



Investigation on Stability of Electroplated-Sulfurized CuInS_2 -based Photocathode Modified with an In_2S_3 Layer for H_2 Evolution under Various pH Conditions

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ABSTRACT

We investigated photoelectrochemical water splitting properties of Pt- In_2S_3 / CuInS_2 photocathodes from near neutral toward basic condition (pH 6, 9, and 13). Half-cell solar-to-hydrogen (HC-STH) of Pt- In_2S_3 / CuInS_2 measured under 0.2 M NaH_2PO_4 was the highest when the pH of the solution was 13 (4.7% at 0.42 V vs. RHE) with a maximum photocurrent density of 16.3 mA cm^{-2} (at 0 V vs. RHE) and onset potential of 0.9 V vs. RHE (defined as cathodic photocurrent of 0.1 mA cm^{-2}). However, it suffers from rapid degradation of the photocurrent over the time course when kept at 0 V vs. RHE under constant illumination. On the other hand, the photocathode showed relatively stable photocurrent when measured under near neutral condition (pH 6): HC-STH of 2.85% (at 0.28 V vs. RHE) with a maximum photocurrent density of 16.3 mA cm^{-2} (at 0 V vs. RHE) and onset potential of 0.72 V vs. RHE were obtained from the photocathode. Passivation using In_2S_3 oxygen-free can stabilize the photocathode at alkaline pH (pH 13).

Keywords: Photoelectrochemical water splitting, Copper indium sulfide, Indium sulfide, Stability.

INTRODUCTION

Hydrogen (H_2) produced by photoelectrochemical (PEC) water splitting via direct

use of sunlight irradiation is considered to be a holy grail to provide sustainable fuel that can support human life for many years to come. PEC approach by using TiO_2 photoelectrode illuminated

with UV light was demonstrated by Fujishima *et al.*, as the first realization of water splitting.¹ This result triggered other researchers to investigate and propose numerous varieties of semiconductors and device configurations to realize an efficient water splitting system to produce H₂.²⁻⁶

Tandem water splitting system has been emerged as the most viable solution for the practical application due to the difficulty in finding a single semiconductor that is able to perform efficiently both water reduction and oxidation simultaneously. It consists of a photocathode and a photoanode where each of which is responsible for the water reduction and oxidation, respectively. Therefore, each of the electrodes allows flexibility to be investigated and optimized its potency as a promising semiconductor to achieve an efficient overall water splitting system using only sunlight (no bias).

Considering the photocathode part, Cu-chalcopyrite materials, for instance CuInSe₂, CuGaSe₂, CuInS₂, CuGaS₂ and their mixed crystals, have emerged as promising candidates to produce H₂.⁷⁻¹¹ Moreover, through bandgap engineering from 1.0 eV to 2.4 eV by varying the In/Ga and/or Se/S ratios in their mixed crystal promises a versatile flexibility to optimize the appropriate tandem design with photoanode as another part. Researchers by using different absorbers had inserted *n*-type thin layers on their surface to improve the photo response, which are widely employed in fabrication of *p-n* junctions for chalcopyrite-based solar cells.¹²⁻¹⁵ We used In₂S₃ by chemical bath deposition (CBD), in our previous study, as an alternative to the commonly-used CdS as the *n*-type layer on CuInS₂ photocathode and obtained in half-cell solar-to-hydrogen (HC-STH) efficiency close to 2%.¹⁶ Moreover, the photocurrent onset was shifted positively, which made this photocathode system become more favorable for the tandem PEC system with unbiased potential.

In₂S₃-modified CuInS₂ photocathode showed higher water reduction properties; however, its behavior under different pH was not well confirmed. Consequently, we wanted to investigate the water reduction properties of In₂S₃-modified CuInS₂ in various pH from near neutral to alkaline conditions.

The photostability of the photocathode under various pH conditions also will be discussed.

Experimental Details

Fabrication of CuInS₂ Thin Films

The CuInS₂ thin film was synthesized by successive stack electrodeposition of Cu and In layers followed by sulfurization. Electrodeposition was carried out potentiostatically using a Hokuto Denko HSV-100 potentiostat-galvanostat under N₂ atmosphere without stirring. A vertical three-electrode setup consisting of an Ag/AgCl reference electrode, a Pt wire counter electrode, and a Mo-coated glass substrate (Mo/glass) as a working electrode (area of the working electrode being 0.7 cm²) was employed. The electrolyte solution for Cu deposition consisted of 50 mM CuSO₄, 150 mM trisodium citrate, and 242 mM citric acid. The solution was adjusted to pH 2.4 using H₂SO₄. For In deposition, the electrolyte solution consisted of 30 mM InCl₃, 242 mM citric acid, and 36 mM trisodium citrate. Potentials used for Cu and In deposition were -0.2 V and -0.76 V (vs. Ag/AgCl), respectively. Electric charges of Cu and In deposition were fixed at 0.73 C and 0.84 C, respectively: this resulted in the composition ratio of Cu and In (Cu/In) in a Cu and In stacked layer of 1.3. The Cu/In stack as-deposited was then heated at 160 °C for 30 min under Ar flow (200 mL min⁻¹), followed by sulfurization at 560 °C under H₂S flow (5% H₂S in Ar, 200 mL min⁻¹) for 10 min in a glass tube furnace. Thus-obtained CuInS₂ films were then etched by immersion in an aqueous KCN solution (10%) for 2 min to remove excess Cu_xS components.

Surface Modification with In₂S₃ Layer

Surface modification was performed by chemical bath deposition (CBD) method on the prepared CuInS₂ film by In₂S₃ layers. In a typical procedure, the prepared CuInS₂ was added to an aqueous solution containing 25 mM In₂(SO₄)₃, 0.1 M CH₃CNSH₂ and 0.1 M CH₃COOH; deposition of In₂S₃ was performed at 65°C for 15 min. Finally the films were washed with and dried by N₂ gas. The deposition gave the formation of Ca. 15 nm thick In₂S₃ layer on CuInS₂ films (labeled In₂S₃/CuInS₂). For revised In₂S₃ deposition we used 25 mM In₂(SO₄)₃, 0.2 M CH₃CNSH₂ and 1 M CH₃COOH in demineralized water after removing the dissolved

oxygen using N_2 for 1 h, the similar procedure for revised In_2S_3 by CBD was used as above.

Surface Modification with Pt

Photoelectrodeposition in three-neck cylindrical flask containing 20 mL solution of 0.1 M Na_2SO_4 and 1 mM H_2PtCl_6 at pH 4 was performed for Pt deposition modified-CuInS₂ films. Three electrodes namely Pt wire, Ag/AgCl and modified CuInS₂ as counter, reference and working electrodes, respectively were inserted into the flask. By continuous illuminating the working electrode through the window the photoelectro deposition was performed at a potential of -0.1 V for 10 min. using electrochemical measurement unit (Solartron SI 1280B) equipped with a solar simulator AM-1.5 (Compact Xenon Light Source, Asahi Spectra HAL-320). Thus obtained $In_2S_3/CuInS_2$ modified with Pt was labeled as Pt- $In_2S_3/CuInS_2$.

Photoelectrochemical Measurements

Photoelectrochemical measurements were done using the same instruments as surface modification with Pt completed with digital function generator 0.1 MHz-2MHz DF 1906, NF Japan (at 0.3 Hz) and Shutter Controller F77 (Suruga Seiki). Solutions of 0.2 M NaH_2PO_4 (at pH 6, 9 and 13) were used for measurements of Pt- $In_2S_3/CuInS_2$ photocathodes. The three electrode setup was immersed in each solution. The measurement was run by chopping 1.5 AM light irradiation to the working electrode under sweep potential with scan rate 10 mV/s.

The potentials in each PEC measurement for Pt- $In_2S_3/CuInS_2$ photocathodes referred to Ag/AgCl electrode ($E_{Ag/AgCl}$) were converted into E_{RHE} using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.199.$$

Half-cell solar-to-hydrogen efficiency (HC-STH) for photocathode was calculated from the data according to the following equation:

$$HC-STH [\%] = J \times (V - V_{H+/H_2}) \times 100\% / P,$$

where J ($mA\ cm^{-2}$) is the measured photocurrent density, V (V vs. RHE), is the bias voltage measured by the reversible hydrogen

electrode (RHE) scale (E_{RHE} , see above), $V - V_{H+/H_2}$ is the equilibrium redox potential of hydrogen (0 V vs. RHE) and P is the photon flux of the AM 1.5 simulated sunlight ($100\ mW\ cm^{-2}$).

Characterizations of Fabricated Photocathodes

Surface morphologies were examined using a Hitachi S-5000 FEG field emission scanning electron microscope (FE-SEM). Surface structures of Pt-CdS/CuInS₂ and Pt- $In_2S_3/CuInS_2$ films were examined by X-ray photoelectron spectroscopy (XPS) using a Shimadzu AXIS ULTRA X-ray photoelectron spectrometer.

RESULTS AND DISCUSSIONS

We investigated the performance of Pt- $In_2S_3/CuInS_2$ photocathodes at various pH conditions from near neutral to alkaline condition. Figure 1 shows current-potential profiles of Pt- $In_2S_3/CuInS_2$ photocathodes in 0.2 M NaH_2PO_4 at pH 6.0, 9.0 and 13.0 (adjusted by NaOH) measured under chopped illumination from AM 1.5 G ($100\ mW/cm^2$) solar simulator. Table 1 summarized photocurrent density (at 0 V vs. RHE), onset potential (defined as cathodic photocurrent of $0.1\ mA\ cm^{-2}$), and half-cell solar-to-hydrogen (HC-STH) efficiency of Pt- $In_2S_3/CuInS_2$ measured under 0.2 M NaH_2PO_4 at various pH. The onset potential was clearly shifted toward positive potential with the increase of pH. This positive shift of the potential with the increase of pH is similar to

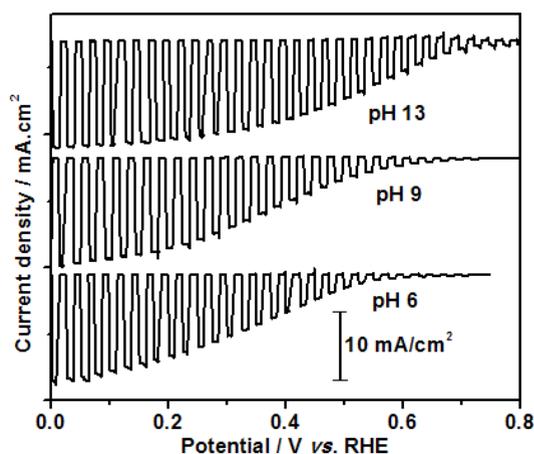


Fig. 1: Current-potential curve of Pt- $In_2S_3/CuInS_2$ in 0.2M NaH_2PO_4 (pH 6, 9, 13) under chopped illumination from AM 1.5 simulated solar irradiation

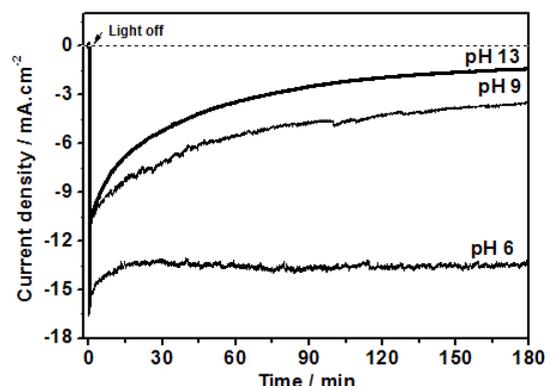


Fig. 2: Current-time profile of Pt-In₂S₃/CuInS₂ measured using 0.2 M NaH₂PO₄ solution at pH 6, 9 and 13 at bias potential of 0 V vs. RHE under chopped illumination from AM 1.5 simulated solar irradiation.

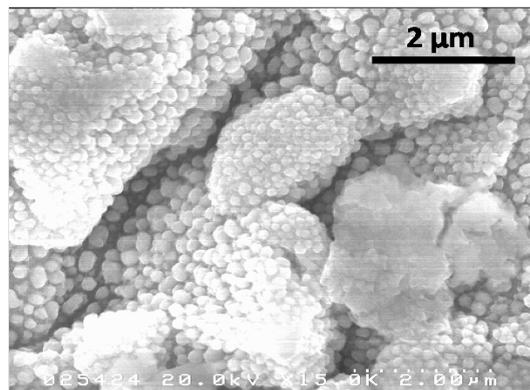


Fig. 3: SEM of Pt-In₂S₃/CuInS₂ photocathode after used. The stability test was done for 15 h at pH 13 in 0.2 M NaH₂PO₄ solution (0V vs. RHE) under continuous illumination from AM 1.5 simulated solar irradiation.

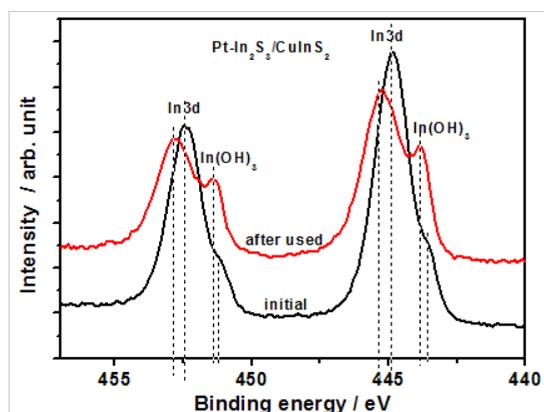


Fig. 4: XPS of indium (In 3d) as Pt-In₂S₃/CuInS₂ before and after used. The stability test was done for 15 h at pH 13 in 0.2 M NaH₂PO₄ solution (0 V vs. RHE) under continuous illumination from AM 1.5 simulated solar irradiation

the behavior of Cu₂ZnSnS₄-based photoelectrode¹³ and flatband potential of Cu(In,Ga)S₂.¹⁷ In our case, similarly, the positive shift of the onset potential could be influenced by the deeper flat-band potential of CuInS₂ with the increase of pH. Photocurrent density of the photocathodes at 0 V vs. RHE were relatively similar (ca. 16 to 17 mA.cm⁻²). Maximum HC-STH of 4.7% (at 0.42 V vs. RHE) was obtained from Pt-In₂S₃/CuInS₂ measured at pH 13.

To investigate the stability of the Pt-In₂S₃/CuInS₂ under reductive condition at various pH, the photocathode was then exposed to continuous

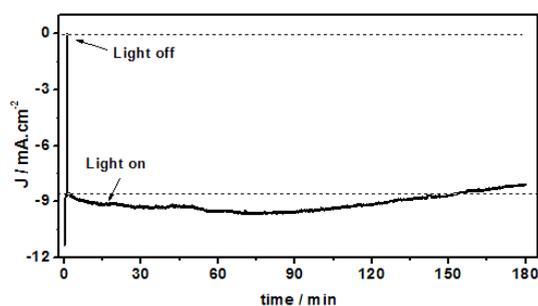


Fig. 5: Current-time profile of Pt-In₂S₃/CuInS₂ (using modified In₂S₃) measured in 0.2 M NaH₂PO₄ solution at pH 13 (0 V vs. RHE) under chopped illumination from AM 1.5 simulated solar irradiation.

Table 1: Photocurrent density (at 0 V vs. RHE), onset potential (defined as cathodic photocurrent of 0.1 mA cm⁻²), and HC-STH of Pt-In₂S₃/CuInS₂ measured under 0.2 M NaH₂PO₄ at various pH

pH	6.0	9.0	13.0
Photocurrent density/ mA cm ⁻²	16.3	16.7	16.3
Onset potential / V vs. RHE	0.72	0.75	0.90
HC-STH / %	2.85(at 0.28 V)	2.85(at 0.30 V)	4.70 (0.42 V)

illumination from AM 1.5 solar simulator while keeping at a bias potential of 0 V vs. RHE. Figure 2 shows current-time profiles of the photocathode at such

measurement conditions. The photocurrent initially started at a relatively similar photocurrent density (ca. 16 mA cm⁻²), then the photocathode measured at pH 6 shows relatively stable photocurrent along the time course, while at the basic conditions the photocurrent keeps degrading and getting worse with the increase of pH: the percentage of degradation compared to initial photocurrent was 16%, 78%, and 91% for pH 6, 9, and 13, respectively.

It is clear from the above results that the alkaline condition is not favorable for the long-term stability of Pt-In₂S₃/CuInS₂ under continuous illumination. In addition, when we repetitively measured the photocathode under cathodic swept at pH 13, both photocurrent and onset potential was gradually decreased: no clear degradation was observed upon such repetitive scan for pH 6 and 9. Further more from SEM images we cannot clearly see the SEM changes from initial photocathode compared with photocathodes after measured in pH 6, 9 and 13 for 3 hours.

In fact, immersion of bare In₂S₃ deposited on FTO substrate at pH 13 for 5h resulted in dissolution of the In₂S₃ layer from the substrate. Accordingly, to know the further change, we treated the photocathode at pH 13 for a longer time (15 h) under continuous illumination at 0 V vs RHE, the result is depicted in Figure 3 and 4.

SEM image of Figure 3 shows the formation grape-like on the photocathode that most probably hydroxide attachments on the indium sulfide layer, as can be seen in Figure 4 the survey scan for In 3d of initial Pt-In₂S₃/CuInS₂ using XPS analysis shows the peaks of 444.8 and 452.4 eV as representation of indium bound as In₂S₃, and small shoulders around 443.6 and 451.2 eV as indium hydroxide peaks. Photocathode of Pt-In₂S₃/CuInS₂ after used there is a little bit shift to higher binding energy for survey scan of In 3d namely 445.3 and 452.9 eV main peaks and also there are increasing peak height at the shoulder with binding energy of 443.9 and 451.4 eV that representing the improvement of indium that binds OH⁻ ions from the solution for sample after used. As we know In₂S₃ prepared by CBD using indium sulfate and thioacetamide will resulted almost 80% of In₂S₃.¹⁸ Therefore the presence of OH⁻ in its

structure will tend to attract other OH⁻ ions from the solution.

Figure 5 represents the current time curve of Pt-In₂S₃/CuInS₂ of using In₂S₃ with oxygen-less content (revised In₂S₃ by CBD), oxygen was not detected (the data not shown). The figure can be seen the photocathode gave stable for 3 h continuous illumination. Moreover the current increased to 90 min and began to decrease after that and finally reduced a little bit after 160 min from the initial measurement. Compared with standard Pt-In₂S₃/CuInS₂ the initial current diminished almost 54% (from 16.8 mA/cm² reduced to 9 mA/cm²). The most probable reason is due to slightly blocking of incident light that reduces In₂S₃ transparency. Another possibility is reducing bandgap of revised In₂S₃ that can degrade the performance of photocathode, since reducing oxygen will lower conduction band position.¹⁹ Similarly as solar cell, therefore, for In₂S₃ there must have been tunable oxygen to improve its performance.

CONCLUSION

PEC water splitting of Pt-In₂S₃/CuInS₂ photocathodes for H₂ evolution showed a more enhanced photocurrent density under 0.2 M NaH₂PO₄ (pH 6). PEC water splitting study of Pt-In₂S₃/CuInS₂ photocathodes reveal that HC-STH and onset potential values are quite influenced by the pH of the solutions, HC-STH and onset potential improve with increasing pH with the maximum value was 4.7% at pH 13. Long term stability test of Pt-In₂S₃/CuInS₂ shows that the photocathode is stable at pH 6 while at basic condition it suffers from rapid degradation of the photocurrent over the time course when kept at 0 V vs. RHE. The used revised In₂S₃ can stabilize of Pt-In₂S₃/CuInS₂ photocathode under long term illumination, although the current decreased compared with standard photocathode.

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