論 文 の 内 容 の 要 旨

論文題目　Study on Cu-chalcogenide Photocathodes toward Solar Hydrogen Production via Water Splitting（水分解によるソーラー水素製造に向けた銅カルコゲナイド系光カソードに関する研究）

氏　　名　熊谷　啓

Chapter 1: General Introduction

For sustainable development into the future, our society needs to reduce current dependence on fossil fuels and CO_2 gas emissions. Renewable energies have gathered much attention as sustainable energy source. The technologies called “artificial photosynthesis”, which for conversion of the solar energy to storable chemicals like hydrogen, become to get much attention from insight of storage and transportation. This “solar hydrogen” can be a clean, sustainable and stockable fuel which can convert into electricity efficiently using fuel cells whenever it is necessary. To obtain solar hydrogen from sunlight and water, photoelectrochemical (PEC) water splitting can be possible candidates. In PEC water splitting system, water reduction or oxidation occurs on photoelectrode surface. Recently many studies about “photoelectrode” or “photoelectrochemical” system for solar hydrogen generation have been reported. Among them, Cu-chalcogenide semiconductors have received significant attention as photocathode for PEC water splitting because of their good p-type semiconducting property with high optical absorption coefficients of more than 10^5 cm^{-1} and usability in the polycrystalline state. The object of the present study is to obtain the knowledge to achieve efficient and largely scalable Cu-chalcogenide based photocathode for practical solar hydrogen generation in future.

Chapter 2: Photoelectrochemical Hydrogen Evolution from Water Using Copper Gallium Selenide Photocathodes Prepared by a Particle Transfer Method

Photocathodes prepared using Cu-Ga-Se powder materials are investigated. From the view point of large scale applicability, the use of powder materials as photoelectrodes is preferable because the preparation method is simple and the cost become lower. Cu-Ga-Se powder materials with various Ga/Cu ratios were prepared by a solid state reaction from selenide precursors. The photoelectrodes are prepared from Cu-Ga-Se powders through the particle transfer method, which was invented for preparation of photoelectrode from semiconductor photocatalyst powders. The

effects of the composition on PEC properties of Cu-Ga-Se and fabrication of a multi-layer structure on the electrode are examined here. The Ga/Cu ratio strongly influenced the crystal structures and the PEC properties of the prepared Cu-Ga-Se particles. Cu-Ga-Se particles with a Ga/Cu ratio of 2 showed the largest cathodic photocurrent and were composed of two phases, a $CuGa_3Se_5$ phase and an intermediate phase between $CuGaSe_2$ and $CuGa_3Se_5$. This intermediate phase has never been reported previously. By surface modification with a CdS layer, the photocurrent density and onset potential of the Cu-Ga-Se electrodes clearly increased. This is due to enhancement of charge separation by the formed p-n junction between CdS and Cu-Ga-Se with appropriate band alignment at the solid-liquid interface. A Pt/CdS/Cu-Ga-Se electrode (Ga/Cu=2) generated a cathodic photocurrent contributing stoichiometric hydrogen evolution from water for 16 h under visible light irradiation. Its HC-STH reached to 0.59% at 0.25 V_{RHE} in 0.1 M Na_3PO_4 aqueous solution with pH12.6. It was almost comparable to 0.83% of modified $CuGaSe_2$ thin film electrode which was reported before. Multi-layered structures on the particles were confirmed to aid photocurrent enhancement as in the case of thin film photoelectrodes. These insights can contribute to asymmetric surface modification of photocatalytic particles. It can be concluded that the Cu-Ga-Se photoelectrodes prepared by the simple particle transfer method show the potential for practical use in large scale photoelectrochemical water splitting, after further study and development.

Chapter 3: Photoelectrochemical Properties of Ag-Cu-Ga-Se and Cu-In-Ga-Se Photocathodes for PEC Water Splitting Prepared by a Particle Transfer Method

The performance of PEC water splitting using Cu-Ga-Se material is limited by its physical properties such as band gap energy and band positon. So the strategy of changing its band structure by element substitution becomes attractive to achieve more efficient utilization of sunlight irradiation. In this chapter, Ag and In were selected as candidates of elements in substitution. Ag-Cu-Ga-Se powders are prepared with composition of $Ag_xCu_{1-x}GaSe_2$ and $Ag_xCu_{1-x}Ga_2Se_{3.5}$. XRD results of $Ag_xCu_{1-x}GaSe_2$ powders revealed that the solid solution of $AgGaSe_2$ and $CuGaSe_2$ is formed by introducing Ag into Cu-Ga-Se. The $Ag_xCu_{1-x}GaSe_2$ electrodes with x of 0.7, 0.9, 1 generated anodic photocurrent under illumination although the electrode with x below 0.5 showed cathodic photocurrent. This result indicates that higher substitution of Ag provides n-type semiconducting properties same as thin film reports. In the case of $Ag_xCu_{1-x}Ga_2Se_{3.5}$, Ag substituted powders have a $CuGa_3Se_5$ phase and an intermediate phase as same as Cu-Ga-Se in chapter 2 and Ag was substituted for Cu site only in the intermediate phase even in the presence of $CuGa_3Se_5$ phase. Ag substituted electrode showed relatively high onset potential although no significant improvement of photocurrent was observed by Ag substitution. Cu-In-Ga-Se powders are prepared with composition of $CuIn_xGa_{1-x}Se_{3.5}$. XRD results revealed that In can be substituted for Ga site not only in an intermediate phase but also $CuGa_3Se_5$ phase. Judging from XRD and DRS results, the solid

solutions of $CuInSe_2$ and $CuGaSe_2$ were formed by In substitution for Ga and the controllability of band gap of Cu-In-Ga-Se was indicated. The $CuIn_xGa_{1-x}Se_{3.5}$ electrodes with x of 0.75, 1 generated anodic photocurrent under illumination and the electrode with x below 0.5 showed cathodic photocurrent although these were smaller than that of Cu-Ga-Se photoelectrode. Through these investigations, significant improvement of PEC properties of partially substituted Cu-Ga-Se has not been observed in contrast with the case of polycrystalline thin film. It may be due to the difficulty of control physical properties such as donor density in present preparation method of powders. Electrochemical impedance spectroscopies explained that the possible reasons of their relatively low photocurrent might be the small resistance of charge transfer in the depletion layer for Ag-Cu-Ga-Se and the big series resistance for Cu-In-Ga-Se. It can be concluded that photocathodes using these powders have rooms to improve after further development to control these properties.

Chapter 4: Surface-modified $Cu(In,Ga)Se_2$ Photocathode for Efficient Solar Hydrogen Production under Neutral Condition

Surface modified $Cu(In,Ga)Se_2$ polycrystalline thin film photocathodes were investigated aiming at get perspectives to increase the performance of the photocathode during PEC water splitting. Firstly the effect of concentrated neutral buffer based solution on photoelectrochemical properties was explored instead of alkaline solution which used in previous reports. In an attempt to improve surface conductivity for the high usability of photo-exited electrons, modification with thin conductor layers was examined next. It was found that CdS/CIGS photocathode modified with Pt catalyst and Mo/Ti thin layer showed significant high photocurrent and HC-STH even in neutral electrolyte solution. Using concentrated neutral buffer based solution as electrolyte instead of alkaline solution, the photocurrent significantly improved and the maximum of HC-STH was 5.4% at 0.30 V_{RHE}. Electrochemical analysis revealed that this is attributed to the promotion of hydrogen evolution reaction on the electrode surface. In addition, modification with thin conductive layers of Mo and Ti provided further improvement of high photocurrent and its HC-STH reached to 8.5% at 0.38 V_{RHE}. These conductive layers assisted to keep surface potential homogeneously and promote the surface mobility of photo-exited electrons on CdS/CIGS. These results provide valuable insights into effective means of improving the solar-to-hydrogen efficiency by employing mediators to ensure smooth surface reactions and charge transfer. It can be concluded that surface modified CIGS photoelectrodes show potential for use as efficient photocathodes in solar hydrogen production via photoelectrochemical water splitting, although further development is required to allow their practical application.

Chapter 5: Summary and Outlooks

This work presents the potentials of Cu-chalcogenide materials as photocathode for efficient solar hydrogen generation via photoelectrochemical (PEC) water splitting. In previous studies there were mainly two problems to overcome for practical use of these photocathodes in future. One is the cost in film preparation of photoelectrode which need high-vacuum process toward large scale expansion. Another is difficulty to achieve the high efficiency which is expected from their physical and optical properties. To solve these problems, this research was intended to obtain the knowledge of (i) applicability of Cu-chalcogenide semiconductor powders for scalable photocathodes (chapter 2 and 3) and (ii) feasibility to improve solar-to-hydrogen efficiency by promotion of surface reaction by reactant supply and of electron transfer to the reaction site. (chapter 4) Through this thesis, the applicability of powder materials for photocathodes and effectiveness of employing mediators to ensure smooth surface reactions by reactant supply and charge transfer to reaction site were confirmed. For the utilization of Cu-chalcogenide photocathode in combined photocathode/photoanode PEC cell, photocurrent and HC-STH at higher potential nearby 0.6 V vs.RHE are essential in order to match balance charges between photocathode and photoanode. The approaches of charge transfer to reaction site by the coating with a material will provide chance for improvement as shown in chapter 4. Furthermore, chapter 2 indicated the possibility to obtain the photocathode using powder by more simple preparation method although there is the difficulty of control physical properties such as donor density in present preparation method of powders, as shown in chapter 3. So the scalable powder-based photocathode also has possibility to achieve high efficiency, after development of appropriate control of the properties of powders.