

論文の内容の要旨

論文題目 **Development of photocatalysts for efficient Z-scheme water splitting using visible light**

(可視光による高効率 Z-スキーム
水分解のための光触媒開発)

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Over the recent years, there has been a growing interest in energy obtained from exploiting nature as an alternative fuel for sustainable development and environmental preservation. Hydrogen, which has been suggested as the main energy source in the future, could offer an answer to the threat of global climate change and help avoid the undesirable effects of the use of fossil fuels. Furthermore hydrogen from renewable energy resources is a clean, green, virtually inexhaustible, environmentally benign energy source that could be our future energy supply. Thus, to meet the growing energy demand, hydrogen produced by solar energy can be considered as one of the desirable approaches. One of the attractive and environmentally friendly methods to harvest solar energy is photocatalytic hydrogen generation from water. [1] Because of its simplicity, water splitting using a powdered photocatalyst has become a subject of much interest, with most research focusing on the visible light sensitization of catalysts in order to effectively utilize incoming solar energy. Since the first report of TiO₂-based photoelectrolysis initiated by Fujishima and Honda, [2] many attempts have been made to achieve efficient energy conversion from solar energy to hydrogen energy. However, the most significant obstacle is the lack of proper semiconductor materials that could meet the demands for efficient and stable water splitting: a band gap of 1.6 to 2.0 eV straddling the redox potentials of the water, and chemical stability. [3, 4]

In this study, construction of a Z-scheme water splitting system has been implemented with the use of various modified visible-light-responsive photocatalysts. [4] The Z-scheme system, which refers to overall water splitting using a two-step photoexcitation system mimicking photosynthesis in a green plant, is made up of two

different photocatalysts for H₂ and O₂ evolution respectively. These photocatalysts are reacted along with a proper reversible shuttle redox couple. Recent studies have also revealed that Z-scheme water splitting proceeds even in the absence of redox couples owing to interparticle electron transfer. In these two-step photoexcitation processes, a wider range of visible light can be utilized through several photocatalysts combinations, with reduction in the energy required to drive each photocatalyst. Therefore, current research work aimed to investigate and optimize the efficiency of Z-scheme water splitting and through the use of new and/or modified past developed photocatalysts that promote overall water splitting into a stoichiometric mixture of H₂ and O₂ (2:1 by volume) under visible light irradiation.

My research work aimed to develop new photocatalyst materials for water splitting reaction and to achieve an artificial photosynthesis. The goals of my Ph.D research were to overcome some of the challenges in application of visible-light-driven photocatalytic materials in particular, oxynitrides, in Z-scheme two-step photocatalytic water splitting process. The major goals of my research were: (1) preparation of active visible-light-responsive photocatalyst; (2) investigation of its photocatalytic activity for water oxidation or water reduction in the presence of redox mediator relays (half reaction); (3) in the application for Z-scheme water splitting system both in the presence and absence of redox relays. Through my research work on the study of photocatalysts for Z-scheme system, the optimized photocatalysts would enhance and enable the process of splitting water into hydrogen and oxygen much more efficiently and therefore viable.

A total of 7 chapters are included in this thesis, all of which has been carried out in the time frame of three years:

Chapter 1 gives a brief introduction to the background and motivation of the research. The general principle of water splitting on semiconductor, available visible light-driven photocatalysts, Z-scheme photocatalytic hydrogen and oxygen generation and factors which affect photocatalytic efficiency, are reviewed extensively. The significance, aim and objectives of the study are described. The scope of the research and the overall structure of the thesis are also outlined in this chapter.

In Chapter 2, the effects of the preparation conditions of ZrO₂-modified TaON (referred to as ZrO₂/TaON) on the photocatalytic activity for H₂ evolution under visible light ($\lambda > 420$ nm) were investigated. ZrO₂/TaON catalysts were prepared by loading

particulate Ta₂O₅ with ZrO₂ using different zirconium precursors, followed by nitridation at 1123 K for different durations (5–20 h) under NH₃ flow. Nitridation of ZrO₂/Ta₂O₅ for 15 h resulted in the production of ZrO₂/TaON, regardless of the zirconium precursors used, but the physicochemical properties varied. The highest activity was obtained for ZrO₂/TaON synthesized from Ta₂O₅ and ZrO(NO₃)₂•2H₂O (Zr/Ta = 0.1 by mole) after nitridation for 15 h. Physicochemical analysis suggested that a lower density of anionic defects in TaON, which was realized using highly-dispersed ZrO₂ nanoparticles (10–30 nm in size), contributed primarily to the enhanced activity.

Chapter 3 covers modified tungsten trioxide (WO₃) powder that is employed as water oxidation photocatalyst under visible light ($\lambda > 420$ nm) irradiation. WO₃ modified with nanoparticulate Pt species (more specifically, PtO) as cocatalysts is capable of photocatalyzing water oxidation under visible light in the presence of iodate (IO₃⁻) ions as an electron acceptor under near-neutral pH conditions (pH \approx 5.9). When PtO/WO₃ was further modified with a very small amount (0.001 wt%) of a metal oxide (e.g., MnO_x, CoO_x, RuO₂ or IrO₂) as a secondary cocatalyst, the water oxidation activity was improved. Among the metal oxide cocatalysts examined, RuO₂ was found to give the highest performance, with an apparent quantum yield of 14.4% at 420 nm. The results of photocatalytic reactions and photoelectrochemical analyses suggest that the main roles of the loaded PtO and RuO₂ on WO₃ are to promote the reduction of IO₃⁻ and water oxidation, respectively.

Chapter 4 present tantalum nitride (Ta₃N₅) semiconductor as a photocatalyst for solar water splitting due to its suitable band edge potentials, capable of producing hydrogen and oxygen from water under visible light ($\lambda < 590$ nm). Ta₃N₅ modified with various O₂-evolving cocatalysts such as CoO_x and IrO₂, was studied as a photocatalyst for water oxidation under visible light irradiation ($\lambda < 500$ nm) in the presence of electron acceptor, AgNO₃. Cocatalyst loaded Ta₃N₅ in particular CoO_x cocatalysts, displays especially good water oxidation performance with apparent quantum efficiencies (AQY) of 2.3 % at 500–600 nm, respectively.

Subsequently, Chapter 5 also reports on highly-active Ta₃N₅ photocatalysts that has been modified with alkaline metal. This chapter describes on the effect of facile modification of Ta₂O₅ with alkaline metal salts on water oxidation in an aqueous AgNO₃ solution under visible light irradiation. Compared with conventional Ta₃N₅, the modified Ta₃N₅ was characterized by better crystallinity, smaller particle sizes with smoother surface and less agglomeration, and more importantly higher photocatalytic activity by six fold. Interestingly, modification with alkaline metal salts was compatible with loading of an oxygen evolution cocatalyst such as CoO_x, suggesting that functions

of the modifiers were distinct from catalytic effect. The present study shows critical roles of alkali metal salts loaded onto Ta₂O₅ upon nitridation toward the highly-active Ta₃N₅.

Chapter 6, various Z-scheme photocatalysis system using the optimized photocatalyst from the previous research as mentioned in earlier chapters was studied. The Z-scheme water splitting reactions were done both in the presence and absence of redox mediators respectively. Strategies to develop a highly active Z-scheme photocatalysis system driven by electron transfer between H₂- and O₂-photocatalyst are discussed on the basis of the structural and activity analysis results. The present results show the possibility of constructing an efficient solar H₂ production system from water using this simple Z-scheme mechanism through interparticle electron transfer.

Chapter 7 brings to a close of the past three years research work with a summary of what has been accomplished. Future research areas based on the information drawn from the results obtained are suggested. Subsequently, an outline is drawn for future work that can be carried out with useful findings from this project.

All in all, the present study demonstrates that suitable cocatalyst loading and surface modifications are effective in minimizing electron-hole recombination and maximizing absorption capability while improving the selectivity for the two-step water splitting (Z-scheme). The present results suggest that an efficient and stable utilization of solar energy using two-step photoexcited Z-scheme water splitting can be achieved by employing high absorption wavelength visible-light-driven photocatalysts. This expands the possibility of using various active (oxy)nitrides in Z-scheme water-splitting systems, by employing suitable modification method to construct reaction sites and promote Z-scheme interparticle electron transfer.

References

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