

## 論文の内容の要旨 (Abstract)

論文題目     Development of Perovskite-type Oxide Photocatalysts for Water Splitting under  
Visible Light Irradiation

(可視光照射下での水分解を目的としたペロブスカイト型酸化物光触媒の開発)

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Photocatalytic water splitting has received much attention for its potential significance in producing clean and renewable H<sub>2</sub> from water. Few oxide photocatalysts show activity for H<sub>2</sub> evolution under visible light even in the presence of an electron donor, because their band gap energies are too large to absorb visible light or their conduction band edges are too positive to reduce water to hydrogen directly. For example, perovskite-type strontium titanate (SrTiO<sub>3</sub>) is a photocatalyst that is active for overall water splitting. However, the photoabsorption band of SrTiO<sub>3</sub> is restricted to the ultraviolet light region because of its wide band gap (3.25 eV).<sup>1</sup> Doping of wide-gap semiconductor photocatalysts with metal cations is a conventional but important approach for production of a visible-light-driven photocatalyst via formation of donor or acceptor levels in the band gap. Among the various dopants examined, Rh is one of the most interesting metals for yielding visible light activity.<sup>2</sup> Rh-doped SrTiO<sub>3</sub> absorbs visible light owing to the transition from electron donor levels formed by Rh<sup>3+</sup> ions to the conduction band composed of the Ti 3d orbital of SrTiO<sub>3</sub>.<sup>2</sup> In contrast, electron transitions associated with coexisting Rh<sup>4+</sup> species are inactive during the H<sub>2</sub> evolution reaction under visible light irradiation, but instead do offer a recombination route for photogenerated electrons and holes.<sup>3</sup> Codoping is a useful strategy for controlling of the valence states of dopants and can result in improvement of the photocatalytic activity of SrTiO<sub>3</sub>.<sup>1,4</sup> It was expected that codoping La ions could improve the photocatalytic H<sub>2</sub> evolution activity of Rh-doped SrTiO<sub>3</sub>. Rh-doped SrTiO<sub>3</sub> can also be applied as a H<sub>2</sub> evolution photocatalyst in Z-scheme overall water splitting, where two types of visible-light responsive photocatalysts are applied for H<sub>2</sub> and O<sub>2</sub> evolution to complete overall water splitting. However, the solar energy conversion efficiency of Z-scheme systems using Rh-doped SrTiO<sub>3</sub> was very low.<sup>2,3,5</sup> BiVO<sub>4</sub> was the most active component for O<sub>2</sub> evolution in the redox-mediator-free Z-scheme system with Rh-doped SrTiO<sub>3</sub>, still yielding a solar energy conversion efficiency of 0.12%.<sup>3</sup> The absorption edge wavelength of BiVO<sub>4</sub> is approximately 520 nm, which limits the potential of the Z-scheme system in harvesting sun light. In earlier studies, Ta<sub>3</sub>N<sub>5</sub> was used instead of BiVO<sub>4</sub> to extend the range of available wavelength for O<sub>2</sub> evolution to 600 nm. However, the solar energy conversion efficiency was much lower (0.013 %) than the expectation from the available wavelengths of

the respective photocatalysts, presumably because of the limited light absorption by Rh-doped SrTiO<sub>3</sub>, insufficient activity of Ta<sub>3</sub>N<sub>5</sub>, and/or poor electron transfer among Rh-doped SrTiO<sub>3</sub> and Ta<sub>3</sub>N<sub>5</sub> particles.<sup>5</sup> In fact, the efficiency of interparticle electron transfer has a significantly effect on the photocatalytic activity.<sup>3</sup> It is essential to ensure a continuous flow of electrons between the photocatalysts.

On the basis of the aforementioned background, it is important to design new materials which are more active for H<sub>2</sub> evolution under visible light and new systems which are more efficient for interparticle electron transfer between photocatalysts. In this research, metal ions were doped in perovskite-type oxide photocatalysts such as La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub><sup>6</sup> and SrTiO<sub>3</sub> in order to develop more active photocatalysts for water splitting under visible light and utilize solar energy more efficiently in redox-mediator-free Z-scheme systems. Besides, a new configuration for the Z-scheme water splitting system consisting of two kinds of photocatalyst particles (one for H<sub>2</sub> evolution and the other for O<sub>2</sub> evolution) and metal layer, called a photocatalyst sheet, was fabricated in order to enhance the interparticle electron transfer efficiency.

In Chapter 1, the urgent need to develop hydrogen production technology, basic principle of one-step and two-step overall water splitting on powdered photocatalysts, and the progress in the development of the photocatalysts with perovskite structure were described.

In Chapter 2, La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> doped with Rh was developed as a novel visible-light-driven material. The effects of the conditions used during molten salt synthesis of Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> on the resultant physical properties and photocatalytic activity were examined. Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> synthesized by the flux method showed single-phase diffraction patterns attributable to the La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> phase. The Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> had a steep absorption edge at around 330 nm and a shoulder absorption extending to the visible light region regardless of the preparation methods, indicating that Rh doping reduced the energy gap. With increasing the amount of doped Rh, the intensity of the visible light absorption band was increased, while remaining the position of the UV absorption edge. La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> prepared by the flux method had no activity for H<sub>2</sub> evolution under visible light, due primarily to the large band gap. Doping Rh into La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, on the other hand, resulted in observable H<sub>2</sub> evolution. However, Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> samples prepared by SSR and PC methods exhibited lower performance. The MSS method yielded a higher photocatalytic activity than the SSR and PC methods owing to the larger surface areas, higher crystallinity, higher phase purity, and stronger light absorption induced by the Rh<sup>3+</sup> ions.

In Chapter 3, Rh and La-codoped SrTiO<sub>3</sub> (SrTiO<sub>3</sub>:La/Rh) was developed to enhance the activity of SrTiO<sub>3</sub>:Rh for H<sub>2</sub> evolution under visible light irradiation. The effects of preparation methods, preparation conditions and La doping concentrations on physiochemical properties and photocatalytic water splitting performance of SrTiO<sub>3</sub>:La/Rh were investigated.

The XRD patterns of La- and Rh-codoped SrTiO<sub>3</sub> (La/Sr=Rh/Ti=1 %) prepared by the two-step SSR and PC methods were assignable to SrTiO<sub>3</sub>, while in the one-step SSR sample, LaRhO<sub>3</sub> was observed as an impurity phase. With increasing the amount of La (Rh/Ti=4 %, La/Sr=1–10%), the crystallinity of La-

and Rh-codoped SrTiO<sub>3</sub> became lower, because heavy doping tended to result in the formation of impurities. Compared with Rh-doped SrTiO<sub>3</sub>, La- and Rh-codoped SrTiO<sub>3</sub> prepared using the two-step SSR method showed weaker absorption in the region from 500 to 800 nm in the UV-Vis DRS spectra. The absorption band of 500–800 nm assigned to Rh<sup>4+</sup> species became weaker by La codoping, and the absorption in 400–500 nm attributed to Rh<sup>3+</sup> became apparent. Besides, with increasing the amount of doped La, the intensity of the visible light absorption in 400–500 nm was increased. The photocatalytic activities of La and Rh codoped SrTiO<sub>3</sub> for H<sub>2</sub> evolution from an aqueous methanol solution under visible light ( $\lambda > 420$  nm). La- and Rh-codoped SrTiO<sub>3</sub> prepared by the PC method showed very low activity for H<sub>2</sub> evolution under visible light, primarily owing to its low crystallinity. On the other hand, photocatalytic activity of the sample synthesized by the one-step SSR method was almost identical to that of Rh-doped SrTiO<sub>3</sub>. The result might be due to the low fraction of Rh<sup>3+</sup> ions as is suggested from XPS and DRS spectra. SrTiO<sub>3</sub> codoped with Rh and La prepared using the two-step SSR method exhibited higher photocatalytic activity than Rh-doped SrTiO<sub>3</sub> when loaded with ruthenium as cocatalysts because of its higher crystallinity and higher fraction of Rh<sup>3+</sup> ions.

The dependence of H<sub>2</sub> evolution rates on the calcination time (from 2 to 10 h) shows that SrTiO<sub>3</sub>:La/Rh calcined for 6 h generated the highest H<sub>2</sub> evolution activity. XPS depth-profiling elucidated the characteristic physical properties of the SrTiO<sub>3</sub>:La/Rh prepared via the two-step SSR calcined for 6 h: The concentrations of the La and Rh ions tended to decrease with increasing etching times. STEM-EDX elemental mapping at different stages of the second calcination in the two-step SSR synthesis supported the formation of core/shell-type structure in SrTiO<sub>3</sub>:La/Rh after 6 h calcination. However, further calcination of the sample yielded particles without obvious core/shell structures, indicating that the SrTiO<sub>3</sub>:La/Rh particles became relatively homogeneous. The highly crystalline SrTiO<sub>3</sub> particles serve as perovskite-type templates that allow dopants to nucleate into the SrTiO<sub>3</sub> phase while suppressing segregation of by-products such as the La<sub>2</sub>O<sub>3</sub> or LaRhO<sub>3</sub> that are observed in the material made by the one-step SSR. Photogenerated carriers can migrate to active sites on the surface more readily and efficiently in particles with a core/shell structure, because photoactive Rh<sup>3+</sup> dopants are densely located near the surface. Moreover, the crystallinity of the material can be maintained owing to the SrTiO<sub>3</sub> core. Therefore, the recombination between photogenerated carriers can be suppressed. However, when SrTiO<sub>3</sub>:La/Rh is calcined excessively, the dopants diffuse into the bulk of the material and the gradient in the dopant concentrations is reduced. As a result, SrTiO<sub>3</sub>:La/Rh calcined for 6 h exhibited the highest degree of activity.

In Chapter 4, SrTiO<sub>3</sub>:La/Rh was applied in a redox-mediator-free Z-scheme overall water splitting system in combination with Ir/CoO<sub>x</sub>/Ta<sub>3</sub>N<sub>5</sub> under visible light irradiation ( $\lambda > 420$  nm). Simultaneous evolution of H<sub>2</sub> and O<sub>2</sub> was observed and the H<sub>2</sub>/O<sub>2</sub> ratio was equal to two. Moreover, the rates of H<sub>2</sub> and O<sub>2</sub> evolution were improved 3.8 times compared with the case Rh-doped SrTiO<sub>3</sub> was used as a H<sub>2</sub> evolution photocatalyst.<sup>5</sup> The solar-to-hydrogen efficiency of the Z-scheme system as measured under

illumination with simulated sunlight (AM1.5G) was found to have improved by a factor of three. The dependence of the photocatalytic activity and reaction conditions was examined. The (Ru/SrTiO<sub>3</sub>:La/Rh)-(Ir/CoO<sub>x</sub>/Ta<sub>3</sub>N<sub>5</sub>) system was found to split water into H<sub>2</sub> and O<sub>2</sub> under irradiation up to 540 nm. This wavelength is in reasonably good agreement with the onset of DRS absorbance observed for SrTiO<sub>3</sub>:La/Rh. The AQY associated with Z-scheme water splitting is 1.1% at 420 nm and this value is observed to decrease as the wavelength of the incident photons increases up to 560 nm. These results make it clear that the photocatalytic activity of this Z-scheme system is limited by the activity of the SrTiO<sub>3</sub>:La/Rh, which exhibits weak visible light absorption at longer wavelengths.

In Chapter 5, a novel Z-scheme water splitting system — a photocatalyst sheet — was invented. The comparison of a powered system, a photocatalyst plate and a photocatalyst sheet was carried out. The relationship between preparation and reaction conditions and the photocatalytic activity of photocatalyst sheets was discussed. For the Z-scheme water splitting system of (SrTiO<sub>3</sub>:La,Rh)-(BiVO<sub>4</sub>), the rates of H<sub>2</sub> and O<sub>2</sub> evolution were evidently improved by a factor of 3.5 and 14 in the photocatalyst sheet compared with the powder suspension system and the photocatalyst panel, respectively. No water splitting was observed when Ru/SrTiO<sub>3</sub>:La,Rh or BiVO<sub>4</sub> alone was used in the same reaction condition, indicating that H<sub>2</sub> and O<sub>2</sub> evolved through interparticulate charge transfer between Ru/SrTiO<sub>3</sub>:La,Rh and BiVO<sub>4</sub> particles. The tremendous enhancement of the photocatalytic activity for Z-scheme water splitting on the photocatalyst sheet compared to the photocatalyst panel was attributed to the presence of the metal layer to receive excited electrons from the O<sub>2</sub> evolution photocatalyst and release them to the H<sub>2</sub> evolution photocatalyst.

In Chapter 6, the results illustrated in Chapter 2-5 were summarized and the future outlook was described.

In this thesis, Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> was developed as a novel oxide photocatalyst that was active for hydrogen evolution from an aqueous methanol solution under visible light irradiation. In addition, the photocatalytic activity of Rh-doped SrTiO<sub>3</sub> was enhanced by codoping with La. Besides, a photocatalyst sheet was fabricated as a new configuration for the Z-scheme water splitting system.

## References

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