

Research Article

Photocatalytic Hydrogen or Oxygen Evolution from Water over S- or N-Doped TiO₂ under Visible Light

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S- or N-doping of TiO₂ 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 TiO₂ showed higher level of activity than that of doped TiO₂ having a rutile phase using ethanol as an electron donor. Furthermore, the activity level of S-doped TiO₂ for hydrogen evolution was higher than that of N-doped TiO₂ photocatalysts under visible light. Photocatalytic oxidation of water on doped TiO₂ having a rutile phase proceeded with fairly high efficiency when Fe³⁺ ions were used as electron acceptors compared to that on doped TiO₂ 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 TiO₂ having anatase and rutile phases for H₂ and O₂ evolution and the I⁻/IO₃⁻ redox couple as an electron relay.

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1. INTRODUCTION

Photocatalytic reactions on the surfaces of TiO₂ 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]. TiO₂ is chemically stable and nontoxic and it has a high oxidation power under photoirradiation. However, a high oxidation power of TiO₂ is only shown under UV light, which is a great disadvantage for practical application. Therefore, the development of a TiO₂ photocatalyst that shows a high level of activity under visible light is needed.

N, S, or C anion-doped TiO₂ 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 TiO₂ photocatalysts containing some carbon species that show photocatalytic activity under visible light [10]. We have also reported the preparation of S cation-doped TiO₂ having anatase and rutile phases and its photocatalytic activity for oxidation of organic compounds [11, 12]. The absorbance of S cation-doped TiO₂ in the visible region is larger than that of N, C, or S anion-

doped TiO₂, and the photocatalytic activity level of S cation-doped TiO₂ for oxidation of organic compounds is relatively high under visible light compared to that of N, C, or S anion-doped TiO₂. It should be noted that S atoms were incorporated into the lattice of TiO₂ as cations and were thought to be replaced by Ti ions in the case of S cation-doped TiO₂.

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 TiO₂ [13], SrTiO₃ [14], and K₄Nb₆O₁₇ [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 TiO₂ for reduction of water into molecular hydrogen and oxidation of water into molecular oxygen under visible

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

2. EXPERIMENTAL

2.1. Materials and instruments

Various kinds of 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, 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 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 $K\alpha$ -ray ($\lambda = 1.5405 \text{ \AA}$). The relative surface areas of the powders were determined by 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 TiO_2 powders were measured using a JEOL JPS90SX photoelectron spectrometer with an Mg $K\alpha$ source (1253.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 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 TiO_2 powders

S- or N-doped TiO_2 powders were synthesized by previously reported methods [11, 12, 17–19].

S- or N-doped 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 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 TiO_2 powder calcined at a temperature higher than 600°C , no absorbance in the visible region was observed. The surface areas of S-doped and N-doped TiO_2 powders having an anatase phase (ST-01) calcined at 400°C were $120 \text{ m}^2/\text{g}$ and $90 \text{ m}^2/\text{g}$, respectively. The surface areas of S-doped TiO_2 powders having a rutile phase (MT-150A, TIO-3, and NS-51) calcined at 500°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 TiO_2 powders having a rutile phase (TIO-3 and NS-51) calcined at 600°C were $26.3 \text{ m}^2/\text{g}$ and $4.9 \text{ m}^2/\text{g}$, respectively. The relative sur-

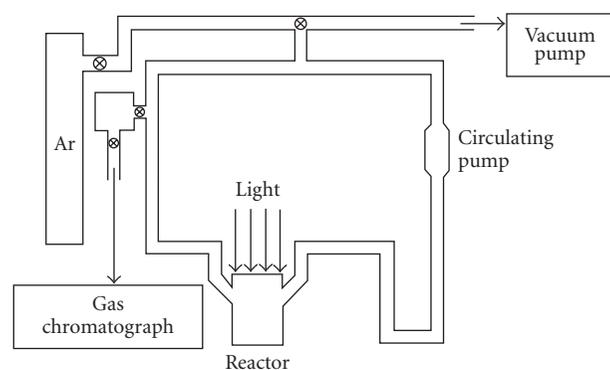


FIGURE 1: Schematic diagram of the closed gas circulating system.

face area decreased with increase in the calcination temperature.

2.3. Preparation of Pt-loaded TiO_2 photocatalysts for hydrogen evolution

Pt-loaded TiO_2 powders were prepared by a photochemical deposition method. The doped TiO_2 photocatalyst was stirred in a 5% ethanol aqueous solution containing H_2PtCl_6 and irradiated by a 500 W high-pressure Hg lamp ($2 \text{ mW}/\text{cm}^2$) for 12 hours. Photoreduction of H_2PtCl_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°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 H_2 evolution and 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 g) was suspended in distilled water using a magnetic stirrer. S- or N-doped TiO_2 having anatase phase (ST-01) was used for hydrogen evolution, and S- or N-doped TiO_2 having rutile phase (NS-51) was used for oxygen evolution. The required amount of sacrificial reagent ethanol for hydrogen evolution and Fe^{3+} for oxygen evolution was added to the suspension. The pH of the solution containing 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 TiO₂ powder having anatase phase (ST-01) and S-doped TiO₂ 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⁻/IO₃⁻ 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 I₃⁻ 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 H₂ or O₂ 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 TiO₂

Diffuse reflectance spectra for the obtained S-doped TiO₂ and N-doped TiO₂ are shown in Figure 2. All doped TiO₂ powders showed absorption in the visible region. Photoabsorption in the visible region of the doped TiO₂ having an anatase phase was stronger than that of the doped TiO₂ having a rutile phase. The TiO₂ 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 TiO₂ shifted to a longer wavelength than that of N-doped TiO₂. The band gap energies of S-doped TiO₂ and N-doped TiO₂ 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 TiO₂ having an anatase phase), 2.58 eV (N-doped TiO₂ having an anatase phase), 2.34 eV (S-doped TiO₂ having a rutile phase), and 2.94 eV (N-doped TiO₂ having a rutile phase).

The chemical states of S atoms or N atoms incorporated into TiO₂ were studied by measuring the XPS spectra of the S-doped TiO₂ or N-doped TiO₂. Figure 3(a) shows the S2p_{3/2} spectrum of S-doped TiO₂. 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 S⁶⁺ and S⁴⁺ states [11, 12]. Figure 3(b) shows the N 1s spectrum of N-doped TiO₂. 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 N₂ molecules adsorbed on the TiO₂ surface [17].

3.2. Selective water oxidation over doped TiO₂ photocatalysts in an aqueous solution containing Fe³⁺ ions

We investigated photocatalytic reduction of water into H₂ or oxidation of water into O₂ over various semiconductor

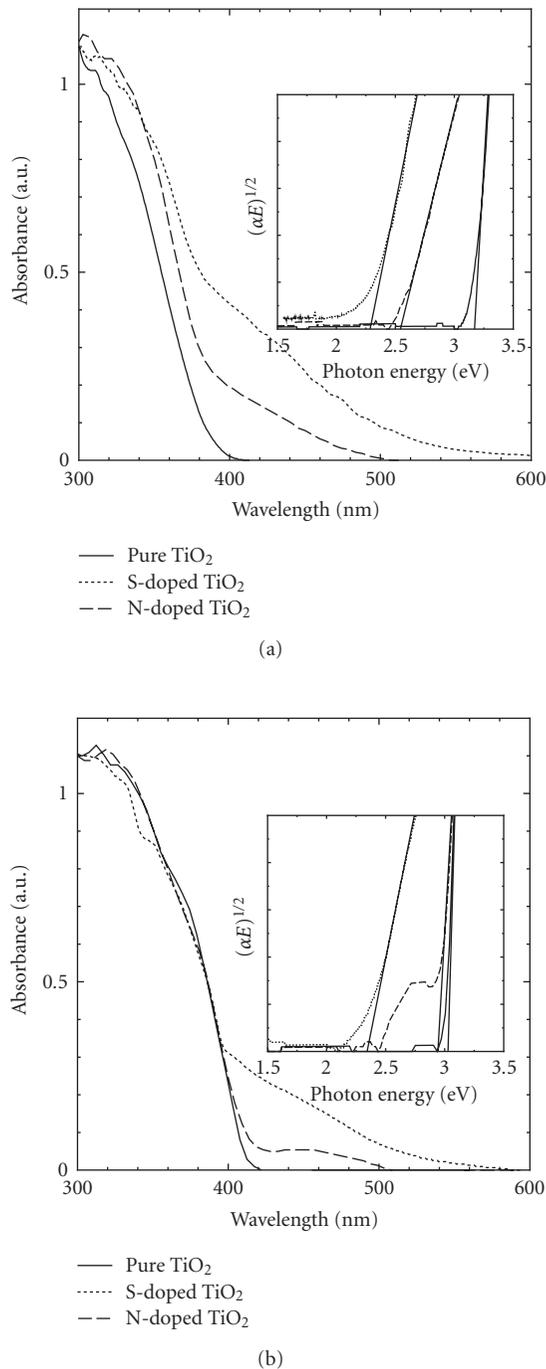
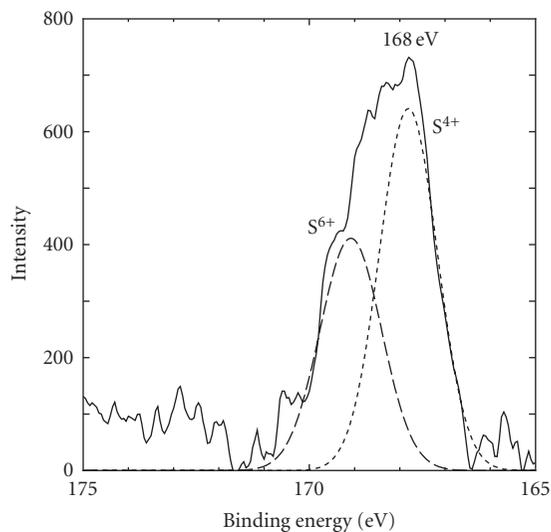
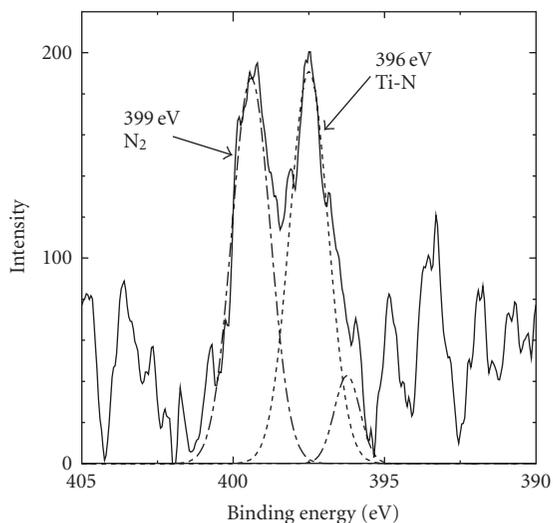


FIGURE 2: Diffuse reflectance spectra for the obtained S-doped TiO₂ and N-doped TiO₂ having an anatase or rutile phase. (a) TiO₂ having an anatase phase (ST-01), (b) TiO₂ having a rutile phase (NS-51).

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 O₂ evolution proceeded over TiO₂ photocatalysts having a rutile



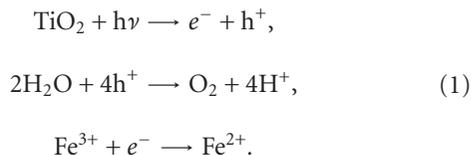
(a)



(b)

FIGURE 3: XPS spectra of S-doped TiO₂ and N-doped TiO₂. (a) S-doped TiO₂, (b) N-doped TiO₂.

phase in the aqueous solution (pH < 3) containing Fe³⁺ ions as electron acceptors with the following reactions [21]:



The optimized concentration of Fe³⁺ ions was 2 mmol/L. The rate of oxygen evolution was lowered by raising the concentrations of Fe³⁺ ions owing to a filter effect of the solution

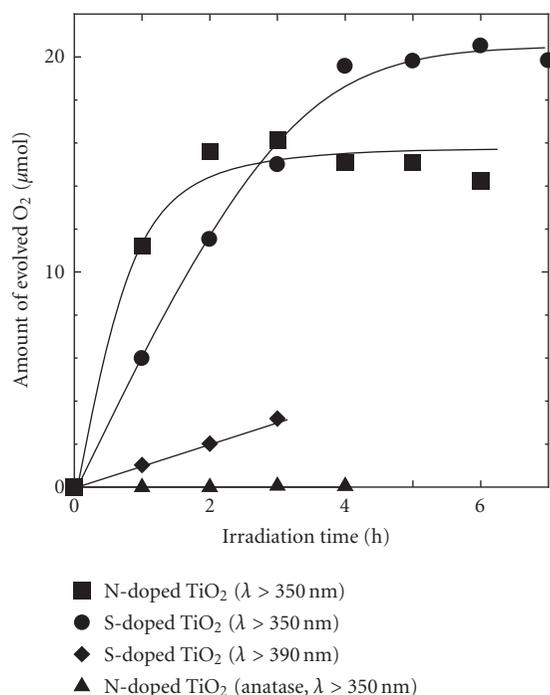


FIGURE 4: Amount of evolved O₂ from water containing Fe³⁺ ions as electron acceptors on S-doped TiO₂ having rutile phase (NS-51), N-doped TiO₂ having rutile phase (NS-51), and N-doped TiO₂ having anatase phase (ST-01).

at a high concentration [21]. Excess Fe³⁺ ions decreased rate of evolved oxygen because Fe³⁺ aqueous solution has absorption in visible light region. Figure 4 shows the amounts of evolved O₂ over S- or N-doped TiO₂ having rutile phase (NS-51) and N-doped TiO₂ having anatase phase (ST-01) from water containing Fe³⁺ ions as electron acceptors. The photocatalytic activity level of S-doped TiO₂ for water oxidation was higher than that of N-doped TiO₂. However, the amounts of evolved O₂ on S- or N-doped TiO₂ did not agree with concentration of Fe³⁺ ions. The backward reaction, oxidation of Fe²⁺ ions with holes, was thought to proceed. S-doped TiO₂ showed photoinduced oxidation of water under visible light irradiation at wavelengths longer than 390 nm. Photocatalytic oxidation of water on doped TiO₂ having a rutile phase proceeded with a fairly high efficiency compared to that on doped TiO₂ having an anatase phase as shown in Figure 4. This result suggested that the activity for the evolution of O₂ from H₂O is dependent on the particle size of doped TiO₂ 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 TiO₂ photocatalysts deposited with Pt in an aqueous solution containing ethanol

H₂ evolution from water containing ethanol as a sacrificial reagent proceeded over platinized TiO₂ having an anatase phase under UV and visible light irradiation. To improve the rate of H₂ evolution on doped TiO₂, Pt was deposited on the TiO₂ surface. The optimized amount of Pt deposited on the surface of TiO₂ was 0.5 wt%. Deposition of an excess amount of Pt (1.0 wt%) decreased photocatalytic activity because aggregated Pt particles on the TiO₂ surface prevented the TiO₂ photocatalyst from absorbing incident light or because TiO₂ surface active sites were covered with Pt particles. The reduction of water containing ethanol is as follows:

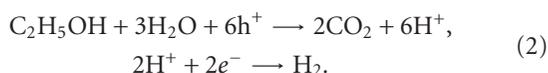


Figure 5 shows the amounts of evolved H₂ from water containing ethanol over S- or N-doped TiO₂ having anatase phase (ST-01) and S-doped TiO₂ having rutile phase (NS-51) under UV light irradiation. The amount of evolved H₂ on doped TiO₂ was smaller than that on pure TiO₂ because impurity level was formed by doping treatment. However, under visible light irradiation at wavelengths longer than 420 nm, the amount of evolved H₂ on doped TiO₂ was higher than that on pure TiO₂ as shown in Figure 5(b). S-doped TiO₂ showed a higher level of activity than that of N-doped TiO₂ for water reduction because S-doped TiO₂ showed higher photoabsorption than that of N-doped TiO₂ in the visible region as shown in Figure 2(a). Photocatalytic reduction of water on doped TiO₂ having an anatase phase proceeded with a fairly high efficiency compared to that on doped TiO₂ having a rutile phase as shown in Figure 5. This result suggested that the activity for the evolution of H₂ from H₂O is dependent on the surface area of doped TiO₂ 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⁺ ions on the surface of TiO₂ having an anatase phase.

3.4. Water splitting over TiO₂ photocatalysts in an I⁻/IO₃⁻ shuttle redox-mediated system

Photocatalytic water splitting into H₂ and O₂ was observed in a two-step redox system using an iodate/iodide redox mediator. In this system, we used Pt-loaded S-doped TiO₂ having an anatase phase (ST-01) for H₂ evolution and S-doped TiO₂ having a rutile phase (NS-51) for O₂ evolution under incident light including UV and visible light. Figure 6 shows the mechanism of the two-step redox system. On TiO₂ having an anatase phase, water is reduced to H₂ 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 O₂ by holes on TiO₂ having a rutile phase. The optimized concentration of I⁻ ions was 20 mmol/L. The oxidation products of I⁻ ions were IO₃⁻ and I₃⁻. An excess concentration of I⁻

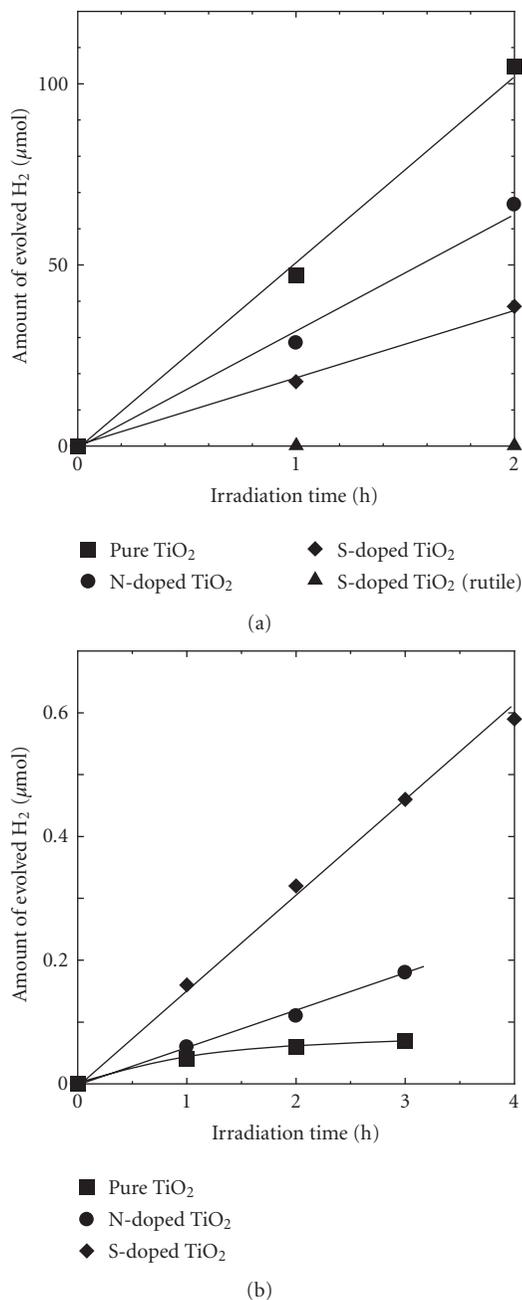
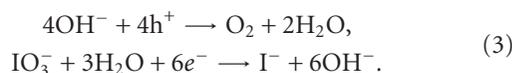


FIGURE 5: Amount of evolved H₂ from water containing ethanol as an electron donor on S- or N-doped TiO₂ (anatase phase: ST-01, rutile phase: NS-51) (a) under UV light irradiation at wavelengths longer than 350 nm or (b) under visible light irradiation at wavelengths longer than 420 nm.

ions resulted in I₃⁻ generation. The accumulation of I₃⁻ caused a light loss due to the strong absorption of I₃⁻ around 350 nm, resulting in a lower efficiency of the photocatalytic reaction [16]. Reactions over a rutile phase are as follows:



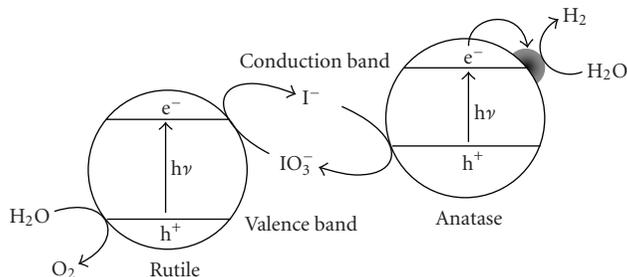


FIGURE 6: Mechanism for water splitting on TiO_2 with an I^-/IO_3^- redox-mediator system.

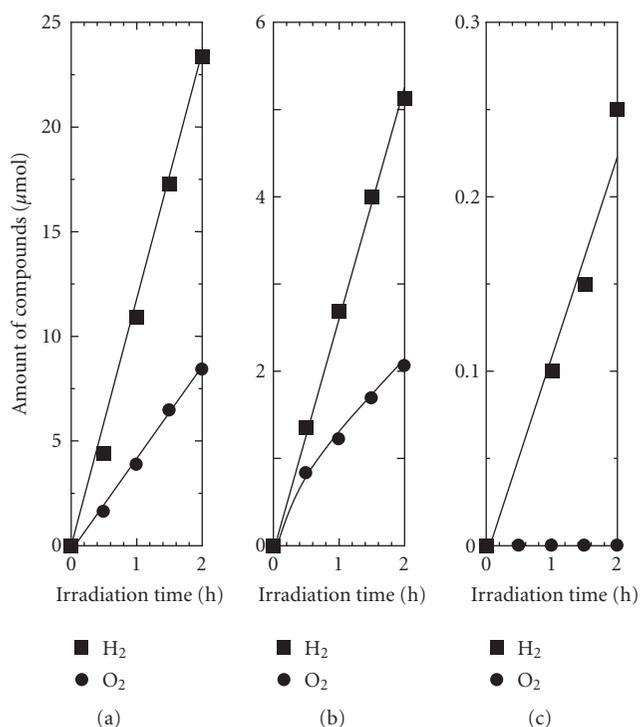
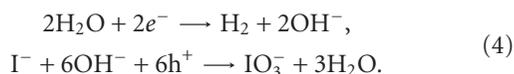


FIGURE 7: Amounts of evolved H_2 and O_2 from water containing I^-/IO_3^- redox on S-doped TiO_2 powders having an anatase phase (ST-01) and a rutile phase (NS-51) under UV or visible light irradiation. (a) under UV light irradiation without a cutoff filter, (b) under UV light irradiation at wavelengths 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 H_2 and 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 H_2 and O_2 evolved. However, the ratio of amount of evolved H_2 to amount of evolved O_2 was not 2 : 1. O_2 molecules generated from water oxidation were

thought to adsorb on the TiO_2 surface [24]. Under visible light irradiation at wavelengths longer than 390 nm, no O_2 evolution was observed because the number of holes is not sufficient for 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

H_2 evolution from water containing ethanol as an electron donor was performed on N- or S-doped TiO_2 under visible light irradiation. An anatase TiO_2 powder showed a higher level of activity than that of a rutile TiO_2 powder. Oxidation of water containing Fe^{3+} ions as electron acceptors proceeded on doped TiO_2 under UV and visible light irradiation. Water splitting was performed in an I^-/IO_3^- redox system on TiO_2 having an anatase phase for H_2 evolution and TiO_2 having a rutile phase for O_2 evolution. Under UV irradiation, both H_2 and O_2 were evolved, though the ratio of amount of evolved H_2 to amount of evolved O_2 was not 2 : 1.

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