Photocatalytic Activities of Noble Metal Ion Doped $SrTiO_3$ under Visible Light Irradiation

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Mn-, Ru-, Rh-, and Ir-doped $SrTiO_3$ possessed intense absorption bands in the visible light region due to excitation from the discontinuous levels formed by the dopants to the conduction band of the $SrTiO_3$ host. Mn- and Ru-doped $SrTiO_3$ showed photocatalytic activities for O_2 evolution from an aqueous silver nitrate solution while Ru-, Rh-, and Ir-doped $SrTiO_3$ loaded with Pt cocatalysts produced H_2 from an aqueous methanol solution under visible light irradiation ($\lambda > 440$ nm). The Rh(1%)-doped $SrTiO_3$ photocatalyst loaded with a Pt cocatalyst (0.1 wt %) gave 5.2% of the quantum yield at 420 nm for the H_2 evolution reaction.

1. Introduction

Development of photocatalysts which can efficiently split water into H_2 and O_2 under sunlight irradiation has extensively been explored. The number of photocatalysts which are active for H_2 evolution under visible light irradiation is limited even for the reaction in the presence of an electron donor. In some cases, visible light responses of photocatalysts with large band gaps are brought by doping of metal cations which form electron donor levels within the band gaps. TiO_2 and $SrTiO_3$ are wide band gap photocatalysts (band gap = 3.2 eV) which can split water into H_2 and O_2 under ultraviolet light irradiation.[1−5] There are some reports that the photocatalysts[6−8] and semiconductor electrodes[9−15] of TiO_2 and $SrTiO_3$ doped with transition metal ions show visible light responses. The present authors have reported that TiO_2 and $SrTiO_3$ photocatalysts with Cr and Sb ions or Cr and Ta ions substituted for Ti sites showed activity for O_2 or H_2 evolution from aqueous solutions containing the sacrificial reagents under visible light irradiation.[7,8] On the other hand, it has been reported that photoelectrodes of $SrTiO_3$ doped with Rh or Pt in the surface region give a photoresponse to visible light.[14,15]

Mn and some noble metals seem to be interesting as dopants that bring the visible light response to the $SrTiO_3$ photocatalyst because of their redox properties. In the present study, the effects of doping of Mn and noble metal cations into the wide band gap photocatalyst $SrTiO_3$ on the photocatalytic activity were examined to create a visible absorption center and an active surface site. The visible light response was discussed with a proposed electronic structure.

2. Experimental Section

$SrTiO_3$ powders doped with Mn, Ru, Rh, Pd, Ir, and Pt ions (denoted as $SrTiO_3$:M(*X* %)) were synthesized in the following manner. The starting materials, $SrCO_3$ (Kanto Chemical; 99.9%, treated in air at 573 K for 1 h before use), TiO_2 (Soekawa Chemical; 99.9%), MnO_2 (Nacalai Tesque; 99%), RuO_2 (Rare Metallic; 99.9%), Rh_2O_3 (Wako Pure Chemical; 95%), PdO (Wako Pure Chemical; 98.0%), IrO_2 (Soekawa Chemical; 85.5%), and PtO_2 (Kojima Chemical; 95%) were mixed with a small amount of methanol in a ratio according to the composition of $SrTi_{1-x}M_xO_3$, and then the mixtures were calcined in air at 1173−1573 K for 5−25 h using an alumina crucible (purity 99.7%). The obtained powders were determined by powder X-ray diffraction (Rigaku; MiniFlex, Cu Kα). Diffuse reflectance spectra were obtained using a UV−vis−NIR spectrometer (Jasco; UbestV-570) and were converted from reflection to absorbance by the Kubelka−Munk method. Pt cocatalysts were loaded in situ by a photoreduction method using an aqueous H_2PtCl_6 solution (Tanaka Kikinzoku; 37.55% as Pt in $H_2PtCl_6 \cdot 6H_2O$).

Photocatalytic reactions of H_2 evolution from an aqueous methanol solution (10 vol %) and O_2 evolution from an aqueous silver nitrate solution (0.05 mol L^{-1}) were carried out in a closed gas circulation system. The photocatalyst powder (0.3 g) was dispersed by a magnetic stirrer in a reactant solution in the cell with a top window made of Pyrex. The light source was a 300 W Xe lamp (ILC Technology; CERMAX LX-300F) attached with cutoff filters (HOYA; L42 and Y44) to control the wavelength of the incident light. The amounts of evolved gases were determined using on-line gas chromatography (Shimazu; GC-8A, MS-5A column, TCD, Ar carrier). The quantum yield was measured using a 300 W Xe lamp (ILC Technology; CERMAX LX-300F) attached with a band-pass filter (Kenko) and a cutoff filter (HOYA). A thermopile (OPHIR; a 3A-P-SH head and a NOVA energy monitor) was used for the measurement of the number of incident photons. The value obtained by this experiment is an apparent quantum yield (percent), calculated by the following equation:

$$\begin{aligned}\text{apparent quantum yield (\%)} = &\\ &[\text{number of reacted electrons or holes}]/\\ &[\text{number of incident photons}] \times 100 =\\ &[\text{number of } H_2 \text{ molecules evolved} \times 2]/\\ &[\text{number of incident photons}] \times 100\end{aligned}$$

3. Results and Discussion

3.1. Characterization. XRD patterns of $SrTiO_3$:M(0.5%) (M = Mn, Ru, Rh, Pd, Ir, and Pt) powders synthesized at 1423 K showed a single phase of $SrTiO_3$ except $SrTiO_3$:Pd(0.5%), in which some peaks assigned to metallic palladium were con-

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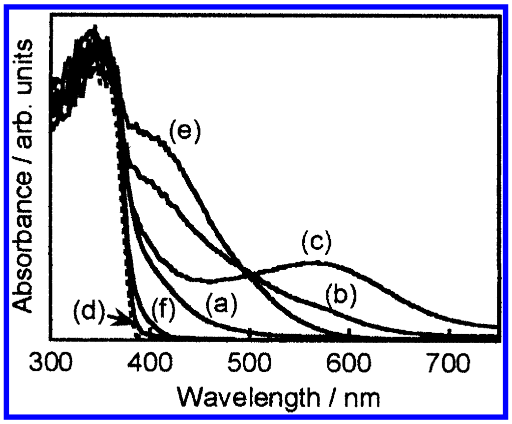

Figure 1. Diffuse reflectance spectra of $SrTiO_3$:M(0.5%). M = (a) Mn, (b) Ru, (c) Rh, (d) Pd, (e) Ir, and (f) Pt. A broken line represents a spectrum of nondoped $SrTiO_3$.

TABLE 1: Photocatalytic Activities of $SrTiO_3$:M(0.5%) for H_2 or O_2 Evolution from an Aqueous Solution Containing Sacrificial Reagents under Visible Light Irradiation[a]

		activity/μmol h^{-1}	
M	E_g/eV	H_2 [b]	O_2 [c]
Mn	2.7	0.2	2.7
Ru	1.9	1.7	3.9
Rh	1.7	17.2	0
Ir	2.3	8.6	0.4

[a] Catalyst, 0.3 g; reactant solution, 150 mL; light source, 300 W Xe lamp with cutoff filter (λ > 440 nm). [b] From 10 vol % aqueous MeOH; cocatalyst, Pt (0.5 wt %). [c] From 0.05 mol L^{-1} aqueous $AgNO_3$.

firmed. Doping of Pd^{2+} seemed to be difficult because its ion radius (0.86 Å) was much larger than that of Ti^{4+} (0.605 Å).

Figure 1 shows diffuse reflectance spectra of $SrTiO_3$:M(0.5%) (M = Mn, Ru, Rh, Pd, Ir, and Pt) powders. In $SrTiO_3$:M(0.5%) (M = Mn, Ru, Rh, and Ir), absorption bands with shoulders in the visible light region were observed in addition to the band gap absorption of $SrTiO_3$. These shapes of the diffuse reflectance spectra were similar to those of the doped sintered electrode that was reported by Matsumura et al.[14] These shapes were the characteristics of doped photocatalysts and indicated that discontinuous levels were formed by the dopants in the forbidden band. The existence of two absorption bands of a shoulder around 420 nm and broad bands around 580 and 1000 nm for the $SrTiO_3$:Rh powder indicated that some doping levels due to different oxidation numbers were formed in the forbidden band. The diffuse reflectance spectrum of $SrTiO_3$ not doped but loaded with Rh or rhodium oxides on the surface by an impregnation method was quite different from that of the present material, demonstrating that the doped material was obtained by the present preparation condition.

3.2. Photocatalytic Activity. Table 1 shows hydrogen evolution from an aqueous methanol solution and oxygen evolution from an aqueous silver nitrate solution under visible light irradiation (λ > 440 nm) on $SrTiO_3$:M(0.5%) which possessed absorption bands in a visible light region. Mn- and Ru-doped $SrTiO_3$ showed photocatalytic activities for O_2 evolution from an aqueous silver nitrate solution while Ru-, Rh-, and Ir-doped $SrTiO_3$ loaded with Pt cocatalysts produced H_2 from an aqueous methanol solution. No O_2 evolution activity of Rh-doped $SrTiO_3$ is due to the lack of an O_2 evolution site as discussed below. In the cases of $SrTiO_3$ doped with Mn and Ru, the dopants might work as active sites for O_2 evolution, resulting in showing the activities for O_2 evolution. In contrast, the low activities for H_2 evolution on these photocatalysts would mainly be due to the surface states created by their dopants below the conduction bands, resulting in difficulty in H_2 evolution.

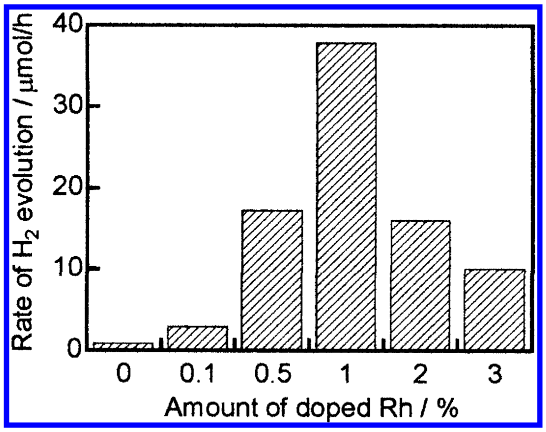

Figure 2. Dependence of H_2 evolution activity of Rh-doped $SrTiO_3$ upon the doping amount. Catalyst, 0.3 g; cocatalyst, Pt (0.5 wt %); reactant solution, 150 mL of 10 vol % aqueous MeOH; light source, 300 W Xe lamp with cutoff filters (λ > 440 nm).

TABLE 2: H_2 Evolution from an Aqueous Methanol Solution under Visible Light Irradiation of $SrTiO_3$:Rh(1%) Photocatalysts Prepared under Different Conditions[a]

calcination condition		
temp/K	time/h	H_2/μmol h^{-1}
1173	25	9
1273	5	46
	10	90
	20	58
1423	5	42
	10	65
	20	24
1573	10	21

[a] Catalyst, 0.3 g; cocatalyst, Pt (0.1 wt %); reactant solution, 150 mL of 10 vol % aqueous MeOH; light source, 300 W Xe lamp with cutoff filters (λ > 440 nm).

Among the photocatalysts listed in Table 1, further investigation was carried out for $SrTiO_3$:Rh, which showed the highest activity for H_2 evolution.

The optimum preparation condition of the $SrTiO_3$:Rh photocatalyst was examined. Pt/$SrTiO_3$:Rh(1%) showed the highest activity for H_2 evolution from an aqueous methanol solution under visible light irradiation among $SrTiO_3$ photocatalysts with different doping amounts of Rh as shown in Figure 2. The increase in the doping amount enhances visible light absorption whereas it makes a recombination center between photogenerated carriers increase. Therefore, the volcano-type dependence was obtained.

The optimal calcination condition of $SrTiO_3$:Rh(1%) was examined as shown in Table 2. Starting materials had to be calcined more than 20 h at 1173 K or 10 h at 1273 K to get a single phase. The best preparation temperature was 1273 K. The suitable calcination time was 10 h for all temperatures. The preparation temperature and time affected the crystallinity, particle size, homogeneity of the dopant, and other natures which were important factors dominating photocatalytic activities.

The $SrTiO_3$:Rh(1%) photocatalyst calcined for 10 h at 1273 K showed the highest activity for H_2 evolution from an aqueous methanol solution under visible light irradiation in the presence of a Pt cocatalyst as shown in Figure 3. An induction period was observed at the early stage of the photocatalytic reaction. The induction period suggests that some reduction process should have proceeded at the beginning stage instead of water

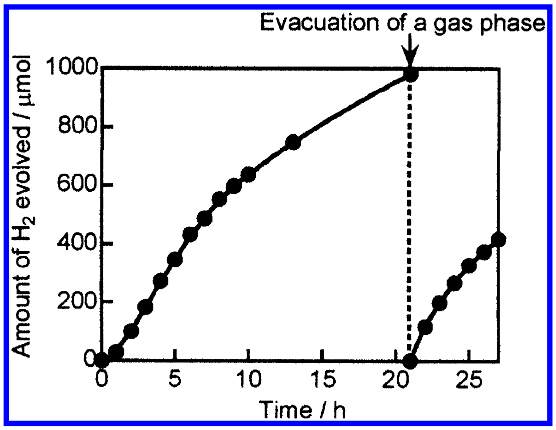

Figure 3. H_2 evolution from an aqueous methanol solution under visible light irradiation over a Pt(0.1 wt %)/$SrTiO_3$:Rh(1%) photocatalyst prepared by solid-state reaction at 1273 K for 10 h. Catalyst, 0.3 g; reactant solution, 150 mL of 10 vol % aqueous MeOH; light source, 300 W Xe lamp with cutoff filters (λ > 440 nm).

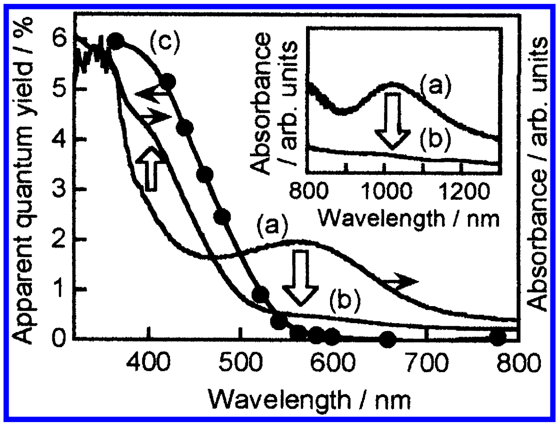

Figure 4. Diffuse reflectance spectra of (a) before and (b) after photocatalytic reaction, and (c) action spectrum for H_2 evolution from an aqueous methanol solution over a $SrTiO_3$:Rh(1%) photocatalyst. The inset shows an expanded view of the spectra in the wavelength region from 800 to 1300 nm. Catalyst, 0.3 g; cocatalyst, Pt (0.1 wt %); reactant solution, 150 mL of 10 vol % aqueous methanol solution; light source, 300 W Xe lamp.

reduction. On the other hand, although the rate of H_2 evolution became slow after ca. 10 h, it was improved by evacuating a gas phase and the induction time was not observed. The decrease in activity with reaction time was probably due to the poisoning by evolved H_2 because H_2 evolution was suppressed by the purposeful addition of H_2 into a gas phase. The maximum rate of H_2 evolution was 117 μmol h^{-1}. The amount of the $SrTiO_3$:Rh photocatalyst used was 1.6 mmol, and it contained 16 μmol of Rh. The number of electrons reacted was estimated to be 2.8 mmol judging from the amount of evolved H_2. The electron turnover number to amounts of doped Rh and surface Ti reached 175 and 300, respectively, after 27 h of irradiation. Therefore, it can be concluded that H_2 evolution photocatalytically proceeded on Pt/$SrTiO_3$:Rh.

Figure 4 shows diffuse reflectance spectra before and after the photocatalytic reaction and an action spectrum for H_2 evolution from an aqueous methanol solution over the optimized Pt(0.1 wt %)/$SrTiO_3$:Rh(1%) photocatalyst. An absorption peak around 580 and 1000 nm observed before the reaction vanished after the reaction, whereas a shoulder around 420 nm grew up. The color of this photocatalyst changed from grayish purple to yellow during the photocatalytic reaction in agreement with the spectral change. The change in color and the observation of an induction period indicate that some doped Rh species with a high oxidation number was reduced by the photoexcited electrons at the early stage of the reaction. The yellow color of the reduced $SrTiO_3$:Rh(1%) photocatalyst approximately returned to the original color as soon as the photocatalyst was exposed to the air. The doped Rh ions were in the condition that they could oscillate between oxidized and reduced forms. The yellow powder was also obtained by reduction with H_2 at 573 K. However, the color of the thermally reduced powder did not return to the original color. Moreover, although the induction period disappeared, the photocatalytic activity (5 μmol h^{-1}) was much lower than that of the photocatalytically reduced sample.

The onset of the action spectrum agreed well with the absorption edge of the diffuse reflectance spectrum of the reduced photocatalyst rather than with that of the original photocatalyst. Visible light up to 540 nm can be used. The action spectrum was similar to those of photocurrent reported by Matsumura et al.[14] and Watanabe et al.[15] The quantum yield of the Pt(0.1 wt %)/$SrTiO_3$:Rh(1%) photocatalyst was 5.2% at 420 nm. This represents a very high value among doped oxide photocatalysts reported in the literature. When a foreign element is added into some host photocatalysts, the quantum yields generally become much lower than those of the undoped materials because the dopant could provide an electron−hole recombination site. However, the apparent quantum yield of the Pt/$SrTiO_3$:Rh(1%) photocatalyst (6% at 365 nm) was almost the same as that of nondoped Pt/$SrTiO_3$ (6% at 365 nm). Moreover, the H_2 evolution rate of the Pt/$SrTiO_3$:Rh(1%) photocatalyst (330 μmol h^{-1}) was faster than that of nondoped Pt/$SrTiO_3$ (166 μmol h^{-1}) even under full arc irradiation. The Rh doping did not make the photocatalytic activity decrease even under the band gap excitation. Rh ions also form recombination centers more or less. However, the similarity in the activity between Rh-doped and nondoped photocatalysts indicates that the contribution of Rh dopant to the formation of a recombination center is less than that of other transition metal dopants such as iron ions. In general, transition metal ions of which the valency is easily changed between relatively stable oxidation numbers tend to form a recombination center. In the present photocatalyst, most Rh ions are trivalent under the working conditions for H_2 evolution as mentioned below. The trivalency is definitely the most stable oxidation number among Rh ions in oxides, suggesting the stability of Rh^{3+}. Therefore, the possibility that Rh ions form a recombination center would be less than that for other ions such as iron ions of which di- and trivalencies are stable.

Some oxide, oxynitride, and oxysulfide photocatalysts which are active for H_2 evolution under visible light irradiation have been reported.[16−18] However, their activities are not high. Pure oxide photocatalysts with a high activity for H_2 evolution under visible light irradiation has not been reported so far. In this regard, the Rh-doped $SrTiO_3$ powder is a unique photocatalyst for H_2 evolution.

3.3. Mechanism. The derived schematic mechanism for the photocatalytic H_2 evolution on Pt/$SrTiO_3$:Rh is illustrated in Figure 5. The visible light absorption bands in the diffuse reflectance spectrum suggested the existence of two different species of the doped Rh at least. They can be assigned to be Rh^{3+} and a rhodium species with a higher oxidation number than Rh^{3+} such as Rh^{5+}. These Rh ions with different oxidation numbers would neighbor each other, judging from the charge and distortion compensation by their cations. The Rh with higher oxidation number can be easily reduced to Rh^{3+} by photogenerated electrons at an early stage of the photocatalytic reaction, indicating that the Rh with higher oxidation number works as an electron acceptor. The highly efficient H_2 evolution

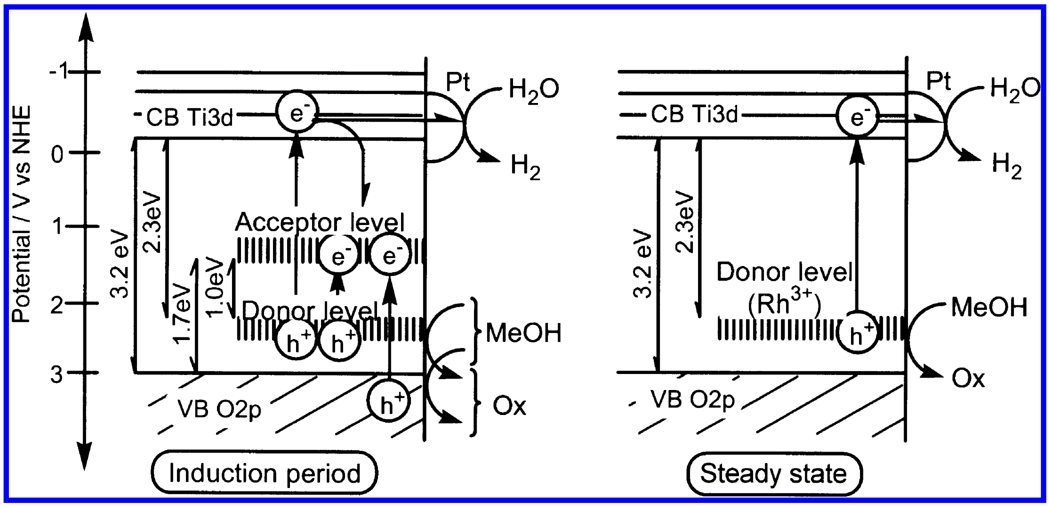

Figure 5. Proposed band structure and visible light response of Rh-doped $SrTiO_3$ photocatalyst.

on the $SrTiO_3$:Rh photocatalyst under visible light irradiation indicates that Rh^{3+} works as an electron donor. Therefore, the absorption bands around 580 and 1000 nm, which have onsets at 1.7 and 1.0 eV, are assigned to the transition from the valence band and the donor level to the acceptor level, respectively. On the other hand, the absorption band remaining after the reduction by photogenerated electrons should be the transition from the donor level formed with Rh^{3+} to the conduction band. It is the key process for the photocatalytic H_2 evolution on Pt/$SrTiO_3$:Rh under visible light irradiation. The electrons photogenerated in the conduction band reduce water to form H_2, while holes formed in the electron donor level possessed thermodynamic and kinetic potentials for oxidation of methanol. This indicates that the doped Rh^{3+} formed the visible light absorption center and the surface reaction center. The optimum doping amount was 1%: it is not low in general. Although the donor levels are basically discrete, they should partly overlap with O 2p orbital to form a hybrid orbital. Therefore, the migration of holes is not so difficult. For example, in the case of ZnS doped with 0.1% of Ni^{2+} ions, high activity has been realized despite a quite small amount of doping.[19] However, O_2 evolution hardly proceeded. The doping level in which holes are generated is estimated to be +2.1 eV as shown in Figure 5. This potential might thermodynamically be deep enough for oxidation of water to form O_2. However, dopants are not easily able to form a reaction center for the O_2 evolution because the reaction is accompanied by four-electron oxidation. The kinetic limitation of the lack of an active site is one of the reasons for no O_2 evolution activity. On the other hand, a photocatalytic reaction efficiently proceeds after Rh species with high oxidation numbers are reduced. These species cannot be reduced in the reaction in an aqueous silver nitrate solution because they work as recombination centers in the absence of a hole scavenger. This is another reason for no photocatalytic activity for O_2 evolution. On the other hand, the methanol oxidation is easy compared to O_2 evolution from water from both thermodynamic and kinetic standpoints. The standard redox potentials for $HCHO/CH_3OH$ and H_2CO_3/CH_3OH are 0.232 and 0.044 V. These redox potentials are considerably more negative than $E°(O_2/H_2O)$ (1.23 V). This indicates that O_2 evolution is thermodynamically difficult more than methanol oxidation. Moreover, it is well-known that the overpotential for O_2 evolution is quite large (more than 0.5 V): it is a kinetic factor. In fact, O_2 evolution from an aqueous methanol solution has never been observed for any photocatalysts even if the photocatalyst possesses a quite high activity for O_2 evolution. It is obvious from this fact that O_2 evolution from water is a tougher reaction than the oxidation of methanol.

4. Conclusion

$SrTiO_3$:Rh(1%) is a novel oxide photocatalyst that is active for H_2 evolution from an aqueous methanol solution under visible light irradiation. The visible light response was due to the transition from the electron donor level formed by Rh ions to the conduction band composed of Ti 3d orbitals of $SrTiO_3$. It was supported by diffuse reflectance spectra and the color change that the reducible Rh species contributed to the formation of visible light absorption band and the surface reaction sites.

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