Improving the interfacial properties of CZTS photocathodes by Ag substitution

Tay, Ying Fan; Hadke, Shreyash Sudhakar; Zhang, Mengyuan; Lim, Nathan; Chiam, Sing Yang; Wong, Lydia Helena

2020

Tay, Y. F., Hadke, S. S., Zhang, M., Lim, N., Chiam, S. Y., & Wong, L. H. (2020). Improving the interfacial properties of CZTS photocathodes by Ag substitution. *Journal of Materials Chemistry A*, 8(18), 8862-8867. doi:10.1039/D0TA02042G

<https://hdl.handle.net/10356/143982>

<https://doi.org/10.1039/D0TA02042G>

© 2020 Royal Society of Chemistry. All rights reserved. This paper was published in *Journal of Materials Chemistry A* and is made available with permission of Royal Society of Chemistry.

Downloaded on 26 Apr 2023 21:55:08 SGT

Journal of Materials Chemistry A

Materials for energy and sustainability

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. H. Wong, Y. F. Tay, S. Hadke, M. Zhang, N. L. J. Lim and S. Y. Chiam, *J. Mater. Chem. A*, 2020, DOI: 10.1039/D0TA02042G.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

COMMUNICATION

Improving the interfacial properties of CZTS photocathode by Ag substitution.

Ying Fan Tay,^a Shreyash Sudhakar Hadke,^b Mengyuan Zhang,^a Nathan Lim,^a Sing Yang Chiam,^c and Lydia Helena Wong^{a*}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Cu₂ZnSnS₄ (CZTS) is a promising photocathode in a water splitting system due to its appropriate conduction band position with the water reduction potential, suitable band gap and high absorption coefficient. However, CZTS has yet to demonstrate unbiased solar to hydrogen efficiency above 1% in a photocathode-photoanode tandem setup unlike its CuInGaSe₂ chalcogenide counterpart due to its low onset potential and photocurrent. This low onset potential and photocurrent is believed to be limited by the large density of defects in CZTS and at the CZTS/CdS interface which limits the open-circuit voltage in CZTS solar cells. In this work (Ag_xCu_{1-x})₂ZnSnS₄ (ACZTS) with Ag⁺ partially replacing Cu⁺ is fabricated by solution process and investigated as a photocathode. Our ACZTS/CdS/Pt photocathode yields a maximum photocurrent of 17.7 mA cm⁻² at 0 V_{RHE} at 4% Ag (x = 0.04) and a maximum onset potential of 0.85 V_{RHE} at 8% Ag (x = 0.08), which is a substantial improvement from our CZTS/CdS/Pt photocathode that has a photocurrent of 13 mA cm⁻² and onset potential of 0.65 V_{RHE}. A combination of incident photon to current efficiency (IPCE) measurements done in a photoelectrochemical (PEC) and photovoltaic (PV) setup attributes the improvement to the interface properties. Other PV measurements such as capacitance-voltage profiling (CV) and Mott-Schottky measurements reveal a lower apparent carrier concentration and higher built-in voltage of ACZTS.

Introduction

The use of solar energy to split water using photoactive semiconductors is a clean and economical route to produce hydrogen. However, due to the redox potential of both water-splitting reactions (water reduction and water oxidation), a potential of at least 1.23 V must be supplied for the overall reaction. This is further complicated when reaction kinetics and entropy change of converting water into gas is taken into account, which further increases the energy required to about 1.8 V to achieve a practical current density¹. As a result, for a single semiconductor to drive the water splitting reaction through solar energy, the photons absorbed must have energy higher than 1.8 eV, which limits the amount of the solar spectrum it can absorb, lowering its overall efficiency. Incorporating two photoactive absorbers (photocathode and photoanode) in tandem to carry out the two water-splitting reactions will optimize the amount of solar irradiation that can be absorbed which allows solar-to-hydrogen efficiencies of 20% to be reached².

Cu₂ZnSnS₄ (CZTS) is an attractive photocathode due to its suitable band edges (i.e. conduction band lying above the water reduction potential), optimal band gap and high absorption coefficient. In addition, it has achieved good success in the photovoltaic field

achieving high efficiencies of 12.6%³. Its first demonstration as a photocathode with a n-type CdS layer achieved photocurrent density of 9 mA cm⁻² at 0 V versus the reversible hydrogen electrode (RHE)⁴. Subsequent deposition of overlayers such as TiO₂ has managed to increase the photocurrent to 11 mA cm⁻², which is the highest photocurrent for sulfide-based CZTS photocathode⁵.

While increasing the photocurrent is important, increasing the onset potential is also crucial to have a higher operating current density when integrated with a photoanode. The onset potential of a photocathode is largely affected by thermodynamic factors such as the position of its VBM relative to the oxygen evolution potential and the surface concentration of electrons^{6,7}. To date, even with a multi-layered photocathode stack (such as with CdS and TiO₂) and the most efficient Pt catalyst, CZTS still suffers from low onset potentials and requires high cathodic potentials to achieve high current densities. This drastically reduces its solar-to-hydrogen (STH) power conversion efficiency and the highest reported STH for a CZTS based photocathode is only about 1%⁸, lagging behind other photocathodes such as Cu₂O⁹, GaInP¹⁰⁻¹² and Cu(In,Ga)Se₂ (CIGS)^{13,14}. Such an onset potential is much lower than the bandgap of CZTS which is about 1.5 eV, thus allowing much room for improvement.

This low onset potential is also reflected in CZTS photovoltaics which is often associated to open-circuit voltage (V_{oc}) loss. It is generally attributed to defects such as interfacial defects at the CZTS/CdS interface^{15,16} or deep and shallow defects within the bandgap of the CZTS absorber^{17,18}. These defects are often associated with the Cu/Zn antisites which arise due to the similar ionic size of Cu⁺ and

^a Address here.^b Address here.^c Address here.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Journal Name

Zn^{2+} . A common strategy used in the photovoltaic community is to partially substitute Cu^+ or Zn^{2+} with another cation with more distinct ionic size. More recently, our group has demonstrated that partial substitution of Zn^{2+} with Cd^{2+} , which has demonstrated much improvement in the photovoltaic field^{19, 20}, yields similar results when applied as a photocathode. When Zn^{2+} is partially substituted with Cd^{2+} , the minority carrier lifetime can be improved due to the reduction of defects leading to a 3 fold increase in photocurrent²¹. In the case of improving the onset potential, substituting Cu^+ with Ag^+ seems to be feasible since the shallower Cu 3d orbitals that make up the VBM are replaced by the deeper Ag 4d orbitals. Furthermore, Ag substitution is shown to increase the V_{oc} in photovoltaics and is also predicted by first principles to reduce certain defects in the CZTS absorber^{22, 23}. This makes Ag substitution interesting to study for the dual purpose of increasing the onset potential and photocurrent.

Recently, Xu et al. have demonstrated solution processed Ag substituted CZTS photocathode which achieved a photocurrent of 3.78 mA cm^{-2} at $0 V_{\text{RHE}}$ and an onset potential of $0.33 V_{\text{RHE}}$ with a Ag/(Ag+Cu) ratio of 30% due to Ag improving the grain size and lowering the valence band maximum²⁴. The onset potential of the reported $(\text{Cu}_{0.7}\text{Ag}_{0.3})_2\text{ZnSnS}_4$ photocathode is rather low since most CZTS/CdS/Pt photocathode stacks have already demonstrated onset potentials of up to $0.6 V_{\text{RHE}}$ and much higher photocurrent densities. In addition, most ACZTS photovoltaic studies report a decline in efficiencies once the Ag/(Ag+Cu) ratio exceeds 20%^{22, 25-27}, which leads us to believe that the optimal ratio of Ag/(Ag+Cu) might not be in the range studied. In this work, we demonstrate a substantial improvement of both photocurrent and onset potential based on low Ag substitutions of 4% to 8% and achieve a photocurrent of 17.7 mA cm^{-2} at $0 V_{\text{RHE}}$ and an onset potential of $0.85 V_{\text{RHE}}$. To our knowledge this is the highest photocurrent and onset potential reported for a CZTS-based photocathode without further modifications beyond an n-type CdS layer. We also investigated the effect of Ag substitution using a combination of wet photoelectrochemical and dry photovoltaic characterizations and attributed the improvement in interface properties as the main cause of the improved onset potential.

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

Figure 1 shows the cross-sectional scanning electron microscopy (SEM) images of $(\text{Cu}_{1-x}\text{Ag}_x)_2\text{ZnSnS}_4$ (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 indicating a good crystallinity. The amount of Ag in the ACZTS films is analysed by energy-dispersive X-ray spectroscopy (SEM-EDX) (Table S1, Supporting Information) and found to be about 1% higher for the films when compared to the as-prepared amount, 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 analysed under angle-resolved X-ray photoelectron spectroscopy (ARXPS) (Table S2, Supporting Information), it is found that the Ag/(Cu+Ag) ratio is much higher than that measured by SEM-EDX. Moreover, the Ag/(Cu+Ag) ratios increased 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 the ACZTS absorbers which may influence the interface properties of ACZTS/CdS. X-ray diffraction (XRD) measurements of CZTS and highest substituted 10% Ag absorbers (Figure S1, Supporting Information) are consistent with previous reports and no secondary phases are observed.^{25, 28}

Figure 2: (a) Current density (J) – vs potential curves (V) 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 2a shows the current density (J) vs potential (V) curves of $(Cu_{1-x}Ag_x)_2ZnSnS_4/CdS/Pt$ photocathodes with different amount of Ag under chopped illumination of simulated sunlight (AM 1.5G) in a 1 M K_2HPO_4/KH_2PO_4 electrolyte (pH 7). The thickness of CdS is first optimized by altering the CdS chemical bath deposition time and comparing the J-V curves (Figure S2, Supporting Information). 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 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 S3, Supporting Information). 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 authors note the inconsistency among different works for the definition on onset potentials hence preventing proper comparison between them. A table showing the different photocathode stacks, reported onset potential and method of determining the onset potential is shown in Table S3 (Supporting Information) with the current work. In this work, the onset potential is defined at the onset of the derivative curve (dJ/dV vs V) as proposed by Le Formal et al.²⁹ as the authors believe this 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. 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 S4, Supporting Information). 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. Amount of H_2 produced by 8%Ag/CdS/Pt photocathode measured by gas chromatography reveals a Faradaic Efficiency close to unity, indicating that the photocurrent shown results in hydrogen production (Figure S5, Supporting Information).

Figure 3: (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 3a 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 3b) is also relatively consistent to the photocurrent from the J-V curves in Figure 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 S6, Supporting Information). 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. To understand the reasons behind this improvement, we perform drift-diffusion simulations using SCAPS-1D software package³⁰. In particular, we simulate the effect of interface and bulk defects on the EQE characteristics in the range 300 nm to 1000 nm (Figure S7, Supporting Information). The parameters used for the simulations are given in Table 4 (Supporting Information). 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 report³¹. Further, we find that acceptor-type interface defects affect the overall EQE. From Figure 3a and S6, 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^{19, 20, 25, 31}. In Figure S8 (Supporting Information), 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

COMMUNICATION

Journal Name

experimentally observed EQE, we attribute the improvement in the overall EQE (Figure 3a) of our samples to the suppression of interface recombination.

Figure 4: (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. (c) PV Mott-Schottky plots of ACZTS/CdS/ITO with linear extrapolation of built in potential and (d) PV Capacitance-Voltage (CV) plots of ACZTS/CdS/ITO.

Figure 4a and 4b show the open-circuit potential-time profile 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 4a), indicating a higher band bending with Ag substitution between ACZTS and CdS in the dark³². This is supported by PV Mott-Schottky plots (Figure 4c) that show a higher built-in potential of ACZTS with increasing Ag concentration. 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 S9, Supporting Information). 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 holes³³. However, based on the band gap derived from PV EQE (Figure S10, Supporting Information), 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 2a. Furthermore, when analysing the XPS valence spectra of the ACZTS absorbers and comparing it with CZTS (Figure S11, Supporting Information), 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 4d, 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^{22, 26, 28}. 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 4d) 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 3a. 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. Furthermore, from Figure 4a, 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 4b is higher), which suggests that there are lesser trap states in the photocathode stack³⁴. These observed improvements in built-in potential, depletion width and reduction in interfacial defects and trap states suggests an improvement in interface properties between ACZTS/CdS, which may reduce interface recombination and increase charge collection, enhancing the photocurrent and onset potential of ACZTS/CdS/Pt photocathode.

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 methods³⁵, 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.

Conclusions

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. This increase in performance when Ag is substituted into CZTS is attributed to the improved interface properties which may be due to a reduction of Cu/Zn antisites and other interface defects at the ACZTS/CdS interface and an increase in 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.

Experimental

Synthesis of ACZTS absorbers

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. 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.¹⁷ 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.

Chemical bath deposition of CdS buffer layer (for thin CdS)

ACZTS thin film substrates were immersed in an aqueous solution containing 25 mmol L^{-1} of $\text{Cd}(\text{CH}_3\text{COO})_2$, 0.375 mol L^{-1} of $\text{SC}(\text{NH}_2)_2$, and 8 mol L^{-1} NH_4OH at 60 °C for 14 min. The solution was continuously stirred throughout the process.

Chemical bath deposition of CdS buffer layer (for thick CdS)

ACZTS thin film substrates were immersed in an aqueous solution of 0.75 M $\text{SC}(\text{NH}_2)_2$, 0.015 M CdSO_4 , and 8 mol L^{-1} NH_4OH at 80 °C for 9 min. The solution was continuously stirred throughout the process.

PEC measurements

PEC measurements were conducted on a CHI 660D workstation (CH Instruments Inc.) using a three-electrode setup with a solar simulator (PEC-L01, Peccell) applying AM 1.5G irradiation at 100 mW cm^{-2} as the light source. A Pt wire and Ag/AgCl in 3 M saturated KCl aqueous solution were employed as counter and reference electrodes respectively.

PEC EQE measurements were carried out using a combination of a Xe lamp (MAX-302, Asahi Spectra Co. Ltd.) and a monochromator (CMS-100, Asahi Spectra Co. Ltd.) from 300 to 900 nm wavelength. The EQE is calculated using the following equation:

$$EQE (\%) = \frac{1240 (V \text{ nm}) \times \text{photocurrent density (mA cm}^{-2}\text{)}}{\text{Incident light power density (mW cm}^{-2}\text{)} \times \text{wavelength (nm)}}$$

The hypothetical HC-STH was calculated from the current-potential curves using the equation $HC - STH = \frac{|I_{ph}|}{P_{sun}} \times 100\%$ where I_{ph} is the photocurrent density obtained under an applied bias of E_{RHE} , E_{H^+/H_2} is the equilibrium redox potential of hydrogen (0 V_{RHE}) and P_{sun} is the power density of the incident solar energy (100 mW cm^{-2}).

PV External Quantum Efficiency

EQE measurements for PV devices was measured using Bentham PVE300. The system was calibrated using a standard Si cell.

PV Capacitance-Voltage

PV CV measurements were performed in the dark at room temperature using Autolab PGSTAT302N with an AC signal of 30 mV rms at 50 kHz.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

This research is partially supported by grants from the National Research Foundation, Prime Minister's Office, Singapore under its Campus of Research Excellence and Technological Enterprise (CREATE) programme and Ministry of Education (MOE) Tier 2 Project (MOE2016-T2-1-030)

References

1. C. Xiang, K. M. Papadantonakis and N. S. Lewis, *Materials Horizons*, 2016, **3**, 169-173.
2. M. S. Prévot and K. Sivula, *The Journal of Physical Chemistry C*, 2013, **117**, 17879-17893.
3. W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu and D. B. Mitzi, *Advanced Energy Materials*, 2014, **4**, 1301465.
4. D. Yokoyama, T. Minegishi, K. Jimbo, T. Hisatomi, G. Ma, M. Katayama, J. Kubota, H. Katagiri and K. Domen, *Applied Physics Express*, 2010, **3**, 101202.
5. W. Yang, Y. Oh, J. Kim, M. J. Jeong, J. H. Park and J. Moon, *ACS Energy Letters*, 2016, **1**, 1127-1136.
6. L. Zhang, T. Minegishi, M. Nakabayashi, Y. Suzuki, K. Seki, N. Shibata, J. Kubota and K. Domen, *Chemical Science*, 2015, **6**, 894-901.
7. J. E. Thorne, S. Li, C. Du, G. Qin and D. Wang, *The Journal of Physical Chemistry Letters*, 2015, **6**, 4083-4088.
8. D. Huang, K. Wang, L. Yu, T. H. Nguyen, S. Ikeda and F. Jiang, *ACS Energy Letters*, 2018, **3**, 1875-1881.
9. L. Pan, J. H. Kim, M. T. Mayer, M.-K. Son, A. Ummadisingu, J. S. Lee, A. Hagfeldt, J. Luo and M. Grätzel, *Nature Catalysis*, 2018, **1**, 412-420.
10. Y. Wang, J. Schwartz, J. Gim, R. Hovden and Z. Mi, *ACS Energy Letters*, 2019, **4**, 1541-1548.
11. M. M. May, H.-J. Lewerenz, D. Lackner, F. Dimroth and T. Hannappel, *Nature Communications*, 2015, **6**, 8286.
12. J. L. Young, M. A. Steiner, H. Döschner, R. M. France, J. A. Turner and Todd G. Deutsch, *Nature Energy*, 2017, **2**, 17028.
13. Y. Goto, T. Minegishi, Y. Kageshima, T. Higashi, H. Kaneko, Y. Kuang, M. Nakabayashi, N. Shibata, H. Ishihara, T. Hayashi, A. Kudo, T. Yamada and K. Domen, *Journal of Materials Chemistry A*, 2017, **5**, 21242-21248.
14. H. Kobayashi, N. Sato, M. Orita, Y. Kuang, H. Kaneko, T. Minegishi, T. Yamada and K. Domen, *Energy & Environmental Science*, 2018, **11**, 3003-3009.
15. L. Yin, G. Cheng, Y. Feng, Z. Li, C. Yang and X. Xiao, *RSC Advances*, 2015, **5**, 40369-40374.
16. A. Crovetto, M. L. N. Palsgaard, T. Gunst, T. Markussen, K. Stokbro, M. Brandbyge and O. Hansen, *Applied Physics Letters*, 2017, **110**, 083903.
17. S. Chen, X. G. Gong, A. Walsh and S.-H. Wei, *Applied Physics Letters*, 2010, **96**, 021902.
18. M. Kumar, A. Dubey, N. Adhikari, S. Venkatesan and Q. Qiao, *Energy & Environmental Science*, 2015, **8**, 3134-3159.
19. Z. Su, J. M. R. Tan, X. Li, X. Zeng, S. K. Batabyal and L. H. Wong, *Advanced Energy Materials*, 2015, **5**, 1500682.
20. S. H. Hadke, S. Levchenko, S. Lie, C. J. Hages, J. A. Márquez, T. Unold and L. H. Wong, *Advanced Energy Materials*, 2018, **8**, 1802540.
21. Y. F. Tay, H. Kaneko, S. Y. Chiam, S. Lie, Q. Zheng, B. Wu, S. Hadke, Z. Su, P. S. Bassi, D. Bishop, T. C. Sum, T. Minegishi, J. Barber, K. Domen and L. H. Wong, *Joule*, 2018, **2**, 537-548.
22. T. Gershon, Y. S. Lee, P. Antunez, R. Mankad, S. Singh, D. Bishop, O. Gunawan, M. Hopstaken and R. Haight, *Advanced Energy Materials*, 2016, **6**, 1502468.
23. Z.-K. Yuan, S. Chen, H. Xiang, X.-G. Gong, A. Walsh, J.-S. Park, I. Repins and S.-H. Wei, *Advanced Functional Materials*, 2015, **25**, 6733-6743.
24. Z. Xu, Z. Guan, J. Yang and Q. Li, *ACS Applied Energy Materials*, 2019, **2**, 2779-2785.
25. A. Guchhait, Z. Su, Y. F. Tay, S. Shukla, W. Li, S. W. Leow, J. M. R. Tan, S. Lie, O. Gunawan and L. H. Wong, *ACS Energy Letters*, 2016, **1**, 1256-1261.
26. W.-C. Huang, S.-Y. Wei, C.-H. Cai, W.-H. Ho and C.-H. Lai, *Journal of Materials Chemistry A*, 2018, **6**, 15170-15181.
27. Y. Qi, Q. Tian, Y. Meng, D. Kou, Z. Zhou, W. Zhou and S. Wu, *ACS Applied Materials & Interfaces*, 2017, **9**, 21243-21250.
28. X. Liang, P. Wang, B. Huang, Q. Zhang, Z. Wang, Y. Liu, Z. Zheng, X. Qin, X. Zhang and Y. Dai, *ChemPhotoChem*, 2018, **2**, 811-817.
29. F. Le Formal, M. Grätzel and K. Sivula, *Advanced Functional Materials*, 2010, **20**, 1099-1107.
30. M. Burgelman, P. Nollet and S. Degraeve, *Thin Solid Films*, 2000, **361-362**, 527-532.
31. S. Hadke, S. Levchenko, G. Sai Gautam, C. J. Hages, J. A. Márquez, V. Izquierdo-Roca, E. A. Carter, T. Unold and L. H. Wong, *Advanced Energy Materials*, **n/a**, 1902509.
32. S. Berglund, F. Abdi, P. Bogdanoff, A. Chemseddine, D. Friedrich and R. Van de Krol, *Chemistry of Materials*, 2016, **28**.
33. J. Van Zeghbroeck, *Principles of Semiconductor Devices*, Bart Van Zeghbroeck, 2011.
34. C. Ros, T. Andreu, S. Giraldo, Y. Sánchez and J. R. Morante, *Solar Energy Materials and Solar Cells*, 2016, **158**, 184-188.
35. Y. Ren, J. J. S. Scragg, M. Edoff, J. K. Larsen and C. Platzer-Björkman, *ACS Applied Materials & Interfaces*, 2016, **8**, 18600-18607.