Long wavelength visible light-responsive SrTiO₃ photocatalysts doped with valence-controlled Ru for sacrificial H₂ and O₂ evolution†

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SrTiO₃ doped with Ru, H₂-reduced SrTiO₃ doped with Ru and SrTiO₃ codoped with Ru and Sb were developed as active photocatalysts for sacrificial H₂ and O₂ evolution under visible light irradiation. H₂-Reduced SrTiO₃:Ru showed the highest activity responding up to 750 nm, almost the whole range of visible light.

Photocatalytic water splitting is a promising chemical reaction to convert solar energy into storable chemical energy, so-called artificial photosynthesis.¹†⁻⁶ Utilization of visible light is a key issue to achieve highly efficient solar energy conversion. Accordingly, development of photocatalysts with responses to a wide range of visible light is an important research topic.

Doping of metal ions is a useful technique to make materials responsive to light with longer wavelengths.²⁻⁷ The doped metal ions form impurity levels in the forbidden band of the host material, and hence new energy gaps appear in addition to the band gap of the host material. For example, Rh-doped SrTiO₃ is an established photocatalyst which is highly active for sacrificial H₂ evolution under visible light irradiation.⁸ In addition to Rh ions, Cr, Ir, and Ni ions are known as effective dopants.⁹⁻¹³ We have preliminarily reported that Ru-doped SrTiO₃ shows photocatalytic activities for sacrificial H₂ and O₂ evolution under visible light irradiation.⁸ However, the details of the photocatalytic properties and the band structure have not been clarified yet. It is important to improve the Ru-doped SrTiO₃ by some modifications.

Codoping with a second dopant can control the oxidation number of the main dopant. For example, Rh ions are mainly doped as Rh⁴⁺ at Ti⁴⁺ sites when only Rh is doped into SrTiO₃.¹⁴ In contrast, the oxidation number of the rhodium species is controlled from Rh⁴⁺ to Rh³⁺ by codoping of Sb⁵⁺ into SrTiO₃ to maintain the charge balance, according to 2Ti⁴⁺ = Rh³⁺ + Sb⁵⁺.¹⁵,¹⁶ As a result, Rh,Sb-codoped SrTiO₃ shows activity for water splitting under visible light irradiation,¹⁶ being different from Rh-doped SrTiO₃. Thus, the oxidation number of the doped metal ions drastically affects the photocatalytic properties.

In the present study, we investigated the photocatalytic properties of Ru-doped SrTiO₃ to develop and improve a photocatalyst responding to long wavelength visible light. Sb-Codoping and H₂-reduction were applied to Ru-doped SrTiO₃ to control the oxidation number of doped Ru. The band structures of Ru-doped SrTiO₃, Ru,Sb-codoped SrTiO₃, and Ru-doped SrTiO₃ after H₂ reduction were also discussed.

Metal ion-doped SrTiO₃ was prepared by a solid-state reaction. The starting materials SrCO₃ (Kanto Chemical, 99.9%), TiO₂ (Soekawa Chemical, 99.9%), RuO₂ (Rare Metallic, 99.9%), Sb₂O₅ (Nakarai Tesque, 98%), Nb₂O₅ (Kojundo Chemical, 99.9%) and Ta₂O₅ (Rare Metallic, 99.99%) were mixed in atomic ratios of Sr/Ti/Ru = 1.015 : 0.997 : 0.003 for Ru⁰.³%-doped SrTiO₃, Sr/Ti/Ru/Sb = 1.015 : 0.9925 : 0.003 : 0.0045 for Ru(0.3%)-doped SrTiO₃, Sr/Ti/Ru/Sb = 1.015 : 0.9925 : 0.003 : 0.0045 for Ru(0.3%)-doped SrTiO₃, and Sr/Ti/Ru/M = 1.015 : 0.991 : x : 0.003 : 0.006 for Ru(0.3%),Nb(0.6%) and Ru(0.3%),Ta(0.6%)-codoped SrTiO₃. The mixture was calcined in an alumina crucible at 1273 K for 10 h. H₂-Reduced SrTiO₃ doped with Ru was prepared by reduction in one atmosphere of H₂ at 473 K or 673 K for 2 h. The crystal phase of the prepared powder was analyzed on an X-ray diffractometer (Rigaku, MiniFlex) using CuKα radiation. Diffuse reflectance spectra were obtained using a UV-vis-NIR spectrometer (JASCO, Ubest-570) equipped with an integrating sphere and were converted from reflection to K-M function by the Kubelka-Munk method. Electron spin resonance (ESR) spectra were recorded at 77 K on an ESR spectrometer (JEOL, JES-FA200).

Photocatalytic reactions of sacrificial H₂ and O₂ evolution were carried out using a gas-tight circulation system with a
top-irradiation cell with a Pyrex window. Photocatalyst powder (0.2 g) was dispersed in an aqueous solution (120 mL) containing 10 vol% methanol as a hole scavenger and a certain amount of H2PtCl6 as a source of a Pt cocatalyst for sacrificial H2 evolution. Photocatalyst powder (0.2 g) was dispersed in an aqueous solution (120 mL) containing 20 mmol L\(^{-1}\) AgNO3 as an electron scavenger for sacrificial O2 evolution. The suspension was irradiated with visible light using a 300 W Xe lamp (PerkinElmer, Cerox PE300BF) with a long-pass filter (HOYA L42). The amounts of evolved gases were determined using an online gas chromatograph (Shimadzu, GC-8A, MS-5A column, TCD, Ar carrier). The apparent quantum yield (AQY) for the sacrificial O2 evolution was estimated using the following equation.

\[
\text{[AQY\%]} = 100 \times \frac{[\text{the number of reacted holes}]}{[\text{the number of incident photons}]} \\
= 100 \times [\text{the number of evolved O2 molecules}] \times 4/ [\text{the number of incident photons}]
\]

The photon flux of the monochromatic light through the band-pass filters (Asahi Spectra, MAX-303) was measured using a silicon diode head (Ophir Optronics, PD300-UV head and NOVA display).

XRD measurements revealed that Ru(0.3\%) -doped SrTiO3 (SrTiO3:Ru) was obtained without noticeable impurities (Fig. S1†), indicating that Ru ions were doped into the SrTiO3 lattice. Judging from the ionic radii of Ru\(^{3+}\) (68 pm, 6 coordination) and Ru\(^{4+}\) (62 pm, 6 coordination) compared to that of Ti\(^{4+}\) (60.5 pm, 6 coordination),\(^{17}\) the Ru ions should be doped at Ti\(^{4+}\) sites. In the ESR measurements, no signal was observed for non-doped SrTiO3, while Ru-doped SrTiO3 gave a small signal, as shown in Fig. 1. The intensity of the signal increased by H\(_2\)-reduction and Sb-codoping, indicating that the observed ESR signal was from either Ti\(^{3+}\) or Ru\(^{3+}\). Upon considering the stability of SrTiO3, Ti\(^{3+}\) may not be formed by H\(_2\)-reduction at 673 K. Thus, we can conclude that Ru was mainly doped as Ru\(^{4+}\) which is ESR inactive and was reduced to Ru\(^{3+}\) by H\(_2\)-reduction and Sb-codoping.

![Fig. 2](Image 14x290 to 26x354)  
**Fig. 1** ESR spectra for Ru\(^{3+}\) in (a) non-doped SrTiO3, (b) SrTiO3::Ru(0.3%), SrTiO3:Ru(0.3%) after H\(_2\)-reduction at (c) 473 K and (d) 673 K and (e) SrTiO3:Ru(0.3%), Sb(0.45%).

The change in the oxidation number of a dopant, especially a transition metal cation with d\(^a\) configuration (\(n = 1\) – 9), usually affects the photoabsorption properties of the material, as observed for Rh-doped SrTiO3 and Ir-doped SrTiO3.\(^{13–16}\) SrTiO3:Ru possessed a wide absorption band in the visible light region in addition to the band gap absorption of the SrTiO3 host (Fig. 2b). Upon reduction with H\(_2\), the absorption at around 500 – 700 nm increased, while the absorption at around 400 – 450 nm decreased (Fig. 2c and d). On the basis of the change in the absorption profile, the absorption bands at around 500 – 700 nm and 400 – 450 nm were assigned to Ru\(^{3+}\) - and Ru\(^{4+}\)-related transitions, respectively. This behavior corresponded to the change in ESR signals.

Sb, Nb and Ta ions were codoped with Ru into SrTiO3 to control the Ru to be trivalent. The XRD patterns of Ru,Sb-, Ru,Nb- and Ru,Ta-codoped SrTiO3 were the same as that of SrTiO3:Ru (Fig. S1†), indicating the successful doping of Sb, Nb and Ta. Upon codoping with Sb ions, the absorption in the diffuse reflectance spectrum at around 500 – 800 nm increased, whereas the absorption at around 400 – 450 nm decreased (Fig. 2e). This is because the doped Ru ions were controlled to be trivalent by codoping with Sb ions. In more detail, two Ti\(^{3+}\) ions were substituted with Ru\(^{3+}\) and Sb\(^{5+}\) ions to maintain the charge balance, according to 2Ti\(^{3+}\) = Ru\(^{3+}\) + Sb\(^{5+}\). Actually, the intensity of the ESR signal also increased by codoping with Sb ions (Fig. 1e). However, the intensities of the absorption at around 500 – 800 nm in the diffuse reflectance spectra and the ESR signal were lower than those of the sample after H\(_2\)-reduction. These lower intensities indicate that Ru\(^{4+}\) ions still existed even in Ru,Sb-codoped SrTiO3. The profile of the diffuse reflectance spectrum of SrTiO3:Ru did not change upon codoping of either Nb or Ta ions (Fig. 2f and g). This indicates that the Nb and Ta ions do not contribute to control of the oxidation number of the doped Ru ions, being different from Sb ions. The codopants should locate close to the Ru ions to maintain the charge balance. Both Ru\(^{3+}\) (68 pm, 6 coordination) of the dopant and Nb\(^{5+}\) or Ta\(^{5+}\) (64 pm, 6 coordination) of the codopants.
possess larger ionic radii than Ti$^{4+}$ (60.5 pm, 6 coordination). Therefore, it is unfavourable that Ru$^{3+}$ and Nb$^{5+}$ or Ta$^{5+}$ are closely located to each other. In contrast, Sb$^{5+}$ (60 pm, 6 coordination) possesses a slightly smaller ionic radius than Ti$^{4+}$ (60.5 pm, 6 coordination). This suggests that Sb$^{5+}$ can locate closely to Ru ions resulting in control of the oxidation number of the doped Ru ions compared to Nb and Ta ions.

Table 1 shows the photocatalytic activities for sacrificial H$_2$ and O$_2$ evolution over SrTiO$_3$:Ru, H$_2$-reduced SrTiO$_3$:Ru and codoped SrTiO$_3$:Ru under visible light irradiation. SrTiO$_3$:Ru showed activities for both sacrificial H$_2$ evolution and O$_2$ evolution, as previously reported. H$_2$-Reduced SrTiO$_3$:Ru showed a higher activity for the sacrificial O$_2$ evolution than the pristine SrTiO$_3$:Ru and the activity increased with increasing temperature of H$_2$ reduction.

In contrast, the activity for the sacrificial H$_2$ evolution was decreased by H$_2$ reduction. The H$_2$-reduced SrTiO$_3$:Ru continuously produced O$_2$ under visible light irradiation, as shown in Fig. 3. The turnover number which is the ratio of the number of reacted holes to the number of doped Ru ions is calculated to be 45 using the amount of evolved O$_2$ (37 $\mu$mol for 4 h) and doped Ru ions (3.3 $\mu$mol in 0.2 g of SrTiO$_3$:Ru). The activity for sacrificial O$_2$ evolution over Ru$_3$Nb-codoped SrTiO$_3$ was also higher than that over SrTiO$_3$:Ru, while the activity for sacrificial H$_2$ evolution was lower. This trade-off between the sacrificial H$_2$ evolution and O$_2$ evolution for the codoped photocatalyst was similar to that for Rh$_3$Nb-codoped SrTiO$_3$.$^{15,16}$ A doped photocatalyst with impurity levels formed by a dopant with an oxidation number stabilized by H$_2$-reduction and Sb-codoping is sometimes not suitable for H$_2$ evolution, as observed for Rh$_3$Nb-codoped SrTiO$_3$.$^{15,16}$ Ru$_3$Nb- and Ru$_3$Ta-codoped SrTiO$_3$ showed similar activities for sacrificial H$_2$ and O$_2$ evolution to that of SrTiO$_3$:Ru. Thus, the activity for sacrificial O$_2$ evolution increased upon increasing the rate of doped Ru$^{3+}$ by H$_2$ reduction and Sb-codoping.

To further understand the relationship between the doped Ru$^{3+}$ ions and the activity for O$_2$ evolution, action spectra were measured, as shown in Fig. 4. SrTiO$_3$:Ru, H$_2$-reduced SrTiO$_3$:Ru and Ru$_3$Sb-codoped SrTiO$_3$ (SrTiO$_3$:Ru$_3$Sb) showed activity for sacrificial O$_2$ evolution using light up to 660 nm (1.88 eV), 750 nm (1.65 eV) and 670 nm (1.85 eV), respectively.

The onset of the action spectrum for the O$_2$ evolution over the SrTiO$_3$:Ru in which doped Ru was mainly tetravalent was similar to that of the photoanodic current of an RuO$_2$-doped SrTiO$_3$ photoelectrode, though the condition of the doped Ru was not clear for the photoanode.$^{18}$ As discussed above, the corresponding absorption bands were assigned to Ru$^{3+}$-related transitions. The possible band structures of SrTiO$_3$: Ru, H$_2$-reduced SrTiO$_3$:Ru and SrTiO$_3$:Ru$_3$Sb judging from the action spectra are summarized in Fig. 5. The valence band maximum consisting of the O$_2p$ orbitals of metal oxides is generally located at around +3.0 V vs. NHE at pH 0, and the band levels of metal oxides shift with −0.059 V pH$^{-1}$. Accordingly, the conduction band minimum and the valence band maximum of SrTiO$_3$:Ru with a band gap of 3.2 eV are estimated to be at −0.61 V and +2.59 V vs. NHE at pH 7, respectively. When the Ru$^{3+}$-related transition is the

Table 1: Sacrificial H$_2$ and O$_2$ evolution over the SrTiO$_3$:Ru, H$_2$-reduced SrTiO$_3$:Ru and codoped SrTiO$_3$:Ru photocatalysts under visible light irradiation

| Photocatalyst | Activity/μmol h$^{-1}$ | H$_2$ | O$_2$ |
|--------------|----------------------|------|------|
| SrTiO$_3$:Ru (0.3%) | 4.0 | 4.4 |
| SrTiO$_3$:Ru (0.3%) with H$_2$-red. (473 K) | 1.7 | 8.0 |
| SrTiO$_3$:Ru (0.3%) with H$_2$-red. (673 K) | 1.8 | 16.1 |
| SrTiO$_3$:Ru (0.3%),Sb (0.45%) | 0.2 | 7.3 |
| SrTiO$_3$:Ru (0.3%),Nb (0.6%) | 3.3 | 3.3 |
| SrTiO$_3$:Ru (0.3%),Ta (0.6%) | 2.4 | 4.3 |

Photocatalyst: 0.2 g; reactant solution: 120 mL; light source: 300 W Xe lamp with a long-pass filter ($\lambda > 420$ nm, L42). $^a$ Prepared at 973 K for 10 h by a solid-state reaction with 1.5 at% excess Sr. $^b$ Pt (0.3 wt%)-Cocatalyst; 10 vol% MeOH aq. $^c$ 20 mmol L$^{-1}$ AgNO$_3$ aq.
There is a negative correlation between the order of the energy gap (SrTiO₃:Ru > SrTiO₃:Ru,Sb > H₂-reduced SrTiO₃:Ru) and the order of the rate of Ru³⁺ ions (SrTiO₃:Ru < SrTiO₃:Ru,Sb < H₂-reduced SrTiO₃:Ru) judging from the ESR spectra (Fig. 1). When the rate of Ru³⁺ increases, the impurity levels formed by Ru³⁺ become wide due to the increased density of states. Accordingly, the energy gap between the conduction band and the impurity levels formed by Ru³⁺ becomes narrow, as shown in Fig. 5. The widened impurity levels are also considered to be favorable for migration of photogenerated holes. Thus, the possible reasons why H₂-reduced SrTiO₃:Ru showed higher activity for the sacrificial O₂ evolution than SrTiO₃:Ru and SrTiO₃:Ru,Sb are the longest response wavelength and favorable impurity levels for hole migration.

Conclusions

In conclusion, the SrTiO₃:Ru,Sb and H₂-reduced SrTiO₃:Ru photocatalysts as well as SrTiO₃:Ru showed activities for sacrificial H₂ and O₂ evolution under visible light irradiation. Ru ions were mainly doped as tetravalent Ru in SrTiO₃:Ru and the Ru⁴⁺ ions became Ru³⁺ ions by Sb-codoping and H₂-reduction. The H₂ evolution activity decreased by controlling Ru to become trivalent, while the O₂ evolution activity increased. Photocatalytic reactions over SrTiO₃:Ru, SrTiO₃:Ru,Sb and H₂-reduced SrTiO₃:Ru proceeded by the excitation from the impurity levels formed by Ru³⁺ to the conduction band of SrTiO₃. Among them, H₂-reduced SrTiO₃:Ru especially showed the highest O₂ evolution activity and the longest response wavelength up to 750 nm, because of widening of the impurity level formed by Ru³⁺. Thus, we successfully developed metal oxide photocatalysts with a response to long wavelength visible light (near infrared) by Ru³⁺ doping. This responsive wavelength is almost the longest among those of photocatalysts which are active for O₂ evolution. Thus, Ru-doping will be one strategy to develop metal oxide photocatalysts responding to a wide range of visible light. Moreover, these photocatalysts can be employed as O₂-evolving photocatalysts in a Z-scheme photocatalyst system.

Conflicts of interest

There are no conflicts to declare.

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