

## 論文の内容の要旨

論文題目 Development of photocatalyst sheets for Z-scheme water splitting under visible light irradiation  
(Zスキーム型可視光水分解反応のための光触媒シートの開発)

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Photocatalytic water splitting is a promising approach for generating clean and renewable H<sub>2</sub> in a wide scale. However, the candidate photocatalysts for this reaction under visible light irradiation are rare as the driving force for reaction decreases with narrower band gaps. For overcoming this problem, a Z-scheme water splitting system was proposed in which the water reduction and oxidation proceed on a hydrogen evolution photocatalyst (HEP) and an oxygen evolution photocatalyst (OEP), respectively. In a typical Z-scheme system, a redox mediator will be used for charge transfer between HEP and OEP. However, the redox mediator will also facilitate the backward reaction working as a recombination center. A redox-mediator-free Z-scheme system was then developed to avoid the side effects of redox mediators, but the charge transfer between particles becomes much poorer.

Recently, an all-solid-state Z-scheme systems was developed to combine the advantages of the other two types of Z-scheme systems while avoid their drawbacks. The photocatalyst sheet prepared by immobilizing SrTiO<sub>3</sub>:La, Rh (HEP) and BiVO<sub>4</sub> (OEP) into gold layer is a successful model for the all-solid-state Z-scheme system with a high water splitting efficiency. However, further improvement of this system is limited by the short absorption edge of photocatalysts, especially the SrTiO<sub>3</sub>:La, Rh (< 520 nm) as a HEP. A HEP with absorption edge up 600 nm which covers a high proportion of visible light in solar spectrum, is desirable.

On the basis of the aforementioned background, it is important to develop new HEPs which are active under visible light up to 600 nm for the photocatalyst sheet system. In this research, LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N, a 600 nm-responsive photocatalyst, was investigated to work as a HEP in photocatalyst sheet systems. Besides, surface

modification on  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  by  $\text{ZrO}_2$  was conducted for improving the performance of photocatalyst sheet. A new configuration for the photocatalyst sheet consisting of two types of solid mediators, Au layer and reduced graphene oxide (RGO), was also fabricated in order to enhance the interparticle electron transfer efficiency.

In Chapter 1, the necessity to develop environmental friendly and renewable energy, basic principle of overall water splitting by powdered photocatalysts, and the progress in the development of one-step and Z-scheme water splitting systems were described.

In Chapter 2, the applicability of  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$ , a 600-nm-class photocatalyst, as a  $\text{H}_2$  evolution photocatalyst (HEP) in Z-scheme systems was investigated. The redox-mediator-free Z-scheme system composed of  $\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  as a HEP and rutile as an  $\text{O}_2$  evolution photocatalyst (OEP) showed higher activity than one-step excitation systems of  $\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  or rutile alone under irradiation ( $\lambda \geq 300$  nm). Moreover, a photocatalyst sheet, which consisted of  $\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  and rutile embedded in a Au layer by the particle transfer method, exhibited a photocatalytic activity one order of magnitude higher than the Z-scheme powder suspension system, although  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  suffered from self-oxidation. Coating the photocatalyst sheet with an amorphous titanium oxide ( $\text{a-TiO}_2$ ) protective layer suppressed the self-oxidation of  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  effectively while maintaining a high photocatalytic activity. This is because the overlying  $\text{a-TiO}_2$  layer stabilized  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  while the underlying Au layer transferred charges between  $\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  and rutile effectively. This chapter demonstrates the feasibility of the use of  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  in Z-scheme systems as a HEP with a long absorption edge wavelength and provides a facile approach to stabilizing oxynitrides in photocatalyst sheet systems.

In Chapter 3,  $\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  and Mo-doped  $\text{BiVO}_4$  ( $\text{BiVO}_4:\text{Mo}$ ), with absorption edges at 600 and 540 nm, were investigated as the hydrogen evolution photocatalyst (HEP) and oxygen evolution photocatalyst (OEP) in photocatalyst sheets, respectively. The  $(\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N})/\text{Au}/\text{BiVO}_4:\text{Mo}$  sheet exhibited water splitting activity about five times higher than that of corresponding powder suspensions. Stable water splitting was achieved under visible light using the  $(\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N})/\text{Au}/\text{BiVO}_4:\text{Mo}$  sheet coated with an amorphous  $\text{TiO}_2$  ( $\text{a-TiO}_2$ ) protective layer. However, it's shown the low  $\text{H}_2$  evolution activity of the  $\text{RhCrO}_x/\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  imposed a ceiling on the activity of the photocatalyst sheet. The surface modification of the  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  with  $\text{ZrO}_2$  effectively enhanced its

H<sub>2</sub> evolution activity. Accordingly, the activity of the photocatalyst sheet was almost doubled when employing ZrO<sub>2</sub>-modified LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N. The solar-to-hydrogen energy conversion efficiency was still low of 1 × 10<sup>-3</sup>%, although this work expands the possibility for the development of photocatalyst sheets capable of functioning under irradiation by long-wavelength photons.

In Chapter 4, photocatalyst sheets consisting of RhCrO<sub>x</sub>/LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N (HEP), BiVO<sub>4</sub>:Mo (OEP) and reduced graphene oxide (RGO) on an underlying Au layer was developed. One of the most important challenges in enhancing the performance of the photocatalyst sheet system is to establish efficient charge transfer among photocatalyst particles often thickly-stacked on the conductive layer. In this chapter, reduced graphene oxide (RGO) was investigated as an additional solid mediator to the conductive layer to bridge particulate photocatalysts for effective charge transfer. Photocatalyst sheets made of RhCrO<sub>x</sub>/LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N as a HEP and BiVO<sub>4</sub>:Mo as an OEP embedded into Au layer together with RGO split water into H<sub>2</sub> and O<sub>2</sub> stoichiometrically and stably under visible light irradiation, demonstrating 3.5 times higher activity than those without incorporation of RGO. SEM-EDS and STEM-EDS analyses revealed that RhCrO<sub>x</sub>/LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N particles tens of nanometers in size were anchored on large BiVO<sub>4</sub>:Mo particles micrometers in size by RGO photoreduced from GO *in situ*. The RGO facilitated the charge transfer between particles that were distant from the underlying Au layer and involved more photocatalyst particles in the water splitting reaction effectively. It is concluded that incorporation of conductive materials into the photocatalyst particle layer can effectively enhance the water splitting activity of photocatalyst sheets.

In Chapter 5, the results presented in Chapter 2-4 were summarized and the future outlook was described. Efforts was made to develop an efficient photocatalyst sheet system for Z-scheme overall water splitting, which is a promising approach for scalable H<sub>2</sub> production. For harvesting the solar spectrum, the application of photocatalysts with long absorption edges is desirable. In Chapter 2, LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N, whose absorption edge up to 600 nm, was tested to work as a HEP in the photocatalyst sheet and stable overall water splitting was achieved after coating the a-TO<sub>2</sub> layer. This study offers useful concepts for preparation of new photocatalyst sheet systems composed of oxynitride-type photocatalysts. In Chapter 3, the photocatalyst sheet composed of RhCrO<sub>x</sub>/LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N and BiVO<sub>4</sub>:Mo was developed for visible-light-driven water splitting. Its activity was improved by ZrO<sub>2</sub> modification on LaMg<sub>1/3</sub>Ta<sub>2/3</sub>O<sub>2</sub>N. However, its efficiency was still low and

further modification on the photocatalysts, especially the  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$ , is necessary for a better performance. The modified photocatalyst sheet with additional RGO developed in Chapter 4 provides a useful approach to promote the charge transfer and involve most photocatalyst particles in water splitting reaction. However, it's still an important issue to accurately control the contact between photocatalyst particles for further promoting the charge transfer between particles.