub> having an anatase phase under UV and visible light irradiation. To improve the rate of H<sub>2</sub> evolution on doped TiO<sub>2</sub>, Pt was deposited on the TiO<sub>2</sub> surface. The optimized amount of Pt deposited on the surface of TiO<sub>2</sub> was 0.5 wt%. Deposition of an excess amount of Pt (1.0 wt%) decreased photocatalytic activity because aggregated Pt particles on the TiO<sub>2</sub> surface prevented the TiO<sub>2</sub> photocatalyst from absorbing incident light or because TiO<sub>2</sub> surface active sites were covered with Pt particles. The reduction of water containing ethanol is as follows:

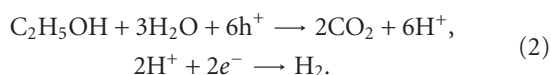


Figure 5 shows the amounts of evolved H<sub>2</sub> from water containing ethanol over S- or N-doped TiO<sub>2</sub> having anatase phase (ST-01) and S-doped TiO<sub>2</sub> having rutile phase (NS-51) under UV light irradiation. The amount of evolved H<sub>2</sub> on doped TiO<sub>2</sub> was smaller than that on pure TiO<sub>2</sub> because impurity level was formed by doping treatment. However, under visible light irradiation at wavelengths longer than 420 nm, the amount of evolved H<sub>2</sub> on doped TiO<sub>2</sub> was higher than that on pure TiO<sub>2</sub> as shown in Figure 5(b). S-doped TiO<sub>2</sub> showed a higher level of activity than that of N-doped TiO<sub>2</sub> for water reduction because S-doped TiO<sub>2</sub> showed higher photoabsorption than that of N-doped TiO<sub>2</sub> in the visible region as shown in Figure 2(a). Photocatalytic reduction of water on doped TiO<sub>2</sub> having an anatase phase proceeded with a fairly high efficiency compared to that on doped TiO<sub>2</sub> having a rutile phase as shown in Figure 5. This result suggested that the activity for the evolution of H<sub>2</sub> from H<sub>2</sub>O is dependent on the surface area of doped TiO<sub>2</sub> powder. Potential of the conduction band of anatase phase is at a more negative position than that of rutile phase. Therefore, the excited electrons easily transfer H<sup>+</sup> ions on the surface of TiO<sub>2</sub> having an anatase phase.

### 3.4. Water splitting over TiO<sub>2</sub> photocatalysts in an I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> shuttle redox-mediated system

Photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> was observed in a two-step redox system using an iodate/iodide redox mediator. In this system, we used Pt-loaded S-doped TiO<sub>2</sub> having an anatase phase (ST-01) for H<sub>2</sub> evolution and S-doped TiO<sub>2</sub> having a rutile phase (NS-51) for O<sub>2</sub> evolution under incident light including UV and visible light. Figure 6 shows the mechanism of the two-step redox system. On TiO<sub>2</sub> having an anatase phase, water is reduced to H<sub>2</sub> by photoexcited electrons and the iodide ions are oxidized to iodate ions by holes. The iodate ions are reduced to generate iodide ions by photoexcited electrons at the same time as water is oxidized to O<sub>2</sub> by holes on TiO<sub>2</sub> having a rutile phase. The optimized concentration of I<sup>-</sup> ions was 20 mmol/L. The oxidation products of I<sup>-</sup> ions were IO<sub>3</sub><sup>-</sup> and I<sub>3</sub><sup>-</sup>. An excess concentration of I<sup>-</sup>

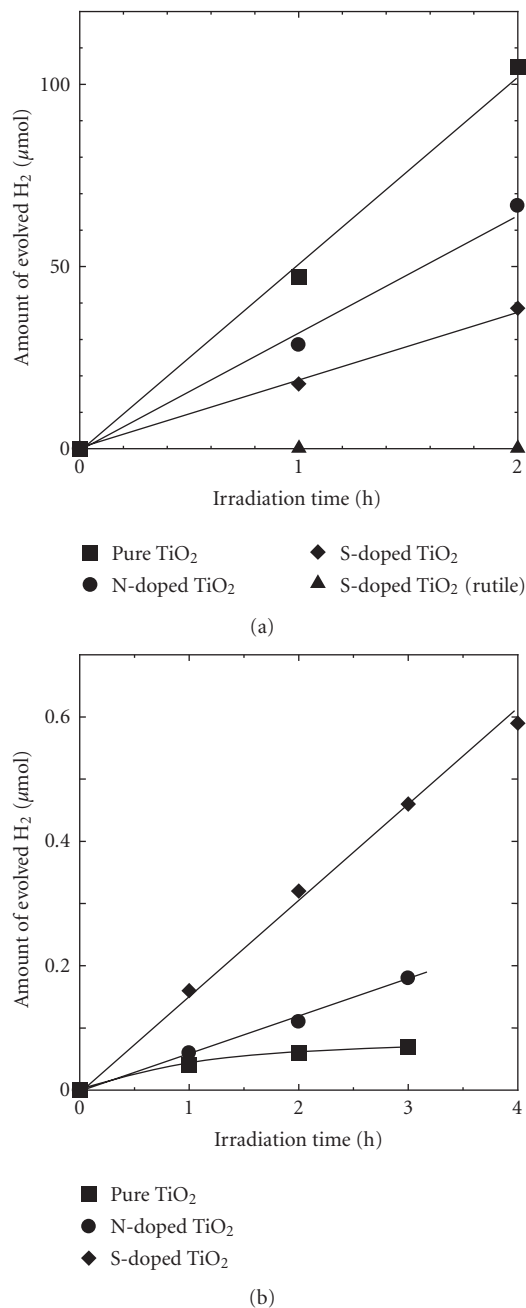
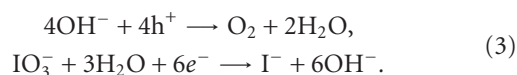


FIGURE 5: Amount of evolved H<sub>2</sub> from water containing ethanol as an electron donor on S- or N-doped TiO<sub>2</sub> (anatase phase: ST-01, rutile phase: NS-51) (a) under UV light irradiation at wavelengths longer than 350 nm or (b) under visible light irradiation at wavelengths longer than 420 nm.

ions resulted in I<sub>3</sub><sup>-</sup> generation. The accumulation of I<sub>3</sub><sup>-</sup> caused a light loss due to the strong absorption of I<sub>3</sub><sup>-</sup> around 350 nm, resulting in a lower efficiency of the photocatalytic reaction [16]. Reactions over a rutile phase are as follows:





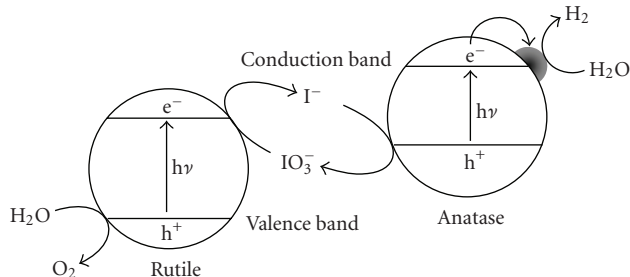


FIGURE 6: Mechanism for water splitting on  $\text{TiO}_2$  with an  $\text{I}^-/\text{IO}_3^-$  redox-mediator system.

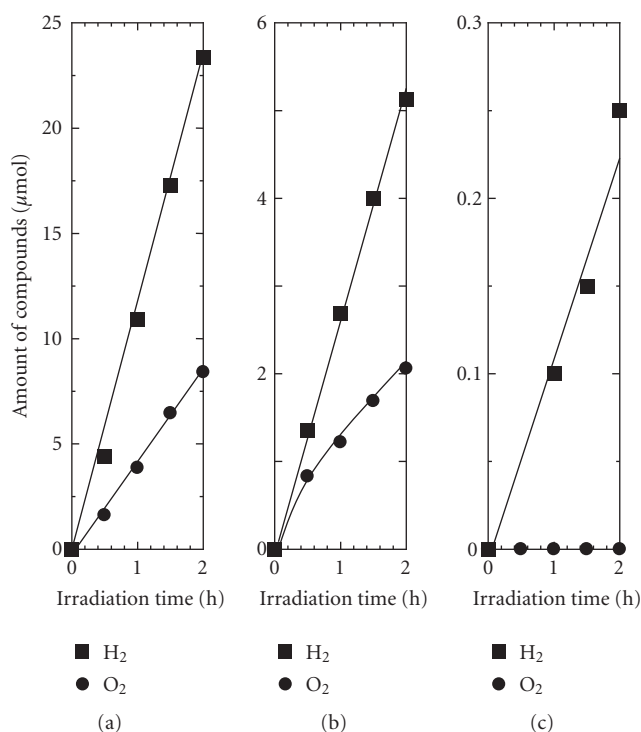
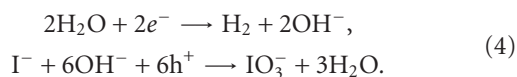


FIGURE 7: Amounts of evolved  $\text{H}_2$  and  $\text{O}_2$  from water containing  $\text{I}^-/\text{IO}_3^-$  redox on S-doped  $\text{TiO}_2$  powders having an anatase phase (ST-01) and a rutile phase (NS-51) under UV or visible light irradiation. (a) under UV light irradiation without a cutoff filter, (b) under UV light irradiation at wavelengths longer than 350 nm, (c) under visible light irradiation at wavelengths longer than 390 nm.

On the other hand, reactions over an anatase phase are as follows:



Amounts of evolved  $\text{H}_2$  and  $\text{O}_2$  in the two-step redox system under incident light including UV and visible light are shown in Figure 7. Under UV light irradiation without a cutoff filter and UV light irradiation at wavelengths longer 350 nm, both  $\text{H}_2$  and  $\text{O}_2$  evolved. However, the ratio of amount of evolved  $\text{H}_2$  to amount of evolved  $\text{O}_2$  was not 2 : 1.  $\text{O}_2$  molecules generated from water oxidation were

thought to adsorb on the  $\text{TiO}_2$  surface [24]. Under visible light irradiation at wavelengths longer than 390 nm, no  $\text{O}_2$  evolution was observed because the number of holes is not sufficient for  $\text{O}_2$  generation under low intensity of incident light. Under these circumstances, the intermediates generated by water oxidation were thought to be reduced by photoexcited electrons.

#### 4. CONCLUSION

$\text{H}_2$  evolution from water containing ethanol as an electron donor was performed on N- or S-doped  $\text{TiO}_2$  under visible light irradiation. An anatase  $\text{TiO}_2$  powder showed a higher level of activity than that of a rutile  $\text{TiO}_2$  powder. Oxidation of water containing  $\text{Fe}^{3+}$  ions as electron acceptors proceeded on doped  $\text{TiO}_2$  under UV and visible light irradiation. Water splitting was performed in an  $\text{I}^-/\text{IO}_3^-$  redox system on  $\text{TiO}_2$  having an anatase phase for  $\text{H}_2$  evolution and  $\text{TiO}_2$  having a rutile phase for  $\text{O}_2$  evolution. Under UV irradiation, both  $\text{H}_2$  and  $\text{O}_2$  were evolved, though the ratio of amount of evolved  $\text{H}_2$  to amount of evolved  $\text{O}_2$  was not 2 : 1.

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