

## 論文の内容の要旨

論文題目 Study on (Ag,Cu)GaSe<sub>2</sub> Thin Film Photocathodes for Water Splitting  
(水分解のための(Ag, Cu)GaSe<sub>2</sub>薄膜光カソードに関する研究)

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Human society has heavily relied on the finite fossil resources as energy sources since the industrial revolution of mid-eighteenth century. The ever-increased consumption of fossil fuels causes gradually depleting of the fossil fuels and corresponding environmental issues such as global warming. For constructing a sustainable society, it is therefore of great importance to develop a carbon-neutral, storable and sustainable energy source. As an infinite and clean energy source, solar energy is the best option. The enormous power of sunlight intercepted by the earth can be roughly estimated to be  $1.27 \times 10^5$  TW based on the sunlight spectrum of AM 1.5G ( $1000 \text{ W m}^{-2}$ ) and interception area of the earth, which exceeds the global energy consumption in 2012 ( $1.66 \times 10^1$  TW) by roughly 3–4 orders of magnitude. It clearly shows that theoretically there is enough solar energy to fulfill energy demand of our society at present and in the future.

For efficient utilization of solar energy, the large-scale energy storage technology is required to overcome the diurnal intermittency of sunlight and non-synchronization between solar energy supply and consumption. One of the potentially efficient routes for solar energy storage is to convert it into storable chemical energy such as hydrogen. Photoelectrochemical (PEC) water splitting for hydrogen production, which directly converts the absorbed photons of sunlight into electron-hole pairs and splits water into hydrogen and oxygen, provides a promising route to convert sunlight into storable and clean energy carrier of hydrogen. The stored hydrogen can then be converted into electricity within fuel cell or directly used as a clean fuel in combustion engine. Constructing the dual-electrode PEC cell, which consists of an n-type photoanode and a p-type photocathode with overlapped band gaps covering the oxygen evolution and hydrogen evolution potentials, is proposed as the most practical one that has potential to achieve practical

solar-to-hydrogen (STH) conversion efficiency larger than 10%.

This dissertation investigates the p-type semiconductor as photocathode for hydrogen evolution based on CuGaSe<sub>2</sub> (CGSe) semiconductor material. As a kind of high-efficiency absorbers for thin film solar cells, CGSe is a promising candidate as photocathode for hydrogen evolution due to its strong optical absorption, suitable band gap (ca. 1.65 eV), usability in polycrystalline state, and high stability for hydrogen evolution in electrolyte. CGSe can efficiently utilize a large portion of visible sunlight with absorption edge ca. 750 nm, which corresponds to a maximum photocurrent of 24 mA cm<sup>-2</sup> and a STH conversion efficiency of 29% based on the AM 1.5 spectrum.

However, the main challenges for high-efficiency PEC water splitting on CGSe is that the valence band maximum (VBM) potential of CGSe is too low in comparison to oxygen evolution, and the crystallinity of CGSe is very poor due to the high melting temperature (ca. 1050 °C). To improve the PEC performance of CGSe electrode, these two disadvantages need to be solved. Partial substitution of Cu in CGSe into Ag to form (Ag,Cu)GaSe<sub>2</sub> (ACGSe) seems to be an effective solution to make the VBM potential more positive and the grain size larger based on the following two facts: (1) the VBM potential of AgGaSe<sub>2</sub> (AGSe) is ca. 0.44 V<sub>NHE</sub> higher than CGSe, which means partial substitution of Cu into Ag to form the ACGSe may have higher VBM potential than CGSe, and thus more suitable band edges for PEC water splitting. (2) The melting point temperature of AGSe is ca. 200 °C lower than CGSe, thus the ACGSe is expected to have better crystallinity than CGSe.

The objectives of this dissertation are to improve the PEC performance of CGSe electrodes through Ag partial substitution and surface modification, and study the relationship between PEC properties and film quality. The following ways have been tried in this dissertation to improve the PEC properties of CGSe electrode: (1) Partial substitution of Cu in CGSe into Ag to form ACGSe thin films. (2) CdS surface modification to form CdS/ACGSe p-n heterojunction. (3) Applying two-step deposition methods to improve the ACGSe film/Mo substrate interface. (4) Introducing CuGa<sub>3</sub>Se<sub>5</sub> thin layer onto ACGSe to form bilayer textured CuGa<sub>3</sub>Se<sub>5</sub>/ACGSe thin films.

In Chapter 1, the necessity of sustainable energy, the properties of sunlight, and the potential of solar energy were firstly introduced. Then, the advantages of PEC water splitting, the fundamentals of semiconductor, the semiconductor/electrolyte interfaces, and the PEC cell configurations were sequentially introduced. Furthermore, the available material candidates for

photoelectrodes and the general strategies for high-efficiency PEC water splitting were briefly reviewed. Finally, the CGSe-based semiconductor material, which is candidate material for this dissertation, was introduced and reviewed in details.

In Chapter 2, the main preparation methods used in this dissertation were presented. The radio frequency (RF) magnetron sputtering and vacuum co-evaporation methods, which were used to preparing the Mo substrates and ACGSe thin films for this dissertation, were introduced in details. In addition, the selection of hydrogen evolution catalyst and the PEC deposition method were briefly introduced.

In Chapter 3, the ACGSe thin films were prepared onto the Mo-coated soda-lime glass substrates by vacuum co-evaporation method using a molecular beam epitaxy (MBE) system. The effects of Ag partial substitution on the structural and PEC properties of CGSe were studied. The structural and electronic characterizations showed that Ag partial substitution largely improved the grain size of CGSe and shifted its valence band maximum (VBM) to more positive potential. The PEC results on bare ACGSe and Pt modified ACGSe showed that ACGSe with Ag/Cu+Ag ratio ca. 5% shows the best PEC activity. The prepared Pt/ACGSe (Ag 5.9%) showed a photocurrent of ca.  $3.8 \text{ mA cm}^{-2}$  at  $0 \text{ V}_{\text{RHE}}$  and onset potential of  $0.51 \text{ V}_{\text{RHE}}$  (defined at cathodic photocurrent of  $0.05 \text{ mA cm}^{-2}$ ), which shows an obvious improvement compared with the Pt/CGSe (ca.  $2.0 \text{ mA cm}^{-2}$  at  $0 \text{ V}_{\text{RHE}}$  and onset potential of  $0.42 \text{ V}_{\text{RHE}}$ ).

In Chapter 4, CdS surface modification of ACGSe was applied to further improve photocurrent of ACGSe films with optimal Ag composition. The CdS was deposited by chemical bath deposition (CBD) method. The role of CdS is to form p-n heterojunction and facilitate the separation of photogenerated electron-hole pairs. A Pt and CdS modified ACGSe (Ag 5.9%) electrode (Pt/CdS/ACGSe) showed a cathodic photocurrent of  $6.2 \text{ mA cm}^{-2}$  at  $0 \text{ V}_{\text{RHE}}$  and an onset potential of  $0.67 \text{ V}_{\text{RHE}}$  (defined as cathodic photocurrent of  $0.05 \text{ mA cm}^{-2}$ ) under simulated sunlight illumination in  $0.1 \text{ M Na}_2\text{SO}_4$  (pH 9.5), which shows obvious improvement than that of Pt/ACGSe (Ag 5.9%) without CdS modification.

In Chapter 5, the Pt/CdS/ACGSe electrode was further improved by applying two-step co-evaporation method. The motivation to try two-step method is to improve the quality of film/substrate interface. A Pt and CdS modified two-step deposited ACGSe showed a cathodic photocurrent of  $8.1 \text{ mA cm}^{-2}$  at  $0 \text{ V}_{\text{RHE}}$  and an onset potential of  $0.70 \text{ V}_{\text{RHE}}$  (defined at cathodic photocurrent of  $0.05 \text{ mA cm}^{-2}$ ) under simulated sunlight illumination, and reached a maximum solar energy conversion efficiency in applied bias photon-to-current efficiency (ABPE) of 1.2%

at  $0.3 V_{\text{RHE}}$ . Further, a Pt/CdS/ACGSe deposited by two-step method showed a stable cathodic photocurrent contributing to hydrogen evolution for over 4 days without clear decrease.

In Chapter 6, the Pt and CdS modified two-step deposited ACGSe was further modified by introducing a  $\text{CuGa}_3\text{Se}_5$  thin layer onto ACGSe to form  $\text{CuGa}_3\text{Se}_5/\text{ACGSe}$  bilayer thin film electrodes. With Pt and CdS modification, the Pt/CdS/ $\text{CuGa}_3\text{Se}_5/\text{ACGSe}$  bilayer electrode with  $\text{CuGa}_3\text{Se}_5$  for 15 min showed a photocurrent of  $8.3 \text{ mA cm}^{-2}$  at  $0 V_{\text{RHE}}$  and an onset potential of ca.  $1.0 V_{\text{RHE}}$  (defined at cathodic photocurrent of  $0.05 \text{ mA cm}^{-2}$ ), which reached a maximum ABPE of ca. 1.8% at ca.  $0.35 V_{\text{RHE}}$ . Moreover, a Pt/CdS/ $\text{CuGa}_3\text{Se}_5/\text{ACGSe}$  electrode showed a cathodic photocurrent contributing stoichiometric hydrogen evolution from water over for ca. 20 days without clear decrease, indicating that ACGSe electrode with suitable modification can act as a highly stable photocathode for PEC hydrogen evolution.

As summarized in Chapter 7, this dissertation investigated the solar-driven PEC hydrogen evolution from water using ACGSe photocathodes under sunlight irradiation. ACGSe electrodes showed largely improved PEC performance than that of CGSe due to the largely increased grain size and more positive shift of VBM potential. The PEC performance of ACGSe electrodes was greatly enhanced through formation of p-n heterojunction with CdS, applying two-step co-evaporation method and designing bilayer structure ( $\text{CuGa}_3\text{Se}_5/\text{ACGSe}$ ). A Pt and CdS modified bilayer-textured  $\text{CuGa}_3\text{Se}_5/\text{ACGSe}$  (Pt/CdS/ $\text{CuGa}_3\text{Se}_5/\text{ACGSe}$ ) thin film electrode showed a stable cathodic photocurrent contributing stoichiometric hydrogen evolution from water over for ca. 20 days without clear decrease, suggesting the feasibility of ACGSe as promising photocathodes for hydrogen evolution from water under sunlight irradiation. In future, constructing a dual-electrode system using the modified ACGSe photocathodes in this dissertation and the state-of-the-art photoanode such as  $\text{Ta}_3\text{N}_5$  to realize bias-free overall water splitting under sunlight irradiation is certainly worth trying. Furthermore, searching for CdS-free modifier is another important research topic to realize environmental friendly and high-efficiency ACGSe photocathodes.