論 文 の 内 容 の 要 旨

論文題目 Development of lanthanum titanium copper oxysulfide ($La_5Ti_2CuS_5O_7$) based photocathodes for solar water splitting
（太陽光による水分解反応を目的としたランタンチタン銅酸硫化物（$La_5Ti_2CuS_5O_7$）系光カソードの開発）

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Chapter 1: General Introduction

Conversion of renewable solar energy into storable and transportable chemical fuels is an important strategy towards realization of a sustainable society. Photoelectrochemical (PEC) water splitting is an ideal means for direct conversion of the solar energy into hydrogen as a renewable chemical energy. Many semiconductors are capable of generating a high photocurrent attributable to hydrogen or oxygen production; however a sufficiently high applied voltage is often required. To solve this problem, a p/n-PEC cell based on two-step excitation of series-connected photocathode and photoanode has attracted much attention, because this system can generate a sufficient photovoltage to drive the water splitting reaction. By matching the photocurrents of the photocathode and the photoanode at the same electrode potential, and the reduction and oxidation of water occur separately on the surfaces of the respective photoelectrodes. The operation photocurrent of a p/n-PEC cell can be estimated from the intersection of steady current-potential curves of the respective photoelectrodes, and it is proportional to the solar-to-hydrogen energy conversion efficiency. Therefore, the onset potential of photocathodes should be more positive to fabricate more efficient p/n PEC cells.

$La_5Ti_2CuS_5O_7$ (LTC) is an oxysulfide semiconductor material with an absorption edge wavelength of 650 nm. LTC consists of series of TiO_xS_{6-x} octahedra and CuS_4 tetrahedra growing along the b-axis and forms rod-like particles. The previous studies revealed that LTC/Au photoelectrodes fabricated by the particle transfer method was active in PEC hydrogen production from water and exhibited a photocurrent onset potential of +0.8 V *vs.* RHE, which was one of the most positive potentials among ever-existing photocathodes. However, the photocurrent observed was lower than the calculated photocurrent of 16.8 mA cm^{-2} assuming the incident photon-to-current efficiency of unity. There is still large room to improve the

photocurrent of LTC.

Chapter 2. Photoelectrochemical activity of doped $La_5Ti_2CuS_5O_7$ electrodes fabricated by particle transfer in hydrogen evolution.

Doping of photoelectrode materials such as $BiVO_4$ and Fe_2O_3 has been widely researched to control the electronic properties and improve the photocurrent. In this chapter, effects of doping LTC with aliovalent cations were investigated.Sc^{3+}, Ga^{3+}, Al^{3+}, Mg^{2+}, Nb^{5+} and Ta^{5+}were doped into the Ti^{4+} site during the synthesis process. As Sc^{3+} and Ga^{3+} have lower valence states than Ti^{4+}, they are expected to provide free holes in LTC. Conversely, Nb^{5+} and Ta^{5+} have higher valence states than Ti^{4+}; hence, they are expected to provide free electrons in LTC.

The successful synthesis of doped $La_5Ti_2CuS_5O_7$ was confirmed by XRD, SEM and DRS. By particle transfer method,[3] undoped and doped LTC particles are prepared into electrode and their PEC properties are measured. The onset potential of 1% Sc doped-$La_5Ti_2CuS_5O_7$ photocathode was +0.88 V vs. RHE, which is 80 mV more positive than undoped one. In addition, the photocurrent density of the 1% Sc doped-$La_5Ti_2CuS_5O_7$ photocathode was 0.80 mA cm^{-2} at 0 V vs. RHE, which was approximately eight-fold compared with the undoped sample. The enhanced PEC activity was also observed for $La_5Ti_2CuS_5O_7$ photocathodes doped with 1% Ga. By contrast, Ta- and Nb-doped $La_5Ti_2CuS_5O_7$ photocathodes showed lower PEC activity. These results suggest that an increase in the majority carrier concentration in $La_5Ti_2CuS_5O_7$ by doping of lower valent cations into Ti sites improved the PEC activity. The PEC activity of $La_5Ti_2CuS_5O_7$ at different doping levels of Sc was also investigated. It was found that the doping level of 1% was the optimum.

Chapter 3. Effect of Particle Size of $La_5Ti_2CuS_5O_7$ on Photoelectrochemical Properties in Solar Hydrogen Evolution

Density functional theory (DFT) calculations have shown that the conduction band minimum and valence band maximum of LTC are localized around linear chains of the $Ti(O,S)_6$ and CuS_4 units, respectively. Therefore, photogenerated electrons and holes can move along the b-axis to the edge surfaces of LTC particles separately through these linear chains. The selective deposition of Pt particles on the edge surface of rod-like LTC particles by the PEC reduction of $[PtCl_6]^{2-}$ has been demonstrated. Based on the one-dimensional carrier transport properties of rod-like LTC particles, it is believed that the morphology of LTC particles have a significant influence on the PEC performance of LTC photoelectrodes. In **section 3.2**, LTC particles with different sizes were prepared by controlling the annealing duration and through sequential centrifugation, and effects of particle size on the PEC properties were investigated.

At first, LTC particles prepared with longer annealing durations were found to exhibit

higher photocurrents, which may due to the higher ratio of large particles formed. In addition, a sequential centrifugation was implemented to more vigorously discuss the effect of particle size on the PEC performances of LTC electrodes. Results indicated that Rod-like LTC particles with larger sizes were found to exhibit higher photocurrents.SEM observations revealed that Pt nanoparticles were PEC-deposited not only on the edge surfaces but also on the lateral surface for small Mg-doped LTC particles, while they were selectively deposited on the edge surfaces for large Mg-doped LTC particles. The use of well-grown, rod-like LTC particles is advantageous for PEC hydrogen production.

Chapter 4. Effect of surface modification of particulate $La_5Ti_2CuS_5O_7$ photocathodes with oxides on charge separation and hydrogen evolution

The surface modification of compact thin film photocathodes composed of materials such as metal oxides, pnictogenides and chalcogenides with n-type semiconducting oxide layers has been widely researched with the aim of enhancing the charge separation and improving both the photocurrent and the stability. TiO_2 is one of the most popular anti-corrosive, passivation and/or charge separation layers, owing to its high chemical stability and the suitable position of its band gap. Despite this, the effects of surface modifications using TiO_2 and similar compounds on the PEC properties of particulate photocathodes with a high degree of inhomogeneity have rarely been studied. In **Chapter 4**, TiO_2, Nb_2O_5, Ta_2O_5 and ZrO_2 were deposited on particulate Mg-doped LTC (Mg-LTC) electrodes by radio-frequency (RF) reactive magnetron sputtering, and effects on the PEC properties were investigated.

As a result, Mg-LTC electrodes modified with Nb_2O_5, Ta_2O_5 and TiO_2 exhibited cathodic photocurrents that approximately doubled over the potential range of 0 to 0.9 V *vs.* RHE compared to the value obtained from an unmodified electrode. In addition, at 0.7 V *vs.* RHE, Mg-LTC photocathodes modified with these oxides maintained a photocurrent attributed to PEC hydrogen evolution. Increases in the population of long-lived photoexcited carriers existing on the microsecond timescale in these materials demonstrated the vital role of the oxide surface modification in obtaining effective charge separation. This work suggests opportunities for improving PEC hydrogen evolution on particulate photocathodes based on surface oxide modifications and also highlights the importance of the band gap alignment.

Chapter 5: Summary and Outlooks

Through the above studies, the photocathodic current of LTC electrodes attributed to PEC H_2 evolution was improved by almost two orders of magnitude. As a consequence, the STH of p/n PEC cells based on LTC photocathodes was estimated to be upgraded by more than 20 times. However, there is still a large gap between the observed and calculated photocurrents of

LTC electrode, indicative of necessity of further improvements.

Considering the one-dimensional carrier transport properties of LTC particles, the orientation of rod-like LTC particles on Au conductive layer should be controlled. In addition, my recent study showed that two-step post-annealing in sulfur vapor enhanced the photocurrent of LTC electrodes, suggesting room for further refinement in the properties of particulate LTC electrodes. The nature of LTC material and electrodes should be investigated further in follow-up studies.In addition, this thesis reveals the necessary of studying oxysulfide materials. The valence band of oxysulfides are often composed of S 3p orbitals as well as O 2p orbitals, hence the band gap of oxysulfides are narrow enough to absorb visible light. On the other hand, due to the involved of oxygen, a relatively stable performance can be expected from those materials.[5] Until now, $La_5Ti_2CuS_5O_7$ is the only oxysulfide material that can be prepared and used as photocathode, but with property experiment design and the help from computer science such as chemoinformatics or density functional theory (DFT), hopefully more oxysulfide materials with high performance will be discovered and utilized in the future.