Photocatalytic H₂ evolution by layered perovskite Ca₃Ti₂O₇ codoped with Rh and Ln (Ln = La, Pr, Nd, Eu, Gd, Yb, and Y) under visible light irradiation

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Layered perovskite Ca₃Ti₂O₇ codoped with Rh and Ln (Ca_{3-x}Ln_xTi_{1.9}Rh_{0.1}O₇; Ln = La, Pr, Nd, Eu, Gd, Yb, and Y; 0 ≤ x ≤ 0.15) was synthesized by a conventional solid-state reaction to investigate the effects of Rh and Ln codoping on the photocatalytic activity. Rh and Ln-codoped Ca₃Ti₂O₇ exhibited a higher photocatalytic activity than Rh-doped Ca₃Ti₂O₇ for H₂ production from an aqueous methanol solution under visible light irradiation (λ > 420 nm). In addition, the induction period for H₂ production was shortened by codoping with Rh and Ln. The codoped elements helped control the oxidation state of Rh ions and suppressed the formation of oxygen defects, improving the activity of the Rh-doped Ca₃Ti₂O₇ photocatalyst.

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1. Introduction

Since the discovery of photoelectrochemical splitting of water on TiO₂ electrodes,¹⁾ much attention has been paid to photocatalytic water splitting to produce H₂ from water using solar light. This would provide a clean energy carrier from a renewable source. Some ceramic materials, which are suitable for the photocatalytic reaction in water because of their resistance to photocorrosion, have shown reasonable activity for splitting water into H₂ and O₂ in a stoichiometric ratio under UV irradiation.^{2)–11)} Unfortunately, few photocatalysts have been found that can accomplish stoichiometric water splitting under visible light irradiation. Thus, there is a strong desire to develop improved catalysts, with higher photocatalytic activity for H₂ production.

A Z-scheme photocatalyst system, which is a combined system involving two photoexcitation processes, is a very attractive research target for effective harvesting of solar energy.^{12)–14)} In this system, two types of visible-light responsive photocatalysts for H₂ and O₂ evolution are applied for overall water splitting under visible light irradiation. It is, therefore, important to design new photocatalysts, which are active in either H₂ or O₂ evolution under visible light irradiation.

The introduction of foreign elements into active photocatalytic compounds with wide band gaps in order to create donor or acceptor levels within the forbidden band is one useful approach to developing new visible-light-driven photocatalysts. Unfortunately, most doped materials are inactive because electron-hole recombination centers are formed by doping. However, there have been some reports that Ti-based photocatalysts such as TiO₂, SrTiO₃, and CaTiO₃, when doped with foreign elements, can produce H₂ or O₂ from aqueous solutions containing sacrifi-

cial reagents under visible light irradiation.^{15)–22)} In particular, Ti-based perovskite compounds doped with Rh showed highly efficient H₂ evolution. In Rh-doped Ti-based perovskite systems, the doped Rh ions were assigned to Rh³⁺. Rhodium species with a higher oxidation number than Rh³⁺, such as Rh⁵⁺, were reduced to Rh³⁺ by photogenerated electrons at an early stage of the photocatalytic reaction.^{20)–22)} As a result, visible-light responsive photocatalytic activity is induced by a transition from the electron donor level of Rh³⁺ to the conduction band composed of the Ti 3d orbital. That is, Rh³⁺ proved very important for efficient H₂ evolution.

We have recently reported the effect of doping Rh into layered perovskite Ca₃Ti₂O₇, which consists of NaCl-type CaO blocks and perovskite-type Ca₂Ti₂O₆ blocks, alternately ordered along the *b*-axis.²³⁾ As-prepared Rh-doped Ca₃Ti₂O₇ showed poor photocatalytic activity under visible light irradiation, unlike Rh-doped SrTiO₃²⁰⁾ or CaTiO₃,²¹⁾ but this activity was drastically enhanced by treating the Rh-doped Ca₃Ti₂O₇ under a reducing atmosphere of 3% H₂. This unique behavior suggests that controlling the oxidation state of Rh ions by external stimuli was very important in the Ca₃Ti₂O₇ system, compared with SrTiO₃ and CaTiO₃ systems. On the other hand, Niishiro et al. reported that rutile-type TiO₂ codoped with Rh and Sb showed high photocatalytic O₂ evolution from an aqueous silver nitrate solution under visible light irradiation.²²⁾ According to their report, the activity depended upon suppressing the formation of Rh⁴⁺ and promoting the formation of Rh³⁺ by codoping high-valence ions, such as Sb⁵⁺. In addition, codoping with Rh and Sb suppressed the formation of oxygen defects, which act as recombination centers.

Thus, we believed that controlling the oxidation state of Rh ions and compensating charge to suppress the formation of oxygen defects by codoping with another high-valence ion improved the photocatalytic activity of the Rh-doped Ca₃Ti₂O₇. In the present study, we synthesized Ca₃Ti₂O₇ codoped with Rh and Ln (Ca_{3-x}Ln_xTi_{1.9}Rh_{0.1}O₇; Ln = La, Pr, Nd, Eu, Gd, Yb, and

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Y; $0 \leq x \leq 0.15$), where Ca²⁺ sites were partially replaced with Ln³⁺ ions, leading to the formation of Rh³⁺ ions at Ti⁴⁺ sites without the formation of oxygen defects. The effects of codoping Ln and Rh on the photocatalytic activities were investigated by measuring photocatalytic H₂ evolution from an aqueous methanol solution under visible light irradiation.

2. Experimental

Powdered Rh and La-codoped Ca₃Ti₂O₇ was prepared by a conventional solid-state reaction, using CaCO₃, TiO₂, Rh₂O₃, and La₂O₃ as starting materials. Before weighing, the La₂O₃ powders were pre-heated at 900°C for 5 h in air to remove absorbed water. The mixture of CaCO₃, TiO₂, Rh₂O₃, and La₂O₃ was pre-heated at 1000°C for 10 h in air. After pre-heating, the mixtures were ground and heated at 1600°C for 6 h in air. Rh and Ln-codoped Ca₃Ti₂O₇ (Ln = Pr, Nd, Eu, Gd, Yb, and Y) was also prepared by the same procedure as was used for Rh and La-codoped Ca₃Ti₂O₇, using CaCO₃, TiO₂, Rh₂O₃, Pr₆O₁₁, Nd₂O₃, Eu₂O₃, Gd₂O₃, Yb₂O₃, or Y₂O₃ as starting materials. The obtained powdered samples were identified by X-ray diffraction (XRD), using a Rigaku Co., RINT2100/PC diffractometer with monochromatic Cu K α radiation. Diffuse reflectance spectra were measured using a Shimadzu Co., UV-2450 spectrophotometer. The specific surface areas of the resulting samples were evaluated by measuring isothermal adsorption of N₂ at 77 K based on the BET method (BEL-Japan BELSORP 18 PLUS).

The behavior of photocatalytic H₂ evolution from an aqueous methanol solution was examined using a closed-gas circulation system. The powdered samples (0.3 g) were dispersed in a 10 vol% aqueous methanol solution (150 mL) in a Pyrex cell under an Ar atmosphere. The suspensions containing the samples were irradiated by a 300 W Xe lamp with attached cut-off filters to control the wavelength of the incident light, and the amount of H₂ produced was measured by gas chromatography, using a Shimadzu GC-8A equipped with a thermal conductivity detector. For the measurements, Pt co-catalysts (0.1 mass%) were loaded in situ by a photo-reduction method, using an aqueous H₂PtCl₆ solution.

3. Results and discussion

Figure 1 shows the XRD patterns of Rh and La-codoped

Fig. 1. XRD patterns of Rh and La-codoped Ca₃Ti₂O₇ (Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇; $0 \leq x \leq 0.15$).

Ca₃Ti₂O₇ (Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇; $0 \leq x \leq 0.15$). The resulting crystalline phases of the samples were indexed using the same crystal structure of the orthorhombic system as was previously reported for Ca₃Ti₂O₇.²⁴⁾ Though a few XRD peaks assigned to Ca₄Ti₃O₁₀ were observed around $2\theta = 13, 19$ and 46° , no impurity peaks due to Rh and La were detected in the XRD patterns. Moreover, the indexed XRD peaks for the Ca₃Ti₂O₇ phase shifted toward lower angles with increasing La doping. This indicates that an expansion of the unit cell was caused by the La doping, because the size of a La ion is larger than that of a Ca ion.²⁵⁾

Figure 2 shows diffuse reflectance spectra of prepared Rh and La-codoped Ca₃Ti₂O₇ (Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇; $0 \leq x \leq 0.15$), together with Ca₃Ti_{1.9}Rh_{0.1}O₇ treated at 200°C for 1 h under a 3% H₂ atmosphere. As described in the previous report, an intense absorption peak was observed at 550 nm for Ca₃Ti_{1.9}Rh_{0.1}O₇ before the reducing treatment. This peak disappeared and a new peak appeared at 360 nm after the reducing treatment.²³⁾ These changes in the spectra were attributed to the reduction of Rh ions to Rh³⁺ ions. It was noted that the peak intensity at 550 nm for Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ ($0 \leq x \leq 0.15$) decreased considerably with increasing La content up to $x = 0.11$, while the peak intensity at 360 nm increased. With further La doping, the peaks at 550 nm remained unchanged. These results indicate that the formation of Rh³⁺ in the samples was systematically promoted by increasing the La content up to $x = 0.11$, and that most of the Rh existed as Rh³⁺ ions in the Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ ($0.11 \leq x \leq 0.15$) samples.

Examining the photocatalytic H₂ evolution from an aqueous methanol solution under visible light irradiation ($\lambda > 420$ nm) revealed that although Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ ($x = 0$ and 0.15) did not generate H₂, Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ ($0.08 \leq x \leq 0.12$) did generate H₂. The H₂ evolution over a Ca_{2.91}La_{0.09}Ti_{1.9}Rh_{0.1}O₇ sample is shown in **Fig. 3** as a typical time course. Hydrogen gas was generated after an induction period of several hours. No reaction took place in the dark. In subsequent reaction after evacuation, H₂ evolution resumed, with no significant decrease in activity. These results demonstrate that Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ ($0.08 \leq x \leq 0.12$) functions as a photocatalyst.

Figure 4 shows the effect of La doping on H₂ evolution from an aqueous methanol solution under visible light irradiation. The induction period and the H₂ evolution rate differed among the samples. The induction period shortened with increasing La con-

Fig. 2. Diffuse reflectance spectra of Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ ($x =$ (a) 0, (b) 0.08, (c) 0.09, (d) 0.1, (e) 0.11, (f) 0.12 and (g) 0.15), as well as (h) Ca₃Ti_{1.9}Rh_{0.1}O₇ treated at 200°C for 1 h under a 3% H₂ atmosphere.

Fig. 3. H_2 evolution from an aqueous methanol solution under visible light irradiation over $\text{Pt}/\text{Ca}_{2.91}\text{La}_{0.09}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$. Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt%), reactant solution; 150 mL of a 10 vol% aqueous methanol solution, and light source; 300-W Xe lamp with a cut-off filter ($\lambda > 420$ nm).

tent up to $x = 0.1$. Then, it lengthened with further La doping. Similarly, the H_2 evolution rate increased with increasing La content up to $x = 0.1$, and decreased drastically with further La doping. Measurements of isothermal adsorption of N_2 at 77 K revealed that the specific surface area of $\text{Ca}_3\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($1.2 \text{ m}^2/\text{g}$) was nearly same as those of $\text{Ca}_{2.9}\text{La}_{0.1}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($1.3 \text{ m}^2/\text{g}$) and $\text{Ca}_{2.8}\text{La}_{0.11}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($1.3 \text{ m}^2/\text{g}$). Although the samples contain the impurity phase ($\text{Ca}_4\text{Ti}_3\text{O}_{10}$) with different contents, which can be roughly estimated from the peak intensity at $2\theta = 46^\circ$, there is no relation between the impurity phase contents and photocatalytic activities (H_2 evolution rate and induction period). Therefore, the difference of the H_2 evolution behaviors can be discussed based on the La doping effect. As shown in Fig. 5, the diffuse reflectance spectra of $\text{Ca}_{2.9}\text{La}_{0.1}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ remained nearly unchanged by the photocatalytic reaction, whereas those of $\text{Ca}_{3-x}\text{La}_x\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($x = 0.08$ and 0.09) changed as follows. The peak intensity at 550 nm weakened, suggesting that Rh with a high oxidation number such as Rh^{5+} ions was reduced to Rh^{3+} by photogenerated electrons during the induction period. In addition, the spectrum of the sample without La doping, $\text{Ca}_3\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$, was not significantly changed by the reaction, although no H_2 was generated. This indicates that La doping facilitates the reduction of Rh by photogenerated electrons. Consequently, these effects caused differences in induction periods for $\text{Ca}_{3-x}\text{La}_x\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($0.08 \leq x \leq 0.1$). Furthermore, the peak intensity at 550 nm for $\text{Ca}_{2.91}\text{La}_{0.09}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ after the photocatalytic reaction was comparable to that of $\text{Ca}_{2.9}\text{La}_{0.1}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ before and after reaction, whereas the same peak for $\text{Ca}_{2.92}\text{La}_{0.08}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ after reaction was weaker than those of $\text{Ca}_{3-x}\text{La}_x\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($x = 0.09$ and 0.1) after reaction. Moreover, most Rh ions existed as Rh^{3+} in $\text{Ca}_{3-x}\text{La}_x\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($0.11 \leq x \leq 0.15$), as evident from the diffuse reflectance spectra, which remained unchanged after the reaction. Consequently, the Rh^{3+} content in the sample was estimated to be on the order of x : $0.08 < 0.09-0.1 < 0.11-0.15$. The activity should increase with Rh^{3+} content, since the visible light responsive photocatalytic activity is induced by a transition from the electron donor level

Fig. 4. (a) H_2 evolution from an aqueous methanol solution under visible light irradiation over $\text{Pt}/\text{Ca}_{3-x}\text{La}_x\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($0.08 \leq x \leq 0.12$). (b) H_2 evolution activity of $\text{Pt}/\text{Ca}_{3-x}\text{La}_x\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ ($0 \leq x \leq 0.15$). Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt%), reactant solution; 150 mL of a 10 vol% aqueous methanol solution, and light source; 300-W Xe lamp with a cut-off filter ($\lambda > 420$ nm).

of Rh^{3+} to the conduction band composed of the Ti 3d orbital. Furthermore, a moderate amount La doping suppressed the formation of oxygen defects due to the charge imbalance caused by the formation of Rh^{3+} , resulting in the increase in activity. On the other hand, further La doping induced the formation of lattice defects. Moreover, a large doping of foreign elements may form excess charge recombination centers. Thus, these effects in balance led to optimal dopant amounts. The considerable decrease in activity caused by excess La doping probably elongated the induction period.

Our previous report revealed that the H_2 evolution rate of as-prepared $\text{Ca}_3\text{Ti}_{2-x}\text{Rh}_x\text{O}_7$ depended on the Rh content, and $\text{Ca}_3\text{Ti}_{1.98}\text{Rh}_{0.02}\text{O}_7$ showed the maximum H_2 generation rate of ca. $0.5 \mu\text{mol/h}$ after a long induction period (~ 20 h).²³⁾ Furthermore, no H_2 generation was observed for $\text{Ca}_3\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$. On the other hand, $\text{Ca}_{2.9}\text{La}_{0.1}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ efficiently produced H_2 after a short induction period (~ 6 h). The H_2 evolution rate of $\text{Ca}_{2.9}\text{La}_{0.1}\text{Ti}_{1.9}\text{Rh}_{0.1}\text{O}_7$ was about 2 times higher than that of $\text{CaTi}_{1.98}\text{Rh}_{0.02}\text{O}_7$. Thus, Rh and La-codoping had a significant

Fig. 5. Diffuse reflectance spectra of Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇ (0.08 ≤ x ≤ 0.1) before (solid lines) and after (broken lines) the photocatalytic reaction.

Fig. 6. Diffuse reflectance spectra of Ca_{2.9}Ln_{0.1}Ti_{1.9}Rh_{0.1}O₇ (Ln = La, Pr, Nd, Eu, Gd, Yb, and Y).

effect on the photocatalytic activity. However, the activity of Ca_{2.9}La_{0.1}Ti_{1.9}Rh_{0.1}O₇ was about half that of Ca₃Ti_{1.9}Rh_{0.1}O₇ treated under a reducing atmosphere of 3% H₂. Rh and Ln-codoped Ca₃Ti₂O₇ (Ln = Pr, Nd, Eu, Gd, Yb and Y) were prepared to investigate the effect of codopant on catalytic activity.

Since the optimum La content was x = 0.1 for Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇, Ca_{2.9}Ln_{0.1}Ti_{1.9}Rh_{0.1}O₇ (Ln = Pr, Nd, Eu, Gd, Yb and Y) were prepared. All samples were indexed on the crystal structure of the same orthorhombic system as Ca₃Ti₂O₇,²⁴⁾ and a few very weak XRD peaks assigned to Ca₄Ti₃O₁₀ were observed at 2θ = 13, 19 and 46°, as observed on the XRD pattern of Ca_{2.9}La_{0.1}Ti_{1.9}Rh_{0.1}O₇. No impurity peaks due to Rh or Ln (Ln = Pr, Nd, Eu, Gd, Yb, and Y) were detected in the XRD patterns. **Figure 6** shows the diffuse reflectance spectra of prepared Rh and Ln-codoped Ca₃Ti₂O₇ samples (Ca_{2.9}Ln_{0.1}Ti_{1.9}Rh_{0.1}O₇, Ln = Pr, Nd, Eu, Gd, Yb, and Y), together with Ca_{2.9}La_{0.1}Ti_{1.9}Rh_{0.1}O₇. All spectra were similar, suggesting that approximately the same amounts of Rh ions were reduced to Rh³⁺ with Ln (Ln = Pr, Nd, Eu, Gd, Yb, and Y) doping.

Fig. 7. H₂ evolution from an aqueous methanol solution under visible light irradiation over Pt/Ca_{2.9}Ln_{0.1}Ti_{1.9}Rh_{0.1}O₇ (Ln = La, Pr, Nd, Eu, Gd, Yb, and Y). Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt%), reactant solution; 150 mL of a 10 vol% aqueous methanol solution, and light source; 300-W Xe lamp with a cut-off filter (λ > 420 nm).

Figure 7 shows the effect of Ln (Ln = Pr, Nd, Eu, Gd, Yb, and Y) doping on H₂ evolution from an aqueous methanol solution under visible light irradiation. All samples produced H₂ after similar induction periods (~6 h). On the other hand, the H₂ evolution rate depended on the codopant. In addition, no dependence of the activity on Ln³⁺ size was observed. According to the previous report, the contribution of the Ln 4f orbital to the O 2p and Ta 5d orbitals in layered perovskite photocatalysts, RbLnTa₂O₇ (Ln = La, Pr, Nd, and Sm), had a significant impact on the photocatalytic activity.^{8),26)} Therefore, the difference in activity was caused by the difference in the contribution of the Ln 4f orbital to the O 2p and Ti 3d orbitals. The maximum H₂ evolution rate was obtained on Rh and Gd-codoped Ca₃Ti₂O₇, and this activity was comparable to that of reduced CaTi_{1.9}Rh_{0.1}O₇.

4. Conclusions

Layered perovskite Ca₃Ti₂O₇ codoped with Rh and Ln (Ca_{3-x}Ln_xTi_{1.9}Rh_{0.1}O₇; Ln = La, Pr, Nd, Eu, Gd, Yb, and Y; 0 ≤ x ≤ 0.15) functioned as a photocatalyst for H₂ production from an aqueous methanol solution under visible light irradiation (λ > 420 nm). The formation of Rh³⁺ in the samples was increasingly promoted by increasing Ln content, resulting in shortening of the induction period. The dependence of the H₂ evolution rate on the La content suggested that a moderate amount of La doping suppressed the formation of oxygen defects due to the charge imbalance caused by the appearance of Rh³⁺, resulting in increased activity. The optimum amount of doping proved to be x = 0.1 for Ca_{3-x}La_xTi_{1.9}Rh_{0.1}O₇. The Ca_{2.9}Gd_{0.1}Ti_{1.9}Rh_{0.1}O₇ sample showed the highest activity in this study, which was comparable to that of reduced CaTi_{1.9}Rh_{0.1}O₇, and about 5 times the maximum activity of as-prepared CaTi_{2-x}Rh_xO₇ samples.

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