Investigation of copper-kesterites for solar water splitting

Tay, Ying Fan

2020

Tay, Y. F. (2020). Investigation of copper-kesterites for solar water splitting. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/145524>

<https://doi.org/10.32657/10356/145524>

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Investigation of Copper-Kesterites for solar water splitting

Tay Ying Fan

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2020

Investigation of Copper-Kesterites for Solar Water Splitting

Tay Ying Fan

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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... 26 March 2020 ...

Date

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Associate Professor Lydia Helena Wong

Authorship Attribution Statement

This thesis contains material from 2 papers published/in preparation in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 4 is published as Tay, Y.F., Kaneko, H., Chiam, S.Y., Lie, S., Zheng, Q., Wu, B., Hadke, S.S., Su, Z., Bassi, P.S., Bishop, D., Sum, T.C., Minegishi, T., Barber, J., Domen, K., and Wong, L.H. Solution processed Cd-substituted CZTS photocathode for efficient solar hydrogen evolution from neutral water. *Joule* **2018**, 2, 537-548
<https://doi.org/10.1016/j.joule.2018.01.012>

The contributions of the co-authors are as follows:

- Associate Professor Lydia Helena Wong and Associate Professor Tsutomu Minegishi provided the project direction and revised the manuscript drafts.
- Dr Sing Yang Chiam, Associate Professor Tze Chien Sum, Professor Kazunari Domen and Professor James Barber edited the revised manuscript drafts.
- I performed the thin film synthesis and characterization at the Energy Research Institute @ NTU. I performed photocathode fabrication, optimization and photoelectrochemical measurements at the University of Tokyo. I performed XPS and UPS characterization at the Institute of Materials Research and Engineering (IMRE). I also analyzed the data and prepared the manuscript drafts.
- Dr Hiroyuki Kaneko assisted in the experiments at the University of Tokyo.
- Dr Qiusha Zheng and Dr Bo Wu assisted with the TAS measurements at NTU.
- Dr Stener Lie assisted with the AC Hall measurements at the Energy Research Institute @ NTU.
- Mr Shreyash Hadke and Prince Saurabh Bassi assisted with the discussion of the manuscript.
- Dr Douglas M. Bishop assisted in the photoluminescence study at the IBM T.J. Watson.
- Dr Oki Gunawan assisted and guided device characterization and analysis at the IBM T.J. Watson facilities

Chapter 5 is published as Tay, Y.F., Hadke, S.S., Zhang, M.Y., Lim, Nathan., Chiam, S.Y. and Wong, L.H. Improving the interfacial properties of CZTS photocathode by Ag substitution. Journal of Materials Chemistry A, **2020**, 8, 8862-8867.

DOI: 10.1039/d0ta02042g

The contributions of the co-authors are as follows:

- Associate Professor Lydia Helena Wong provided the project direction and revised the manuscript drafts.
- I performed the thin film synthesis and characterization at School of Materials Science and Engineering and the Energy Research Institute @ NTU. I performed device fabrication and analysis at NTU. I also analyzed the data and prepared the manuscript drafts.
- Mr Shreyash Hadke assisted with the PV Mott-Schottky, CV data collection and analysis at the Energy Research Institute @ NTU. He also helped in the manuscript revision.
- Mr Nathan Lim assisted with some of the device fabrication.
- Dr Sing Yang Chiam and Meng Yuan Zhang assisted in manuscript revision.

.....26 March 2020.....

Date

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Tay Ying Fan

Abstract

Solar water splitting is a promising method to store energy by utilizing renewable solar energy to electrolyze water and generate hydrogen as a fuel. For this vision to succeed, both photoanode and photocathode driving the water oxidation and reduction reaction respectively must be able to both split water efficiently and be able to guarantee a sufficient lifetime to make economic sense. In the field of photocathodes, copper chalcogenides has been extensively studied, with Cu(In,Ga)Se₂ (CIGS) achieving up to 3.7% unbiased solar-to-hydrogen (STH) conversion efficiency in 2018. While the results are attractive, the scarcity of Indium and Gallium makes the alternative Cu₂ZnSnS₄ (CZTS) a promising candidate due to its similar characteristics as CIGS. Extensive research in the field of photovoltaics has advanced CZTS device efficiencies up to 12.7%, providing a template for its application to water splitting.

The first part of the thesis aims to explore the influence of cation substitution in CZTS photocathodes (Cd²⁺ replacing Zn²⁺ and Ag⁺ replacing Cu⁺) which alters the band positions and the carrier transport properties of CZTS. Both Ag⁺ and Cd²⁺ were chosen to replace Cu⁺ and Zn²⁺ to maintain charge neutrality and to increase the difference in ionic size between Cu⁺ and Zn²⁺ which may help reduce the amount of Cu_{Zn} antisite defects. Firstly, different amounts of Ag and Cd are substituted into CZTS and fabricated through solution processed spin coating. Next, the optimum amount of substitution is determined by studying its photoelectrochemical (PEC) performance, along with advanced characterizations to investigate its band structure and carrier transport properties. The next part of the thesis focuses on investigating Indium Tin Oxide (ITO) as a charge transport layer and a protective layer. ITO is deposited between the CdS buffer layer and the Pt catalyst to increase the stability and performance of the cation substituted CZTS photocathode.

For Cd²⁺ substitution, PEC measurements reveal that the photocurrent increases steadily with increasing Cd²⁺ substitution reaching a maximum when 40% of Zn is substituted with

Cd^{2+} . A 3 fold increase in carrier mobility and lifetime is observed along with a reduction in radiative recombination, which may be due to the reduction of antisite defects. Cd^{2+} substitution is confirmed to be beneficial to reduce bulk defects in CZTS and improve the carrier transport. However, onset potential of the Cd^{2+} substituted photocathode decreases when compared to pristine CZTS, which may be due to the lower bandgap and the spike like heterojunction with CdS.

For Ag^+ substitution, PEC performances follow a similar gaussian trend as Cd^{2+} substitution, with a maximum photocurrent observed at 4% Ag substitution and a maximum onset potential observed at 8% Ag substitution. Ag^+ substitution is found to affect mainly the CZTS/CdS interface instead of the CZTS bulk, helping to reduce the interfacial defects and leading to an increased photocurrent and onset potential. A bilayer Cd^{2+} substituted CZTS (near the bulk) and Ag substituted CZTS (near the CdS interface) may reap the benefits of bulk and interface improvement from both cation substitution and could be studied in the future to push the efficiency of CZTS photocathode further.

To address the issue of stability usually observed in photocathodes and possibly also reap the superior charge transport properties of a transparent conducting oxide (TCO), amorphous thin Indium Tin Oxide (ITO) is DC sputtered unto CZTS/CdS at room temperature. It is found that during photoelectrodeposition of Pt on ITO, In and Sn near the ITO surface is partially reduced, creating a new metallic interface formed between ITO and Pt. While the photocurrent of the ITO protected photocathode decreases with time during stability test (under $0V_{\text{RHE}}$ with illumination), stopping the stability test and doing repeated linear sweep voltammetry (LSV) in the dark is able to recover the photocurrent to its original value. This leads to the hypothesis that the decrease in photocurrent observed initially is due to phosphate ions from the potassium phosphate electrolyte adhering on the surface of ITO and Pt, preventing efficient charge transfer instead of the photocathode degrading. Further investigations on the reason for dark linear sweep voltammetry (LSV) in removing the phosphate ions and the adhesion of phosphate on ITO may help in the design of other protective layers for photocathodes.

In summary, this thesis succeeds in employing cation substitution to selectively improve the bulk and interface properties of CZTS photocathodes, enhancing photocurrent and onset potential considerably. The function of ITO as a protective charge transport layer for the photocathode is also demonstrated. This thesis utilizes cation substitution to improve bulk and interface properties of CZTS photocathode and recommends that such techniques can be employed for other defective photocathodes. Furthermore, a corrosion resistant TCO capable of forming a metallic interface with Pt is studied for the first time and shown to be able to enhance the photocurrent substantially while also preventing the degradation of the underlying CdS and CZTS.

Lay Summary

With an increasing energy price and depletion in fossil fuels coupled with a growth in projected energy demand of 37% by 2040, there is a growing need to shift our energy production towards renewable energy that is sustainable. Furthermore, the rise in global temperature due to carbon dioxide emissions from burning fossil fuels raises the urgency to find such clean renewable energy. Solar energy is highly attractive in this regard, as it has the largest theoretical potential requiring just 0.17% of Earth surface to produce 15 TW of carbon-neutral power needed to stabilize carbon dioxide emissions in 2050 at 6.6 GtC per year. However, despite the advantages of solar energy, there is still a problem of intermittency with the energy source, which requires us to look into storage of electrical energy for utilization and transportation. Storing renewable energy in a chemical fuel like hydrogen is favorable because of its high energy density and ability to utilize existing infrastructure. Furthermore, combustion of hydrogen is environmentally friendly and does not produce any carbon products, creating the potential to reduce total amount of carbon dioxide in the atmosphere and slow down global warming.

The use of photoactive semiconductors to produce hydrogen photoelectrochemically by splitting water therefore encompasses the ideals of utilizing renewable solar energy and storage in a clean chemical fuel. In water splitting, the two half reactions of water oxidation and water reduction are handled by photoanodes and photocathodes respectively. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a well-studied material in photovoltaics whose conduction band lies above the water reduction potential, making it thermodynamically favorable to reduce water into hydrogen as a photocathode. To raise the efficiency of the water splitting reaction, a photocathode should have high photocurrents and onset potentials.

This thesis addresses the limitations of CZTS by first improving its performance through incorporating other isovalent cations to substitute the cations in CZTS. Two cation substitutions are investigated which helps improve two different aspects of the CZTS photocathode. Next, stability of the CZTS photocathode is improved by adding an additional Indium Tin Oxide (ITO) overlayer. Through these two studies, this thesis aims

to promote cation substitution as a viable technique in improving the performance of photocathodes and in using ITO to enhance its stability.

Acknowledgements

The author would like to express his deepest gratitude and appreciation to:

Assoc. Prof. Lydia Helena Wong for always giving the author freedom and space to conduct experiments on his ideas, faith in the author even in the down times and continued guidance throughout this PhD journey. Thanks also for the opportunity to collaborate with other groups, without which the author would have been completely at a loss in the beginning. The author is deeply thankful for the chance to undertake research under her since his undergraduate years.

Dr. Chiam Sing Yang, the author's co-supervisor for the continued guidance, encouragement and support during the course of the PhD. Thanks for the lunches we had and the wild long hours of brain storming. Also, thanks for always helping in the scientific discussions and also the voice of reason when the author is going off track.

The author's collaborators in the University of Tokyo, Hiroyuki Kaneko and Prof Tsutomu Minegishi. Without them giving a kick start to the author's knowledge in photocathodes, there is no way this thesis would have been completed. Thanks for the warm hospitality shown to the author during his stay in Tokyo. Thanks also for the unwavering support given to the author for the first work on CCZTS.

The author's group members, Dr. Joel Tan, Dr. Leow Shin Woei, Dr. Wang Hao, Dr. Asim Guchhait, Dr. Su Zhenghua, Mr. Li Wenjie, Dr. Prince Bassi Dr. Nguyen Thi Hiep, Dr. Wilman Septina, Dr. Zhang Mengyuan, Dr. Monika Rai, Dr. Stener Lie, Mr. Hadke Shreyash Sudhakara, Mr. Ahmad Ibrahim, Mr. Jin Xin, Mr. Sadhu Anupam, Mr. Mahmoud Gamal Mahmoud Ahmed and Mr. Daniel Goh. Thanks for the time we had together, it has been such a blessing to have you all as my groupmates. Thanks for all the drop ins, lunches, discussions, talks, help, cheering ups, motivating and time spent together trudging on in this journey of research! Special mention to Dr. Leow Shin Woei who helped the author in proof reading the thesis and also acting as a mentor for all the young PhD

students; Dr. Joel Tan for all the valuable advice given especially with regard to chemistry stuff and being such a willing person to help; Dr. Zhang Mengyuan for all the help in lab management and collaborative work; Shreyash Hadke for all the collaborative work, photovoltaic advice, defects advice and Stener Lie for the meals, random talks and for being such a great help.

My Thesis Advisory Committee (TAC) members Prof. Martial Duchamp and Prof. Nripan Matthews for their valuable advice on the author's research. It has been a wonderful experience collaborating with their group members in various projects and having a relationship beyond that of a typical TAC member.

My family and friends, who have followed the author on this journey since forever and has been the author's pillar of support throughout this long journey. Without those random dinners and entertainment, it would have been impossible to disconnect from work. Thanks for also all the motivation given to the author. Life will not be complete without them.

Last but most importantly, to God, the almighty creator who have seen through all the author's faults and failures, and yet given the author the greatest privilege and grace to know of Him. Thanks for planning the author's future and chastening the author when needed. Thanks for making the author who he is and thanks for never giving up on him.

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Abbreviations

AC	Alternating Current
BEI	Backscattered Electron Images
CBD	Chemical Bath Deposition
CBM	Conduction Band Minimum
CIGS	Copper Indium Gallium Selenide
CV	Capacitance-Voltage
CZTS	Copper Zinc Tin Sulfide
DFT	Density Functional Theory
DOS	Density of States
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-ray
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FWHM	Full Width Half Maximum
HC-STH	Half-Cell-Solar-To-Hydrogen conversion efficiency
ITO	Indium-doped Tin Oxide
IPCE	Incident Photon-to-Current Conversion Efficiency
IV	Current-Voltage
JCPDS	Joint Committee on Powder Diffraction Standards
JV	Current Density-Voltage
NTU	Nanyang Technological University
PCE	Power Conversion Efficiency
PEC	Photoelectrochemical cell
PED	Photoelectrochemical Deposition
PL	Photoluminescence
PV	Photovoltaic
RHE	Reversible Hydrogen Electrode
SEI	Secondary Electron Images

SEM	Scanning Electron Microscopy
UV	Ultraviolet
VB	Valence Band
VBM	Valence Band Maximum
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

An outline of the thesis is laid out in the first chapter. A brief introduction of the project background is first presented followed by the hypothesis of replacing Zn^{2+} and Cu^{+} in copper zinc tin sulfide photocathode absorber to improve its performance while retaining the isovalency. The 2nd hypothesis of the thesis focuses on using Indium Tin Oxide (ITO) as a protective layer to enhance the performance and stability of CZTS/CdS/ITO/Pt photocathode. The objective and scope of the thesis will then be described, along with a summary of each subsequent chapter. Research findings on Cd^{2+} and Ag^{+} partial substitution on CZTS photocathode and ITO overlayer are highlighted in the last part.

1.1 Hypothesis/Problem Statement

Figure 1.1: (a) Energy consumption of OCED vs non-OCED countries projected to 2050.^[1](b) Global mean temperature anomalies for May 2019.^[2]

Energy demand is predicted to increase by nearly 50% between 2018 and 2050 largely contributed from non-OECD (Organization for Economic Cooperation and Development) countries owing to strong economic growth and high population growth. Projections to year 2050 suggest that the world energy consumption will total 911 quadrillion British Thermal Units (Btu) (267 trillion kWh) with the upper limit at 1090 quadrillion Btu (319 trillion kWh). This is coupled with an increasing global surface and ocean temperature, higher CO₂ emissions, rising sea levels, sea acidification and further ice melt in the Arctic and Antarctic regions. In May 2019, certain key anomalies were recorded, such as new maximum temperature records for Japan and Hawaii while Antarctic recorded its smallest sea ice area, which is 13% below the 1981-2010 average. These effects and anomalies are usually associated with increasing emissions of greenhouse gasses from burning fossil fuels to supply our increasing energy need. Furthermore, with the volatility of oil prices and the diminishing reserves of fossil fuels, there is a need to shift our energy production towards renewable energy that is more sustainable. Solar energy is highly attractive in this regard, as it has the highest theoretical potential to satisfy our energy needs.

Figure 1.2: Energy storage technologies comparison^[3]

Despite the advantages of solar energy, there is still a problem of intermittency of the energy source which requires efficient storage of energy for practical utilization and transportation. Each type of storage method has its own advantages and short comings in factors such as price, energy capacity, scale-up potential and energy density. In Figure 1.2, discharge time at rated power is plotted as a function of system power rating and size (scale-up potential). Electrical storage in the form of supercapacitors allow for mid-range discharge time (minutes to hours) but have a small scale-up size in the kW range. Electrochemical storage in form of batteries occupies the middle in terms of discharge time and scale-up size. While pumped hydropower has the largest discharge time and scale-up size, it is highly dependent on geographical conditions and is not always applicable. Storage of energy in a chemical fuel such as hydrogen is favorable as it has the advantages of higher discharge time and scalability, while also having the ability to integrate and utilize existing fossil fuel infrastructure. Furthermore, the switch to hydrogen fuel has the added advantage of resolving the current greenhouse emission problem as the combustion of hydrogen is environmentally friendly and does not produce any carbon compounds. It is thus advantageous to store renewable solar energy in hydrogen fuel.

The application of semiconductors to produce hydrogen from water photoelectrochemically by harnessing solar energy has been widely studied since the first demonstration in 1972 by Honda and Fujishima^[4]. Such a method utilizes semiconductors to absorb solar energy and generate electron hole pairs which can then drive the 2 separate water splitting half reactions shown below:

Water reduction reaction:

Water oxidation reaction:

Overall reaction:

Figure 1.3: (a) Single light absorber (S2) configuration for full water splitting. (b) Corresponding maximum theoretical solar-to-hydrogen (STH) conversion efficiency vs band gap for S2 configuration. (c) Dual light absorbers (D4) side-by-side configuration. (d) Corresponding maximum theoretical STH conversion efficiency vs band gap for D4 side-by-side configuration. (e) Dual light absorbers stacked (D4) configuration. (f) Corresponding maximum theoretical STH conversion efficiency vs band gap for D4 stacked configuration.^[5]

The two water splitting reactions (i.e. water reduction and oxidation) requires a total of 1.23 V to thermodynamically split water. When kinetics and the large entropy change to convert water to gas is taken into account, a much higher operating voltage is often necessary. This results in a requirement of a large band gap semiconductor to carry out the reaction (Figure 1.3a), limiting the photocurrent density generated and resulting in a poor solar-to-hydrogen (STH) conversion efficiency (Figure 1.3b). Thus, a common strategy is to incorporate two photoabsorbers (photoanode and photocathode) to carry out the water oxidation and reduction reactions respectively. This allows the photovoltage required for overall water splitting to be divided between two materials and allows for higher current densities. Such photoelectrochemical (PEC) tandem cells makes it possible to attain solar-to-hydrogen conversion efficiencies of over 20%.^[6] For practical water splitting applications, a photocathode/photoanode tandem should attain a STH efficiency of about 10% and operate stably for at least 10 years.^[7] In order to achieve this efficiency, the photocathode-photoanode tandem must be operating at a current density of about 8 mA cm^{-2} . The operating potential is estimated to be about $0.6 \text{ V}_{\text{RHE}}$ since it is in the middle of the water potential window and should allow both the photocathode and photoanode to achieve appreciable photocurrents. Hence, a photocathode should achieve a photocurrent of 8 mA cm^{-2} at potentials above $0.6 \text{ V}_{\text{RHE}}$ to meet the target for commercialization.

Figure 1.4: Main components of a photoelectrochemical (PEC) water splitting system.

As discussed earlier, the photovoltage required to split water can be split into two with the photocathode carrying out the water reduction while the photoanode carrying out the water oxidation. With respect to photocathodes, the material must have its conduction band minimum (CBM) positioned more cathodic than the water reduction potential to ensure that photoelectrons have sufficient potential to reduce water. Furthermore, it needs to be p-type such that it produces electrons as minority carriers upon light irradiation, and driven to the semiconductor/electrolyte interface. Other requirements such as good carrier transport properties, high absorption coefficient and an optimal band gap helps to improve the solar to hydrogen conversion efficiency. For the selection of materials, a common method is to utilize well studied p-type photoabsorbers that is used for photovoltaic applications and apply it as a photocathode.

Figure 1.5: Photocurrent density values for different n-type photoanodes and p-type photocathodes at 1.23 V_{RHE} and 0 V_{RHE} respectively^[5].

While crystalline Si is still the most dominant photoabsorber, the emergence of thin film second-generation photoabsorbers have been gaining interest due to its high absorption coefficient which allows for thinner and flexible devices. Among them, copper chalcogenides such as CuInGaS_2 (CIGS)^[8-9], CuInGaSe_2 (CIGSe)^[10-14], CuZnSnS_4 (CZTS)^[15-20], CuInS_2 ^[21-22] and CuGaSe_5 ^[23-24] have been widely studied and have demonstrated good photocurrents. CIGSe in particular has seen much research and has recently managed to set a record for unbiased solar to hydrogen conversion efficiency at 3.7% with a photocurrent of 28 mA cm^{-2} at 0 V_{RHE} which is about 80% of its theoretical

limit^[10] (Figure 1.5). However, due to the scarcity of In and Ga in CIGSe, kesterite CZTS is a highly attractive substitute material, as it has the same absorption properties as CIGSe, suitable band gap and band alignment with respect to water reduction potential while utilizing elements that are more abundant in the earth crust (Zn and Sn replacing In and Ga). However, to date, CZTS photocathodes have only shown photocurrents of up to 18 mA cm⁻² at 0 V_{RHE}^[17] which is much lower than its theoretical photocurrent density of 32 mA cm⁻² (56% of theoretical limit) and an unbiased solar to hydrogen conversion efficiency of 0.25%^[20]. This gap in performance between CZTS and CIGSe despite their similar optical properties presents an opportunity to improve the properties of CZTS to enhance its performance.

Figure 1.6: Intrinsic defect transition energy levels within band gap of Cu₂ZnSnS₄.^[26]

The limitation of performance for CZTS is usually attributed to interface defects, bulk antisite defects, secondary phases and band alignment^[25]. Among the many defects in the CZTS band gap, the Cu_{Zn} antisite received considerable attention due to its low formation energy, which results in a much higher concentration compared to other defects. Furthermore, the similarity in ionic size between Cu⁺ (0.74 Å) and Zn²⁺ (0.74 Å) allows interchanging of the ions within the Zn-Cu layer in the <001> orientation of the kesterite supercell without a large energy change to the overall system as the octet rule is still fulfilled^[26]. These Cu_{Zn} antisites occupy a deeper energy level in the band gap (Figure 1.6),

acting as non-radiative recombination centers for photogenerated minority carriers which decreases carrier mobility and lifetime^[27]. Furthermore, these defects tend to form defect clusters (such as $\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}$ defect cluster) which results in other deep level defect states, further increasing carrier recombination. While the concentration of Cu_{Zn} antisite defects can be altered by changing the concentration of Cu in the CZTS system during growth^[28], the amount of off-stoichiometry is being limited by its thermodynamic phase stability.

Figure 1.7: (a) Intrinsic point defect calculated transition energy levels for band gap of $\text{Ag}_2\text{ZnSnS}_4$. (b) Calculated formation energies of possible acceptor and donor defects in $\text{Ag}_2\text{ZnSnS}_4$ as a function of Fermi energy.^[29]

Cation substitution in CZTS with isovalent elements has been shown to change the grain sizes, band levels, carrier concentration and defect concentration^[29-33]. More specifically, the replacement of cations Cu^+ and Zn^{2+} is preferred with the objective of suppressing Cu_{Zn} antisites. Such substitution can alter the defect formation energy of the substituted element, enhancing the absorber bulk and interface quality, which leads to better electron transport properties. Furthermore, the carrier concentration can be altered to increase the depletion width allowing for better light absorption and carrier separation while the band levels (conduction band minimum and valence band maximum) can be adjusted which may lead to higher onset potentials. Such substitution has been demonstrated in the photovoltaic field with beneficial effects if the substitution is in low amounts. Su and coworkers investigated Zn^{2+} (0.74 Å) substitution with Cd^{2+} (0.92 Å) and demonstrated an increase in grain size,

suppression of ZnS secondary phase and reduction in Cu_{Zn} antisites, leading to an enhancement in efficiency from 5.3% of CZTS to 9.24% with 40% Cd substitution^[30]. Following this, other reports on Cd substitution has also been reported with consistent improvements in efficiency^[34-35]. With regard to substituting Cu^+ , Ag^+ (1.14 Å) has emerged as a promising candidate with consistent enhancement in efficiencies and open circuit voltage due to decreasing defects^[31, 33, 35-37]. While cation substitution to reduce defects is practiced in photovoltaics, this approach has not been studied in the solar driven photoelectrochemical reaction. This makes Cd^{2+} and Ag^+ substitution interesting to study to improve the properties of CZTS photocathode.

Figure 1.8: Reported stabilities of photocathodes with its reported stability vs pH of electrolyte used. Chart only shows photocathodes with more than 1 day of reported stability. Degradation is calculated by taking the ratio of photocurrent after the stability to the initial photocurrent.^[38]

While improving the performance of CZTS photocathode is necessary, the stability of the photocathode in electrolyte is another important factor for practical applications. Most of the photocathodes show degradation under stability test and long-term durability has not been demonstrated even with different forms of protective layers (Figure 1.8). While TiO_2 is the most commonly used protective layer, utilizing transparent conducting oxides have the added benefit of increasing electronic conductivity of photogenerated carriers while providing additional band bending. Indium tin oxide (ITO) seems promising to investigate

as such a multi-purpose layer due to its high electronic conductivity, high transmittance and compatibility with the CdS buffer layer used for CZTS.

Hypothetically, cation substitution of Zn^{2+} with Cd^{2+} and Cu^+ with Ag^+ in CuZnSnS_4 photocathode should lead to reduced defect concentration due to reduction of Cu_{Zn} antisites. This should translate to a higher photocurrent and a higher onset potential due to reduced carrier recombination. Furthermore, cation substitution might change the band gap and carrier concentration of the photoabsorber, allowing for higher photocurrents and a larger depletion width. The combined effect should improve the performance of the photocathode similar to that observed for photovoltaics. However, similar to most cation substitution work done on photovoltaics, an optimized amount of substitution might be needed to achieve the optimum properties. Following that, ITO transparent conducting oxide is **hypothesized** to enhance the transport of charge carriers from the buffer layer to the catalyst while also improving the stability of the photocathode stack. An optimized thickness for ITO should be determined which may be different from that used for photovoltaics.

1.2 Objectives

The **objective of this thesis** is to investigate the effect of cation substitution in CuZnSnS_4 (CZTS) photocathodes, and to determine the optimum amount of substitution for the 2 cations (Cd^{2+} and Ag^+). Subsequently, ITO is investigated as a protective layer for the CZTS photocathode stack. To fulfill the objective, the **scope** of the thesis is as follows:

1. Synthesis, fabrication and characterization of Cd-substituted ($\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$) and Ag-substituted CZTS ($(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$) with varying amounts of x to study effects of Cd^{2+} and Ag^+ on structural, optical and photocathode properties of onset potential, photocurrent.

2. Understanding the mechanism for the improvement in PEC performance for these substituted CZTS by studying band alignment, charge transport properties and optical absorption properties.
3. Fabrication and optimization of Indium tin oxide (ITO) overlayer for CZTS with thickness and oxygen content as variables.
4. Understanding the role of ITO for the improvement in PEC performance for the photocathode stack. Catalytic efficiency, band alignment and charge transport and stability will be assessed.
5. Integrating of best substituted CZTS with optimized ITO overlayer.

1.3 Dissertation overview

The thesis investigates the effect of cation substitution on the photoelectrochemical performance of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) photocathode. Two substitutions are investigated, Zn^{2+} with Cd^{2+} and Cu^+ with Ag^+ . Following that Indium tin oxide (ITO) is investigated as a protective charge transport layer for CZTS photocathode stack. The outline of this thesis is given as:

Chapter 1 provides the research rationale and outlines the goals and scope of the project.

Chapter 2 reviews the literature regarding the development of CZTS photocathode and effect of cation substitution observed in photovoltaics. Following that, the stability of CZTS photocathodes is also reviewed and the various protective layers utilized in literature to protect photocathodes.

Chapter 3 details the fabrication methods and various characterization techniques utilized. The rationale for the chosen methods is also covered.

Chapter 4 elaborates upon the effects of Zn^{2+} substitution with Cd^{2+} in CZTS photocathode. Cd substitution enhances the photocurrent but decreases the onset potential of the photocathode which is due to an increase in carrier mobility and lifetime which originates from the reduction in defects.

Chapter 5 elaborates the effects of Cu^+ substitution with Ag^+ in CZTS photocathode. Ag substitution enhances both the photocurrent and onset potential of the photocathode which is due to the reduction in interface defects at the Ag-substituted CZTS/CdS interface.

Chapter 6 elaborates the development of Indium tin oxide (ITO) as a conductive protective overlayer for the CZTS/CdS photocathode stack. ITO is able to enhance both the photocurrent and onset potential of CZTS photocathode which is due to the lower charge transfer resistance, additional heterojunction and the better catalytic activity from the synergy with Pt catalyst. ITO also enhances the stability of CZTS photocathode stack

through a “recovery” effect where Potassium and Phosphate ions can be removed from the surface by doing linear sweep voltammetry in the dark.

Chapter 7 summarizes the findings of this thesis and discusses on reconnaissance work on SnO₂ protective layer and other CZTS studies and improvement strategies which will be carried out in the future.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating the viability of using cation substitution to improve CZTS photocathode for the first time and identifying the specific role that each cation substitution plays.
 - a. Cd²⁺ substitution is shown to improve the CZTS absorber bulk by reducing the near band-edge defects, which leads to higher carrier mobility and lifetimes contributing to a much higher photocurrent. The spike-like band alignment at the Cd-substituted CZTS (CCZTS)/CdS buffer layer heterojunction is experimentally revealed by Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) for the first time. Time-resolved femtosecond transient reflectivity measurements reveals a fluence dependence for CCZTS which is distinctly different from CZTS, demonstrating passivation of defects for the first time.
 - b. Ag⁺ substitution on the other hand is shown to improve the CZTS/CdS interface, leading to less charge trapping near the interface, contributing to a higher photocurrent and onset potential. Segregation of Ag is revealed by XPS for the first time, which may lead to the reduction in interface defects at the Ag-substituted CZTS (ACZTS)/ CdS interface. Open circuit potential measurements reveal less charge trapping for ACZTS/CdS/Pt when compared to CZTS/CdS/Pt which provides evidence for the reduction in interface defects. Lastly, a record onset potential of 0.8 V_{RHE} is demonstrated through Ag⁺ substitution helping to pave the way for CZTS to be integrated with a photoanode for practical tandem water splitting application.

2. Indium tin oxide (ITO) is being assessed as a protective overlayer for the first time and several new findings are elaborated below:
 - a. Thickness of ITO is being assessed for an effective charge transport layer and a much thinner ITO of 80 nm compared to that usually used by photovoltaics of about 300 – 400 nm demonstrates optimal performance for the CZTS photocathode. This leads to a significant enhancement of photocurrent at 0 V_{RHE} from 15 mA cm⁻² of CZTS/CdS/Pt to 24 mA cm⁻² of CZTS/CdS/ITO/Pt and onset potential from 0.5 V_{RHE} to 0.7 V_{RHE}.
 - b. In-Pt interaction at ITO/Pt interface leads to higher catalytic activity and better charge transport from ITO to Pt catalyst. ITO is experimentally revealed by XPS to undergo surface reduction (In³⁺ and Sn⁴⁺ is reduced to In and Sn metal) when Pt is photoelectrodeposited on the surface. This interaction between In and Pt (as In is in higher concentration than Sn) leads to a higher electron density on Pt, allowing it to demonstrate better catalytic activity.
 - c. Hysteresis of CZTS/CdS/Pt photocathode (when current-voltage curve is scanned in the cathodic vs anodic direction) is experimentally revealed for the first time, suggesting the presence charged trap states at the CdS/Pt interface, leading to charge trapping. This may be a reason for the poor performance of CZTS photocathode to date. ITO overlayer is shown to be able to reduce the hysteresis.
 - d. ITO is shown to be an effective protective layer for the CZTS/CdS photocathode. Initial decrease in photocurrent for the CZTS/CdS/ITO/Pt photocathode during the stability test is shown to be due to the adhesion of K⁺ and PO₄³⁻ ions on the surface of ITO/Pt. With linear sweep voltammetry done in the dark at regular intervals to remove any K⁺ and PO₄³⁻ ions adhered on the surface, it is shown experimentally that the photocurrent can be recovered. Using this recovery method, a stable operation of 12h is shown for the CZTS/CdS/ITO/Pt photocathode.

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Chapter 2

Literature Review

This chapter outlines the development of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) photocathode since its first application in 2010. Next the improvement strategies employed for CZTS in photovoltaic field is highlighted and explained. Lastly, the reason for instability for photocathodes and different protection layers employed by literature is also discussed.

2.1 $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) as a photocathode

This section starts with a description on CZTS as a photoabsorber followed by the advancement in CZTS as a photocathode material. Lastly, the limitations of CZTS as a photocathode will be explored.

2.1.1 Derivation of CZTS kesterite structure

Figure 2.1: Derivation of the kesterite structure.^[1]

The kesterite structure of the $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) originates from the cubic Zinc blende structure which is the structure of materials like ZnS, CdTe and GaAs. Taking ZnS as an example, the charge neutrality is fulfilled in a II-VI binary structure. When two cations of +2 charge (Zn^{2+} in ZnS case) is substituted with elements of +1 and +3 charge in the case of chalcopyrite CuInS_2 (Cu^+ and In^{3+}), the structure changes to ternary to maintain charge balance. This is due to Cu^+ and In^{3+} having an average charge of 2+ which is similar to that of Zn^{2+} if 2 cubic structures are considered as a single unit cell in the case of the ternary structure. The two cations are substituted along the (201) chalcopyrite plane to satisfy the thermodynamic requirement of lowest energy formation due to each anion being bonded with two of each +1 and +3 charge element.^[2] Further substitution of two elements with

+3 charge with a pair of +2 and +4 charge element will result in the kesterite structure of CZTS.

2.1.2 $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) properties

Figure 2.2: (a) Band gaps of $\text{Cu}_2\text{ZnSn(S,Se)}_4$ experimentally derived from external quantum efficiency and photoluminescence measurements as a function of $\text{S}/(\text{S}+\text{Se})$ ratios.^[3] (b) Absorption coefficient of $\text{Cu}_2\text{ZnSnS}_4$ experimentally derived from spectroscopic ellipsometry (SE) and RT derived from spectrophotometry methods (RT).^[4] (c) Carrier density calculated from capacitance-voltage and Hall-effect measurements for CZTS polycrystalline films (px) and single crystal films (x) as a function of $\text{S}/(\text{S}+\text{Se})$ ratios.^[5] (d) Corresponding mobilities measured from Thz (TRTS) measurements and Hall-effect.^[5]

CZTSSe has a band gap varying from 1 eV to about 1.5 eV according to its $\text{S}/(\text{S}+\text{Se})$ ratio of 0 to 1 respectively. The conduction band density of states is made up of hybridization between Sn-s and anion chalcogenide-p orbitals while the valence band consists of hybridization between Cu-d and anion chalcogenide-p orbitals. The density of states near the lower energy region of the valence band also comprise of contributions from Cu-s, Zn-

spd and Sn-p.^[6] With higher Se content (i.e. lower S/(S+Se) ratios) the conduction band shift downwards by about 0.3 eV while the VBM shifts upwards about 0.15 eV.^[6-8] The absorption coefficient is approximately $2 - 3 \times 10^4 \text{ cm}^{-1}$ at 1.6 eV. Hence a CZTS film of about 1 μm thickness will be enough to absorb 90% incoming light of up to wavelength of 760 nm.^[9] CZTS is p type and its carrier density lie in the range of $10^{15}/\text{cm}^3$ for pure sulfide CZTS, and increases with Se content. However, this can be further increased when the Cu/(Zn+Sn) ratio is increased due to the increase in formation of Cu_{Zn} antisites which will be discussed in the later section.^[5] Carrier mobilities of CZTS lie in the range of $10 - 40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and increases with increasing Se content. The difference in mobilities measured by Hall and Terahertz spectroscopy (TRTS) (Figure 2.2d) suggests that the low mobility in CZTS may be due to grain boundary scattering since TRTS is able to probe intragrain transport while Hall does not. This indicates that polycrystalline CZTS films should have grain sizes that are large ($> 500 \text{ nm}$) to avoid long range carrier transport from being limited by grain boundaries. The minority carrier lifetime of CZTS is measured to be within hundreds of picoseconds,^[10-11] which is much smaller than that measured of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGSe) (about 10 - 100 ns).^[12] As the minority carrier lifetime is a measurement of the overall recombination rate, this will consequently affect the open-circuit voltage of the photoabsorber (onset potential of a photocathode) as it is dependent on the minority carrier density^[13] based on the following equation:

$$V_{oc} = \left(\frac{kT}{q}\right) \ln\left[\left(\Delta n \frac{N_A + \Delta p}{n_i^2}\right) + 1\right]$$

Where Δn is the excess photogenerated minority carrier density. These differences in optical and electrical properties discussed earlier results in a huge performance gap between CZTS and CIGS and limits its ability to replace it. A summary of the above mentioned points on the optical and electrical properties of CIGS and CZTS is given in the Table 2.1 below.

	$\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$	$\text{Cu}_2\text{ZnSnS}_4$
Minority carrier lifetime	10 - 100 ns ^[12]	Hundred of ps ^[10-11]
Carrier mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	75 - 230 ^[14]	10 – 40 ^[5]
Absorption coefficient (cm^{-1})	10^5 ^[15]	3×10^4 ^[5]

Table 2.1: Summary of electronic and optical properties of CIGSe and CZTS.

2.1.3 Operation of a photocathode/photoanode tandem setup

Figure 2.3: (a) Photocathode-photoanode tandem cell. (b) Current voltage curve of a photocathode/photoanode tandem cell.^[16] Photovoltage is indicated as V_{ph} in diagram.

Under the working conditions of a photocathode/photoanode tandem cell, the water reduction process is divided into two parts. (1) At the photoanode side (usually on top of the photocathode), light is first absorbed generating photogenerated electron and hole pairs, with the holes then oxidizing water forming O_2 . The photogenerated electrons then travel through an external circuit to the photocathode. (2) At the photocathode side, remaining unabsorbed light from the photoanode is absorbed by the photocathode and similarly electrons and holes are generated. The photogenerated electrons then reduce water, forming H_2 while the photogenerated holes recombine with the photogenerated holes generated from the photoanode. The operating current which directly affects the H_2 production rate is determined by the point of crossing between the photocurrent of the photocathode and photoanode.^[17-18] In order to achieve higher current densities and thus higher H_2 production rates, the photocurrent at the crossing point should be improved. This can be done by enhancing the onset potential of the photoabsorbers (increasing onset potential for photocathode, decreasing onset potential for photoanode), which is loosely defined in the

literature as the potential at which the photocurrent begins.^[17, 19] An additional way to visualize the improving of onset potential is increasing the photovoltage (V_{ph} in Figure 2.3b) of both the photocathode and photoanode. Thus, usual terms used to study photocathode performance is the onset potential and the photocurrent at 0 V_{RHE} which is the onset of H_2 production.

2.1.4 Development of CZTS photocathode

Figure 2.4: Band edges of different semiconducting materials with respect to water reduction and oxidation potential.^[20] (b) Unbiased solar water splitting utilizing a CZTS/CdS/In₂S₃/Pt photocathode stack and a NiOOH/BiVO₄ photoanode stack reported by Jiang et al.^[18]

CZTS is a suitable photoabsorber to be employed as a photocathode as it possesses p-type characteristics and has a conduction band straddling the water reduction potential (Figure 2.4a), hence its photogenerated electrons is thermodynamically favourable to reduce water. The first application of CZTS as a photocathode was in 2010 by Yokoyama et al. where a photocurrent of 9 mA cm⁻² at 0 V_{RHE} was achieved with CZTS/CdS/TiO₂/Pt as the photocathode stack.^[21] Following that, many other reports of CZTS emerged but there has been limited improvement since then and the highest photocurrent densities at 0 V_{RHE} are 12.5 mA cm⁻² reported by Yang et al. in 2016,^[22] and 18 mA cm⁻² reported by Feng et al in 2019 using an electrolyte of very low pH.^[23] The only two reported unbiased tandem cell using CZTS as a photocathode was reported by Jiang et al. in 2015 where a solar-to-hydrogen (STH) efficiency of 0.28% was reported using a CZTS/CdS/In₂S₃/Pt photocathode stack with an overlapping photocurrent of only about 0.3 mAcm⁻² at 0.5 V_{RHE} ,^[18] and by Huang et al. in 2018 using a CZTS/CdS/HfO₂/Pt photocathode stack with

a STH efficiency of 1.04% and an overlapping photocurrent of 0.64 mA cm^{-2} at $0.57 V_{\text{RHE}}$.^[24] This is in comparison to its CIGSe counterpart which has achieved photocurrent of 26 mA cm^{-2} , onset potential of $0.7 V_{\text{RHE}}$ with a smaller band gap of 1.32 eV (vs CZTS of 1.5 eV) and unbiased solar to hydrogen conversion efficiency of 3.7% and overlapping current of 3 mA cm^{-2} at $0.6 V_{\text{RHE}}$.^[17] The low photocurrent and onset potential achieved to date for CZTS limits its application in a photocathode/photoanode tandem cell. A summary of different works utilizing CZTS as a photocathode is summarized in Table 2.2 below.

Photocathode stack	Year	Photocurrent at $0V_{\text{RHE}}$	Onset potential	Electrolyte pH
CZTS/CdS/TiO ₂ /Pt ^[21]	2010	9 mA cm^{-2}	$0.6 V_{\text{RHE}}$	9.5
CZTS/CdS/AZO/TiO ₂ /Pt ^[25] I	2013	0.8 mA cm^{-2}	-	9
CZTS/CdS/In ₂ S ₃ /Pt ^[18]	2015	9.3 mA cm^{-2}	$0.63 V_{\text{RHE}}$	6.5
CZTS/CdS/TiO ₂ /Pt ^[22]	2016	12.5 mA cm^{-2}	$0.85 V_{\text{RHE}}$	7
Ge-CZTS/CdS/In ₂ S ₃ /Pt ^[26]	2017	11.1 mA cm^{-2}	$0.6 V_{\text{RHE}}$	6.5
CZTS/CdS/HfO ₂ /Pt ^[24]	2018	11.9 mA cm^{-2}	$0.65 V_{\text{RHE}}$	6.5
Cd-CZTS/CdS/Ti/Mo/Pt ^[27]	2018	17.5 mA cm^{-2}	$0.65 V_{\text{RHE}}$	7
CZTS/CdS/MoS _x ^[23]	2019	14 mA cm^{-2}	$0.6 V_{\text{RHE}}$	6.5
		18 mA cm^{-2}	$0.6 V_{\text{RHE}}$	3
CIGSe/CdS/Pt ^[17]	2018	26 mA cm^{-2}	$0.7 V_{\text{RHE}}$	6.8

Table 2.2: Selected works of CZTS photocathode since its first application in 2010. Highest reported efficiency of CIGS photocathode is included. Additional note is the inconsistency in literature on determination of onset potentials.

2.2 Limitations in CZTS photocathodes

2.2.1 Phase stability in CZTS

Figure 2.5: (a) Pseudoternary phase diagram together with crystal structures of the formation of CZTS and other secondary phases.^[28] (b) Theoretically calculated chemical potential stability diagram for CZTS.^[29-31]

The formation of CZTS quaternary compound from its elemental precursors is in competition with other secondary phases such as CuS , SnS , ZnS and Cu_2SnS_3 .^[32-34] The calculated formation window of CZTS based on its thermodynamic chemical potential is only in a small regime (Figure 2.5a) and a slight deviation especially in zinc ratios will cause secondary phases to form (Figure 2.5b). Hence, control of zinc ratios is essential during the growth process of CZTS. With regards to the secondary phases that are formed, ZnS is insulating and has a band gap of about 3.5 eV. It affects the overall device by reducing the total photoabsorbing active area, thus diminishing the photocurrent generated.^[35] Cu_2S is extremely conductive with a band gap of 1.21 eV, which may short the solar cell,^[36] reducing its shunt resistance and hence its fill factor. Cu_2SnS_3 has a band gap that is lower than CZTS at about 1 – 1.35 eV, but is not as efficient as CZTS.^[37-38] Hence it may compete with CZTS in the absorption of light and reduce the overall device efficiency. SnS_2 is n-type with a band gap of 2.2 eV,^[39] and may form a secondary diode within the CZTS absorbing layer, enhancing recombination of photocarriers.^[36] Reduction of such secondary phases is essential for higher device performance. Studies have shown a Cu poor Zn rich composition during growth to be optimal to produce CZTS of good efficiencies as it optimizes formation of V_{Cu} ,^[30, 40] while favoring the formation of wider

gap ZnS secondary phase which is predicted not to trap electrons and shunt the absorber unlike the other conductive secondary phases.^[41]

2.2.2 Defects in CZTS absorber

Figure 2.6: (a) Open circuit voltage (V_{oc}) vs band gap (E_g) of photovoltaic devices amorphous Si (a-Si), Methylammonium lead iodide (MAPI), crystalline Si (c-Si), poly crystalline Si (pc-Si), Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe), $Cu(In_xGa_{1-x})S_2$ (CIGS). V_{oc} deficit ($E_g/q - V_{oc}$) of each material is labelled in brackets while the oblique lines signify constant V_{oc} deficit from 0 to 0.8 V.^[42] (b) Schematic representation of electrostatic and band gap fluctuations.^[5] (c) Defect complexes within the CZTSSe bandgap that is heavily doped.^[43] (d) Calculated defect formation energy for point defects as a function of Fermi energy.^[32, 44]

The main limitation in CZTS photovoltaics has always been attributed to the limited open circuit voltage (V_{oc}) where the V_{oc} of CZTS is unable to achieve beyond 60% of its Shockley-Queisser (SQ) limit, which leads to its efficiency residing below 30% of the SQ limit^[42] whereas other parameters such as short circuit current density (J_{sc}) and fill factor

(FF) has already reached 80% of the SQ limit. In contrast, its counterpart CIGS has already reached 50% of its efficiency limit, with V_{oc} lying in the 80-85% range of SQ limit and J_{sc} and FF lying above 90%. This V_{oc} deficit ($\text{Bandgap}/q - V_{oc}$) is largely attributed to the short minority carrier lifetime and the significant amount of band tails in the absorber.^[10, 45-46] These band tails mainly originates from spatial potential fluctuations induced by highly charged defects within the forbidden gap^[45] (Figure 2.6b) while the short lifetime of minority carriers is usually attributed to Shockley-Read-Hall (SRH) recombination caused by point defects and other recombination pathways like grain boundary scattering,^[47] which reduces carrier density and lowers the quasi-fermi level splitting.

These defects exist as vacancies, interstitials and antisites which are formed due to the minimization of crystal's Gibbs free energy. Compensating charged point defects may in turn form complexes (Figure 2.6c), which together with the point defects form donor and acceptor levels, mid-gap states and deep trap states within the band gap.^[30] Such defect complexes have a smaller formation energy than individual defects due to charge transfer and Coulomb attraction between the negative and positive defects.^[32] These defect complexes may exist as stoichiometric conserving complexes (e.g. $\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}$) or non-stoichiometric conserving complexes (e.g. $\text{V}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$). The latter will cause spatial variation in stoichiometry and create more band tails.^[42] Based on the calculated defect formation energy (Figure 2.6d) the defect which has the lowest formation energy is the Cu_{Zn} antisite defect and the corresponding defect cluster ($\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}$).^[30] This Cu_{Zn} and Zn_{Cu} antisite defect has low enthalpy of formation due to the similar cation size.^[32] Hence, due to the low formation energy of these defects, they exist in CZTS in higher concentrations when compared to the other defects such as V_{Cu} , V_{Zn} , Zn_{Sn} and Cu_{Sn} and is expected to be largely contributing to the p-type character of CZTS. As Cu_{Zn} antisite is deeper within band gap as compared to V_{Cu} (which is preferred), electrostatic potential fluctuation and band tailing is introduced.^[42, 48] Furthermore, a high concentration of these Cu_{Zn} antisite defects on the surface of CZTS pins the interfacial Fermi level to a lower energy level, reducing band bending and hence V_{oc} of the device.^[49]

2.2.3 Poor stability of CZTS absorber and CdS buffer in electrolyte under photoillumination

Figure 2.7: (a) Calculated reduction ϕ^{re} (black bars) and oxidation ϕ^{ox} (red bars) potential of selected semiconductors relative to Normal Hydrogen Electrode (NHE) in pH 0 electrolyte at temperature of 298.15K and pressure of 1 bar. Water redox potential is plotted as $E(\text{O}_2/\text{H}_2\text{O})$ (red) and $E(\text{H}_2/\text{H}_2\text{O})$ (black) together with valence (green) and conduction (blue) band positions.^[50] (b) Current-time curve of CZTS/CdS/Pt (blue) and CZTS/CdS/In₂S₃/Pt (red) in 0.2M Na₂HPO₄/NaH₂PO₄ electrolyte (pH 6.5) under applied bias of 0 V_{RHE} under constant illumination from simulated sunlight (AM 1.5G).^[18]

While the performance of the CZTS photocathode is crucial to advance this material towards practicality, the stability of the photocathode is another important factor to be considered. Figure 2.7a shows the calculated semiconductor reduction and oxidation potentials with reference to the potentials for water reduction and oxidation. These semiconductor potentials represent the semiconductor thermodynamic stabilities against photocorrosion. A semiconductor is theoretically resistant against self-reduction from photogenerated electrons when its self-reduction potential (ϕ^{re}) is higher compared to the water reduction potential.^[51] While majority of these p-type materials including CZTS fulfills the above requirement, they however have their self reduction potential lying between the conduction band and the water reduction potential. This means that the stability of CZTS is dependent on the competitive reaction between material reduction and water reduction since transfer of photogenerated electron from the conduction band to both these reactions is thermodynamically favorable.^[52] Fast and efficient kinetics of extracting photogenerated charges from CZTS is thus necessary to mitigate the self-reduction of the

material. This is usually overcome by depositing a catalyst with high hydrogen evolution kinetics at the semiconductor surface, allowing fast transfer of charges to the electrolyte. Despite CZTS having its self-reduction potential above the water reduction potential, its self-oxidation potential is higher than the water oxidation potential. This means that CZTS may undergo anodic decomposition from the photogenerated holes if they are not transferred fast enough to the photoanode through majority carrier conduction in the bulk. The common n-type buffer layer commonly used for CZTS is CdS which can be easily grown using solution-based processes. However, CdS is prone to photocorrosion due to inefficient electron and hole separation and transportation.^[53-54] Such photocorrosion leads to a degradation in photocurrent over time as seen in Figure 2.7a and hence drop in efficiency of hydrogen generation over time.

Furthermore, most photocathodes studied are susceptible to corrosion when placed in contact with a high ionic strength electrolyte and have a narrow stability window based on Pourbaix diagram.^[50, 55] This suggests that an electrolyte of low salt concentration and neutral pH will be preferred for operation for most photocathodes. However, this leads to high Ohmic losses and overpotentials related to pH gradients in the electrolyte, producing a low photocurrent and onset potential. The above-mentioned strategy of depositing a layer of catalyst for improved transfer of charges to stabilize the electrode is not comprehensive as its stability relies upon the maintaining of the cathodic bias. A dark condition where photovoltage produced is insufficient will ultimately cause these electrodes to degrade.^[52, 56] Thus, other improvement strategies must be developed that will allow these semiconductors to function stably while not compromising with its performance.

2.3 Strategies used to improve CZTS photocathode

This section highlights the different strategies used by literature to improve CZTS in the photovoltaic field and also to improve performance of photocathodes (not limited to CZTS) for water splitting applications. Lastly, different protective layers used by literature to protect photocathodes are also explored.

2.3.1 Strategies used to enhance CZTS performance

a) Cation substitution in CZTS absorber

Figure 2.8: Schematic of Cd^{2+} and Ag^+ substitution into kesterite CZTS lattice.^[57]

Based on the earlier discussion, the similar ionic sizes of Cu^+ (0.74 Å) and Zn^{2+} (0.74 Å)^[58] result in a low enthalpy of formation for Cu_{Zn} and Zn_{Cu} antisites. A strategy used by the photovoltaic field is to introduce cations of larger or smaller ionic sizes as a substitute for Cu^+ or Zn^{2+} . Such substitutions must take into account the structural stability after the substitution to avoid lattice disorder.^[59] Through substitution, the formation energy of related antisite defects (in this case Cu_{Zn} and Zn_{Cu}) can be increased, hence lowering the overall concentration of these defects. This strategy of reducing defects have not been investigated in the photocathode field. Thus, it will be interesting to employ such strategy on CZTS photocathodes and improve its efficiency. Two such substitutions (Cd^{2+} (0.92 Å) substituting Zn^{2+} (0.74 Å) and Ag^+ (1.14 Å) substituting Cu^+ (0.74 Å)) are discussed further in this section.

I. Cd^{2+} substitution of Zn^{2+} in $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ (CCZTS)

Figure 2.9: (a–f) Cross-sectional Scanning Electron Microscope (SEM) images of $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ (CCZTS) absorbers for compositions of $x = 0$ to 1. (g) Corresponding current density-voltage curves of the CCZTS photovoltaic devices with additional CdS, ZnO and Aluminium Zinc Oxide (AZO) layers. Efficiencies of CZTS ($x=0$, black triangle) and 40% Cd ($x=0.4$, blue square) are labelled.^[60] (h) Calculated formation energy of point defects of $\text{Cu}_2\text{CdZnS}_4$ as function of Fermi Energy.^[61]

Cd^{2+} (0.92 Å) has a larger ionic radius than Cu^+ (0.74 Å) and Zn^{2+} (0.74 Å) and is expected to increase the formation energy of Cd_{Cu} and Cu_{Cd} antisites. Su et al. reported Cd^{2+} substitution with Zn^{2+} in CZTS increases the grain size (Figure 2.9 a – f), suppress the formation of ZnS secondary phase and reduces Cu_{Zn} antisites, leading to an increase in external quantum efficiency and overall efficiency enhancement (Figure 2.9 g) from 5.3% of CZTS to 9.24% with 40% Cd substitution ($\text{Cu}_2\text{Cd}_{0.4}\text{Zn}_{0.6}\text{SnS}_4$).^[60] Since then, other reports on Cd^{2+} substitution on CZTS and CZTSSe have consistently shown improved

efficiencies with optimal Cd substitution of 30 - 40% for CZTS^[62-64] and 5% for CZTSe.^[65] However, despite these positive results, Density Functional Theory (DFT) calculations on $\text{Cu}_2\text{CdSnS}_4$ (Figure 2.9 h) reveal that the formation energy of the antisite defect Cu_{Cd} is still lower than V_{Cu} and the lowest among all the defects. As a result, the defect complex $\text{Cu}_{\text{Cd}} + \text{Cd}_{\text{Cu}}$ and $2 \text{Cu}_{\text{Sn}} + \text{Sn}_{\text{Cd}}$ also has a low formation energy.^[61] Hence, Cd substitution is expected not to resolve the Cu_{Zn} antisite problem. Despite this, studies done on Cd substitution in CZTS have shown consistent improvements in band tailing,^[60, 63, 66] increase in grain size^[60, 65] which should lead to less recombination via grain boundary scattering and preventing the formation of secondary ZnS phase.^[60, 65] Cd^{2+} substitution is thus still viable to improve the performance of CZTS and further studies can be done to better understand the reasons for the improvements consistently observed.

II. Ag^+ substitution of Cu^+ in $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ (ACZTS)

Figure 2.10: (a) Calculated point defect formation energy for $\text{Ag}_2\text{ZnSnS}_4$ as a function of Fermi energy.^[61] (b) Calculated shifts in band-edge due to defect complexes.^[61]

Similar in concept to substitution of Cd^{2+} with Zn^{2+} , substitution of Cu^+ (0.74 Å) with the much larger Ag^+ (1.14 Å) is expected to increase the formation energy of Cu_{Zn} antisites and its related defect complexes. Based on DFT calculations, formation energy of Ag_{Zn} antisite (red line in Fig 2.10a) and its related defect complexes ($\text{Ag}_{\text{Zn}} + \text{Zn}_{\text{Ag}}$ and $2\text{Ag}_{\text{Zn}} + \text{Sn}_{\text{Zn}}$) is significantly higher than the original Cu_{Zn} antisite in CZTS.^[61] As a result, the total concentration of defects is predicted to be at least an order of magnitude lower than that of CZTS.^[61] In addition, the defect energy levels of Zn and Ag related defects are much

shallower which will result in a smaller shift in band edge as compared to Zn and Cu defects in CZTS (Fig 2.10b). Thus, Ag^+ substitution with Cu^+ is predicted to improve the performance of CZTS through reduction of defect concentration and replacement with shallower defect levels.

Figure 2.11: (a) Carrier density (b) Mobility measured from Hall effect measurements as a function of Ag content.^[67]

Gershon et al. investigated substitution of Ag into CZTSSe and found that band tailing decreased with increasing Ag content and managed to improve the V_{oc} deficit of CZTSSe from 660 meV to 580 meV, with the consequence of efficiency improving from 9% for CZTSe to 10.2% for $(\text{Ag}_{0.1}\text{Cu}_{0.9})_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (ACZTSSe).^[67] Carrier density decreases and inverts to n-type at high Ag contents^[68] (Ag_x , $x > 0.8$) while mobility increases with increasing Ag content and lifetime is enhanced.^[69] Similar reports of Ag enhancing photovoltaic performance of CZTS was replicated by Wu et al. with 3% Ag substitution for CZTSSe^[70] and Guchhait et al with 7% Ag substitution for CZTS.^[71] These promising results supports theoretical calculations of Ag reducing the amount of defects in CZTS and suggests that Ag substitution is a viable strategy to overcome the V_{oc} deficit of CZTS and enhance the onset potential of the photocathode. In addition, as the valence band maximum (VBM) of CZTS is made up of hybridized Cu 3d and S 3p orbitals, Ag substitution is shown to lower the VBM due to the deeper Ag 4d orbitals compared to Cu 3d.^[61] This may help increase the onset potential of photocathode as it is also affected by the VBM position with respect to the oxygen evolution potential.^[72]

b) Deposition of n-type buffer to form buried p-n junction

Figure 2.12: (a) Current density-voltage curve of Cu₂O/Aluminium Zinc Oxide (AZO)/TiO₂/RuO_x and Cu₂O/Ga₂O₃/TiO₂/RuO_x in 0.5 M Na₂SO₄ and 0.1 M phosphate solution (pH 5) under chopped AM 1.5G light illumination. (b) Corresponding band edge diagram measured from XPS valence spectra.^[73] (c) Current density-voltage curve of InP/Pt and InP/TiO₂/Pt in 1M HClO₄ solution under 100 mW/cm² light irradiation.^[74] (d) Current density-voltage curve of (ZnSe)_{0.85}(CIGS)_{0.15} photocathodes with different surface modifications in 1 M phosphate buffer (pH 7) under chopped AM 1.5G light illumination.^[75]

Deposition of an additional n-type layer above p-type photocathodes increases the charge separation efficiency of the photocathode through formation of a buried p-n junction. This leads to increased photocurrent and onset potential and reduces the reliance on the band bending formed at the semiconductor/electrolyte interface. The ideal band alignment is extensively studied by Pan et al. where the offsets of two different n-type buffers (AZO and Ga₂O₃) were compared (Figure 2.12 a and b).^[73] AZO which has a conduction band offset (CBO) of 1.08 eV results in a much smaller quasi Fermi level splitting with Cu₂O as compared to Ga₂O₃ which has a CBO of -0.26 eV. Using Ga₂O₃ with a larger quasi Fermi level splitting results in a 0.5 V anodic shift in onset potential (despite the negative CBO

which may lead to interface recombination). In a separate study, TiO_2 is shown to be a promising n-type layer for InP and reduces surface recombination by extracting the minority carriers.^[74] For copper chalcogenides, the common n-type buffer used is CdS due to its easy deposition method and relatively compatible electrical properties.^[21, 72, 76-77] However, reports in photovoltaic field suggests that the band alignment between CZTS and CdS is not ideal due to a large cliff offset which limits the Fermi level splitting^[78], presence of surface states on CZTS surface that extends to the forbidden gap, hence narrowing the band gap at CZTS/CdS interface^[79-80] and presence of defects in CdS.^[81]

c) Deposition of overlayers

Figure 2.13: Current density-potential curves of CIGSe/CdS/M/Pt photocathodes in 0.5 M Na_2SO_4 , 0.25 M $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ electrolyte (pH 6.8) under AM 1.5 G light irradiation (M = Ti, Mo, Ti/Mo and none).^[77] Current density-potential curves of CZTS, CZTS/CdS/Pt and CZTS/CdS/TiO₂/Pt photocathodes in phosphate buffer (pH 6.85) under chopped AM 1.5 G light irradiation.^[22]

CZTS is known to have poorer carrier lifetimes as compared to its CIGS counterpart as discussed in section 2.12 above where the minority carrier lifetime of CZTS is in picoseconds whereas CIGS is in the nanosecond regime. Majority of the photogenerated electrons may undergo recombination before reaching the Pt catalyst, especially with the limitation of slow kinetics of charge transfer into the electrolyte to reduce water. While this can be solved to a certain extent through improving the CZTS absorber by reducing its defects, an additional strategy to improve charge transfer from CZTS absorber to the

catalyst is preferred. A multilayer design will be able to achieve build in electric field through band bending, facilitating charge transfer and reducing recombination. Such additional overlayers have been widely utilized in the photocathode field with majority of the layers providing better charge extraction from CdS through additional band grading such as TiO_2 ,^[21-22, 82] ZnO ,^[83] In_2S_3 ,^[18] Aluminum Zinc Oxide (AZO)^[84] and ZnS .^[85-86] An additional method is to utilize conductive metals such as Ti/Mo to improve charge conductivity from CdS to Pt catalyst.^[77] However, such a method requires the deposited metals to be very thin due to the low optical transmittance of metals.

2.3.2 Strategies to improve CZTS stability

a) Deposition of overlayers

Figure 2.14: (a) Schematic diagram of CZTS/CdS/HfO₂/Pt photocathode and BiVO₄ tandem cell.^[24] (b) Chronoamperometry photoelectrochemical measurement of CIGS/CdS/reduced graphene oxide (rGO)/Pt and CIGS/CdS/Pt in 0.5 M phosphate buffer (pH 6.8) under AM 1.5G illumination at applied potential of 0 V_{RHE}. Yellow dotted lines signify photocurrent at 0 V_{RHE} measured from current-voltage curve.^[87] (c) Chronoamperometry photoelectrochemical measurement of multicrystalline Si n+p/Al₂O₃ photocathodes in H₂SO₄ and 0.5 M K₂SO₄ solution under 100

mW/cm⁻² Xe lamp at applied bias of -0.8V vs RHE. Insert shows the current-voltage curves of photocathode before and after 100h of stability test.^[88] (d) Chronoamperometry photoelectrochemical measurement of Cu₂BaSn(S,Se)₄/CdS/TiO₂/Pt photocathode in 0.5 M KH₂PO₄/ 0.5 M Na₂SO₄ (pH 4.3) under 100mW/cm⁻² illumination at applied bias of 0 V_{RHE}.^[82]

Due to the instability of CZTS and CdS in an electrolyte of high salt concentration and under illumination, overlayers of high chemical stabilities must be deposited above to allow these photocathodes to function stably without compromising its performance. To date, many protective layers have been studied with various levels of enhanced stability under water reducing conditions (applied bias = 0 V_{RHE}). Most of these layers also provide additional band bending and hence enhance the photocurrent and onset potential of the whole photocathode stack, increasing the attractiveness of using such a layer. Protective layers such as TiO₂,^[22, 56, 73, 82, 89] In₂S₃,^[18] ZnS,^[85] HfO₂,^[24, 90] and Al₂O₃,^[88, 91] have demonstrated almost no degradation in the various testing durations mentioned in the many works cited. While the protection of the underlying CdS and CZTS is important, another factor that may cause photocurrent loss is the delamination of commonly used Pt catalyst.^[27, 87, 92] Thus, the adhesion of Pt on the surface of the photocathode is another factor of consideration. With this consideration, the scope is expanded to the deposition conditions and deposition methods of Pt catalyst. Adhesion of Pt catalyst deposited by chemical processes such as photoelectrochemical and electrochemical deposition versus physical deposition processes such as thermal evaporation and sputtering can be further studied. Recently, Koo et al. attempts to address this issue of Pt loss by depositing a layer of reduced graphene oxide (rGO) to bind the Pt catalyst. rGO demonstrates multiple functions of preventing degradation of underlayers, enhancing charge transport and binding Pt.^[87]

However, as noted by Kaneko et al. in his recent work,^[93] most of the stability tests conducted by the community focuses on highly negative potentials (high cathodic bias) where a bias of 0 V_{RHE} or lower is applied during the test. At high cathodic potentials, photocathode stacks have an added advantage of having a large degree of band bending induced by the external bias, hence enhancing charge separation and transport. This potential applied does not reflect the actual working conditions of an unbiased photocathode-photoanode tandem cell which have operating voltages around 0.6 V_{RHE}.^{[17-}

^{18, 24]} Under applied bias of 0.6 V_{RHE}, the photocathode stack is subjected to oxidative corrosion of surface layers (e.g. $\text{CdS} + 2 \text{h}^+ \rightarrow \text{Cd}^{2+} + \text{S}$)^[75, 77, 94] and delamination of Pt catalyst.^[95] Photocathode stacks that have demonstrated high stability at 0 V_{RHE} no longer remain stable at higher applied anodic bias.^[77, 95] This lack of stability without the high applied cathodic bias is shown when photocurrent degrades when the photocathode is in tandem with a photoanode.^[24] ^[17]

b) Replacement of Pt catalyst

Figure 2.15: (a) Chronoamperometry photoelectrochemical measurement of $(\text{ZnSe})_{0.85}(\text{CIGSe})_{0.15}/\text{CdS}/\text{RuO}_2$ and $(\text{ZnSe})_{0.85}(\text{CIGSe})_{0.15}/\text{CdS}/\text{Ti}/\text{Mo}/\text{Pt}$ in 1 M potassium phosphate buffer (pH 13) under AM 1.5G illumination at an applied bias of 0.6 V_{RHE}.^[93] (b) Chronoamperometry photoelectrochemical measurement of $\text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3/\text{TiO}_2/\text{NiMo}$ in 0.5 M Na₂SO₄ and 0.1 M phosphate buffer (pH 9) under AM 1.5G illumination at an applied bias of 0.5 V_{RHE}.^[73] (c) Chronoamperometry photoelectrochemical measurement of CZTS/CdS/Pt and CZTS/CdS/MoS_x (with different photoelectrochemical deposition times) in 0.2 mol dm⁻³ Na₂HPO₄/NaH₂PO₄ solution (pH 6.5) under AM 1.5G illumination at an applied bias of 0 V_{RHE}.^[23]

Another way of overcoming the delamination of Pt catalyst is to replace it with other catalysts that binds stronger to the underlying substrate. The search for new catalysts is

also motivated by the scarcity and cost of Pt, which hinders large-scale deployment. Furthermore, as most photoanodes and oxygen evolution catalysts operate in alkaline electrolytes,^[96-98] it is important to design photocathodes that also work well in alkaline medium. Kaneko et al. deposited RuO₂ on his (ZnSe)_{0.85}(CIGSe)_{0.15}/CdS photocathode and found that RuO₂ performs not just as a hydrogen evolution reaction (HER) catalyst, but also a conductive surface and a protective layer.^[93] With RuO₂ thickness of 25 – 30nm, the photocathode stack demonstrates 10 h of stability (Figure 2.15a) without degradation at an applied anodic bias of 0.6 V_{RHE} for both neutral (pH 7) and alkaline electrolytes (pH 13). Pan et al. investigated NiMo as a HER catalyst and found that NiMo is able to enhance the onset potential of Cu₂O/Ga₂O₃ photocathodes (as compared to RuO_x) to more than 1 V_{RHE} and improve its stability in alkaline electrolytes. Interestingly, NiMo have shown to have a higher current density at similar overpotentials as compared with Pt/C in alkaline electrolytes.^[99] MoS_x is also widely studied as a replacement catalyst for Pt in HER reactions^[100] and is more stable than Pt in acidic conditions.^[101] Recently, MoS_x is applied to CZTS/CdS photocathode for the first time and demonstrates higher stability than Pt in pH 3 and pH 6.5 electrolyte.^[23] TaO_x is also another multifunctional layer capable of protecting the underlying layers, conducting HER activity and passivating the surface. Chae et al. recently demonstrated a CuInS₂/TaO_x photocathode which displays higher photocurrent densities at 0 V_{RHE} (but lower onset potential) and higher stabilities when compared to CuInS₂/Pt in 0.5 M H₂SO₄ electrolyte.^[102] A summary of different overlayers and catalysts used to improve photocathode stabilities and their reported stabilities are shown in the table below.

Photocathode stack	Electrolyte used	Testing potential	Test duration	Photocurrent decay
CZTS/CdS/TiO ₂ /Pt ^[22]	Phosphate buffer (pH 6.85)	0 V _{RHE}	5h	70%
CZTS/CdS/In ₂ S ₃ /Pt ^[18]	Phosphate buffer (pH 6.5)	0 V _{RHE}	3h	0%
CZTS/CdS/MoS _x ^[23]	Phosphate buffer (pH 3)	0 V _{RHE}	3h	~0%
	Phosphate buffer (pH 6.5)		10h	30%

	Phosphate buffer (pH 9)		3h	~50%
	Phosphate buffer (pH 11)		3h	~80%
CZTS/CdS/ZnS/Pt^[85]	Phosphate buffer (pH 6.5)	0 V _{RHE}	2h	~20%
CZTS/CdS/HfO₂/Pt^[24]	Phosphate buffer (pH 6.5)	0 V _{RHE}	10h	~5%
mc-Si n⁺p/Al₂O₃^[88]	H ₂ SO ₄ 0.5M K ₂ SO ₄	-0.8 V _{RHE}	100h	0%
CuO/Al/Al₂O₃^[91]	1 M NaOH (pH 13.6)	-0.55 V _{Ag/AgCl}	1h	10.5%
CIGSe/CdS/rGO/Pt^[87]	0.5 M Na ₂ SO ₄ , 0.5 M Na ₂ HPO ₄ , 0.5 M NaH ₂ PO ₄ (pH 6.8)	0 V _{RHE}	7h	~0%
(ZnSe)_{0.85}(CIGSe)_{0.15}/CdS/RuO₂^[93]	1 M Potassium buffer (pH 7)	0.6 V _{RHE}	22h	~0%
	1 M Potassium buffer (pH 13)	0.6 V _{RHE}	17h	~0%
Cu₂O/Ga₂O₃/NiMo^[73]	0.5 M Na ₂ SO ₄ , 0.1 M phosphate buffer (pH 9)	0.5 V _{RHE}	8h	10%

Table 2.3: Summary of selected works showcasing different protective strategies for photocathodes with the reported stabilities and the testing conditions.

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Chapter 3

Experimental Methodology

In this chapter, details on the experimental procedure for the fabrication of photoabsorber, buffer layer, overlayer and catalyst are listed. These descriptions may provide an initial understanding to the subsequent chapters. The different characterization techniques are also introduced to supplement the following results.

3.1 Rationale for selection

Chapter 4 and 5 adopts spin coating method to fabricate various cation substituted CZTS photoabsorbers, $\text{Cu}_2\text{Zn}_2\text{SnS}_4$ (CZTS), $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ (CCZTS) and $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ (ACZTS). This fabrication method is chosen due to the following reasons: (i) spin coating is both low cost and scalable for the industry; (ii) amount of cation substitution can be easily tuned through altering the precursor solution; (iii) spin coating has been shown in many works to produce high efficiency CZTS photovoltaics

Subsequently, the photoabsorbers are subjected to annealing in a Sulphur environment to complete the crystallization into single phase CZTS films. The n-type CdS buffer layer is deposited using a chemical bath deposition while the Indium Tin Oxide conductive layer in **Chapter 6** is deposited using DC sputtering. Altering of the deposition time was adopted to optimize these overlayers.

Detailed descriptions on the steps of these fabrication methods are listed in the following section.

3.2 Experimental methods

3.2.1 Fabrication of $\text{Cu}_2\text{ZnSnS}_4$

A precursor sol solution was prepared by dissolving $\text{Cu}(\text{Cl})_2 \cdot \text{H}_2\text{O}$ (0.36 mol L^{-1}), $\text{Zn}(\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ (0.25 mol L^{-1}), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 mol L^{-1}) and $\text{SC}(\text{NH}_2)_2$ (1.83 mol L^{-1}) into 2-methoxyethanol and stirred at 50°C in a water bath for 2h to obtain a dark yellow solution as reported by Su et al.^[1] All precursors were purchased from Sigma-Aldrich Company. The ratio of $(\text{Cu}+\text{Ag})/(\text{Zn}+\text{Sn})$ was adjusted to about 0.86 and Zn/Sn to be 1.25 following a Cu-poor, Zn-rich composition commonly used for high efficiency CZTS photovoltaic devices.^[2] The prepared sol solution was spin coated on Molybdenum glass substrates at 3000 rpm for 30 s followed by preheating at 280°C for 4 min on a hot plate in air. The spin coating was repeated 12 times to obtain the desired thickness. The precursor films were then subjected to sulfurization at 600°C for 40 min in sulphur atmosphere to

obtain CZTS thin films (ramp time 30 min). The sulphur atmosphere was obtained by heating elemental Sulphur in a separate zone at 200 °C in the furnace. The films were cooled naturally in the furnace in sulphur atmosphere.

3.2.2 Fabrication of $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ (CCZTS)

A precursor sol solution was prepared by dissolving $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.38 mol L^{-1}), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, + $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$ (0.25 mol L^{-1}), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 mol L^{-1}) and $\text{SC}(\text{NH}_2)_2$ (1.6 mol L^{-1}) into 2 methoxyethanol and stirred at 50°C in a warm water bath for 2h to obtain a dark yellow solution. All precursors were purchased from Sigma-Aldrich Company. The ratio of $\text{Cu}/(\text{Zn}+\text{Cd}+\text{Sn})$ was adjusted to about 0.86 and $(\text{Zn}+\text{Cd})/\text{Sn}$ to be 1.25 following a Cu poor, Zn rich composition. The prepared sol solution was spin coated on Molybdenum glass substrates at 3000 rpm for 30 s followed by preheating at 280°C for 2 min on a hot plate in air. The spin coating was repeated 13 times to obtain the desired thickness. After that the precursor films were subjected to sulphurization at 580°C in Sulphur atmosphere to obtain CCZTS thin films. The Sulphur atmosphere was obtained by heating elemental Sulphur in a separate zone at 200°C in the furnace. The films were cooled naturally in the furnace under Sulphur atmosphere.

3.2.3 Fabrication of $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ (ACZTS)

A precursor sol solution was prepared by dissolving $\text{Cu}(\text{Cl})_2 \cdot \text{H}_2\text{O}$ + $\text{Ag}(\text{NO}_3)_3$ (0.36 mol L^{-1}), $\text{Zn}(\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ (0.25 mol L^{-1}), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 mol L^{-1}) and $\text{SC}(\text{NH}_2)_2$ (1.83 mol L^{-1}) into 2-methoxyethanol and stirred at 50 °C in a water bath for 2h to obtain a dark yellow solution as reported by Su et al.^[1] All precursors were purchased from Sigma-Aldrich Company. The ratio of $(\text{Cu}+\text{Ag})/(\text{Zn}+\text{Sn})$ was adjusted to about 0.86 and Zn/Sn to be 1.25 following a Cu-poor, Zn-rich composition commonly used for high efficiency CZTS photovoltaic devices.^[2] The prepared sol solution was spin coated on Molybdenum glass substrates at 3000 rpm for 30 s followed by preheating at 280 °C for 4 min on a hot plate in air. The spin coating was repeated 12 times to obtain the desired thickness. The precursor films were then subjected to sulfurization at 600 °C for 40 min in sulphur atmosphere to

obtain ACZTS thin films (ramp time 30 min). The sulphur atmosphere was obtained by heating elemental Sulphur in a separate zone at 200 °C in the furnace. The films were cooled naturally in the furnace in sulphur atmosphere.

3.2.4 Deposition of n-type CdS layer

CdS was deposited using chemical bath method. CCZTS and CZTS thin film substrates are immersed in an aqueous solution containing 25 mmol/L of $\text{Cd}(\text{CH}_3\text{COO})_2$, 0.375 mol/L of $\text{SC}(\text{NH}_2)_2$, and 8 mol/L NH_4OH at 60°C for 14min.

3.2.5 Deposition of overlayers (Ti, Mo and ITO)

Deposition of Ti and Mo conduction layers was done using our previous method as reported by Kumagai et al.^[3] Ti and Mo were sputtered onto CCZTS and CZTS thin films by 30W RF sputtering using high purity Ti and Mo targets with a Ar pressure of 1.2×10^{-1} Pa for 3 min at room temperature.

Indium Tin Oxide (ITO) (Kurt J. Lesker, $\text{In}_2\text{O}_3/\text{SnO}_2$ 90/10 wt%, 99.99%) was sputtered at room temperature with Ar pressure of 4.5×10^{-1} Pa for 7 min at a sputtering power of 75W.

3.2.6 Deposition of Pt catalyst

Three different methods of Pt deposition is investigated in this report: sputtering, evaporation and photoelectrodeposition. For photoelectrodeposition, an electrolyte of pH 9.5 Na_2SO_4 was used and 200 μl of 1 mg Pt/ ml H_2PtCl_6 was added into the electrolyte. The potential used for Pt deposition was at 0 V_{RHE} and the deposition is deemed to have

completed when the current density saturates. An example of current saturation during Pt deposition is shown in Figure 3.1 below.

Figure 3.1: Pt deposition Current-potential curve

3.2.7 Electrode contact fabrication

Figure 3.2: Fabricated photocathode stack with epoxy sealing.

For the fabrication of the electrode contacts, the top of the absorber was exfoliated to expose the underlying Mo back contact. An insulating electric wire was welded using In metal unto the Mo to reduce the series resistance of the photocathode. Finally, the sides and exposed Mo and In were sealed using Epoxy resin to prevent contact of the electrolyte.

3.3 Characterizations

3.3.1 X-ray Diffraction (XRD)

Figure 3.3: Schematic showing diffraction of X-ray beams across plane hkl .^[4]

The structure and phases of the absorber was characterized using X-Ray Diffraction (XRD) using a Bruker D8 Advance. The measurements were conducted in the 2theta configuration since most of the work involves thin films. In this configuration, the angle of the incoming X-rays is fixed while the sample is placed at a small tilt angle (usually 0.5° to 1°). Signals from all directions is obtained by rotating the detector around in a sphere. The scattering of X-rays when the incident X-ray interacts with the atomic planes of the crystal lattice produces a characteristic diffraction pattern. This diffraction pattern gives data on the crystal structure of the material such as its phase and lattice constants. The wavelength of the X-ray is correlated to the inter-planar spacing of the atoms through Bragg's law: $n\lambda = 2d \sin\theta$ where the d represents inter-planar spacing of planes hkl and is correlated to the incident X-ray wavelength λ and angle θ . Only angles where constructive interference occurs will reflect a signal of high intensity in the diffraction pattern.

3.3.2 Scanning Electron Microscope (SEM)

Morphology of thin film top surface was examined using a Hitachi S-5000 FEG field emission scanning electron microscope. Cross section morphology of thin films was

examined using FESEM (JEOL, JSM-7600F). FESEM makes use of electrons to provide high-resolution imaging. These electrons are generated from a cathode, which are then accelerated and focused using a series of objective and condenser lenses. As the electrons come into contact with the sample, they are decelerated and a string of X-rays and electrons are emitted which are then collected by the different detectors.

Figure 3.4: (a) Different information available from scanning electron microscope.^[5] Characteristic X-rays and emitted electrons from interaction between electron-beam and sample with their escape depths.^[5]

These samples were examined using the Secondary Electron (SEI) mode where the secondary electrons that are produced from inelastic scattering of the electron beam and the outer k-shell. Such electrons are low in energy and have a low escape depth, thus reflecting only the surface morphology of the thin film.

On top of SEI, Energy Dispersive X-Ray spectroscopy (EDX) measurements are also conducted on samples to characterize their composition. EDX is done by collecting the characteristic X-rays emitted from electron-sample interactions. When an electron in the inner shell leaves the sample due to excitation from the incident electron beam, other outer shells electrons can fill the inner shell vacancy. This filling of inner shell emits X-ray corresponding to the energy difference between the outer shell and the inner shell which it fills. Due to the dependence of the shell energy level on the atomic configuration and the nuclei size, the emitted X-ray will thus be unique to every element. This allows us to identify the elements present by collecting these X-ray signals. However, the accuracy of EDX is limited due to the electron beam large interaction volume and the presence of overlapping energy peaks from different elements.

3.3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) accelerates electrons to much higher voltages (100 – 300 kV) as compared to SEM.^[6] This results in a beam of much higher energy comprising of coherent electrons travelling through the condenser lens in the column to the specimen. Part of the beam is transmitted through the sample while other regions are scattered and images are formed based on the different imaging modes (i.e. dark field, bright field, high-resolution TEM (HRTEM) and diffraction mode). In bright field imaging, unscattered electrons are used to construct the TEM image, hence elements of high mass or regions of high crystallinity will appear dark. Alternatively, dark field imaging excludes the primary beam and instead uses the scattered electrons to form images and areas of high mass will appear bright while regions of no scattering will appear black. Diffraction mode results in diffraction images formed through Bragg scattering when the primary beam transmit through a crystalline sample and gets diffracted due to the lattice spacing of atoms. The crystal structure of the sample will result in specific angles of diffraction, constructing an image of series of dots with each dot representing a satisfied diffraction condition.

3.3.3 AC Hall

AC Hall measurements were done by using a rotating parallel dipole line AC Hall system. This system is capable of performing Hall measurement by generating a pure harmonic and unidirectional strong magnetic field which is followed by a lock-in detection of the Hall signal. An electron moving perpendicular to magnetic field and along an electric field will experience a Lorentz force in a direction normal to both electric and magnetic fields. Electrons will accumulation at one side due to the Lorentz force and cause a buildup of excess charge, which drifts away from the current direction. This difference in charges allows us to obtain the carrier density and by further inputting the sample thickness and resistivity, the carrier mobility can be obtained.

For materials with low mobility, misalignment voltage (due to misalignment in point contacts on sample) and thermoelectric voltage (due to contact between two dissimilar materials) may outweigh Hall voltage causing errors if DC Hall is used. AC Hall allows higher resolution compared to DC Hall for materials with low mobility since the lock in amplifier is able to separate contributions from AC and DC (which is affected by V_{mis} and V_{TE}).

3.3.4 X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS)

X-ray and Ultraviolet photoelectron spectroscopy (XPS) and (UPS) measurements were carried out using a VG ESCALAB 2201-XL instrument. The X-ray source for XPS is a monochromatic Al K α (1486.7 eV) and the UV source for UPS is a He I discharge lamp (21.2 eV). The measurements were conducted with a base pressure that is lower than 5×10^{-10} mbar. Due to photoelectric effect, a sample surface that is irradiated with X-rays will excite the electrons, generating photoelectrons which may leave the surface if its energy exceeds that of its binding energy. However, due to the short diffusion length of electrons, only electrons near the surface can escape, thus making XPS a surface sensitive technique with a probing depth of only about 10 nm. The chemical state of the element can be characterized by XPS by comparing their binding energies as it is affected by the oxidation state of the element and the electronegativity of the surrounding atoms. This allows us to characterize the material's elemental composition and also its chemical state. UPS is similar to XPS in working principle, but uses a lower energy UV source to irradiate the sample, hence resulting in only electrons near the VBM of the material to be excited, providing us only with information at the VBM.

The obtained kinetic energy spectrum of the photoemitted electrons is reflected on a binding energy scale and it has 2 regions, the highest and lowest energies respectively. The electrons at the highest binding energies (secondary cut-off) are the inelastically scattered electrons and have the lowest kinetic energies, reflecting the state where they barely have enough energy to overcome their work function. The electrons at the lowest binding energy

have the highest kinetic energies, corresponding to the electrons originating from the Fermi level of the material.

Figure 3.5: Photoemission spectra from a semiconductor.^[7]

3.3.5 Photoluminescence

Photoluminescence measurements were conducted at room temperature using a 532nm pulsed laser with a monochromator, and an InGaAs photomultiplier tube detector. High injection conditions are expected due to the pulsed nature of the measurement. The principle of photoluminescence spectroscopy involves an excitation of electrons from VBM to CBM using a laser source. These excited electrons are then relaxed from their excited states to the lowest energy states in the CBM by collisions. They then recombine with the holes in the VBM while simultaneously emitting a light if a band-to-band transition is observed. This emitted light is then analyzed by a monochromator and the corresponding energy reflects either the band gap or the defect level within the band gap. Such electronic transitions are able to give us information of the amount of band tailing within the band gap and with time-resolved photoluminescence, the lifetime of the electron can also be obtained. In our study, the energy difference between the photoluminescence peak (which likely comes from a defect-to-VBM transition) and the measured band gap

from Incident Photon to Current Efficiency (IPCE) will give us an idea of the degree of band tailing.

3.3.6 Transient Reflection Measurement

Transient reflection measurements were conducted using a commercial Helios setup from Ultrafast Systems LLC. The setup works in a nondegenerate pump-probe configuration with the time window 5 ns. The pump pulses (600 nm) were generated from an optical parametric amplifier (Light Conversion TOPAS) that was pumped by a 1-kHz regenerative amplifier (Coherent Legend; center wavelength: 800 nm; pulse width: 150 fs; power: 1 mJ per pulse), which was in turn seeded by an 80 MHz Coherent Vitesse oscillator. The probe beam was a white light continuum generated from a sapphire plate using 800-nm femtosecond pulses, and collected by a CMOS detector. Transient Reflection Spectroscopy involves promoting a small fraction of molecules to an electronically excited state by applying a pump pulse. A relatively weaker probe pulse is then sent to the sample after a delay and the difference in absorption or reflection is calculated. This provides us electronic information regarding the transient states and from there, decay profiles can be constructed which provides us lifetime information on these transient states. In our experiment, the pump intensity is varied to investigate if the recombination is defect dominated or free-carrier dominated. If the decay profile is dependent on the pump fluence, it indicates a free-carrier dominated recombination while a decay profile that is independent of pump fluence will indicate that the recombination is dominated by defect states. A defect-dominated recombination is indicative of a material with a high density of defects.

3.3.7 Photoelectrochemical measurement

A 3 electrode setup was used to conduct PEC measurements with a 100 mW cm^{-2} AM 1.5G simulated light from a solar simulator (XES-40S2-CE, SAN-EI Electric). A saturated 3 M KCl Ag/AgCl electrode was used as a reference electrode while a Pt wire was used as the counter electrode. Two different electrolytes are utilized during different stages of the

measurement. Na_2SO_4 was chosen as the electrolyte for Pt deposition and for the PEC measurement before the Pt deposition due to the abundance of SO_4^{2-} ions which helps prevent the decomposition of CdS. However, as Na_2SO_4 is not a buffer and also has poor conductivity, this will result in local pH gradients near the surface of the electrode and also poorer conductivity. Hence, after photoelectrodeposition of Pt, potassium phosphate buffer $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (KPI) was chosen to be the electrolyte for PEC measurement due to its ability to retain the pH during the measurement and also for its high conductivity as discussed by Kumagai et al.^[3]

The hypothetical Half-Cell-Solar-to-Hydrogen conversion efficiency (HC-STH) equation:

$\text{HC-STH} = |I_{\text{ph}}| \times \frac{(E_{\text{RHE}} - E_{\text{H}^+/\text{H}_2})}{P_{\text{Sun}}} \times 100\%$ was used to calculate the HC-STH of a photocathode using the obtained current–potential curves where:

- I_{ph} represents the measured photocurrent density under external applied potential of E_{RHE}
- $E_{\text{H}^+/\text{H}_2}$ represents the hydrogen equilibrium redox potential (0 V_{RHE})
- P_{sun} represents the power density of the AM 1.5G incident light source (100 mW cm^{-2})

3.3.8 Faradaic Efficiency

The Faradaic efficiency measurement was conducted by measuring the amount of H_2 and O_2 gases produced using an online gas chromatography system (Agilent 490 Micro GC gas analyzer equipped with a MS-5A column and a thermal conductivity detector). This gas chromatography system is connected directly to the PEC cell which is evacuated using a pump before the experiment. To prevent temperature rise due to continued exposure of light, the PEC cell was covered by a water jacket.

3.3.9 Photovoltaic (PV) measurements

PV External Quantum Efficiency (EQE) measurements were measured using Bentham PVE300. The system was calibrated using a standard Si cell.

PV Capacitance Voltage (CV) measurements were performed in the dark at room temperature using Autolab PGSTAT302N with an AC signal of 30 mV_{rms} at 50 kHz.

The charge density (N_{cv}) and profiling equation were calculated using:

$$\begin{aligned} N_{cv} &= -\frac{2}{e\epsilon\epsilon_0 A^2} \left[\frac{d(C^{-2})}{dV_{dc}} \right]^{-1} \\ &= -\frac{C^3}{q\epsilon\epsilon_0 A^2} \left(\frac{dC}{dV_{dc}} \right)^{-1} \end{aligned}$$

And

$$C = \epsilon\epsilon_0 A/W$$

Where C = capacitance, A = area and W = profiling position or depletion width.

3.3.10 SCAPS (Solar Cell Capacitance Simulator) Simulations

The main functionality of SCAPS is to solve the one-dimensional semiconductor equations (Poisson equation and continuity equation for electrons and holes). Up to seven layers can be defined and in the bulk of the layers these equations are given by:

- 1) Poisson equation, which is the starting point to obtain qualitative solutions for semiconductor electrostatic variables:

$$\frac{\partial}{\partial x} \left(\epsilon_0 \epsilon \frac{\partial \phi}{\partial x} \right) = -q(p - n + N_D - N_A)$$

Where $q(p - n + N_D - N_A) = \rho$ charge density assuming donors to be fully ionised. N_D and N_A are the donor and acceptor impurity concentrations.

- 2) Continuity equations which represent the various carrier transport mechanisms in a semiconductor. This include phenomena that are time dependent such as carrier generation, low level injection and recombination. Effects from drift, diffusion and thermal generation or recombination also affects carrier concentration. The net change in carrier concentration is given by the difference between carrier generation and recombination together with the net current flowing at that particular region:

$$-\frac{\partial J_n}{\partial x} - U_n + G = \frac{\partial n}{\partial t}$$

$$-\frac{\partial J_p}{\partial x} - U_p + G = \frac{\partial p}{\partial t}$$

Where G is the generation rate and U_n and U_p is the net recombination rate for electrons and holes.

- 3) Constitutive equations which represents current conduction by two components, drift influenced by electric field and diffusion influenced by carrier concentration gradient:

$$J_n = q\mu_n n\varepsilon + qD_n \frac{dn}{dx} = q\mu_n \left(n\varepsilon + \frac{kT}{q} \frac{dn}{dx} \right) = \mu_n n \frac{dE_{Fn}}{dx}$$

$$J_p = q\mu_p p\varepsilon + qD_p \frac{dp}{dx} = q\mu_p \left(p\varepsilon + \frac{kT}{q} \frac{dp}{dx} \right) = \mu_p p \frac{dE_{Fp}}{dx}$$

Where μ_n and μ_p are the mobilities of electrons and holes respectively, J_n and J_p are the electron and hole current density respectively, D_n and D_p are the Diffusion coefficient of electrons and holes respectively, E_{Fn} and E_{Fp} are the Quasi Fermi level for electron and hole respectively.

In the SCAPS software, physical parameters are input to solve the basic semiconductor equations above.

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Chapter 4*

Improvement of carrier mobility and lifetime of CZTS bulk through Cd²⁺ substitution

Cd²⁺ substitution has shown consistent improvements in the photovoltaic field through its reduction in band tailing as well as increasing grain size of CZTS. This chapter details the study of Cd-substituted CZTS photocathodes and its impact on the photoelectrochemical performance. Cd-substituted CZTS is fabricated through solution processed spin coating with different amounts of Cd substitution. 40% Cd substitution ($\text{Cu}_2\text{Cd}_{0.4}\text{Zn}_{0.6}\text{SnS}_4$) shows best performance and photocurrent of CZTS is enhanced from 5 mA cm^{-2} to 17.5 mA cm^{-2} . This better performance is attributed to the increase in grain size and the reduction in bulk defects, leading to reduction in band tailing and increase in carrier mobility and lifetime. This chapter demonstrates the advantages of utilizing cation substitution to reduce the defects in CZTS leading to an increase in its photocurrent. Subsequent cation substitution in Chapter 5 is built upon knowledge gained in this study.

*This section has been published substantially as YF Tay., et al., *Solution-Processed Cd-substituted CZTS photocathode for Efficient Solar Hydrogen Evolution from Neutral Water*. *Joule*, 2018, 2 (3), 537-548.

4.1 Introduction

As discussed in **Chapter 1** and **2**, the performance of CZTS is predicted by theoretical studies to be limited by the presence of secondary phases and large concentration of Cu_{Zn} , Zn_{Cu} antisites and its related defect clusters.^[1-3] To suppress the conductive secondary phases, CZTS with non-stoichiometric Cu-poor and Zn-rich ratios are usually fabricated which often shows the highest efficiencies in the photovoltaic field.^[4-5] However, this favors the formations of ZnS, which as an insulator reduces photoabsorbing active area.^[6] Substitution of Zn with other cations of larger or smaller ionic size is hypothesized to reduce the formation of ZnS secondary phase and increase the formation energy of Cu_{Zn} antisites. Cd^{2+} substituting Zn^{2+} has shown positive results in the photovoltaic field, capable of reducing the ZnS secondary phase while increasing the photovoltaic efficiency through the reduction of Cu_{Zn} antisites and increase in grain size. However, there is a lack of study on substitution of CZTS in the photocathode field where CZTS photocathodes suffer from the same disparity in performance when compared to CIGS. Furthermore, the electronic properties of Cd substituted CZTS such as carrier lifetime, mobility and band alignment have not been explored yet. Hence, by studying Cd^{2+} substitution into CZTS photocathodes, a new approach into improving CZTS photocathodes can be introduced along with providing additional insights to the influence of Cd^{2+} substitution on the electronic properties of CZTS.

In this chapter, CZTS photocathode is first optimized through different Pt deposition methods and CdS deposition times. Using the optimized deposition conditions, Cd^{2+} substituted CZTS photoabsorbers are fabricated through inexpensive solution-based method. The amount of Cd^{2+} substitution is controlled through the ratio of Cd^{2+} vs Zn^{2+} salt added in the precursor. 40% Cd^{2+} substitution ($\text{Cu}_2\text{Cd}_{0.4}\text{Zn}_{0.6}\text{SnS}_4$) shows the highest photocurrent and results in an enhancement in External Quantum Efficiency (EQE) throughout the visible spectrum (400nm – 800nm) and a sharpening of the absorption edge which suggests an increase in minority carrier diffusion length, correlating to better bulk properties of the absorber film. Through femtosecond transient reflection measurements, 40% Cd^{2+} substitution is shown to have a substantial improvement in the minority carrier

lifetime and a reduction in surface defects, validating the effect of Cd^{2+} substitution in passivating defects in CZTS.

4.2 Photoelectrochemical measurements of CZTS photocathode

An optimization of CZTS/CdS/Pt photocathode is first conducted before the discussion on Cd substituted CZTS to set the standards for the catalyst deposition as well as to optimize the baseline comparison.

4.2.1 Optimization of Pt catalyst deposition method

Figure 4.1: Current density – potential curves of CZTS/CdS/Pt photocathodes with different methods of Pt deposition (Pt sputter – DC sputtering, Pt VE – Vacuum evaporation and Pt PED – Photoelectrodeposition)

Figure 4.1 above shows the current density-potential curves of the different CdS coated CZTS samples with Pt deposited using different methods, sputtering, vacuum evaporation (VE) and photoelectrodeposition (PED). The deposition using sputtering was optimized by adjusting the different sputter operating current and duration. Deposition through vacuum evaporation is controlled by adjusting the deposition rate to 0.1 nm/s and stopping the deposition process once the crystal monitor reads 2 nm. Deposition through photoelectrodeposition is controlled by adjusting the applied potential and is stopped when the current density saturates. It is worth noting that Pt deposited by sputtering has a high dark current and this is probably due to improper design of the electrode where the metal

contacts might be exposed and in contact with the electrolyte, causing a shorting of current. The other 2 deposition methods have the metal electrodes sealed using an epoxy resin which accounts for the negligible dark current at potentials above the water reduction potential. It can be seen that Pt deposited by photoelectrodeposition has a better fill factor than that deposited by vacuum evaporation although the maximum photocurrent at 0 V_{RHE} is almost similar. This might be due to the etching of surface oxide phases during the photoelectrodeposition process, allowing a better interface with Pt and reducing the interfacial resistance. Photoelectrodeposition is thus chosen to deposit our Pt catalyst nanoparticles.

4.2.2 CdS thickness

Figure 4.2: Current density – potential curves of CZTS/CdS/Pt with different CdS deposition times. CdS-solar cell is included as a reference for the optimized CdS recipe for photovoltaic applications.

The thickness of CdS buffer layer for the CZTS photocathode affects the depletion width of the photocathode which will affect the internal electric field and thus affect the collection efficiency. If the CdS is too thin, leakage current might be too high due to insufficient coverage of CdS unto absorber. On the other hand, a CdS layer that is too thick will have higher absorption losses in the shorter wavelength region, which will decrease the current density.^[7-8] The CdS thickness optimized for CZTS photovoltaics is in the range of 50-70nm. However, when the same CdS thickness is used for application in photocathode, the photocurrent of the CZTS/CdS photocathode is almost zero (indicated as CdS-solar cell in Figure 4.2), suggesting that the CdS thickness is too thick. A change of chemical bath

deposition (CBD) recipe for optimization of CdS thickness is conducted by using $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ which has a much slower reaction rate as compared to CdSO_4 . The thickness is controlled by altering the duration of the chemical bath process and the optimum duration is determined by comparing the corresponding current-potential curve. A deposition time of 14 minutes is determined to be optimum for the CZTS photocathode and used for further deposition of surface layers.

4.2.3 Surface layers

Figure 4.3: Current density-potential curves of CZTS/CdS/Pt using optimized Pt and CdS deposition conditions with different overlayers deposited between CdS and Pt.

To increase the charge transfer and performance of the CZTS photocathode, surface layers of TiO_2 and Ti/Mo are deposited onto the CZTS/CdS photocathode before Pt deposition. TiO_2 behaves as a charge extractor as well as an intermediate layer for additional band bending to enhance the charge separation of the photogenerated carriers along with preventing back recombination of photogenerated electrons. Such a layer has been implemented in the past by previous groups studying photocathodes and has shown improved performance in onset potential and photocurrent.^[9-10] TiO_2 should not be deposited directly on CZTS as it will behave as a recombination center due to its large band gap difference.^[11] However, the reduced performance of our deposited TiO_2 layer in Figure 4.3 is probably due to the thickness of TiO_2 being too thick for effective tunneling of electrons. This can be optimized in the future.

A second type of conducting layer Ti/Mo is also investigated as a possible electron conducting layer. The principle of such metallic Ti/Mo layers is different from TiO_2 where an additional grading in band gap is provided to reduce carrier recombination. The purpose of these electron-rich metallic conductor layers are to reduce the surface recombination at the Pt interface with the photocathode by providing a pathway of low resistance for the photogenerated electrons to reach the Pt catalyst. Based on a study by Kumagai et al, 3 nm of Ti followed by 3 nm of Mo is optimum for CIGS/CdS photocathode is able to increase both its onset potential and photocurrent.^[12] Mo is able to enhance the photocurrent while Ti is added as a necessary interface with CdS before Mo. Furthermore, Mo is easily reduced and Pt deposition during PED can be easily deposited onto these reduced Mo-surfaces without any interference by external species. This conducting layer is demonstrated on the CZTS/CdS photocathode, and the photocurrent is doubled, achieving a photocurrent of almost 3 mAcm^{-2} . It is to be noted that this similar CZTS photocathode when employed as a solar cell achieved a short circuit current density of at least 20 mAcm^{-2} (Figure A.1, Appendix A). This gap in performance between similar absorbers employed for different applications suggests a limitation of charge transfer from the CZTS absorber to the electrolyte. Furthermore, by comparing a study by Yang et al who managed to achieve a photocurrent of at least 11 mAcm^{-2} using a similar solution processed CZTS with a CdS and TiO_2 overlayer with our current study, surface conductor layers of Ti/Mo does not seem to work as efficiently as compared to similar applications in CIGS absorbers where band gap grading and surface conductor layers both work efficiently.^[12-13] This suggests that there is an inherent bulk limitation within the CZTS absorber as compared to CIGS absorber that severely limits its charge transfer. Band gap grading to reduce recombination of photogenerated minority carriers seems to be a more efficient strategy.

4.3 Optimization of Cd content and optimal CdS buffer layer thickness for Cd substituted CZTS photocathode

4.3.1 Optimum Cd substitution content

Figure 4.4: (a) Current density (J) - potential (V) curves of Cu₂Cd_xZn_{1-x}SnS₄/CdS/Pt photocathode stacks in 1 M K₂HPO₄/KH₂PO₄ solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation for x = 0, 0.2, 0.4, 0.6 and 0.8. (b) Corresponding stacked J-V curves.

Figure 4.4 shows the current density (J) – potential (V) curves for Cu₂Cd_xZn_{1-x}SnS₄/CdS/Pt photocathode stacks in 1 M K₂HPO₄/KH₂PO₄ solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation for x = 0, 0.2, 0.4, 0.6 and 0.8 (henceforth labelled as CZTS, 20% Cd, 40% Cd, 60% Cd and 80% Cd). Photocurrent is observed to increase with increasing Cd% till a maximum at 40% Cd and subsequently decreases thereafter. 40% Cd was chosen for further optimizations due to the optimal photocurrent generated and referred to as CCZTS.

4.3.2 Optimization of CdS buffer layer for CCZTS photocathode

Figure 4.5: Current density-potential curves of 40%Cd/CdS/Pt photocathodes with different CdS deposition timings in a 1M K_2HPO_4/KH_2PO_4 (pH7) under chopped AM1.5G irradiation. Onset potential is indicated by a vertical arrow for each of the curves.

An optimization of the CdS thickness is conducted for CCZTS/CdS/Pt photocathodes and it is shown that the onset potential of the CCZTS/CdS/Pt photocathode stack can be improved by 0.1 V through depositing a thicker CdS layer (Figure 4.5). Further increase in CdS thickness decreases the photocurrent, which is not shown. A deposition time of 28 min is chosen to be the optimum for CdS deposition and will be used for further deposition of Ti/Mo.

4.4 Comparison between CZTS and CCZTS photocathode

4.4.1 Physical characterization

Figure 4.6: (a) Cross sectional SEM images of CZTS (b) and CCZTS absorber films. (c) X-ray diffraction (XRD) of CZTS and CCZTS (d) zoom in on (112) peak for CZTS and CCZTS.

Figure 4.6 shows the cross-sectional Scanning Electron Microscope (SEM) images of the CZTS and CCZTS absorber layers fabricated by sol-gel spin coating. Grain size was noted to increase with Cd substitution, growing from 400 nm for pure CZTS to 700 nm for CCZTS. The chemical composition of CZTS and CCZTS are determined to be $\text{Cu}_{1.71}\text{Zn}_{1.08}\text{SnS}_{5.91}$ and $\text{Cu}_{1.78}\text{Zn}_{0.63}\text{Cd}_{0.42}\text{SnS}_{4.42}$ using Energy-dispersive X-ray spectroscopy (EDX) (Table A.1, Appendix A). The crystal phases of CZTS and CCZTS was confirmed by X-ray diffraction (XRD) where both the CZTS and CCZTS films show a likely I4-kesterite phase (Figure 4.6c). The shifting of the (112) XRD peak (28.5° - 28.2°) shows the expansion in crystal lattice as the larger Cd^{2+} ion replaces Zn^{2+} .

4.4.2 Photoelectrochemical performance before addition of surface Ti/Mo layer.

Figure 4.7: (a) Current density (J) -potential (V) curves of CCZTS/CdS and CZTS/CdS in 0.1 M Na₂SO₄ (pH 9.5) electrolyte before Pt deposition. (b) Corresponding J-V curves of the same electrodes after Pt deposition in 1 M K₂HPO₄/KH₂PO₄ (pH 7) electrolyte. All measurements are conducted under chopped solar-simulated AM 1.5G solar irradiation.

Figure 4.7 shows the current density-potential curves of Cd-substituted CZTS (CCZTS) photocathode with and without Pt catalyst. In Figure 4.7a, considering that the surface interface of both photocathodes with the electrolyte is CdS, the catalytic activity of both photocathodes can be considered to be similar. However, a significant enhancement in photocurrent can be seen by comparing CZTS/CdS with CCZTS/CdS. This enhancement is further amplified when Pt catalyst is deposited onto the photocathodes, resulting in an increase of photocurrent from 2 mAcm⁻² for CZTS to 16 mAcm⁻² for CCZTS. This photocurrent enhancement cannot just be attributed to the smaller band gap of CCZTS which is determined by IPCE (Figure A.2, Appendix A), as the difference in band gaps of the 2 absorbers is only 0.15 eV, which is not enough to justify the 8 times increase in photocurrent. An improvement in bulk properties is hypothesized which will be discussed further in the report under the characterization section.

4.4.3 Photoelectrochemical performance after addition of surface Ti/Mo layer.

Figure 4.8: (a) Current density-potential curves of CZTS/CdS/TiMo/Pt and CCZTS/CdS/TiMo/Pt in 1M K₂HPO₄/KH₂PO₄ solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation (b) and corresponding half-cell-solar-to-hydrogen-conversion-efficiency (HC-STH) curves.

Figure 4.8 shows the current density-potential curves of optimized CZTS/CdS/TiMo/Pt and CCZTS/CdS/TiMo/Pt photocathodes. The optimized CCZTS photocathode stack shows an enhancement of photocurrent from 4 mAcm⁻² of CZTS to 17 mAcm⁻² with a 0.1 V drop in onset potential, requiring more cathodic potentials to be applied before appreciable photocurrent of at least 1 mAcm⁻² can be achieved. This increased onset potential despite the huge increase in photocurrent may be an indication that the CCZTS absorber has either an unfavourable band alignment with the water reduction potential or the CdS buffer layer. This will be discussed in the following section under band alignment. Calculation of the Half-cell-to-hydrogen-conversion-efficiency (HC-STH) (Figure 4.8b) using the current-potential curves reveals a HC-STH of 4% for CCZTS/CdS/TiMo/Pt photocathode and 1.1% for CZTS/CdS/TiMo/Pt photocathode.

4.4.4 Incident photon to current efficiency (IPCE)

Figure 4.9: Incident Photon to Current efficiency (IPCE) of CZTS/CdS/TiMo/Pt and CCZTS/CdS/TiMo/Pt in 1 M K_2HPO_4/KH_2PO_4 (pH 7) electrolyte under applied bias of 0 V_{RHE} .

Figure 4.9 shows the obtained IPCE spectrum for CCZTS and CZTS photocathode stacks. The band gaps of CZTS and CCZTS was determined to be 1.55 eV and 1.40 eV respectively by plotting the derivative of the IPCE spectrum with the photon energy (Figure A.2, Appendix A). The integrated photocurrent obtained from IPCE is also consistent with photocurrent obtained by current potential curves shown in (Figure A.3, Appendix A). CCZTS photocathodes show much higher IPCE as compared to CZTS across wavelengths 400-800 nm, indicating improved separation of charges and transport to the electrolyte. The higher IPCE together with the sharpening of the long wavelength suggests increasing diffusion lengths of minority carriers and hence better bulk properties of the film. Band tailing is also considered to improve with addition of Cd, but the large changes in collection length mean that more detailed optical studies will be necessary to confirm. Therefore, further optical and electrical studies of the bulk CCZTS absorber will be presented in the subsequent sections.

4.4.5 Faradaic efficiency and stability test

Figure 4.10: (a) Time course curves of H₂ and O₂ evolution for CCZTS/CdS/TiMo/Pt in 1M K₂HPO₄/KH₂PO₄ solution (pH 7) at 0 V_{RHE} under photoirradiation from simulated sunlight (AM 1.5G). The dotted line represent the time course curve of one-half of the electrons passing. (b) Figure on the right shows the corresponding Current density-time curve.

To check that the photocurrent measured is due to hydrogen evolution and does not arise from any corrosive side reactions, the amount of H₂ and O₂ evolved from the CCZTS/CdS/TiMo/Pt photocathode was measured by an in-line gas chromatography using three-electrode configuration at 0 V_{RHE} under illumination of simulated sunlight. Figure 4.10 shows the time course curve of H₂ and O₂ evolution together with corresponding curves showing electrons flowing in outer circuit for H₂ ($e^-/2$) and for O₂ ($e^-/4$). As shown in Figure 4.10a, the amount of H₂ produced by the modified CCZTS photocathode stack follows the time course curve of ($e^-/2$) indicating a Faradaic efficiency that is close to unity. This indicates the CCZTS/CdS/TiMo/Pt photocathode is able to reduce water without inducing other appreciable reactions.

A stability test was also conducted on the CCZTS electrodes by measuring the time-dependent photocurrent profiles at 0 V_{RHE} for 1h and the results show a 20% photocurrent decay after 1h of stability test (Figure 4.10b). This seems to indicate that the Ti/Mo conductor layer is inadequate to protect the photocathode stack and there is some photocorrosion occurring either in the CCZTS or CdS layer.

Figure 4.11: Top view SEM of CCZTS/CdS/TiMo/Pt stack before 1h stability test (a and b) and after stability test (c and d)

To investigate the reason for the photocurrent decay, SEM images of the CCZTS/CdS/TiMo/Pt stack was taken before and after the stability test. From the SEM image in Figure 4.11, we observe that the Pt nanoparticles had detached from the surface after the stability test and there appears to be no degradation of the main photocathode stack visually. To confirm this, the electrolyte used for the stability test was tested with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and no trace of Cu, Sn, Cd or Zn can be detected in the electrolyte, indicating that there is no ion leeching from the photocathode. This leads us to believe that the main reason for the photocurrent decay is not due to photocathode degradation but the delamination of Pt. This is further supported by subsequent redeposition of Pt which recovers the photocurrent after 1h of stability test (Figure A.4, Appendix A). Other methods of Pt deposition can be investigated which might

achieve better adhesion. We also note the incomplete coverage of the deposited Ti and Mo conducting layers due to the requirement of ultra-thin deposition, which may lead to exposure of unstable CdS to the electrolyte, leading to photodegradation. A more complete coverage of Ti and Mo can be used to prevent such a photocurrent decay.

4.4.6 Band alignment

Figure 4.12: Calculated band diagram for CZTS/CdS and CCZTS/CdS with respect to vacuum using XPS and UPS

To elucidate the reason behind the onset potential drop and the large increase in photocurrent for the current potential curves, XPS and UPS measurements were done on CZTS and CCZTS films to investigate the band alignment profiles. The band profiles of the CCZTS/CdS and CZTS/CdS heterojunctions are shown Figure 4.12. The heterojunction valence band offsets between the bulk absorber and CdS at the interface were determined using depth profiling XPS of the CZTS/CdS and CCZTS/CdS layers to gradually probe the CZTS/CdS and CCZTS/CdS interfaces. The XPS core-levels of Cd $2p_{3/2}$ and the Cu $2p_{3/2}$ peak were used as references to calculate the valence band offset (VBO) between the CZTS/CdS and CCZTS/CdS layers. The valence band alignment was extracted when both Cu $2p_{3/2}$ and Cd $2p_{3/2}$ peaks are present, with reasonable intensity for valence band comparison. The CZTS and CCZTS VBM positions relative to E_F were also measured to be 0.56 eV and 0.52 eV respectively after carbon correction (Figure A.5, Appendix A). The work function of the bulk CZTS and CCZTS absorber was determined

by the UPS secondary electron slope to be 4.31 eV and 4.74 eV respectively (Figure A.6, Appendix A).

Figure 4.13: Mott Schottky plots of CZTS and CCZTS at 1 kHz, 2 kHz and 5 kHz in 1M K_2HPO_4/KH_2PO_4 (pH 7).

The deeper VBM position of the CCZTS absorber is consistent with the higher measured flatband potential of CCZTS when compared to CZTS from Mott Schottky plots analysis in Figure 4.13. We hypothesize that the lowering of the VBM of CCZTS is due to the strain induced in the kesterite lattice of CZTS when the larger Cd^{2+} ion replaces Zn^{2+} as reported before.^[14] From our earlier study, at 40% Cd substitution, the CCZTS compound is at its maximum solubility limit for the kesterite phase and further substitution will cause a transition to the stannite phase. We hypothesize that a partial substituted compound at maximum solubility limit of the kesterite phase should be in a state of higher strain as compared to when it is relaxed to the more stable stannite phase which was investigated by Yuan et al.^[14] Thus, partial substituted compound could have a higher lowering of its VBM even though a fully substituted stannite phase only has its VBM lowered by 0.1 eV. This could be investigated further.

Figure 4.14: (a) XPS valence scan for the 3 stages after correcting valence before etching by -0.1 eV for CZTS/CdS (b) and XPS valence scan for the 3 stages after correcting valence before etching by +0.17 eV for CCZTS/CdS

Figure 4.14 shows the superimposed valence scan of the 3 stages (CdS, Interface and at absorber) for CZTS/CdS and CCZTS/CdS. The valence scans have been corrected by aligning the respective Cd and Cu core level peaks at each of the respective stages. The VBO were determined to be 1.12 eV and 0.87 eV for CZTS/CdS and CCZTS/CdS respectively by following a similar method done by other studies.^[15-18] We observe that CZTS show a “cliff-like” heterojunction with a 0.27 eV conduction band offset (CBO) consistent with other reports.^[15, 19] On the other hand, the CCZTS shows a “spike-like” heterojunction with a 0.13 eV conduction band offset with CdS (Figure 4.14b and Figure 4.12). “Cliff-like” interfaces are often undesirable in photovoltaics as they lead to high interface recombination. Under forward bias, the flow of injected electrons from the buffer to absorber is blocked, accumulating at the interface and increasing the recombination rate with the holes in CZTS, thus reducing the open circuit voltage.^[20-21] A favourable conduction band offset is estimated to be around 0 – 0.4 eV with a “spike-like” alignment.^[22] The favourable 0.13 “spike-like” heterojunction between CCZTS and CdS may contribute in reducing recombination and improving the photocurrent. However, on the hand, the onset potential is reduced by about 0.15 V for CCZTS/CdS (Figure 4.8a), which may be due to the 0.13 eV barrier formed when potential is applied close to flat band condition.

4.4.7 Hall mobility and carrier concentration

	Hall Mobility (cm^2/Vs)	Carrier Concentration ($/\text{cm}^3$)
CZTS	0.8672	4.54×10^{15}
CCZTS	2.786	6.75×10^{14}

Table 4.1: AC Hall measurements of bulk CZTS and CCZTS samples using a rotating parallel dipole line AC Hall system.^[21]

To further characterize the electrical properties of CCZTS and CZTS, AC Hall measurements were done on exfoliated bare absorber layers using a rotating dipole system as reported by Gunawan et al.^[23] From Table 4.1, we observe that CCZTS have more than 3 times higher Hall mobility and an order of magnitude lower carrier concentration. As the majority carriers in CCZTS have a much higher mobility than CZTS, this could lead to higher carrier lifetimes which will increase the photocurrent of the photocathode. The lower bulk carrier concentration of CCZTS may increase the space charge region and improve charge collection. This improved charge collection is consistent with the earlier IPCE measurement in Figure 4.9.

4.4.8 Room temperature photoluminescence measurement

Figure 4.15: (a) Valence band density of states profile for CZTS and CCZTS bulk absorbers using XPS (b) Room-temperature photoluminescence peak positions measured using a 532nm laser with dotted line showing band gap values obtained through IPCE.

It is shown previously through AC Hall measurements that CCZTS have an order of magnitude lower carrier concentration than CZTS. This lower carrier concentration however is not observed in the near valence band edge density of states from XPS in Figure 4.15a. This drop in carrier concentration for CCZTS may then be explained by a reduction in defects caused by the introduction of the Cd^{2+} ion which is hypothesized to reduce the Cu_{Zn} antisite defects. This reduction in defects is also supported by room temperature photoluminescence data of bulk CZTS and CCZTS absorbers (Figure 4.15b), where the difference between the bandgap determined by IPCE and the photoluminescence peak was much smaller for CCZTS (0.16 eV) as compared to CZTS (0.23 eV). This difference in position of photoluminescence peak and measured room temperature band gap suggests shallower radiative defects are present in CCZTS sample, either through reducing band tailing in the absorber material or by reducing near-band edge isolated defects.^[24] This result confirms that Cd substitution improving the quality of the absorber bulk.

4.4.9 Carrier lifetime and dynamics

Figure 4.16: Femtosecond transient reflectivity decay dynamics at their respective photobleaching wavelengths normalized to their maximum intensities using a 600nm pump probe with varying pump fluences at room temperature. (a) The decay was fitted using triple exponential function for CZTS (b) and first and second order recombination for CCZTS.

From the previous sections, we have presented that Cd substitution is able to reduce band-edge defects, leading to an increase in majority carrier mobility. This coupled with a

“spike-like” interface with CdS, leads to a 3-fold enhancement in photocurrent. To shed more light on charge transport and lifetime, femtosecond transient reflectivity was conducted on bare CCZTS and CZTS absorbers to determine the minority carrier lifetimes of these photocathodes. From Figure A.7 (Appendix A), photobleaching was observed at 690 nm for CZTS and 795 nm for CCZTS with the redshifting of CCZTS photobleaching indicating a smaller bandgap. From the decay dynamics in Figure 4.16a, we observe that there is little fluence-dependence on the decay dynamics of CZTS and by fitting using triple exponential functions, we obtain $t_1 = 12 \pm 1$ ps (34%), $t_2 = 94 \pm 8$ ps (42%) and $t_3 = 830 \pm 70$ ps (24%), where t_1 represents fast relaxation and trapping, t_2 represents surface recombination and t_3 represents the trapped carrier lifetime which recombines mainly through bulk defects.^[25] We notice that there is a dominance of fast components (t_1 and t_2) which shows that the carrier dynamics is dominated by trapping and surface recombination, indicating a large amount of surface and bulk defects in CZTS. The dominance of defect-mediated carrier recombination is also consistent with minor fluence-dependence found in the system; while the free-carrier band edge recombination is a second-order recombination process, which accelerates with higher fluence. However, for CCZTS (Figure 4.16b) the decay dynamics is highly intensity dependent and can be well-fitted using the first-order and second-order recombination terms:

$$\frac{dN}{dt} = -AN - BN^2$$

Where A is the recombination rate via mid-gap traps through Shockley-Read-Hall model or photogenerated minority carriers with doped carriers and B is the bimolecular recombination coefficient by free electrons and holes in the CBM and VBM respectively. We found the bimolecular recombination coefficient for CCZTS reaches $2.6 \pm 0.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, indicating the presence of large amounts of band edge free carriers which is in striking contrast with that of CZTS, as the carriers are easily trapped by the surface and bulk defects and are not affected by the increasing pump fluence. These findings validate the lower density of surface and bulk defects in CCZTS, supporting the earlier studies that Cd substitution in CCZTS is able to passivate these defects. The trapped carrier lifetime ($\frac{1}{A}$) of CCZTS is fitted to be 2.9 ± 0.2 ns, which is also much longer than the ~ 0.8 ns bulk carrier lifetime of CZTS, not forgetting that the latter has significant surface recombination.

This increased lifetime for minority carrier in photocathodes is more crucial for photocathodes when compared to similar materials used for photovoltaics since the limiting step of the process of hydrogen evolution is the transfer of electrons from the surface of the semiconductor to the electrolyte. This transfer of electrons is inefficient if the lifetime is short and hence restricting the diffusion of photogenerated electrons to Pt particles on the surface of the photocathode and eventually reducing the photocurrent generated for hydrogen evolution. This is highlighted when compared to similar devices used for photovoltaic applications in other reports where the difference in photocurrent between CZTS and CCZTS was only about 2 times.

4.5 Conclusions

In summary, we have shown that through substitution of Cd into CZTS, the PEC performance of the CZTS photocathode can be enhanced drastically. We have also investigated the CCZTS/CdS band profiles for the first time and show that a “spike-like” interface was formed which may reduce interface recombination. Rotating dipole Hall measurements reveal that the CCZTS have a much higher carrier mobility and a reduced carrier concentration, which may be due to the reduction of Cu_{Zn} antisites. This leads to an increase in space charge region and better charge collection, which is also supported by IPCE measurements. Photoluminescence measurements show that CCZTS have smaller difference between the bandgap and the photoluminescence peak which suggests shallower radiative defects either through reducing band tailing in the absorber material or by reducing near-band edge isolated defects. Lastly, femtosecond transient reflectivity measurements reveal that CCZTS have much longer trapped carrier lifetime and a lifetime that is fluence-dependent, which indicates a reduction of surface defects, supporting the claim that Cd substitution is able to passivate these defects. Therefore, we can conclude that the improved hydrogen evolution performance of the CCZTS photocathode is mainly attributed to the improved bulk transport properties of CCZTS. Further optimization of the overlayers may have further improved the interface charge transfer efficiency and increase the hydrogen evolution efficiency.

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Chapter 5*

Improvement of interface CZTS/CdS through Ag substitution

Similar in theory to Cd^{2+} substitution, Ag^+ substitution with Cu^+ in CZTS lattice utilizes the larger ionic size of Ag^+ (1.14 Å) compared with Zn^{2+} (0.74 Å) to increase defect formation energy of Cu_{Zn} antisites and reduce its density. Ag^+ substitution has also shown consistent improvements in the photovoltaic field. More notably, it is shown that with substitution of Ag^+ , the open circuit voltage deficit of CZTS has been reduced significantly. This should translate to a higher onset potential when applied in photocathodes, allowing for higher photocurrents with lower applied cathodic biases, potentially increasing the solar-to-hydrogen conversion efficiency when combined with a photoanode. In this chapter, solution processed $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ was fabricated together with a n-type CdS layer and Pt as a catalyst. The optimized $(\text{Ag}_{0.08}\text{Cu}_{0.92})_2\text{ZnSnS}_4$ (8%Ag) photocathode stack is able to increase the onset potential of CZTS by 0.2 V and photocurrent by 2 mA cm^{-2} . This improvement in onset potential and photocurrent is investigated using a combination of photoelectrochemical and photovoltaic characterizations and attributed to the reduction of interface defects between ACZTS/CdS, resulting in a reduced recombination at the interface.

*This section has been published substantially as YF Tay., et al., *Improving the interfacial properties of CZTS photocathode by Ag substitution*. Journal of Materials Chemistry A, 2020, 8, 8862-8867.

5.1 Introduction

Based on work done in **Chapter 4** on $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ (CCZTS) photocathode, cation substitution has been demonstrated to be viable for application in photocathodes and possess the same enhancement effect as demonstrated in photovoltaics. Cd^{2+} substitution is able to reduce defect density and increase carrier transport properties, thereby increasing the photocurrent of CCZTS photocathode. However, the onset potential of the CCZTS photocathode is reduced upon Cd^{2+} substitution, which may be due to the reduction in band gap. While the photocurrent at 0 V_{RHE} is greatly enhanced, a lower onset potential limits the working potential of the tandem photocathode-photoanode cell, hence lowering the solar-to-hydrogen conversion efficiency. On top of potentially reducing the density of defects in the absorber, Ag^+ substitution is predicted by theoretical calculations to lower the valence band maximum (VBM) due to the deeper Ag 4d orbitals compared to Cu 3d.^[1] The photocurrent can be enhanced through reducing defects and onset potential also increased through lowering of VBM.

Studies on Ag^+ substitution in CZTS has been investigated in the photovoltaic field and shown a consistent improvement in open circuit voltage (V_{oc}), resulting in an increase in photovoltaic efficiency.^[2-5] This improvement in efficiency is attributed to the increase in mobility and lifetime as well as the reduction in band edge shift. Density Functional Theory (DFT) calculations also supports the increase in formation energy of Ag_{Zn} antisite and its related defect complexes, hence reducing the concentration of defects by an order of magnitude compared to CZTS.^[1] In the case of photocathodes, the substitution of Ag in CZTS is not well established and the only study of Ag substitution with CZTS is investigated by Xu et al. which achieved a photocurrent of 3.78 mA cm^{-2} at 0 V_{RHE} and an onset potential of 0.33 V_{RHE} with a $(\text{Ag}_{0.3}\text{Cu}_{0.7})_2\text{ZnSnS}_4/\text{CdS}/\text{Pt}$ photocathode stack (Ag/Ag+Cu ratio of 30%). The improvement in performance is attributed to the increase in grain size and lowering of valence band maximum.^[6] However, the onset potential of the Ag substituted CZTS photocathode is rather low since most CZTS/CdS/Pt photocathode have already demonstrated onset potentials of up to 0.6 V_{RHE} and much higher photocurrent densities.^[7-8] Furthermore, most $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ (ACZTS)

photovoltaic studies report a decline in efficiencies once (Ag/Ag+Cu) ratios exceeds 20%,^[2, 4-5, 9] which leads to the belief that the optimal (Ag/Ag+Cu) ratio might not be in the range investigated. In this study, Ag substituted CZTS photoabsorbers are spin coated onto Mo-coated glass using the same sol-gel recipe presented in Chapter 4 with the focus on small amounts of Ag substitution (0-10% Ag). The optimized ACZTS/CdS/Pt photocathode shows a maximum onset potential of 0.85 V_{RHE} and photocurrent of 15 mA cm⁻² at 0 V_{RHE}. Through a combination of electrochemical and photovoltaic characterizations, we are able to attribute the improvement to the reduction of interface defects at the ACZTS/CdS interface, resulting in a higher built in potential and larger depletion width.

5.2 Results and discussion

5.2.1 Physical characterization

Figure 5.1: Cross-sectional scanning electron microscope images of $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ absorbers for (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.08$ and (d) $x = 0.1$. Scale bars represent length of 1 μm .

Figure 5.1 shows the cross-sectional scanning electron microscopy (SEM) images of $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ (ACZTS) absorbers for (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.08$ and (d) $x = 0.1$ (henceforth labelled as CZTS, 4% Ag, 8% Ag and 10% Ag). The grain size and thickness are approximately similar for all Ag compositions with grains spanning the whole thickness of the film (approximately 800nm), indicating a good crystallinity. Substitution of Ag in this study does not appear to increase its grain size due to the good crystallinity of the CZTS absorber. The amount of Ag is analyzed by energy-dispersive X-ray spectroscopy (SEM-EDX) (Table B.1, Appendix B) and found to be about 1% higher for the films when compared to the as-prepared amount in the sol-gel solution, but with sufficient differentiation between each stated composition for the study to be valid (4% Ag results are not shown as the amount of Ag in the film is too low to be detected accurately by SEM-EDX). However, when the films are analyzed under angle-resolved X-ray photoelectron spectroscopy (ARXPS) (Table B.2, Appendix B), it is found that the Ag/(Ag+Cu) ratio is much higher than that measured by SEM-EDX. Furthermore, the Ag/(Ag+Cu) ratios increases when the take-off angle channel increases (i.e. higher take-off angle being more surface sensitive). These results suggest that there is Ag segregation near the surface of ACZTS absorbers which may influence the interface properties of ACZTS/CdS. X-ray diffraction (XRD) measurements shows a kesterite structure for both CZTS and highest substituted 10% Ag absorbers (Figure B.1, Appendix B) which is consistent with previous reports and no secondary phases are observed.^[4, 10]

5.2.2 Photoelectrochemical measurement

Figure 5.2: Current density (J) – vs potential (V) curves of ACZTS/CdS/Pt in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under chopped solar-simulated AM 1.5G light illumination and (b) corresponding dJ/dV vs V curves extracted from J vs V curves under constant illumination.

Figure 5.2a shows the current density (J) vs potential (V) curves of $(Ag_xCu_{1-x})_2ZnSnS_4/CdS/Pt$ photocathodes with different amounts of Ag under chopped illumination of simulated sunlight (AM1.5G) in a 1M K_2HPO_4/KH_2PO_4 electrolyte (pH 7). The thickness of CdS for the ACZTS samples are first optimized by altering the CdS chemical bath deposition time and comparing the J - V curves (Figure B.2, Appendix B). For 4% Ag substitution ($x = 0.04$) the photocurrent at 0 V_{RHE} of CZTS is increased from 12.8 mA cm^{-2} to 17.7 mA cm^{-2} and onset potential (defined as start of derivative slope in Figure 5.2b) is also enhanced from 0.65 V_{RHE} to 0.8 V_{RHE} resulting in a half-cell solar-to-hydrogen efficiency (HC-STH) of 5.2% (Figure B.3, Appendix B). Upon further addition of Ag ($x = 0.08$, 8% Ag), the photocurrent decreases to 14.8 mA cm^{-2} but the onset potential continues to increase further to 0.85 V_{RHE} which is the highest reported onset potential for CZTS-based photocathodes without further modifications beyond a n-type CdS layer. The highest HC-STH efficiency is also pushed towards higher potentials but decreases slightly to 4.0% for 8% Ag. This increase in photocurrent and onset potential for 4% and 8% Ag is also evident before Pt catalyst deposition, confirming the effect of Ag on CZTS/CdS (Figure B.4, Appendix B). Subsequent addition of Ag ($x = 0.1$, 10% Ag) decreases both the onset potential and photocurrent. Hence subsequent analysis will be done on 4% Ag and 8% Ag.

Photocathode stack	Method of Onset Potential Determination			
	Potential at photocurrent of 0.05 mA cm ⁻²	Potential at photocurrent of 0.1 mA cm ⁻²	Potential where photocurrent almost disappears	Start of derivative curve
CZTS (this work)	0.7 V _{RHE}	0.55 V _{RHE}	> 0.7 V _{RHE}	0.65 V _{RHE}
8%Ag (this work)	0.88 V _{RHE} (excluding photocurrent transients) > 0.95 V _{RHE} including photocurrent transients	0.72 V _{RHE}	> 0.9 V _{RHE}	0.85 V _{RHE}
[¹¹] ZnSe.CIGSe/CdS/Ti/Mo/Pt	0.89 V _{RHE}			
[¹²] CIGSe/CdS/Pt			0.75 V _{RHE}	
[¹³] CIGZS/CdS/TiO ₂ /Pt			1 V _{RHE}	
[¹⁴] ACGSe/CdS/Pt	0.7 V _{RHE}			
[⁷] CZTS/CdS/TiO ₂ /Pt	0.86 V _{RHE}			
[¹⁵] CZTGS/CdS/In ₂ S ₃ /Pt	0.6 V _{RHE}			
[¹⁶] CBTSSe/CdS/TiO ₂ /Pt	0.56 V _{RHE}			
[¹⁷] p-InP/TiO ₂ /Pt	0.8 V _{RHE}			
[¹⁸] CIGS/CdS/Pt	0.89 V _{RHE}			
[¹⁹] Cu ₂ O/AZO/TiO ₂ /Pt		0.7 V _{RHE}		
[²⁰] Cu ₂ O/NiMo		0.53 V _{RHE}		

Table 5.1: Selected photocathodes reported in literature with the different photocathode stacks, method of determining onset potential and reported onset potentials. Papers reporting onset potential without definition of how it is derived is not being listed here.

As shown in Table 5.1, there is an inconsistency among different works for the definition on onset potentials hence preventing proper comparison between them. The method of onset potential determination for this study is defined at the onset of the derivative curve (dJ/dV vs V) as proposed by Le Formal et al.^[21] as it is able to reflect the gain of current with potential accurately and minimize human error. Furthermore, the derivative curve should be obtained from the linear-sweep voltammetry under constant illumination to prevent transient spikes usually observed at high anodic potentials in chopped curves from being erroneously considered. Nevertheless, 8% Ag in this work is shown to improve the

onset potential by about 0.2 V and appears to have the highest reported onset potential for kesterite photocathodes.

Figure 5.3: (a) Time course curve for H₂ and O₂ evolution over 8%Ag/CdS/Pt in 1M K₂HPO₄/KH₂PO₄ solution (pH 7) under simulated sunlight (AM 1.5G) at 0 V_{RHE} applied potential. Solid line represents time course curve for one-half of the electrons passing for H₂ and one-quarter of the electrons for O₂. (b) Corresponding current-time curve for the Faradaic efficiency measurement.

To check if the photocurrent measured is due to hydrogen evolution and does not arise from any corrosive side reactions, the amount of H₂ and O₂ evolved from the 8%Ag/CdS/Pt photocathode was measured by gas chromatography using a three-electrode configuration at 0 V_{RHE} under constant illumination of simulated sunlight (AM 1.5G). Figure 5.3a shows the time course curve of H₂ and O₂ evolution together with the corresponding curves showing electrons flowing in the outer circuit for H₂ (e⁻/2) and O₂ (e⁻/4). The Faradaic efficiency calculated was close to unity, providing confidence in the photocurrent data. The 8%Ag/CdS/Pt photocathode stack appears to undergo certain form of degradation during the 1h Faradaic efficiency test, suggesting that additional protective layers are necessary to retain the high initial photocurrent.

5.2.3 Role of Ag in improving the ACZTS/CdS interface

Figure 5.4: (a) External Quantum Efficiency (EQE) of ACZTS/CdS/Pt photocathode in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under continuous AM 1.5G light illumination. (b) Corresponding integrated photocurrent derived from PEC (photoelectrochemical) EQE.

Figure 5.4a shows the External Quantum Efficiency (EQE) of ACZTS/CdS/Pt photocathodes done in a photoelectrochemical (PEC) setup in a similar 1 M K_2HPO_4/KH_2PO_4 electrolyte (pH 7). Ag substitution improves the overall EQE of CZTS/CdS/Pt with better uniformity across the visible spectrum. The integrated photocurrent derived from PEC EQE (Figure 5.4b) is also relatively consistent to the photocurrent from the earlier J-V curves in Figure 5.2a. In order to exclusively study the ACZTS/CdS stack without the additional electrolyte interface, the ACZTS/CdS stacks are deposited with an additional Indium Tin Oxide (ITO) layer and the EQE is repeated in a photovoltaic (PV) setup (Figure B.5, Appendix B). Another advantage of conducting the PEC EQE measurements (on ACZTS/CdS/Pt) with PV EQE measurements (on ACZTS/CdS/ITO) is the high sensitivity of catalyst (Pt) loading on the roughness of the absorber film, which leads to different effective surface areas for different surface roughness; in contrast, the ITO deposition for PV devices is relatively insensitive to the surface roughness. From PV EQE, a similar trend of Ag improving the overall EQE is observed.

Figure 5.5: (a) Drift-diffusion simulations of CZTS/CdS with bulk and interface defects and a combination of both. (b) PV EQE of ACZTS/CdS/ITO with CdS optimized for PV.

To understand the reasons behind this improvement, we perform drift-diffusion simulations using SCAPS-1D software package.^[22] In particular, we simulate the effect of interface and bulk defects on the EQE characteristics in the range 300 nm to 1000 nm (Figure 5.5). The physical parameters used were taken from a combination of similar works done in literature^[23-24] and from kesterite data files provided by SCAPS developers and are given in Table B.3 (Appendix B). The CZTS/CdS interface was simulated to contain a distribution of acceptors and donors near the middle of CZTS valence band and CdS conduction band. The bulk defects were added according to the depth of acceptor defects typically observed in CZTS^[25] while interface defects were added to get surface recombination velocity in the range that was reported for similar works.^[23,26] We find that bulk defects affect the slope of the EQE in the wavelength range corresponding to absorption in bulk CZTS, consistent with our recent report.^[27] Further, we find that acceptor-type interface defects affect the overall EQE. From Figure 5.4a and B.5, we note that the most significant effect of Ag is to shift the overall EQE, rather than to improve the slope in the wavelength range corresponding to absorption in bulk CZTS. Hence, comparing the simulated EQE with the experimentally observed EQE, we attribute the improvement in the overall EQE of our samples to the suppression of interface recombination. To further confirm that the effect of Ag is not significant in improving the bulk characteristics of these samples, we prepared additional samples for PV EQE measurements using the CdS that is optimized for PV applications^[4, 25,27-28]. In Figure 5.5b,

we plot the EQE for these samples and observe that the slope of EQE in the wavelength range corresponding to bulk absorption in ACZTS is similar, suggesting that the bulk defect properties are similar in these samples. Hence, comparing the simulated EQE with the experimentally observed EQE, we attribute the improvement in the overall EQE (Figure 5.4a) of our samples to the suppression of interface recombination.

Figure 5.6: (a) Open circuit potential (OCP) vs time curves of ACZTS/CdS/Pt in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation and (b) the corresponding derivative of $d(OCP)/d(time)$ vs time.

Figure 5.6a and b show the open-circuit potential-time profile (OCP) of $(Cu_{1-x}Ag_x)_2ZnSnS_4/CdS/Pt$ photocathodes with different Ag substitution and their corresponding derivative curves at the light-dark transition region. The difference between the light and dark open-circuit potential increases from 0% to 8% Ag (Figure 5.6a), indicating a higher band bending with Ag substitution between ACZTS and CdS in the dark.^[29] Furthermore, from Figure 5.6a, with increase in Ag concentration from 0 to 8%, the open-circuit voltage transient during the transition from an illuminated state to the dark state is sharper (i.e. the derivative peak in Figure 5.6b is higher), which suggests that there are lesser trap states in the photocathode stack.^[30]

Figure 5.7: (a) PV Mott-Schottky plots of ACZTS/CdS/ITO with linear extrapolation of built in potential and (b) PV Capacitance-Voltage (CV) plots of ACZTS/CdS/ITO.

PV Mott-Schottky plots (Figure 5.7a) indicates that the built-in potential increases with increasing Ag concentration, supporting the larger band bending observed in earlier OCP measurements. Mott-Schottky is chosen to be conducted in the PV setup to probe the absorber/CdS interface without the complications of additional interfaces caused by the electrolyte when done in the PEC setup (only 1 interface observed in PV Nyquist plot seen in Figure B.6, Appendix B). The increase in built-in potential and band bending is usually attributed to a change in band alignment or an increase in carrier concentration which leads to a larger difference in quasi Fermi level of electrons and holes^[31]. However, based on the band gap derived from PV EQE (Figure B.7, Appendix B), the increase in band gap is too small to account for a significant change in the built-in potential and the onset potential shift observed in the earlier current-density potential curves in Figure 5.2a. Furthermore, when analysing the XPS valence spectra of the ACZTS absorbers and comparing it with CZTS (Figure B.8, Appendix B), it is observed that the separation of valence band maximum positions (VBM) relative to E_F for ACZTS is higher than that of CZTS, indicating a lower carrier concentration at the surface. This is also supported by PV Capacitance-Voltage (CV) measurements in Figure 5.7b, which shows a decrease in the apparent carrier concentration (i.e. free carrier and defect density) with increase in Ag substitution. This reduction in the apparent carrier concentration with Ag is consistent with other reports^[2, 5, 10]. The increase in built-in potential coupled with a decrease in apparent carrier concentration suggests that the increased band bending is possibly due to a reduction

in interfacial defects at the ACZTS/CdS interface. PV CV measurements (Figure 5.7b) also indicate an increase in depletion width, which supports the observed decrease in apparent carrier concentration. This increase in depletion width when the amount of Ag increases helps compensate the loss in depletion width through the use of thin CdS, helping to recover the EQE in visible range seen in Figure 5.4a. Since the surface of the ACZTS absorbers is Ag rich, there may be a graded carrier concentration profile with the surface of the ACZTS photoabsorber having a lower carrier concentration than the bulk.

In addition, we observe that 8% Ag has a lower PEC EQE and lower photocurrent than 4% Ag despite having a higher built-in potential, depletion width, OCP decay and onset potential. This may be due to the increase in band gap and the subsequent change in electronic properties (such as carrier concentration and band alignment) which may lead to a poorer junction formation with CdS that is optimized for CZTS. The observed Ag segregation at the surface of ACZTS may also impact CdS growth by conventional chemical bath methods^[32], which may affect the coverage and thickness of the CdS. Further optimization of the CdS buffer layer is necessary to reap the maximum benefits from Ag substitution.

5.3 Conclusion

In summary, we have demonstrated an improvement in both the onset potential and photocurrent of CZTS photocathodes with Ag substitution, and achieved a maximum onset potential of 0.85 V_{RHE} for 8% Ag and a maximum photocurrent of 17.7 mA cm⁻² for 4% Ag. These improvements can be attributed solely to the reduction in interface defects due to the largely similar morphologies, optical absorption properties and band alignment with CdS between CZTS and Ag substituted CZTS. This is different from other cation substitution works in the literature where the focus is largely on altering the bandgap,^[33] increasing the grain size for better charge transport,^[15] or altering the band alignment for better onset potential.^[12,14] In this work, Ag substitution is utilized to improve the ACZTS/CdS interface, reducing the interface defects (Cu/Zn antisites and other interface defects) and increasing the depletion width. This enhancement in interfacial properties is reflected in the larger built-in potential and reduction of trap states at the ACZTS/CdS interface as revealed by a combination of OCP and Mott-Schottky measurements. EQE measurements also show an enhancement in charge carrier collection due to these better interfacial properties. In addition, a thinner CdS (than that used in PV) is required for the PEC photocathode stack to mitigate carrier recombination arising from the poor transport properties in CdS due to the slower charge transfer kinetics in a PEC setup. Further optimization of the CdS buffer layer may improve the photocurrent the ACZTS photocathodes with higher Ag content and increase the hydrogen evolution efficiency.

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Chapter 6

Improvement of performance and stability of CZTS/CdS/Pt photocathode through incorporation of Indium Tin Oxide overlayer

CZTS/CdS/Pt has been reported to be unstable under photo reducing conditions and stability tests usually observe a decrease in photocurrent over time. In this chapter, Indium Tin Oxide (ITO) is being investigated as both a charge transfer and protective layer for the conventional CZTS/CdS/Pt photocathode. ITO is shown to improve the photocurrent and onset potential substantially while showing a “recovery” effect that enables CZTS/CdS/ITO/Pt photocathode to be stable under the photo reducing conditions when dark linear sweep voltammetry runs are done after the stability test. Initial studies reveal that the recovery effect is probably due to the removal of phosphate ions adhering on the surface of ITO

6.1 Introduction

Chapter 4 and 5 explored the effect of cation substitution on CZTS photocathode and show that the photocurrent is greatly enhanced due to reduction of bulk and interfacial defects in CZTS and CZTS/CdS interface. However, as demonstrated in **Chapter 4**, even with a Ti/Mo overlayer preventing the degradation of CCZTS/CdS, the photocurrent of CCZTS/CdS/Ti/Mo/Pt still decreases overtime and the cause is attributed to the delamination of Pt catalyst. This indicates that stability of photocathodes can be affected by both the degradation of the photocathode stack as well as the delamination of the Pt catalyst. The typical protective layers employed for photocathodes are TiO_2 ^[1-2], Ti/Mo ^[3-4], RuO_2 ^[5-6], Al_2O_3 ^[7], reduced graphene oxide^[8] and HfO_2 ^[9]. Most of these layers also enhance the photocurrent of the photocathode by providing an additional band bending through the formation of a new heterojunction. Other layers such as Ti/Mo provides better charge transport to the Pt catalyst through electrically conductive metallic layers, but with the disadvantage of the lack of transparency. It will therefore be interesting to study conductive transparent conducting oxides which possess the advantages of being electrically conductive while also being transparent and able to form an additional heterojunction with the underlying layers. Indium Tin Oxide (ITO) is chosen due to its superior conductivity and relatively higher stability (from pourbaix diagram) as compared to aluminium zinc oxide (AZO).

In this chapter, room temperature direct current (DC) sputtering was employed to deposit ITO on CZTS/CdS photocathodes. This was followed annealing treatment in Argon atmosphere at 280 °C to improve its conductivity and crystallinity^[10]. Lastly, Pt catalyst is photoelectrodeposited unto CZTS/CdS/ITO under similar deposition conditions as CZTS/CdS. The photocurrent and onset potential was found to be greatly enhanced when ITO is deposited. Furthermore, while the photocurrent also decreases during the stability test, it was found that this photocurrent loss can be recovered by doing linear sweep voltammetry (LSV) in the dark. Preliminary findings lead to the hypothesis that the initial decrease in photocurrent observed during the stability test is due to the adhesion of

potassium and phosphate ions from the phosphate buffer electrolyte unto the photocathode stack.

6.2 Optimization of ITO overlayer

Figure 6.1: (a) Current density-potential curves of CZTS/CdS/ITO(x)/Pt with different ITO sputtering duration (x) in 1M K₂HPO₄/KH₂PO₄ solution (pH 7) under constant solar-simulated AM 1.5G light irradiation. (b) Open circuit potential (OCP) measurements of the corresponding photocathodes in the same electrolyte.

Figure 6.1 shows the current density-potential curves of CZTS/CdS/ITO/Pt with different ITO sputtering durations (and hence thickness) under the same applied sputtering DC power of 75 W under constant illumination of AM 1.5G sunlight. The thickness of ITO with sputtering duration of 6 min, 7 min, 10 min and 15 min was determined by SEM cross section images to be about 50 nm, 80 nm, 100 nm and 170 nm respectively (Figure C.1, Appendix C). The PEC performance peaks at 7 min of sputtering duration before dropping with higher sputtering durations. As sputtering duration is directly correlated with thickness of ITO deposited, it can be hypothesized that charge transfer of the photocathode improves with thickness of ITO, and deteriorates when the thickness is too high. The open circuit potential (OCP) measurement reveals a huge increase in photovoltage (especially the OCP in light) when sputtering duration is increased from 6 min to 7 min, which may be due to the formation of a heterojunction between CdS and ITO. An additional heterojunction helps promote charge separation and reduce recombination, leading to a

higher minority carrier quasi Fermi level (reflected in a higher OCP in light).^[11-12] A minimum thickness might be required to form a continuous heterojunction. External Quantum Efficiency (EQE) measurement for ITO with different sputtering duration (Figure C.2, Appendix C) reveals a maximum EQE for 7 min. The maximum EQE decreases at ITO 15min, which indicates that when the ITO is thin and more transparent, more visible light are absorbed by CZTS resulting in more charge carriers collected across all wavelengths^[13-14] or a decrease in roughness which causes light scattering when grain size is increased. A trade-off between resistivity (decreases with increasing ITO thickness) and transmittance may be necessary.

Figure 6.2: Nyquist plots of CZTS/CdS/ITO(x)/Pt with different ITO sputtering duration (x) in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under constant solar-simulated AM 1.5G light irradiation at (a) 0 V_{RHE} and (b) 0.2 V_{RHE} .

Figure 6.2 shows the Nyquist plots of CZTS/CdS/ITO/Pt with different ITO thickness controlled by the sputtering durations under applied potential of (a) 0 V_{RHE} and (b) 0.2 V_{RHE} . The semicircle arc observed at high frequencies for the Nyquist plots is usually associated to the charge transfer process at the photocathode/electrolyte interface with the diameter of the semicircle equal to the charge transfer resistance^[8, 15]. Under applied bias of 0 V_{RHE} , the 3 ITO sputtering durations of 7 min, 9 min and 11 min appears to have similar charge transfer resistance while 5 min is significantly larger. This may be due to the lack of heterojunction formed by ITO 5min as hypothesized earlier from the OCP measurements. However, when the applied cathodic bias is reduced to 0.2 V_{RHE} , the

difference between ITO 7 min, 9 min and 11 min is more obvious, with 7 min having the lowest charge transfer resistance. This suggests that ITO 7 min has lower charge transfer resistance at lower cathodic potentials compared to the others, which results in a higher onset potential observed in the current density-potential curves in Figure 6.4a. Having an ITO layer that is too thick may not affect the maximum photocurrent at higher cathodic potentials but might result in a lower onset potential due to the higher charge transfer resistance at lower cathodic potentials. The sputtering duration of 7 min is thus chosen for further optimizations.

Figure 6.3: (a) Current density-potential curves of CZTS/CdS/ITO 7min/Pt with different O₂ content (partial pressure ratios O₂/Ar) used during sputtering in 1M K₂HPO₄/KH₂PO₄ solution (pH 7) under constant solar-simulated AM 1.5G light irradiation. (b) Corresponding derivative of photocurrent/ potential vs potential curves for the photocathodes in the same electrolyte.

Figure 6.3a shows the current density-potential curve of CZTS/CdS/ITO/Pt photocathodes with different O₂ content (partial pressure of O₂ (x)/Ar (25sccm) used during sputtering) under constant illumination of simulated sunlight (AM 1.5G). Adjusting the O₂ partial pressure ratios will affect the carrier density of the sputtered ITO films through altering the amount of oxygen vacancies^[16]. Our measurements show that about 2.3% O₂ content (0.6 sccm O₂ pressure) shows the best performance with highest onset potentials for 7 min of sputtered ITO. 3.8% O₂ content (1 sccm O₂ pressure) is not chosen despite having the largest photocurrent at 0 V_{RHE} due to its significantly lower onset potential, which limits its application in a photocathode/photoanode tandem setup. This optimized ITO overlayer (7 min sputtering, 0.6 sccm O₂ pressure) will be used in the subsequent results.

6.3 CZTS/CdS/ITO/Pt physical characterization

Figure 6.4: (a) Bright field STEM images of CZTS/CdS/ITO before Pt deposition. (b) HR TEM images of CZTS/CdS/ITO/Pt after Pt deposition.

Figure 6.4 shows the Transmission Electron Microscope (TEM) image of CZTS/CdS/ITO (6.4a) before and (6.4b) after photoelectrodeposition of Pt. From the TEM images in Fig 6.4a and b, the thickness of CdS is estimated to be around 20 nm and the ITO deposited by sputtering is around 80 nm and amorphous (also confirmed by XRD in Figure C.3 in Appendix C). Atomic ratio of ITO as determined by X-ray photoelectron spectroscopy (XPS) is relatively similar to ITO target used for sputtering (10% Sn doping with respect to In (Table C.1)). After Pt photoelectrodeposition, the thickness of ITO layer seems to decrease to 50 nm with an intermixing layer with Pt at the interface of about 20 nm. Pt nanoparticles (40 nm in diameter) are uniformly distributed on the surface of the intermixed layer. Atomic ratio of ITO after Pt photoelectrodeposition reveals a decreased Sn/In ratio and significantly more O, which may be due to the surface hydroxides adsorbed on the surface of the film (Table C.1).

Figure 6.5: (a) In 3d XPS spectra of CZTS/CdS/ITO before (frame above) and after photoelectrodeposition (PED) of Pt (frame below) after normalizing peak area. (b) Corresponding Sn 3d XPS spectra

Figure 6.5 shows the XPS (a) In 3d fitted peaks and (b) Sn 3d fitted peaks for CZTS/CdS/ITO and CZTS/CdS/ITO/Pt (CZTS/CdS/ITO after Pt photoelectrodeposition). All elemental spectra are first referenced to adventitious C 1s at 284.6 eV and further cross referenced between each other and adjusted if further correction is necessary to achieve a good match across all elements. The XPS spectra are normalized to total area to allow easy comparison between peak positions and observation of additional chemical states. For CZTS/CdS/ITO the In 3d is fitted with 3 components, 443.93 eV, 444.77 eV and 445.35 eV. The first two components are assigned to Indium oxide (In_2O_3), Indium hydroxide while the last component is unassigned and may be due to surface contaminants^[17]. For CZTS/CdS/ITO/Pt after Pt photoelectrodeposition (PED), a clear shoulder at lower binding energy is observed and 3 components are used to fit the spectra with binding energies 443.12 eV, 443.97 eV and 444.77 eV. The last two components (443.97 eV and 444.77 eV) are assigned to Indium oxide and Indium hydroxide similarly to that of ITO. However, the first component at 443.12 eV is not detected for CZTS/CdS/ITO and indicates a new chemical environment that is less electron withdrawing forming around In when Pt is photoelectrodeposited on ITO. The full width half maximum of this new component is also smaller than those assigned to In_2O_3 (0.8 eV vs 1.2 eV) which suggests that the new phase of In is more metallic as reported previously^[18]. This new phase is likely to be metallic In based on the earlier observations and by comparing it to other works^[17]. A similar lower

binding energy shoulder is also observed in the Sn 3d spectra after Pt deposition (Figure 6.5b), which suggests that it may be Sn metal^[19].

Figure 6.6: (a) In 3d XPS spectra of CZTS/CdS/ITO before (frame above) and after immersing in electrolyte used for photoelectrodeposition (Na_2SO_4) and applying the same potential (0 V_{RHE}) for 1h (frame below) after normalizing peak area. (b) Corresponding Sn 3d XPS spectra

This new metallic In and Sn component is only formed when ITO is in the presence of Pt ions, light and applied bias. This conclusion is based on our control experiment when ITO is immersed in the same electrolyte and applied a similar bias of 0 V_{RHE} used for the Pt photoelectrodeposition for 1 h but without the Pt source. The In 3d and Sn 3d peak in the control experiment (Figure 6.6) does not differ to that of original ITO, which suggests that the reduction of In_2O_3 and SnO_2 only occurs when Pt is depositing on it. Furthermore, when comparing ITO deposited with sputtered Pt and photoelectrodeposited Pt (Figure C.4), the metallic Indium only forms Pt is deposited chemically through photoelectrodeposition instead of the physical sputter deposition. This is consistent with reports of Pt sputter deposited on ITO where the In from ITO retains its In^{3+} state^[20]. Comparing the Pt 4f binding energies of CZTS/CdS/ITO/Pt sputter and CZTS/CdS/ITO/Pt photoelectrodeposition (PED) shows that Pt that is photoelectrodeposited has a lower binding energy (Figure C.5). This suggests a form of chemical interaction between Pt and In which results in a Pt with a higher electron density.

Figure 6.7: O 1s XPS spectra of CZTS/CdS/ITO before (frame above) and after photoelectrodeposition (PED) of Pt (frame below) after normalizing peak area.

The O 1s spectra for CZTS/CdS/ITO in Figure 6.7 is fitted with 4 components, 529.42 eV, 530.45 eV, 531.32 eV and 532.14 eV. For the first two components (529.42 eV and 530.45 eV), it is assigned to oxygen in the In_2O_3 lattice, with the higher binding energy component to oxygen adjacent to oxygen deficient positions. For the other 2 components (531.32 eV and 532.14 eV), the lower binding energy component is assigned to surface hydroxide or oxyhydroxide while the other is due to oxygen contaminants^[17]. When Pt is photoelectrodeposited, a significant drop in lattice O in In_2O_3 is observed, suggesting that oxygen is lost when Pt is interacting with In. These new chemical environment changes are also confirmed to be not existing on the surface of ITO before Pt deposition as seen from angle resolved XPS of CZTS/CdS/ITO from Figure C.6 which reveals that the surface of ITO has roughly the same chemical state as the bulk within the detection limits of XPS.

Figure 6.8: (a) Pt 4f XPS spectra of CZTS/CdS/ITO/Pt (red) and CZTS/CdS/Pt (blue) both with Pt deposited through photoelectrodeposition (PED) after normalizing peak area. (b) Current density-potential curves of CZTS/CdS/Pt PED (black) and CZTS/CdS/ITO/Pt PED (red) in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) solution without illumination under scan rate of 1 mV/s without stirring of the electrolyte. (c) Corresponding extracted Tafel plot.

With this information, we suggest that a possible explanation for the above shifts would be the loss of Oxygen atoms in coordination of Indium through a formation of a bond between In and Pt (O-In-Pt). This hypothesis is also supported by the Pt 4f XPS peak of CZTS/CdS/ITO/Pt and CZTS/CdS/Pt where the deposition of Pt on ITO when compared with CdS caused the Pt 4f peak to shift towards lower binding energy, which is consistent with S in CdS having a more withdrawing effect when compared to In (Cd-S-Pt) (Figure 6.8a). Such a bond between Pt and In is also supported by works where an increase in activity of Oxygen reduction reaction (ORR) was being reported due to electron transfer between In and Pt or alloying effect^[21]. Furthermore, interaction between Sn and Pt was also reported to enhance the activity of Pt by other works for the same ORR application^[22-23]. For our work, we observe an increase in catalytic activity when Pt is bonded to In as

compared S as observed by the dark current measurement in Figure 6.8b where the dark current of CZTS/CdS/ITO/Pt requires lower overpotentials to achieve higher currents as compared to CZTS/CdS/Pt. This increase in catalytic activity may be due to the similar reported synergistic effect between In and Pt which supplements the advantages of using ITO as a charge transport layer. However, due to the possibility of ITO forming an additional heterojunction, it might not be accurate to compare the dark current directly. Hence Tafel plots was extracted from the dark currents to further investigate the kinetics of the hydrogen evolution reaction (Figure 6.8c). CZTS/CdS/ITO/Pt shows a smaller Tafel slope (48 mV/dec) as compared to CZTS/CdS/Pt (58 mV/dec) supporting the hypothesis that the interaction between In-Pt enhances the catalytic activity of the Pt catalyst.

6.4 PEC performance of optimized ITO overlayer

Figure 6.9: (a) Current density-potential curves of CZTS/CdS/Pt and optimized CZTS/CdS/ITO/Pt in 1M K₂HPO₄/KH₂PO₄ solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation. (b) Corresponding derivative of photocurrent/ potential vs potential curves for CZTS/CdS/Pt and CZTS/CdS/ITO/Pt in the same electrolyte.

Figure 6.9 shows the current density-potential curve of CZTS/CdS/Pt and CZTS/CdS/ITO/Pt photocathodes under chopped illumination of simulated sunlight (AM 1.5G). A significant enhancement of photocurrent from 15 mA cm⁻² to 24 mA cm⁻² was

achieved when ITO overlayer is introduced between CdS and the Pt catalyst. This increase in photocurrent was also observed before Pt deposition where the additional ITO layer is able to increase the photocurrent generated especially at higher onset potentials (Figure C.7, Appendix C). The transients in photocurrent shown before Pt deposition for CZTS/CdS/ITO confirms the enhanced electronic conductivity of the photocathode stack through the incorporation of the ITO layer, where more electronic charges were initially generated and transported to the semiconductor/electrolyte interface, but due to the slow kinetics at the surface without a proper catalyst, many of the charges recombine and fall to a steady state current which matches the slow kinetics. This enhancement in photocurrent due to the ITO layer is attributed mostly to the better electronic conductivity of the ITO layer with lesser contribution from additional band bending formed due to the relative similarities in measured work function (Figure C.8) for both ITO (4.3 eV) and CdS (4.4 eV), which results in a low build in potential. It was also observed that ITO is able to increase the onset potential of the photocurrent for CZTS/CdS/ITO/Pt by about 0.2 V as seen from the derivative of photocurrent/potential vs potential curve in Figure 6.7b. This increased in onset potential indicate a better charge transport to the electrolyte (since the absorber is the same), which may be either due to an increase in catalytic activity at the surface or a better electronic transport to the catalyst.

Figure 6.10: (a) Current density-potential curves of CZTS/CdS/Pt in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation for different scan directions (forward: negative to positive and reverse: positive to negative) at a scan rate of 0.01V/s. (b)

Corresponding current density-potential curves for CZTS/CdS/ITO/Pt in the same electrolyte under similar test conditions.

Figure 6.10 shows the current density-potential curves for (a) CZTS/CdS/Pt and (b) CZTS/CdS/ITO/Pt with both forward (anodic direction) and reverse (cathodic direction) superimposed on the same graph. It can be observed that without ITO overlayer (Figure 6.26a), CZTS/CdS/Pt suffers from severe hysteresis where the onset potential, photocurrent at 0 V_{RHE} and the shape of the curve changes drastically for the different scan directions. Repeating the previous forward and reverse measurements at different scan rates of 0.005, 0.01 and 0.02 V/s (Figure C.9) does not recover the hysteresis, which suggests that the of the charge trapping process time constant is slower than the scan rate. Such hysteresis is explained with different reasons in the literature such as photochemical stability^[24], transient pH shifts within pores of photocathode^[25] and negative charge trapping/detrapping at interfaces^[26-27]. For our study, we hypothesize that there is a capacitive build up at the CdS/Pt interface, which may be due to charged trap states where Pt grows on CdS since the bottom layers are similar. With ITO overlayer, due to the metallic interaction between In and Pt, this may reduce the amount of charge traps in this layer and reduce the hysteresis. This is also supported by the open circuit potential measurement of CZTS/CdS/Pt and CZTS/CdS/ITO/Pt (Figure C.10) where CZTS/CdS/Pt shows a much gradual decrease in open circuit voltage upon turning off illumination which indicates a slow release of charges in trap states. An interesting point to note here is the much higher illuminated open circuit voltage of CZTS/CdS/ITO/Pt (0.4V) when compared to CZTS/CdS/Pt (0.1V), which may be another indication of an additional heterojunction formed between CdS and ITO despite the relatively similar work functions.

Figure 6.11: (a) Nyquist plot of CZTS/CdS/Pt photocathodes under AM 1.5G illumination in 1 M in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ solution in pH 7 under different applied potentials (b) Corresponding Nyquist plot for CZTS/CdS/ITO/Pt photocathodes tested in similar electrolyte and under similar conditions. (c) Plot of extracted charge transfer resistance (diameter of semicircle at high frequency) vs applied potential for CZTS/CdS/Pt and CZTS/CdS/ITO/Pt under illumination. (d) Mott Schottky plot of extracted $1/C^2$ vs applied potential for the same photocathodes.

Figure 6.11a and b shows the electrochemical impedance Nyquist plots of CZTS/CdS/Pt and CZTS/CdS/ITO/Pt under different applied potentials with AM 1.5G illumination. The extracted charge transfer resistance (R_{ct}) and capacitance is plotted vs applied potential (Mott-Schottky) in Figure 6.11c and d respectively. The Mott-Schottky plot in Figure 6.9d shows a similar positive slope for both CZTS/CdS/Pt and CZTS/CdS/ITO/Pt, indicating that the probing depletion region is n-type and is most probably the CdS layer. From the extracted R_{ct} , we observe that with the introduction of ITO between CdS and Pt, the R_{ct} clearly decreases by 1 to 2 orders of magnitude, indicating an improvement in charge transfer to the electrolyte which may be the result of better catalytic efficiency or from the better charge transport to the Pt catalyst from CdS due to the ITO layer. Furthermore, when

comparing the trend of R_{ct} with applied potential for CZTS/CdS/Pt and CZTS/CdS/ITO/Pt, we observe that with the ITO overlayer, the R_{ct} decreases linearly with applied cathodic potential, which is consistent with the behavior of a photocathode. However, for CZTS/CdS/Pt, the resistance first increases to a maximum at 0.15 V_{RHE} then decreases to a minimum at 0 V_{RHE} with increasing cathodic potential applied. Applying cathodic potentials should increase depletion width and increase band bending, allowing more charges to reach the semiconductor/electrolyte junction. This suggests that there is some sort of limiting factor in CZTS/CdS/Pt that prevents charge transfer to the electrolyte in applied potential range of 0.40 V_{RHE} to 0.15 V_{RHE} , hence limiting the performance of the CZTS/CdS/Pt photocathode. A hypothesis proposed by the author at this juncture for this behavior is the presence of defect levels in CdS/Pt interface as supported by earlier OCP decay and current density-voltage hysteresis that prevents the band levels of CZTS/CdS from being equilibrated with the electrolyte. Further research can be done to investigate the reason for this behavior. This finding shed light on the one of the limitations of CZTS/CdS/Pt photocathode without an intermediate charge transport layer and provides a direction for future research to focus on.

6.5 Stability tests

6.5.1 Without recovery

Figure 6.12: (a) Current-time curve of CZTS/CdS/ITO/Pt in 1 M K₂HPO₄/KH₂PO₄ (pH 7) under solar simulated AM 1.5G light irradiation for the measured duration of 1h at an applied bias of 0 V_{RHE}. (b) Corresponding time-course curves of H₂ and O₂ evolution of CZTS/CdS/ITO/Pt photocathode in the same electrolyte under the same measurement conditions. Solid lines represent the time-course curve for e⁻/2 (black) and e⁻/4 (red) determined from current measured and dots representing H₂ (blue) and O₂ (green) measured by Gas Chromatography (GC) at regular intervals of 10 min.

To check if the generated photocurrent is due to H₂ production, the Faradaic Efficiency of the CZTS/CdS/ITO/Pt photocathode is determined by measuring the amount of H₂ generated using gas chromatography during a chronoamperometry test at 0 V_{RHE}. Figure 6.12a shows the current-time curve of CZTS/CdS/ITO/Pt in 1 M K₂HPO₄/KH₂PO₄ (pH 7) under solar simulated AM 1.5G light irradiation at an applied bias of 0 V_{RHE}. The corresponding graph in Figure 6.10b shows the time-course curve of H₂ (blue dots) and O₂ (green dots) evolution measured by gas chromatography (GC) and electrons passing through the outer circuit for H₂ (e⁻/2) and O₂ (e⁻/4). As seen from the figure, the time course curve for H₂ production for CZTS/CdS/ITO/Pt follows close to the time-course curve for e⁻/2, indicating a Faradaic efficiency close to unity. The current-time curve shows a photocurrent decay of 65% after 1h of stability test. Such a decay of photocurrent is usually attributed to the degradation of the photocathode stack during the stability test or Pt delamination.

Figure 6.13: XPS spectra of CZTS/CdS/ITO/Pt before (black) and after 1h stability test (red). XPS spectra of after 1h stability test is multiplied by factor to match peak intensity for easy comparison due to difference in intensity of survey spectrum. (a) Pt 4f spectra. (b) In 3d spectra (c) Sn 3d spectra. (d) Survey spectra with K 2p spectra as insert. Survey spectra is not multiplied.

Figure 6.13 shows the XPS spectra of CZTS/CdS/ITO/Pt before (black) and after 1h stability test (red) for (a) Pt 4f, (b) In 3d, (c) Sn 3d, (d) Survey with insert showing K 2p XPS spectra. The spectra for after stability test is multiplied by a factor to compensate for the difference in intensity as evidenced from the difference in C 1s intensity and background of survey spectrum in Figure 6.13d. A similar multiplication factor for all the spectra suggests that the difference in intensity for the elements before and after the stability is related to the XPS measurement conditions and not due to an absolute decrease in intensity which may suggest a degradation in ITO or Pt. The difference in multiplication factor for Pt 4f XPS spectra may be due to the lack of control in the Pt photoelectrodeposition process with different samples being deposited with different amounts of Pt (samples for before and after stability are not similar). Furthermore, the

absence of any chemical changes in the In 3d and Sn 3d spectra gives support to the hypothesis that the ITO layer is not degraded. The survey spectra before and after the stability test appears similar, except for the presence of a new peak originating from K 2p seen in the insert of Figure 6.13d. This suggests that K may be the reason for the photocurrent decay seen in the stability test and the influence of K on CZTS/CdS/ITO/Pt photocathode stack will be presented in the subsequent section 6.5.2.

6.5.2 Influence of K_2HPO_4/KH_2PO_4 electrolyte on photocathode stack

Figure 6.14: (a) Current density-potential curves of 8%Ag/CdS/Pt under chopped solar-simulated AM 1.5G light irradiation before and after immersing in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) for 1 day in the dark. (b) CZTS/CdS/ITO/Pt under same testing conditions.

From the previous discussion, the reason for the degradation of photocurrent during the stability test appears to be due to the coating of K on the surface of ITO/Pt rather than the dissolution of ITO or delamination of Pt. Figure 6.14 shows the current density-potential curves of photocathodes (a) with and (b) without ITO overlayer under chopped solar-simulated AM 1.5G light irradiation before and after immersing in 1 M K_2HPO_4/KH_2PO_4 solution (pH 7) for 1 day in the dark. The difference in performance before and after soaking in the electrolyte is significant, where the maximum photocurrent and onset potential clearly decreased. This influence of potassium phosphate soaking does not appear to be dependent on the surface as both the performance of CdS/Pt and ITO/Pt deteriorates sharply after the soaking. This suggests that the K and PO_4^{3-} ions reacting with the ITO/Pt

might be a surface adsorption and not a chemical reaction since the XPS results from Figure 6.13 does not show any change to the chemical environment of ITO. The lack of any applied bias or illumination for the reaction gives further support to the hypothesis that the degradation is probably due to a physical surface adsorption.

Figure 6.15: Scanning Electron Microscope (SEM) of CZTS/CdS/ITO/Pt (a) before and (b) after immersing in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ solution (pH 7) for 12h in the dark without any applied potential.

Figure 6.15 shows the Scanning Electron Microscope (SEM) images for CZTS/CdS/ITO/Pt (a) before and (b) after immersing in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ solution (pH 7) in the dark for 12h. From the SEM images, a distinct layer is shown to be coated on the sample after the soaking experiment (Figure 6.13b) which is not observed in the control sample (Figure 6.13a). Energy dispersive X-ray (EDX) measurements from SEM (Figure C.11) is able to detect presence of K and P from the soaked sample. This supports the hypothesis that the degradation is probably due to a layer of K^+ and PO_4^{3-} coating unto the ITO/Pt surface. This layer of K^+ and PO_4^{3-} is probably physically adsorbed on the surface and blocking efficient transport of electrons from the Pt to the electrolyte, hence causing the decrease in the photocurrent. Since the adsorption of these ions is a physical adsorption, if these surface ions can be removed, the performance of the photocathode can be recovered.

Figure 6.16: (a) Current density-potential curves of CZTS/CdS/ITO/Pt under chopped solar-simulated AM 1.5G light irradiation before (red) and after immersing in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ solution (pH 7) (blue) and after certain number of consecutive linear sweep voltammetry scans in the dark from $-0.2 V_{\text{RHE}}$ to $0.8 V_{\text{RHE}}$. (green) (b) Linear sweep voltammetry scans done in the dark from $-0.2 V_{\text{RHE}}$ to $0.8 V_{\text{RHE}}$ in the same electrolyte for removal of Potassium Phosphate ions. Regions of change at low and high potentials are circled in red.

Based on the previous discussion, it was established that the reason for the degradation of photocurrent is possibly due to the adhesion of K^+ and PO_4^{3-} on the ITO/Pt surface. An effective way of removing adsorbates on the surface is to do cyclic voltammetry where at high potentials, certain species will desorb due to $\text{O}(\text{OH})$ adsorption (needed to oxidize certain species) while low potentials will cause anions to desorb due to loss of coulomb attraction with $\text{Pt}^{[28]}$. Figure 6.16a shows the current density-potential curves of CZTS/CdS/ITO/Pt before (red) and after the KPI soaking (blue) (similar to Figure 6.12b) while the subsequent curves after applying consecutive dark linear sweep voltammetry (LSV) in the anodic direction is overlayed in progressive green. It can be observed that with increasing number of dark LSV scans, the photocurrent recovers sharply and recovers to its original photocurrent. Figure 6.16b shows current density-potential curves of the applied dark LSVs. A change in shape of the current density-potential curve is observed at the high potential ($0.5 V_{\text{RHE}} - 0.8 V_{\text{RHE}}$) and low potential ($0 V_{\text{RHE}}$) which may be an indication of a similar desorption process observed by Ramaker et al^[28]. Further studies can be done to investigate this phenomenon.

6.5.3 Stability test with dark LSV recovery

Figure 6.17: (a) Current-time curve of CZTS/CdS/ITO/Pt in 1 M K₂HPO₄/KH₂PO₄ (pH 7) under solar simulated AM 1.5G light irradiation at an applied bias of 0 V_{RHE}. Stability test is conducted at 2h intervals with 3 recovery dark LSV sweep at every interval to recover the photocurrent before resuming the stability test. (b) Corresponding LSV under chopped solar simulated AM 1.5G light irradiation before the stability test and at every 2h interval after the recovery dark LSV sweep.

Figure 6.17a shows the current-time curve of CZTS/CdS/ITO/Pt in 1 M K₂HPO₄/KH₂PO₄ (pH 7) solution under solar simulated AM 1.5G light irradiation at an applied bias of 0 V_{RHE}. The stability test is conducted at 2h intervals whereupon after the 2h of constant light irradiation and applied bias, the light irradiation and bias is switched off and 3 linear sweep voltammetry (LSV) sweep is done in the anodic direction from -0.2 V_{RHE} to 0.8 V_{RHE}. The photocathode stack is not removed out of the electrolyte at any point during the whole 12h measurement process to ensure that the removal of surface adsorbed ions is only due to the LSV sweep. With the recovery dark LSV sweeps, the photocurrent is able to recover to its original value despite decreasing to 64% of its original value after the 2h stability test (Figure 6.15b). Using this recovery method, the stability test is repeated for 6 intervals (total 12h) of which no decrease in photocurrent is observed after the recovery LSV sweep. Furthermore, upon resuming every stability test, a similar gradient of photocurrent decrease is observed, which suggests a similar mechanism of degradation (coating of phosphate and potassium ions on ITO/Pt) at every point.

Figure 6.18: SEM images of CZTS/CdS/ITO/Pt after 12h stability test in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) under AM 1.5G constant illumination and applied bias of 0 V_{RHE} . (a) Sample with recovery dark LSV sweeps at every 2h interval. (b) Sample without recovery dark LSV sweeps.

Figure 6.18 shows the SEM images of CZTS/CdS/ITO/Pt after 12 h of stability test in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) under AM 1.5G constant illumination and at an applied bias of 0 V_{RHE} (a) with and (b) without recovery LSV sweeps at constant intervals. In the case of the sample with recovery LSV sweep (Figure 6.16a), the surface morphology composes of individual grains of CZTS with small nanoparticles of Pt (approximately 40 nm in size) on the surface similar to that of Figure 6.13a (CZTS/CdS/ITO/Pt control). However, without the recovery LSV sweeps (Figure 6.16b), the morphology is drastically different and the whole surface appears to be covered by a significant layer of particles with sizes of about 100 nm. The coverage of these particles appears to be significant and uniform enough to totally obscure the underlying CZTS grains. By comparing Figure 6.16b with Figure 6.13b where the CZTS/CdS/ITO/Pt is immersed in the 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) without illumination and applied bias, it appears that the growth of the top K^+ and PO_4^{3-} layer seems to be more significant when light and bias is applied. The ability of the implemented recovery LSV sweep to remove this layer is confirmed and supports the earlier hypothesis that the photocurrent decay can be recovered by removing this top ionic layer. SEM EDX (Figure C.11) indicates a significant difference in K and P ratios between the 2 samples with almost no K and P detected for the sample with recovery LSV sweep (as the detected value is within the confidence margin).

Figure 6.19: Current-time curve of CZTS/CdS/Pt in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) under solar simulated AM 1.5G light irradiation at an applied bias of 0 V_{RHE} . Stability test is conducted at 2h intervals with 3 recovery dark LSV sweep at every interval in an attempt to recover the photocurrent before resuming the stability test (similar to that of CZTS/CdS/ITO/Pt). (b) Corresponding LSV under chopped solar simulated AM 1.5G light irradiation before the stability test and at every 2h interval after the recovery dark LSV sweep. (c) LSV after 3rd interval of stability test and after the recovery dark LSV sweep. (d) LSV after 4th interval of stability test and after the recovery dark LSV sweep.

When the same stability test with regular intervals of recovery dark LSV sweeps every 2h is conducted for CZTS photocathode without the ITO layer (CZTS/CdS/Pt) as seen in Figure 6.19a and b, the sample is unable to recover its photocurrent but instead its maximum photocurrent at 0 V_{RHE} decreases overtime. Conducting the recovery dark LSV sweeps is shown to cause the maximum photocurrent at 0 V_{RHE} to decrease instead (Figure 6.17c and d), suggesting that the degradation process of CZTS/CdS/Pt is not only a surface adhesion of K^+ and PO_4^{3-} but another mechanism that cannot be recovered by doing such LSV sweeps. Such degradation caused by phosphate buffer electrolyte has been reported

for other materials such as BiVO_4 ^[29-30] (due to dissolution, which is accelerated by high pH, bias and illumination) while also shown to be able to enhance stability for materials such as Fe_2O_3 ^[31] (prevent accumulation of photogenerated holes on surface of Fe_2O_3). This indicates that the stability of the material in potassium phosphate buffer is related to the stability of the complex formed between the semiconductor/electrolyte interface. For CZTS photocathode with ITO overlayer, it was demonstrated that the process of soaking in phosphate electrolyte in the dark (Figure 6.14b) and during illumination throughout the stability test (Figure 6.17a) appears to be similar with K^+ and PO_4^{3-} adhering on the surface of ITO/Pt. Due to the absence of dissolution, the photocurrent can be recoverable when the surface ions are removed. However, for CZTS/CdS/Pt, there is insufficient evidence to conclude whether the two process (dark and light degradation) is similar since the recovery is not conducted yet for CZTS/CdS/Pt soaked in the dark. Further experiments can be done to affirm this. Furthermore, when the dark LSV is done for CZTS/CdS/Pt, in spite of the maximum photocurrent at 0 V_{RHE} decreasing, the onset potential is seen to be increased which may be due to a decreasing CdS thickness because of dissolution.

6.6 PEC performance of 8%Ag photoabsorber with optimized ITO overlayer

Figure 6.20: Current density-potential curves of 8%Ag/CdS/ITO/Pt and 8%Ag/CdS/Pt in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ solution (pH 7) under constant solar-simulated AM 1.5G light irradiation. (b) Corresponding open circuit potential measurement of the same photocathodes.

As 8% Ag in Chapter 5 shows the highest onset potential, the optimized ITO is deposited onto 8%Ag/CdS in a bid to achieve a CZTS based photocathode with the highest photocurrent and onset potential. From Figure 6.20a, the improvement of onset potential and photocurrent can be clearly seen when ITO is deposited with a high photocurrent of 19 mA cm^{-2} at 0 V_{RHE} while retaining the high onset potential of about 0.8 V_{RHE}. The open circuit potential (OCP) is also enhanced greatly with 8%Ag/CdS/ITO/Pt showing the highest OCP of 0.5 V, which is higher than the 0.4 V of CZTS/CdS/ITO/Pt and 0.2 V of 8%Ag/CdS/Pt. While the improvement from incorporating the ITO layer is not as significant as when CZTS/CdS/Pt is compared with CZTS/CdS/ITO/Pt, a definite improvement is observed which confirms the effect of the ITO layer. Furthermore, there appears to be room for further optimization of ITO layer on 8%Ag/CdS due to the huge improvement in OCP which should reflect in the onset potential of the photocathode.

Figure 6.21: Current-time curve of 8%Ag/CdS/ITO/Pt in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) under solar simulated AM 1.5G light irradiation at an applied bias of 0 V_{RHE} . Stability test is conducted at 2h intervals with 3 recovery dark LSV sweep at every interval in an attempt to recover the photocurrent before resuming the stability test (similar to that of previous recovery conditions). (b) Corresponding LSV under chopped solar simulated AM 1.5G light irradiation before the stability test and at every 2h interval after the recovery dark LSV sweep.

The stability of the 8%Ag/CdS/ITO/Pt photocathode follows the same trend as that of CZTS/CdS/ITO/Pt where the degradation of the photocurrent can be recovered by applying dark LSV. This confirms the effect of ITO in enhancing the stability of the Ag substituted CZTS photocathode stack. A summary of all the above work in this thesis is shown in the Table 6.1 below.

Photocathode stack	Photocurrent at 0 V_{RHE}	Photocurrent at 0.6 V_{RHE}	Onset potential	Stability (Until degradation of 20% photocurrent)
CZTS/CdS/Pt	12.5 mA cm^{-2}	0.8 mA cm^{-2}	0.6 V_{RHE}	<2h
CZTS/CdS/ITO/Pt	22 mA cm^{-2}	4 mA cm^{-2}	0.75 V_{RHE}	>12h
CCZTS/CdS/Pt	16 mA cm^{-2}	0.2 mA cm^{-2}	0.6 V_{RHE}	-
CCZTS/CdS/TiMo/Pt	17.5 mA cm^{-2}	0.5 mA cm^{-2}	0.6 V_{RHE}	>1h
8%Ag/CdS/Pt	15 mA cm^{-2}	6 mA cm^{-2}	0.85 V_{RHE}	1h
8%Ag/CdS/ITO/Pt	20 mA cm^{-2}	7 mA cm^{-2}	0.85 V_{RHE}	>6h

Table 6.1: Summary of performances from all different photocathode stacks in this thesis.

6.7 Conclusion

Transparent conducting oxide Indium Tin Oxide (ITO) is being assessed as a potential overlayer for CZTS/CdS/Pt photocathode in order to both enhance its stability and its performance. The performance is enhanced due to a combination of 3 factors: 1) A better charge conduction from CdS to Pt due to the higher electronic conductivity of the ITO layer. 2) A larger band grading from CdS to Pt due to an additional ITO heterojunction inserted between CdS and Pt which helps promote electron and hole separation, hence preventing recombination. 3) A better catalytic activity at the semiconductor/electrolyte interface due to a partial reduction of In and Sn on the surface of ITO forming an In-Pt and Sn-Pt interaction which helps increase the density of electrons on the Pt surface, hence enhancing its catalytic activity. A probable limitation of CZTS/CdS/Pt was identified due to the presence of charge states at the CdS/Pt interface which causes hysteresis of the CZTS/CdS/Pt photocathode when the potential scan direction is reversed and accounts for higher charge transfer resistance identified by electrochemical impedance spectroscopy. An intermediate layer might always be necessary to passivate these states and realize the full potential of the CZTS/CdS/Pt photocathode.

With regard to stability, the inclusion of the ITO layer has helped prevent degradation of the CZTS/CdS/ITO/Pt photocathode. Linear sweep voltammetry (LSV) curves show almost no decline after more than 12h of stability test if recovery dark LSV runs are done at regular intervals. These recovery dark LSVs are essential to remove the K^+ and PO_4^{3-} ions adhesion on the surface of the ITO/Pt which causes the photocurrent to drop. XPS scans reveals the lack of a new chemical state forming after the stability tests which supports the stability of the ITO layer under illumination and applied bias in the K_2HPO_4/KH_2PO_4 electrolyte. This recovery effect is only demonstrated by the photocathode stack with the ITO intermediate layer and the CZTS/CdS/Pt photocathode does not demonstrate this. This suggests that the mechanism for the degradation of photocurrent for CZTS/CdS/Pt is different from that of CZTS/CdS/ITO/Pt. Further studies can be done to investigate the mechanism of degradation for both photocathode stacks and help design other overlayers to improve the performance and stability of photocathodes.

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Chapter 7

Discussion and Future Work

This chapter serves as the concluding chapter for the thesis and provides general discussion on the main results obtained on cation substituted $\text{Cu}_2\text{ZnSnS}_4$ and Indium Tin Oxide (ITO) overlayer. The role of each cation substitution is highlighted and the role of Indium Tin Oxide as an overlayer for CZTS/CdS/Pt photocathode. Based on the completed work in this thesis, reconnaissance unpublished work on other protective layers such as SnO_2 is discussed along with future work on improving this overlayer. In conclusion, CZTS photocathode can be improved through cation substitution and ITO is a viable protection layer for photocathodes if recovery steps are taken.

7.1 Discussions

The focus of this thesis is to develop $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) photocathode for water splitting applications through the improvement of its performance and stability. In **Chapter 1**, CZTS is identified as a promising photocathode but with limitations such as the high concentration of defects in the absorber. Of these defects the highest concentration involves Cu^+ and Zn^{2+} in the form of Cu_{Zn} and Zn_{Cu} antisites and its related complexes largely due to the similar ionic sizes of these two cations. The impact of these defects on the electrical properties of CZTS are discussed in **Chapter 2** along with evaluation of two promising cations (Cd^{2+} and Ag^+) used to substituted Cu^+ and Zn^{2+} which have shown consistent improvements in the photovoltaic field. Next, factors that affect the stability of photocathodes are discussed along with different strategies used by literature to improve the stability. The hypothesis and objective are stated at the end of Chapter 1.

Zn^{2+} substitution with Cd^{2+} in $\text{Cu}_2\text{Cd}_x\text{Zn}_{1-x}\text{SnS}_4$ (CCZTS) was investigated in **Chapter 4** via solution processed sol-gel spin coating. For the first time, the impact of cation substitution in CZTS photocathode is investigated and its corresponding impact on the onset potential and photocurrent. Cd substitution from 0% to 100% (i.e. $\text{Cu}_2\text{ZnSnS}_4$ to $\text{Cu}_2\text{CdSnS}_4$) was investigated and 40% Cd ($\text{Cu}_2\text{Cd}_{0.4}\text{Zn}_{0.6}\text{SnS}_4$) shows the best photocurrent at 0 V_{RHE} . 40% Cd^{2+} substitution is shown to be able to enhance carrier mobility and lifetime by 3 times when compared to CZTS and band tailing is also shown to be reduced. This results in an enhancement of photocurrent at 0 V_{RHE} from 5 mA cm^{-2} of CZTS/CdS/Ti/Mo/Pt to the 17.5 mA cm^{-2} of CCZTS/CdS/Ti/Mo/Pt. This study validates the use of cation substitution to reduce bulk defects in CZTS photocathode and supports the earlier hypothesis that the carrier mobility and lifetime is one of the main limitations of CZTS.

Chapter 5 investigates the effect of Cu^+ substitution with Ag^+ in $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnS}_4$ (ACZTS). ACZTS films of (0 – 15%Ag) were fabricated via solution processed sol-gel spin coating. Due to the inversion of carrier type from p-type to n-type for high Ag substitutions,^[1-2] low amount of Ag substitution was investigated. The photocurrent at 0

V_{RHE} was shown to increase to a maximum of 17.7 mA cm^{-2} for 4% Ag (i.e. $(\text{Ag}_{0.04}\text{Cu}_{0.96})_2\text{ZnSnS}_4$) and decreases after. However, the onset potential increases steadily beyond $0.75 V_{\text{RHE}}$ of 4% Ag to a maximum of $0.85 V_{\text{RHE}}$ at 8% Ag and decreases after. EQE of ACZTS photocathodes in a photoelectrochemical (PEC) setup reveal that substitution of Ag improves the overall EQE. Drift-diffusion simulations reveal that the improvement in overall EQE fits better with an improvement in interface acceptor defects rather than improvement in bulk defects which should affect the slope of EQE in the visible range. This may be due to the segregation of Ag on the surface of ACZTS revealed by angle resolved X-ray photoelectron spectroscopy (XPS). Open circuit potential (OCP) measurements show that the OCP transient at the illumination-dark transition point is sharper for ACZTS, indicating lesser trap states at the ACZTS/CdS interface. Ag substitution is thus shown to be able to reduce the defects at the ACZTS/CdS interface, reducing some of the voltage loss commonly seen in CZTS/CdS photoabsorbers. With this study, the impact of interface defects on onset potential is revealed, and a small amount of cation substitution is shown to be able to enhance the onset potential greatly. Furthermore, the role of different cations improving different limitations of CZTS is demonstrated, with Ag^+ improving the CZTS/CdS interface and Cd^{2+} improving the bulk properties of CZTS.

Chapter 6 investigates Indium Tin Oxide (ITO) as a conductive protective overlayer for CZTS photocathodes. ITO films of 80 nm were sputtered onto CZTS/CdS films followed by photoelectrodeposition of Pt. Photoelectrodeposition of Pt on ITO is shown to reduce the top layer of In and Sn, resulting in a top layer of In and Sn metal. This top layer of In and Sn metal is hypothesized to have an interaction with Pt catalyst, resulting in a higher electron density on Pt and hence higher activity for Pt deposited on ITO when compared with Pt on CdS. The additional ITO layer also enhances the open circuit voltage from about 0.1 V of CZTS/CdS/Pt to 0.4 V of CZTS/CdS/ITO/Pt suggesting an additional heterojunction formed from ITO. Electrochemical impedance spectroscopy reveals a linear decreasing charge transfer resistance with increasing applied cathodic potentials for CZTS/CdS/ITO/Pt. This is in contrast with CZTS/CdS/Pt where the resistance follows a bow profile with a maximum observed at $0.15 V_{\text{RHE}}$ and decreases to a minimum at $0 V_{\text{RHE}}$. This finding reveals that CZTS/CdS/Pt has an inherent limitation that prevents efficient

charge transfer when cathodic potentials are applied and ITO is able to overcome it. ITO is also shown to be able to reduce the charge transfer resistance when compared with CZTS. Lastly, stability measurements reveal that ITO is able to protect the underlying CZTS/CdS layers and the photocurrent can be recovered if recovery sweeps are conducted. Through this study ITO is an attractive overlayer to increase the conduction of photogenerated electrons, prevent charge recombination from formation of an additional heterojunction, increase the catalytic activity of Pt catalyst and protect the CZTS photocathode stack.

This thesis demonstrated a methodical study in firstly improving CZTS bulk and interface through cation substitution and further improving its performance and stability through ITO overlayer. Some optimizations can be further included to improve the performance of CZTS photocathode and some questions are yet to be resolved. These are listed in the following section.

7.2 Reconnaissance and future works

7.2.1 Improving the photoabsorber properties through double cation substitution of Ag and Cd

Figure 7.1: Solar Cell device parameters of double cation (Ag and Cd) substituted CZTS reported by Hadke et al.^[3]

Based on the earlier work on Cd^{2+} and Ag^+ substitution, each substitution has shown to be unique in their improvements to CZTS. Cd^{2+} substitution is shown to improve the CZTS absorber and hence increase its mobility and lifetime while Ag^+ substitution is shown to improve the CZTS/CdS interface due to segregation of Ag on the surface of CZTS and hence increase the photocurrent and onset potential of the photocathode. A double substitution of both cations will thus be interesting to study as it might bring the benefit from both cations and enhance the performance of the CZTS photocathode further. Such double substitution of Ag^+ and Cd^{2+} was investigated by Hadke et al.^[3] and the efficiency of the $(\text{Cu}_{0.95}\text{Ag}_{0.05})_2\text{Cd}_{0.3}\text{Zn}_{0.7}\text{SnS}_4$ (30% Cd and 5% Ag substitution) achieved efficiency of 10.1% which is higher than that of pure 30% Cd substitution. Through double substitution a synergistic effect of the two cations might increase the performance of CZTS photocathode further.^[4] A design of bulk absorber graded with Cd substituted CZTS and a thin Ag substituted CZTS at the surface might utilize this synergy of double cation substitution to full effect.

7.2.2 Studying of surface phosphate complexes on ITO surface using X-ray absorption near edge structure (XANES)

Potassium phosphate is one of the most common buffers used for water splitting (both photocathode and photoanode) due to its high ionic conductivity and ability to reduce chemical bias resulting from pH variations at the electrode surface.^[5-7] However, as demonstrated by many studies, most photocathodes experience stability problems in phosphate related buffers. This degradation in photocurrent is usually attributed to the breakdown in photocathode structure due to photoelectrochemical corrosion, limitation in mass transport, electron accumulation at protective layer or formation of bubbles on the surface.^[8-11] Similar degradation has also been observed in photoanode studies (BiVO_4) where the degradation is attributed to dissolution,^[12-13] while other materials such as Fe_2O_3 have their stability enhanced due to prevention of hole accumulation on the surface.^[14] From our study, we observe a recovery in photocurrent for ITO protected photocathodes when current voltage cycling is applied in the dark to remove the phosphate ions, while the photocathode without protection (i.e. CZTS/CdS/Pt) does not recover the photocurrent.

This suggests that the phosphate complex formed at the two different surfaces (i.e. CdS/phosphate and ITO/phosphate) might be of different chemistry which affects whether the phosphate adhesion can be reversed. It will be hence be beneficial to study and potentially harness the complexes formed at the semiconductor/electrolyte interface as a new direction to improve the stability instead of applying chemically stable layers on top of the photocathode as such layers usually result in a reduction in performance of the photocathode and most layers are unable to demonstrate long term stability. However, at this juncture the results are unable to determine the cation which phosphate is bonded to which may be the main cause of the difference in stability. X-ray absorption near edge structure (XANES) will be useful to identify the bonding between phosphate and ITO and phosphate and CdS and accurately determine the coordination environment. This is shown by another study by He et al in his study of phosphate anion poisoning of Pt/C catalysts where XANES is able to tell the strength of the of the phosphate-metal adsorbates and identify preferential bonding of phosphate on different cations.^[15] With this information, it will be possible to tell the difference in chemistry of adsorbed phosphate on both surfaces and hence identify stable cation-phosphate complexes. Further design on protective layers can harness this information and further engineer such overlayers with surface terminating with such cations.

7.2.3 Further investigation into role of ITO layer using Intensity Modulated photocurrent spectroscopy (IMPS)

Based on the Nyquist plot obtained for CZTS/CdS/Pt (Figure 6.11) the charge transfer resistance (R_{ct}) appears to follow a bowing trend with a maximum resistance obtained at 0.15 V_{RHE}. This result obtained is very unique because in general when more cathodic potentials are applied, band bending and depletion width should increase, resulting in increased light absorption and charge separation. The behavior of most photocathodes show a decrease in R_{ct} with applied potential^[16-18] and although one study shows a non-linear trend, it was attributed to higher H₂ generation rates for the better photocathode which results in accumulation of H₂ gas at the electrode surface causing fluctuation in the photocurrent.^[16] However, in our case the photocathode that exhibits this non-linear R_{ct}

trend was the lower performing CZTS/CdS/Pt photocathode instead of the CZTS/CdS/ITO/Pt photocathode which has a higher photocurrent and should have more accumulation of H_2 gas at electrode surface. This increase in R_{ct} despite the increasing cathodic potential applied suggests an inherent limitation within CZTS/CdS/Pt which may be either due to band alignment that prevents further band bending with applied potential or defects that prevents charges from effectively transferring to the electrolyte. The extracted R_{ct} at 0 V_{RHE} (point of maximum photocurrent) for CZTS/CdS/Pt is only slightly smaller than the R_{ct} at 0.45 V_{RHE} where the photocurrent almost decreases to 0. This leads to the hypothesis that the photocurrent of CZTS/CdS/Pt at 0 V_{RHE} will be much larger if the R_{ct} follows a similar trend as other photocathodes, where the R_{ct} is a minimum at 0 V_{RHE} . When ITO is deposited, the non-linear behavior is eliminated and the resulting photocurrent and onset is greatly enhanced. Intensity modulated photocurrent spectroscopy can be employed to distinguish whether the limitation is due to band alignment or a defective surface hence resulting in Fermi level pinning. Extracting the surface recombination rate constant (k_{rec}) with different applied potentials will indicate the extent of surface recombination (hence amount of surface defects) as well as presence of Fermi level pinning if k_{rec} does not decrease with increasing applied cathodic potential.^[19] In addition, extracting charge transfer efficiency (k_{tr}) from IMPS will be able to distinguish better support the increase in catalytic activity from In-Pt bonding on top of the extracted Tafel slopes.

7.2.4 Mo-doped Indium oxide as new overlayer

Conductivity of ITO is controlled mainly through Sn doping, which increases the carrier concentration but with the detrimental effect of lowering carrier mobility.^[20-21] As Sn 5s orbitals interacts with the In 5s and O 2p orbitals in the valence band maximum of ITO, an increase in Sn doping will increase the effective mass of electrons and hence lower the carrier mobility.^[22] A tradeoff between carrier concentration and carrier mobility is usually achieved, with 10wt% of SnO_2 with respect to In_2O_3 most commonly used. Mo-doped Indium oxide (IMO) is an attractive overlayer to study beyond ITO to further improve the photocurrent of the CZTS photocathode stack while retaining the benefits of enhancing

stability and performance from ITO. Unlike Sn doping in ITO, Mo 4d states are energetically separated from the CBM and do not interact with the In 5s and O 2p orbitals.^[23] This allows IMO to achieve higher amounts of carrier doping while retaining its high mobility, potentially increasing its conductivity further. Earlier works on IMO have consistently shown higher carrier mobilities and higher conductivities when compared with ITO with the same carrier concentration.^[23-24] An IMO overlayer with an optimized Mo content will potentially increase both the onset potential and the photocurrent of the CZTS photocathode while allowing it to perform stably without degradation.

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List of Publications

- **Ying Fan Tay**, Sing Yang Chiam, Stener Lie, et al. Solution processed Cd-substituted CZTS photocathode for efficient solar hydrogen evolution from neutral water. *Joule*, 2018, 2 (3), 537-548.
- **Ying Fan Tay**, Shreyash Sudhakar Hadke, Mengyuan Zhang, Nathan Lim, Sing Yang Chiam, and Lydia Helena Wong. Improving the interfacial properties of CZTS photocathode by Ag substitution. *Journal of Materials Chemistry A*, 2020, 8, 8862-8867.
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APPENDIX A

Appendix figures and tables for Chapter 4

	Efficiency (%)	Jsc (mAcm ⁻²)	Voc (V)	FF (%)
CZTS	7.3199	20.5262	0.6306	56.5475

Figure A.1: Photovoltaic parameters of CZTS solar cell in stack CZTS/CdS/ITO.

	Cu	Zn	Cd	Sn	S
CZTS	17.62	11.18	0	10.30	60.90
CCZTS	21.77	7.67	4.88	12.00	53.68

Table A.1: Atomic mass concentrations of Cu, Zn, Cd, Sn and S taking the average of 3 readings in 3 different spots.

Figure A.2: Derivative of IPCE with respect to $h\nu$, $d(EQE)/d(h\nu)$, vs band gap energy ($h\nu$) plot and the peak position corresponding to the band gap of the absorbers.

Figure A.3: Integrated photocurrent derived from IPCE in Figure 4.9.

Figure A.4: (a) Current-time curve for CCZTS/CdS/TiMo/Pt in 1M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) under solar-simulated AM 1.5G light irradiation and after subsequent Pt redeposition after 1h of (b)

stability test. (b) Current density-potential curves of CZTS/CdS/TiMo/Pt and CCZTS/CdS/TiMo/Pt in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation before stability test, after stability test and after subsequent Pt redeposition.

Figure A.5: (a) CZTS XPS valence scan after carbon correction (C 1s 284.6 eV) (b) CCZTS XPS valence scan after carbon correction.

Figure A.6: UPS He(I) spectra at -10 V applied bias for (a) CZTS and (b) CCZTS according to method presented in previous work.^[26]

Figure A.7: Room-temperature transient reflection profiles using 600 nm pump and white light probe at different delay times for (a) CZTS and (b) CCZTS. Clear photo-bleaching signals due to the band-filling effect were observed for CZTS and CCZTS centered at around 695 nm and 795 nm respectively. The artifact at around 750 nm for CCZTS is due to the white continuum being uneven near 800 nm. In addition, CZTS exhibits strong photo-induced absorption below the band edge, which could be attributed to the carrier absorption in the subgap trap states. For CCZTS, we did not observe the photoinduced-absorption in the visible range.

APPENDIX B

Appendix figures and tables for Chapter 5

	Cu	Ag	Zn	Sn	S	Ag/(Cu+Ag) (%)
CZTS	2.60	0	1.56	1	5.80	0
8% Ag	1.53	0.15	1.19	1	6.04	9.38
10% Ag	1.68	0.22	1.08	1	5.45	11.58

Table B.1: Atomic ratios of ACZTS films determined by SEM-EDX by taking the average of 5 points.

	4% Ag	8%Ag
0° - 30°	13.87%	22.15%
30° - 50°	18.25%	25.33%
50° - 70°	21.59%	32.63%

Table B.2: Ag/(Cu+Ag) ratios determined by angle resolved XPS for 4%Ag and 8% Ag absorbers for 3 different take-off angle channels.

Figure B.1: X-ray diffraction spectra for CZTS and highest substituted 10%Ag thin films.

Figure B.2: Current density (J) – vs potential curves (V) of CZTS/CdS(x)/Pt in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under chopped solar -simulated AM 1.5G light illumination. X represents CdS chemical bath deposition time. 14min is determined to be the optimized CdS thickness for PEC setup.

Figure B.3: HC-STH efficiency curve for $(Ag_xCu_{1-x})_2ZnSnS_4/CdS/Pt$ photocathodes in 1M K_2HPO_4/KH_2PO_4 solution (pH 7) under constant solar-illuminated AM 1.5G light irradiation.

Figure B.4: Current density-potential curves of ACZTS/CdS photocathodes in Na_2SO_4 (pH 9.5) solution under chopped solar-simulated AM1.5G light irradiation before platinum catalyst deposition.

Figure B.5: PV EQE of ACZTS/CdS/ITO photovoltaic (PV) cells with CdS optimized for PEC.

	CZTS	CdS
Bandgap (eV)	1.5	2.4
Electron affinity (eV)	4.0	4.2
Dielectric constant	6.8	10
Conduction band effective DOS (cm^{-3})	2.2×10^{18}	2.2×10^{18}
Valence band effective DOS (cm^{-3})	1.8×10^{19}	1.8×10^{19}
Electron thermal velocity (cm/s)	10^7	10^7
Hole thermal velocity (cm/s)	10^7	10^7
Electron mobility (cm^2/Vs)	100	100
Hole mobility (cm^2/Vs)	25	25
Carrier concentration (cm^{-3})	10^{15}	10^{17}
	Bulk defect	Interface defect
Type	Single acceptor	Acceptor
Electron capture cross section (cm^2)	10^{-14}	5×10^{-14}
Hole capture cross section (cm^2)	10^{-16}	10^{-14}
Energetic distribution	Gaussian, 0.25 V above VB	Gaussian, 0.6 V above VB
Total defect density	$2.3 \times 10^{15} \text{ cm}^{-3}$	$8 \times 10^{12} \text{ cm}^{-2}$

Table B.3: Parameters used for SCAPS simulation in Figure 5.5a.

Figure B.6: Nyquist plots of CZTS/CdS/ITO and 8%Ag/CdS/ITO done in PV setup.

Figure B.7: (a) $d(EQE)/dE$ plots of ACZTS/CdS using optimized PV CdS. (b) Corresponding extracted bandgap of ACZTS.

Figure B.8: XPS Valence scans of (a) CZTS, (b) 4%Ag and (c) 8%Ag absorbers.

APPENDIX C

Appendix figures and tables for Chapter 6

Figure C.1: SEM cross section images of ITO sputtered on Mo coated glass for ITO sputtering durations of (a) 6 min, (b) 7 min, (c) 10 min and (d) 15 min. Scale bars are representative of 100 nm. Note the difference in magnification between Figures (a) (b) and (c) (d).

Figure C.2: External Quantum Efficiency (EQE) of CZTS/CdS/ITO/Pt photocathode stacks with different ITO sputtering durations in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) solution under applied potential of 0 V_{RHE} .

Figure C.3: X-ray diffractogram of ITO sputtered on glass at room temperature under DC power of 75 W for 7 min.

	Sn	In	O	Sn/(In+Sn) ratio
Before Pt deposition	4.19	38.27	57.55	0.0987
After Pt deposition	1.61	22.32	76.07	0.0672

Table C.1: Atomic ratios of ITO before and after Pt photoelectrodeposition determined by XPS.

Figure C.4: In 3d XPS spectra of CZTS/CdS/ITO/Pt with Pt deposited through sputtering (frame above) and CZTS/CdS/ITO/Pt with Pt deposited through photoelectrodeposition (PED) of Pt (frame below) after normalizing peak area.

Figure C.5: Pt 4f XPS spectra of CZTS/CdS/ITO/Pt with Pt deposited through sputtering (black) and Pt deposited through photoelectrodeposition (PED) of Pt (red) after normalizing peak area.

Figure C.6: XPS spectra of CZTS/CdS/ITO, CZTS/CdS/ITO with 45° tilt, CZTS/CdS/ITO/Pt PED and CZTS/CdS/ITO/Pt PED with 45° tilt after normalizing peak area. (a) In 3d XPS spectra. (b) O 1s XPS spectra. (c) Sn 3d XPS spectra.

Figure C.7: Current density-voltage curves of CZTS/CdS/Pt and CZTS/CdS/ITO/Pt before Pt deposition in 0.1 M Na₂SO₄ (pH 9.5) solution under chopped AM 1.5 G light irradiation.

Figure C.8: UPS He(I) spectra at an applied bias of -10V for CZTS/CdS (black) and CZTS/CdS/ITO (red).

Figure C.9: Current-density potential curves of CZTS/CdS/Pt at different scan rates of 0.01 V/s, 0.02 V/s and 0.005 V/s in 1 M K₂HPO₄/KH₂PO₄ (pH 7) solution under chopped AM 1.5G light irradiation for (a) Anodic and (b) Cathodic directions.

Figure C.10: Open circuit potential (OCP) measurements of CZTS/CdS/Pt (black) vs CZTS/CdS/ITO/Pt (red) in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) solution under constant AM 1.5G light irradiation

Figure C.11: Box plots of SEM EDX measured Wt% of (a) K and (b) P. Each plot is divided into 3 sections representing 3 different experimental conditions: (1-black) 12h stability test of CZTS/CdS/ITO/Pt PED at 0 V_{RHE} in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) solution under constant AM 1.5G illumination with recovery dark LSV done at every 2h interval. (2-red) 12 stability test of CZTS/CdS/ITO/Pt PED under same applied bias in same electrolyte and illumination without any recovery dark LSV. (3-green) CZTS/CdS/ITO/Pt PED soaked in 1 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (pH 7) solution in the dark without any bias applied. Within each section, 2 box plots are presented. First is the box plot of 10 measured EDX points. Second is labelled confidence is the degree of overlap with other surrounding peaks.