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# Stable photoelectrochemical salt-water splitting using the n-ZnSe/n-$Ag_8SnS_6$ photoanodes with the nanoscale surface state capacitances

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ABSTRACT

Interest in the photoelectrochemical water splitting using the metal sulphide photoelectrodes increases due to their good photoelectrochemical performances in aqueous solutions under illumination. However, the accumulation of photo-excited holes at the surfaces of samples results in their poor stabilities for photoelectrochemical water splitting during light illumination. We report the systemic investigations of the physical properties, photoelectrochemical performances and the influence of surface states for the silver-tin-sulphides ($Ag_8SnS_6$) photoelectrode in order to find out the reason about its poor stability for photoelectrochemical salt-water splitting. From the electrical impedance spectra of samples in the salt-water solution with various applied voltages, the Fermi-level pinning effect occurs in the $Ag_8SnS_6$ photoelectrode due to its high density of surface states. The accumulation of holes in the surface states results in the photocorrosion of the photoanode rather than the photoelectrochemical salt-water splitting. With the ZnSe/$Ag_8SnS_6$ heterogeneous junction as the photoelectrode, these surface states at the $Ag_8SnS_6$ sample act as the capacitances that can extract photo-excited electrons from the ZnSe layer and holes from the $Ag_8SnS_6$ sample. They make the increase in the charge separation rate for photo-excited carriers in the samples, which enhances its photoelectrochemical performance and stability in the salt-water solution.

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## 1. Introduction

Photoelectrochemical (PEC) water splitting is one of the interesting processes for the production of hydrogen gas, which is in consideration as the useful secondary energy carrier for the future clean energy demands [1–4]. The PEC water splitting involves in an electrochemical cell with the p-n semiconductor electrodes or the semiconductor/metal electrodes as the photoelectrode and counter electrode in a suitable electrolyte, respectively. Under light irradiation, the photoelectodes absorb the incident light and the photo-excited electron-hole pairs in the bulk semiconductor are generated. The holes migrate to the interface of the n-type photoelectrode/electrolyte junction and electrons transfer to the counter electrode, respectively, under the given applied bias of more positive than its flat-band potential. The p-type samples show the opposite current direction compared with the n-type sample in the PEC water splitting process. The photo-excited holes then react with the water and the electrons react with the protons in the electrolyte, respectively, making the water decompose into hydrogen and oxygen gases. Taking the requirement of solar-to-hydrogen efficiency (STH) for PEC water splitting into consideration, the current density from the photoelectrode to the counter electrode has to be set as large as possible at a given applied voltage [4–6]. In order to improve the STH efficiency of PEC water splitting, the developments of visible-light-active semiconductors are thus necessary and many possible candidate semiconductors such as metal oxide [2,7,8], metal sulphides [2,9,10], metal selenides [11,12], and their solid solutions [6,13–15] used for PEC water splitting have been reported in the literatures. Although the STH efficiency of greater than 10% for PEC water splitting process has been reported, which approaches the STH target of 2018 set by US department of energy, the main challenges for the industrial applications using the PEC water splitting are the high production cost and long-term instability of these photoelectrodes in electrolytes under light irradiation [5]. The major reason for the long-term instability of a photoelectrode is due to the influence of surface states at the samples. Recently, the role of surface states in a photoelectrode and the possible surface modification technologies for these visible-light-active semiconductors have been reported for the enhancements of their PEC water splitting efficiency and stability

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in the electrolyte under light irradiation [6,16–21]. These studies focused on the understanding of the role of the surface states for these metal oxides samples (for example: $\alpha$-hematite) and the improvements of their PEC performances by the surface modification [17,19–26]. In contrast, few discussions about the surface states of the metal sulphide or metal selenide samples are reported compared with the metal oxide photoelectrodes [27,28]. The metal sulphides such as CdS are also the interesting photoanodes with suitable energy band gap (for example $E_g = 2.4$ eV for CdS) and the suitable conduction and valence band positions for water splitting. However, the photocorrosion effect at these metal sulphides is easily observed during the PEC water splitting because of the accumulations of photo-excited holes at the sample surface. Although the hole scavengers such as sacrificial agents with faster oxidation rate than water oxidation reaction can be used to inhibit the photocorrosion of these metal sulphide photoelectrodes, the reactions in electrolyte become the semi-water splitting reaction rather than real water splitting [5,29]. In order to improve the weakness of these metal sulphide photoanodes, we have developed several multi-component metal sulphide/selenides as the photoelectrodes for the solar-driven water splitting [10,11,30,31]. We also developed some possible multi-component metal sulphide/selenide candidates that can split salt-water into the hydrogen and oxygen gases without the toxic $Cl_2$ gases output [32–34]. Although these multicomponent metal sulphide/selenide photoanodes show good PEC performances in the salt-water solutions, the stabilities of the photoanodes are not good enough for the further industrial applications. The possible reason is due to the influence of surface states formed in these photoanodes, which resulted in the accumulations of photo-excited holes at the surface of the photoanode. Considering the PEC salt-water splitting is a good way for the production of hydrogen gases for further industrial applications, it is necessary to understand the influence of the surface states at the sample surface and try to find out the possible way for the enhancements of their PEC performances and stability in the salt-water solution under light irradiation. Liu et al. [16] reviewed the influence of surface states of the metal oxide photoanodes and showed that the passivation/co-catalyst layers can be deposited onto these photoanode surfaces for the inhibition of photocorrosion taking place at the sample surface and reduction for the recombination rate of photo-excited electron-hole pairs. A very thin semiconductor or catalyst layer is deposited onto the sample surface in order to prevent the parasitic light absorption. Another possible approach is to design the heterogeneous semiconductor junctions that can enhance the separation rate of photo-excited carriers in the photoelectrode or use the so-called Z-scheme effect occurred at the interface between these heterogeneous junctions [23]. Although the $Ag_8SnS_6$ (ATS) sample theoretically has the STH efficiency of around 40% under solar light irradiation, the current density-applied voltage plots of ATS samples in the salt-water solution showed the poor photovoltage and instability (only 5% of initial current density remained after a 1000 sec stability test) [4,32]. The possible way for the improvement of its PEC performance and stability in salt-water has to be further discussed. In our pervious study [32], the incident-photo-conversion efficiency of ternary ATS is around 20% with the incident light wavelength of less than 700 nm and increase to 35% at the light wavelength of around 800 nm. For the design of heterogeneous semiconductor junction with good stability in the aqueous solution, ternary ATS has to be the inner layer due to the photocorrosion taking place at the sample surface. The p-type metal oxide semiconductor as the passivation layer with the energy band gap of around 2.5 eV, high water oxidation rate and few surface states may be the good choice for the outer layer of the heterogeneous semiconductor junctions. The p-n semiconductor junction can decrease the photo-excited carrier recombination rates and shift the onset potential in the current density-applied voltage curves of the photoelectrode in electrolyte under light irradiation [6]. However, the possible p-type semiconductors that meet the above requirements are rare. The n-type metal selenide such as ZnSe may be also the candidate as the outer layer for the design of heterogeneous junctions. The heterogeneous semiconductor junctions can also have better PEC performances compared with single layer semiconductor photoelectrode due to the Z-scheme effect occurred at the interface between these semiconductors or the suitable band positions of these tandem structure photoelectrodes [35–41]. The energy band gap of the ZnSe is in the range of 2.3–2.7 eV with the suitable band positons for water splitting [14,35,42]. The charge transfer resistance of ZnSe samples in an aqueous 0.5 M $Na_2SO_4$ solution is around 689 $\Omega$ with the good stability in electrolyte [35]. The reason for the low PEC performance of ZnSe sample is still unclear but the stability of ZnSe photoelectrode is better than CdS in electrolyte [43]. Many reports in the literatures about the n-n type heterogeneous semiconductor junctions for water splitting are the semiconductor with narrow energy band gap as the outer layer and large energy band gap semiconductor as the inner layer, respectively [35–41]. The amounts of light that are absorbed by the inner layer may decrease because of most light absorbed by the narrow energy band gap semiconductor (outer layer). However, Davi et al. [44] reported about the enhancement of PEC performance for the $CuWO_4$ photoelectrode ($E_g \sim 2.21$ eV) with the surface modification of $Ag_2NCN$ ($E_g \sim 2.24$ eV) compared with that for single $CuWO_4$ photoelectrode in the 0.1 M buffer solution. With the suitable band position alignment of $CuWO_4/Ag_2NCN$ composite photoanode, the PEC performance of composite photoanode increased due to the increase in the charge separation rate between the interfaces of $CuWO_4/Ag_2NCN$ composite photoanode under light irradiation. Although the n-n semiconductor junctions with narrow energy band gap semiconductor as the inner layer and large energy band gap semiconductor as the outer layer may increase their PEC performances, the band diagrams of our heterogeneous composite junction are not well match with that reported by the Davi et al. [44]. It may result in the mismatch with the requirement of the electrical field built at the interface for our semiconductor junction. Because the properties of interface of the n-n type semiconductor junctions may also determine the charge separation efficiency of photo-excited electron-hole pairs, the detail observation about the interface properties of samples has to be carried out. In this study, the systemic investigations about the single ATS, ZnSe and the ZnSe/ATS heterogeneous photoelectrodes prepared using the sulfurizaion and selenization of thermal evaporated metal precursors were carried out. The PEC performance tests and electrochemical impedance spectra (EIS) of samples in the salt-water solution were carried out to investigate the reaction mechanisms taking place at the samples in the dark and under light irradiation in order to improve their PEC performance in the salt-water solution.

## 2. Experimental process

### 2.1. Preparation of multi-metal nanolayers using thermal evaporation

The detail preparation processes for the metal sulphides/selenides are similar with our previous study [32–34]. Here shows the brief descriptions of the preparation procedures for these samples. The ATS, ZnSe and the ZnSe/ATS heterogeneous thin films were prepared on the fluorine-doped tin oxide (FTO)-coated glass substrates (10 $\Omega cm^{-2}$, Union-Chemicals Co. Taiwan) using the reactive sulfurization or/and seleinzation of thermal evaporation of the metal precursors. The samples prepared on the glass substrates for the analysis of their compositions, crystal phases, optical and electrical properties were carried out in order to avoid the influence of conductive layer of substrates. The thermal evaporation

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