

# 博士論文(要約)

## 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. 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. For example, 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>. 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. Codoping is a useful strategy for controlling of the valence states of dopants and can result in improvement of the photocatalytic activity of doped SrTiO<sub>3</sub>.

Rh-doped SrTiO<sub>3</sub> can 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, presumably because of the limited light absorption by Rh-doped SrTiO<sub>3</sub> and/or poor electron transfer among hydrogen evolution photocatalysts and oxygen evolution photocatalysts. In fact, the efficiency of interparticle electron transfer has a significant effect on the photocatalytic activity. 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> 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 a 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 (MSS) 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. The MSS method yielded a higher photocatalytic activity than the solid state reaction (SSR) and polymerized complex (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. The highest H<sub>2</sub> evolution rate was obtained with Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> prepared by MSS (1.0 mol% Rh; calcination temperature: 1373 K; mass ratio of molten salts to reactant: unity). The photocatalytic activity of Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> could be enhanced by improving the reversibility of the valence states of the Rh dopant.

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 two-step SSR method was found to be an effective means of preparing SrTiO<sub>3</sub>:La/Rh particles with core/shell structures, in which the surfaces of the particles were enriched with the dopants. The resulting SrTiO<sub>3</sub>:La/Rh exhibited high photocatalytic activity during H<sub>2</sub> evolution. The use of crystalline SrTiO<sub>3</sub> as a precursor was essential to suppress the formation of impurities, presumably because it worked as a perovskite-type template. The valence states of Rh doped at Ti sites in SrTiO<sub>3</sub>:La/Rh could be controlled by the codoping of La at Sr sites. Compared with SrTiO<sub>3</sub>:Rh, SrTiO<sub>3</sub>:La/Rh accommodated a higher proportion of Rh<sup>3+</sup> ions and exhibited enhanced activity for H<sub>2</sub> evolution from an aqueous

methanol solution.

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). SrTiO<sub>3</sub>:La/Rh exhibited 3.8 times higher rates of H<sub>2</sub> evolution during redox-free Z-scheme overall water splitting in combination with Ir/CoO<sub>x</sub>/Ta<sub>3</sub>N<sub>5</sub>, compared to SrTiO<sub>3</sub>:Rh. The solar-to-hydrogen efficiency of the Z-scheme system measured under illumination with simulated sunlight (AM1.5G) was found to have improved by a factor of three. The photocatalytic activity in this Z-scheme system was limited by the relatively wide energy gap of Ru/SrTiO<sub>3</sub>:La/Rh. The efficiency of the present system could be further improved by enhancing the absorption of long-wavelength photons by SrTiO<sub>3</sub>:La/Rh.

In Chapter 5, a novel Z-scheme water splitting system – a photocatalyst sheet – was invented. The comparison of a powder suspension system, a photocatalyst panel 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 improved by a factor of 3.5 and 14 in the photocatalyst sheet compared with the powder suspension system and the photocatalyst panel, respectively. The enhancement of the photocatalytic activity for Z-scheme water splitting on the photocatalyst sheet was attributed to the presence of the metal layer to enhance the efficiency of interparticle electron transfer.

In Chapter 6, the results illustrated in Chapter 2–5 were summarized and the future outlook was described. It is generally accepted that particle sizes dramatically influence the photocatalytic reaction. The distance that photoexcited carriers have to migrate to reach the surface active sites is shorter and thereby charge recombination probability is lower when the particle size is smaller. However, it is challenging to prepare doped SrTiO<sub>3</sub> with high purity, high crystallinity, and small particle sizes. In Chapter 3, the present research offers another strategy, that is, a core/shell structure. The core/shell structure is prepared by a facile two-step solid state reaction. The migration distance of photogenerated carriers generated in the dopant-enriched shell is short as in nanoparticles. On the other hand, crystallinity of the material is maintained owing to the presence of SrTiO<sub>3</sub> as a crystalline

core. The core/shell structure actually suppressed formation of impurity phases and led to higher photocatalytic activity. This research offer useful concepts for preparation of active metal-doped oxide photocatalysts. In addition, the enhancement of the efficiency of electron transfer between two kinds of photocatalysts is a challenge in Z-scheme overall water splitting system. The photocatalyst sheet developed in Chapter 5 provides a useful approach to promote the efficiency of electron transfer between photogenerated carriers so as to improve the charge separation on the photocatalyst surface and photocatalytic activity.