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Photocatalytic oxidation of water by visible light using ruthenium-doped titanium dioxide powder

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Abstract

In order to expand the effective wavelength of TiO_2 particulate photocatalyst into the visible region, Ru-doped TiO_2 particles were prepared and their properties as the photocatalyst were investigated. With this photocatalyst, the oxygen evolution reaction occurred by irradiation of visible light at wavelengths longer than 440 nm using iron(III) ions as the electron acceptor. To clarify the mechanistic aspects of the effect of Ru-doping, photoelectrochemical properties of Ru-doped TiO_2 sinter electrodes were investigated.

Keywords: Ruthenium; Titanium dioxide; Iron ion; Oxidation of water; Oxygen evolution; Photocatalyst

1. Introduction

Semiconductor photocatalized reactions with positive free energy changes have attracted great interest with a view to constructing new energy conversion and storage systems. Among these reactions, splitting of water by solar light has long been a goal of the studies [1–4]. Some oxide particles are capable of splitting water into hydrogen and oxygen under UV irradiation [5–7]. However, these particles have difficulties in continuously splitting water under visible light. To overcome the difficulties, we have been working to combine two photocatalytic reactions, i.e., the reduction of water [8] and the oxidation of water [9,10], via electrodes [11] and via redox reactions of quinone compounds dissolved in an oil phase [12–14]. In principle, the combined system is advantageous to the decomposition of water by visible light because the large energy required for the splitting of water can be divided into two steps.

In order to achieve oxidation of water by visible light using semiconductor particles, their band gaps must be smaller than 3.0 eV or they must have gap states which are sensitive to visible light. In this study, we utilized Ru-doped TiO_2 photocatalysts, which have photoresponse at wavelengths up to 700 nm.

2. Experimental

2.1. Materials

TiO_2 powder (JRC-TIO-5) having a rutile crystalline form was obtained from Catalysis Society of Japan. Guaranteed-grade ruthenium(III) chloride and iron(III) nitrate were obtained from Wako Pure Chemicals. 2,4,6-tris(2-pyridyl)-*s*-triazine (TPTZ) was obtained from Dojindo Laboratories. All other chemicals used in the experiments were purchased from commercial sources as guaranteed-grade reagents and used without further purification.

2.2. Preparation and characterization of Ru-doped TiO_2 powder

The TiO_2 powder was added to the aqueous solutions of $RuCl_3$ to obtain $RuCl_3$-loaded TiO_2 particles. After the solutions were stirred vigorously for 30 min at room temperature, they were vacuum-evaporated at 80°C. The loading level of $RuCl_3$ on the TiO_2 powder was controlled by changing the concentration of the $RuCl_3$ solutions. The $RuCl_3$-loaded TiO_2 powder was heat treated at different temperatures in air for 2 h. The diffuse-reflectance spectra of the powder were obtained using Shimadzu UV-2500PC spectrophotometer equipped with an integrating sphere.

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2.3. Photocatalytic reaction

Photocatalytic reactions were carried out in evacuated 100 ml flasks, to which Ru-doped TiO_2 powder(100 mg) and an aqueous solution (50 ml) of iron(III) chloride were added. The pH of the solution was adjusted to 2.4 by adding a small amount of aqueous solution of sulfuric acid. Oxygen dissolved in the solution was removed by repeated freeze-pump-and-thaw cycles. A 500 W xenon lamp (Wacom, KXL-500F) was used as the light source. The light beam was passed through an L-44 glass filter (Hoya) to cut-off wavelengths shorter than 440 nm. The oxygen evolved by the photocatalytic reaction was determined by gas chromatography and the amount was determined using an oil manometer. Changes in the concentration of iron(II) and iron(III) ions in solution were determined from UV–VIS absorption spectra. Before the spectroscopic measurements, iron(II) ions were colored by complexing with 2,4,6-tris(2-pyridyl)-*s*-triazine (TPTZ) at pH 4.6. For determining the quantum efficiency of the photocatalytic reactions, the suspension of TiO_2 was irradiated at wavelengths around 435 nm from the high-pressure mercury lamp. Light at the wavelengths was selected using band pass filters, and the number of photons irradiated on the flask was determined using an iron(III) oxalate actinometer.

2.4. Photoelectrochemisty of Ru-doped TiO_2 sinter electrodes

The Ru-doped TiO_2 powder was pressed into disks 1 cm in diameter and sintered at 1300°C for 2 h The sintered disks were heated in a stream of hydrogen at 900°C for 1 h so as to gain the electrical conductivity. The ohmic contact with a copper wire was made via an indium layer evaporated on the back surface of the sintered disks.

The electrochemical measurements were carried out in aqueous solutions containing 1.0×10^{-2} M (M = mol/dm^{-3}) H_2SO_4 and 0.5 M Na_2SO_4 under potentiostatic conditions using a potentiostat (Nikkokeisoku, NPOT-2501) and an Ag/AgCl electrode as a reference electrode. A platinum plate was used as a counter electrode. Photoelectrochemical measurements were carried out using a 500 W xenon lamp (Wacom, KXL-500F) as the light source. The light beam was passed through an L-44 glass filter (Hoya) to cut-off wavelengths shorter than 440 nm. For the measurements of the photocurrent action spectra, the light was monochromatized using a monochromator (Jobin-Yvon, Type H.20).

3. Results and discussion

3.1. Photocatalytic oxidation of water

From the diffuse reflectance spectra shown in Fig. 1, it is obvious that the undoped TiO_2 powder shows strong photoabsorption only at wavelengths shorter than 420 nm. On the other hand, the Ru-doped TiO_2 powders show photoabsorption in the visible region, which gradually decreases with the wavelength. The intensity of the absorbance in the visible region increases with the concentration of the doped Ru ion.

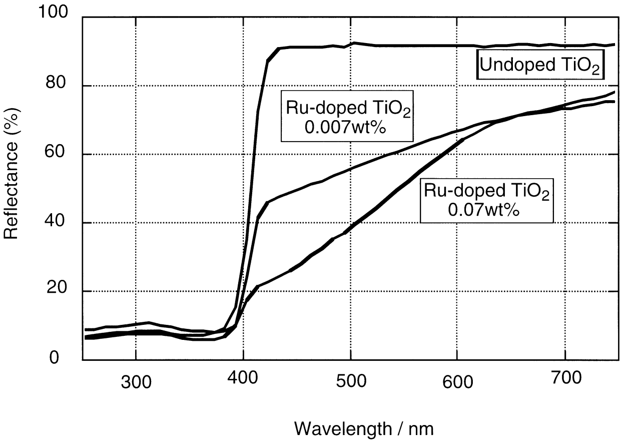

Fig. 1. Diffuse reflectance spectra of undoped and Ru-doped TiO_2 powders. The doped powders were calcined in air at 1200°C for 2 h.

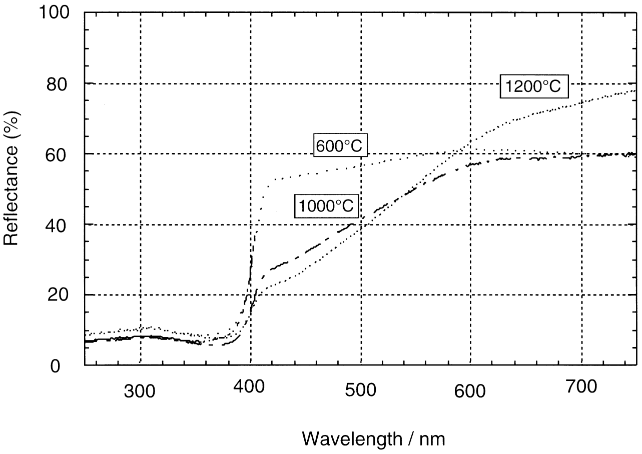

Fig. 2. Diffuse reflectance spectra of Ru-doped (0.07 wt.%) TiO_2 powders calcined at different temperatures.

The intensity of the absorbance in the visible region was also dependent on the calcination temperature. When the powder was calcined at 600°C, the photoabsorption in the visible region is very weak, as shown in Fig. 2. This result suggests that Ru ions are not effectively incorporated into the lattice of TiO_2 by the calcination at low temperatures. The absorption in the visible region becomes intense by calcination at temperatures above 1000°C. The diffuse reflection spectra of the powders calcined at low temperatures showed lower reflectance in the long wavelength region than those calcined at 1200°C, as seen in Fig. 2. The low reflectance for the former powders is due to the $RuCl_3$ compound remaining on the surface of the TiO_2 particles.

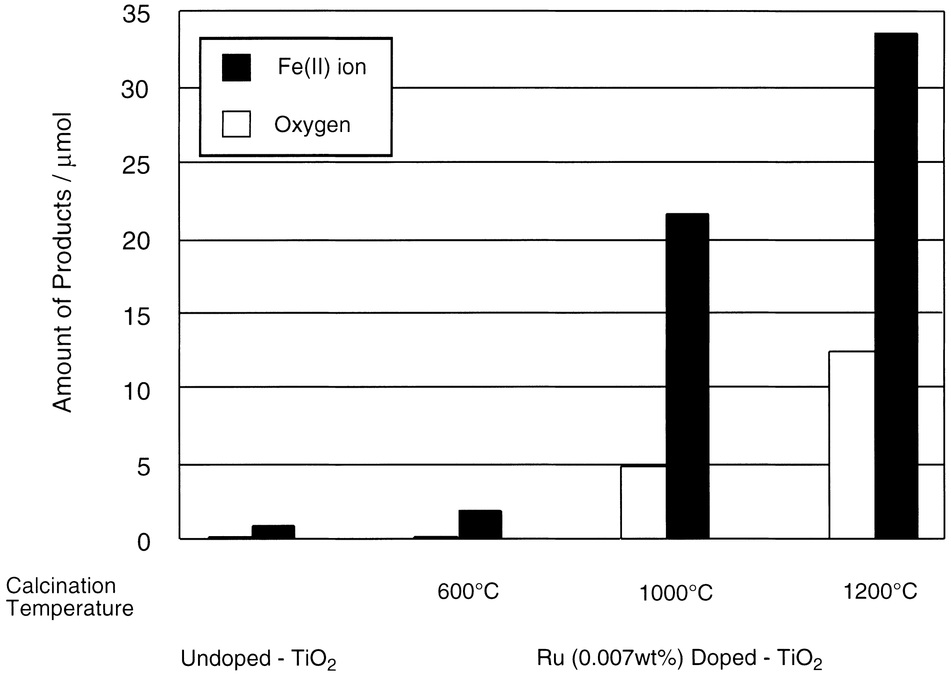

Fig. 3. Amounts of iron(II) ion and oxygen produced by photoirradiation of undoped and Ru-doped (0.007 wt.%) TiO_2 particles. The irradiation was continued for 16 h in a solution containing 8 mM iron(III) nitrate. The calcination temperature of the Ru-doped TiO_2 powder is shown beneath the graph.

There are three possible explanations for the less-than-band gap absorption of the Ru-doped TiO_2 particles; (1) the formation of the localized energy level of the Ru^{3+} species, (2) the change of the band gap by the formation of the $Ti_{1-x}Ru_xO_2$ phase, and (3) the formation of defects in the TiO_2 lattice by the inclusion of Ru^{3+} ions in the lattice. We consider that the last explanation is most plausible, because the content of Ru^{3+} is very low, and the similar absorption bands have been reported for the TiO_2 particles doped with other metal ions [15] The concentration of the Ru^{3+} species was too low to obtain the detailed information about their states by XPS or EXAFS.

Photo-oxidation of water on the Ru-doped and undoped TiO_2 powders was carried out in evacuated flasks containing a deaerated aqueous solution at pH 2.4 under irradiation of visible light. In the absence of iron (III) ion in the solution, practically no oxygen evolved on the undoped or Ru-doped TiO_2 powder. In contrast, when iron(III) ion was added to the solution, oxygen evolved photocatalytically on the Ru-doped TiO_2 powder. Typical results obtained with the undoped and Ru (0.007 wt.%)-doped TiO_2 powders are shown in Fig. 3. The amount of oxygen evolved using the Ru-doped powder increased with the calcination temperature and reached a maximum at 1200°C. At temperatures above 1200°C, the activity lowered (not shown in Fig. 3) probably owing to the decreased surface area of the particles.

With the evolution of oxygen on the Ru-doped powders, iron(III) ions were converted to iron(II) ions. The molar ratio of oxygen and iron(II) ion produced using the powder calcined at temperatures above 1000°C was in the range of 2.9–4.3, being roughly in agreement with the stoichiometry of the reaction. For the powder calcined at 600°C, practically no oxygen was obtained, although a small amount of iron(II) ions are generated in the solution. In such a case, the generation of the iron(II) ions is probably accompanied with the oxidation of unknown impurities.

The evolution of oxygen continued for a long period under photoirradiation. By irradiation of Ru-doped (0.007 wt.%) TiO_2 (100 mg) with visible light for 5, 12.5 µmol of oxygen was obtained as shown in Fig. 3. On the other hand, the content of Ru ions in the photocatalyst is only 6.9×10^{-2} µmol. These results indicate the stability of the Ru-doped TiO_2 photocatalysts.

The activity of the Ru-doped TiO_2 powder for the photo-oxidation of water was dependent on the doping concentration, and was highest at about 0.007 wt.% Ru. The quantum efficiency of the reaction was 0.14% at 435 nm, which was observed using the powder doped with 0.007 wt.% Ru and calcined at 1200°C. Although the efficiency is still low, it is important that the oxidation of water is demonstrated under visible light using the Ru-doped TiO_2 powder. For the photocatalysts doped with a large amount of Ru, the activity is lowered probably by the formation of recombination centers at high concentrations. To prevent the generation of the recombination centers, the ion-implantation method may be useful, as has been reported by Anpo et al. [16].

3.2. Photoelectrochemistry of Ru-doped TiO_2 electrodes

Fig. 4 shows the I–V curves for undoped and Ru-doped TiO_2 sinter electrodes under visible light irradiation. The

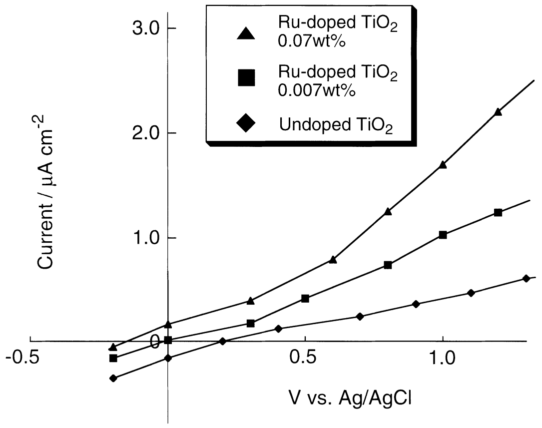

Fig. 4. I–V curves for TiO_2 sinter electrodes undoped (◆) and Ru-doped at the concentrations of 0.007 wt.% (■) and 0.07 wt.% (▲). The electrodes were irradiated with visible light ($\lambda > 440$ nm) in an aqueous solution at pH 2.0.

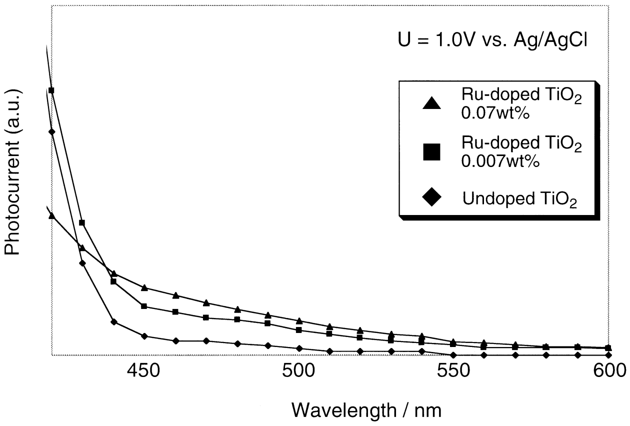

Fig. 5. Action spectra of the photocurrent for the undoped and Ru-doped (0.07 and 0.007 wt.%) TiO_2 sinter electrodes in an aqueous solution at pH 2.0.

dark current at these electrodes was lower than 5 μA/cm^2 at potentials lower than 1.0 V vs. Ag/AgCl. The undoped TiO_2 electrode shows small photoresponse to visible light. The photocurrent is attributable to the defects included in the lattice of TiO_2, which was heated in hydrogen atmosphere to make conductive. On the other hand, the Ru-doped electrodes show the photocurrent under visible light irradiation. The photocurrent increased with the concentration of the doped Ru ion, probably because the concentration of the gap states increased [17,18].

The action spectra of the photocurrent for the Ru-doped and undoped TiO_2 sinter electrodes are shown in Fig. 5. The doped electrode shows photoresponse in the wavelength region where the photoabsorption is observed in the diffuse reflectance spectra of the Ru-doped TiO_2 powder (Fig. 2). The photocurrent at wavelengths above 440 nm increases with the concentration of the doped Ru ions. On the other hand, as seen in Fig. 5, at wavelengths below 440 nm the photocurrent of the Ru-doped TiO_2 electrode at a low doping level (0.007 wt.%) is larger than that of the electrode at a high doping level (0.07 wt.%). This result suggests that too much Ru-doping generates the recombination centers at high concentrations. The doping at high concentrations had also harmful effects on the shape of the I–V curves. These results are consistent with the photocatalytic properties of the Ru-doped TiO_2 photocatalyst, which was most active at the doping level of about 0.007 wt.%.

4. Conclusion

We demonstrated that photo-oxidation of water takes place on the Ru-doped TiO_2 powder under visible light using iron(III) ion as the electron acceptor. This result gives us a basis for the construction of the water splitting system, which operates under visible light, by a combination of oxygen evolution and hydrogen evolution systems.

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