Significant role of the initial precursor sulfur concentration in the photoelectrochemical hydrogen production of Cu₂ZnSnS₄ photocathode prepared by thermal evaporation

Lahiru K. Abeykoon[®],^a Hong-Yi Tan,^{b,c,d} Chang-Feng Yan,^{b,c,d,e} and Jayasundera Bandara[®]^{a,*}

^aNational Institute of Fundamental Studies, Kandy, Sri Lanka ^bChinese Academy of Sciences, Guangzhou Institute of Energy Conversion, Guangzhou, China ^cGuangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou, China ^dChinese Academy of Sciences, Key Laboratory of Renewable Energy, Guangzhou, China

^aChinese Academy of Sciences, Key Laboratory of Renewable Energy, Guangzhou, China ^eUniversity of Chinese Academy of Sciences, Beijing, China

Abstract. The thermal evaporation of Cu_2ZnSnS_4 (CZTS) nanoparticles synthesized by changing the sulfur ratio in the precursor solution was used to investigate the critical role of sulfur concentration in the photoelectrochemical (PEC) water splitting reactions of the CZTS photocathode. X-ray diffraction, transmission electron microscopy, UV–visible spectroscopy, impedance spectroscopy, capacity measurement, and PEC performance measurement were used to investigate the effect of precursor sulfur concentration on the structural, morphological, optical, and PEC performance of films. The half-cell solar-to-hydrogen efficiency of CZTS photoelectrodes increased as the sulfur content increased. The power conversion efficiency of the CZTS cathode constructed with CZTS nanoparticles synthesized with a 0.8 to 1.0 M precursor sulfur concentration was 0.32% at 0 V versus RHE under AM 1.5 illumination. The increase in crystallite size and charge carrier concentration is observed with increasing precursor sulfur concentration. By carefully adjusting the crystallite size and thus the charge carrier concentration of the CZTS material, the PEC water splitting efficiency of the CZTS photocathode can be improved. © 2022 Society of Photo-Optical *Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JNP.16.016001]

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1 Introduction

The conversion of solar energy into chemical fuels or electrical energy can successfully alleviate the current global energy issue.^{1,2} Photoelectrochemical (PEC) and photocatalytic methods are promising methods for producing chemical fuels such as hydrogen by splitting water or hydrocarbons by reducing CO_2 .^{3–7} In comparison to conventional chemical fuel production technologies, such as natural gas reforming/gasification reactions, hydrocarbon and methanol reforming, water electrolysis, the production of chemical fuels by artificial photosynthesis is an appealing method for achieving a fossil-fuel-free economy. Furthermore, the process is cost-effective, abundant, environmentally friendly, and requires little maintenance.^{8,9}

In the field of PEC-based water splitting systems, a remarkable amount of development has lately been made.¹⁰ Achieving a greater solar-to-hydrogen (STH) energy conversion efficiency is a great challenge; however, a 30% STH efficiency have been reported recently for a device fabricated coupling of a photovoltaic cell and an electrolyzer.¹¹ However, current research focuses

^{*}Address all correspondence to Jayasundera Bandara, jayasundera.ba@nifs.ac.lk

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on developing low-cost, extremely stable water splitting systems using PEC devices.¹² Copper zinc tin sulfide (CZTS) and NaSbS₂ are two potential solar semiconductor materials.^{13–15} CZTS, in particular, was discovered to be an important material due to its optimum bandgap of 1 to 1.5 eV and high absorption coefficient of 10⁴ cm⁻¹, as well as the fact that it is composed of Earth-abundant, low-cost, and low-toxicity elements.^{16,17} In a recent publication, a half-cell solar-to-hydrogen efficiency (HC-STH) of 2.1% has been reported by Wang et al. by forming a p-n junction through coupling of n-type CdS with p-type CZTS and protecting the CdS-CZTS photocathode with a thin ZnS layer,¹⁸ whereas Ros et al. reported a 7% HC-STH at 0V versus RHE with a CZTS/Se-based photocathode.¹⁹ Despite recent progress in CZTS photocathode for water splitting reactions, the major barrier and inherent problem in CZTS film fabrication is the formation of a high density of intrinsic defects and binary compounds within the film during deposition, which would result in reduced carrier diffusion length and carrier lifetime.²⁰ The characteristics of CZTS were enhanced by partially replacing Zn with Cd, which passivates the intrinsic defect, and Tay et al. found a fourfold increase in photocurrent and an HC-STH of 4%.²¹ Using hierarchical flower-like CZTS and dense CZTS nanosheets, improved PEC performance was recently reported, and the improved PEC performance was attributed to improved charge separation and a higher electrochemical active surface area.²² More research into CZTS synthesis methods is needed to prevent the creation of intrinsic defects and binary compounds in CZTS nanostructures, as they considerably lower the PEC performance.^{20,23,24}

The presence of ZnS and Cu₂S as secondary phases, as well as Cu_{Zn} antisites in CZTS films, has been identified as the primary factor limiting electrode performance.^{20,25} The formation of impure phases in CZTS films has been minimized or completely eliminated by varying the CZTS deposition methods, i.e., when CZTS films are fabricated in a vacuum by evaporation,²⁶ sputtering,²⁷ and pulsed laser deposition,²⁸ and the formation of ZnS and Cu₂S has been partially retarded. On the other hand, selective removal of Cu₂S and ZnS phases with etchants such as KCN and HCl, respectively, has been shown to improve solar cell performance.²⁹ Doping and alloying kesterites with alkali and other metals have also been proven to be effective methods of removing intrinsic structural defects.³⁰ The substitution of Cu_{Zn} antisites.²¹ Though several methods have been attempted to mitigate the formation of secondary phases during the synthesis of CZTS, none has shown to be highly effective.

In the mitigation and control of intrinsic defects and binary compounds in CZTS nanostructures, the research was mainly focused was on the role of the cations present in CZTS.³¹ Despite the sulfurization step, the source of sulfur, and the precursor sulfur concentration could also significantly contribute to minimizing the intrinsic defects in CZTS films, only the influence of sulfurization steps, i.e., varying the sulfurization temperature, time, sulfur quantity, atmospheric conditions, etc., has been thoroughly investigated, and less attention has been paid to the source of sulfur as well as the precursor sulfur concentration.^{32–35} However, the impact of precursor sulfur content on the quality of CZTS films and their PEC performance has yet to be thoroughly investigated. According to a review of the literature, the tendency for secondary phase formation increased as the concentration of thiourea increased. Changing the concentration of thiourea has also resulted in a high S content or S-rich CZTS thin film.^{36,37} In another study, Gupta et al. reported that a near-ideal stoichiometry could be achieved in CZTS by adding excess thiourea in a controlled manner.³⁸ Because there have been few studies on the influence of the precursor sulfur concentration on the structural, optical, morphology, and electrical properties of CZTS thin films prepared by thermal evaporation.

2 Experimental Details

2.1 Synthesis of CZTS Nanoparticles and the Fabrication of Thin Film CZTS Photocathodes

In this study, CZTS films were fabricated using a two-step process. First, CZTS powder was prepared by varying the sulfur ratio of the precursor solution, followed by thermal evaporation of CZTS powder on a fluorine-doped tin oxide (FTO) glass substrate. For the preparation of

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CZTS nanoparticles, a precursor solution was prepared from aqueous solutions consisting of CuCl₂·2H₂O (0.2 M), ZnCl₂ (0.1 M), and SnCl₂·2H₂O (0.1 M). For this solution mixture, 0.2, 0.4, 0.6, 0.8, and 1.0 M thiourea in a solvent mixture of acetic acid, distilled water, and ethanol in the ratio of 2:3:5 were added separately and stirred at room temperature for 1 h at a 500 rpm rotating speed to form a clear yellow solution. The solution was evaporated, and the powdered sample was sintered with a sulfur stream under nitrogen gas flow for 1 h at 350°C. S01, S02, S03, S04, and S05 were assigned to CZTS samples synthesized with thiourea concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 M, respectively. For thermal evaporation of CZTS onto the conducting substrate, a pellet was made from the CZTS powder generated after sintering and the evaporation was carried out by applying 5 V voltage, 75 A current, and 1×10^{-4} mBar vacuum.

2.2 Characterization and PEC Performance Measurement of CZTS Films

A PANalyticalX'pert diffractometer (X'Pert PRO MPD, PW3040/60) with Cu K α (= 0.154060 nm) radiation and a scanning step of 10 deg per minute was used to study the crystal structure of the various phases of the CZTS powder samples and films. A Hitachi S-4800 field emission scanning electron microscope (SEM) was used for surface morphology analysis, and JEM-2100 microscopes operating at 200 kV were used for transmission electron microscopy (TEM) and high-resolution TEM images. The elemental compositions of the samples are determined using energy-dispersive x-ray spectroscopy (EDS). A HORIBA JY, LabRAM HR800 Raman Spectroscopy System with a 514-nm laser was used for Raman spectroscopy measurements. A Shimadzu UV-2450 UV-VIS spectrophotometer was used to examine the optical properties of the samples.

The electrode performance of the CZTS thin-film photocathode was investigated in a threeelectrode PEC cell using the ZAHNER ZENNIUM electrochemical workstation under chopped illumination. The current density-potential curves were measured both in the dark and with a 300-W Xe lamp (calibrated with a standard Si solar cell to simulate AM 1.5 illuminations) at a light intensity of 100 mW/cm² and an electrolyte solution of $0.5 \text{ M Na}_2\text{SO}_4$ (pH 6.5). The linear sweep voltammetry scan rate was 10 mVs⁻¹. The capacitance and impedance of the CZTScoated FTO glass plates were measured at different frequencies at pH 6.5 in a 0.5 M Na₂SO₄ electrolyte solution with a ZAHNER ZENNIUM electrochemical workstation. All measurements were taken with a 100 mW/cm² irradiation. The incident photon to current efficiency (IPCE) was measured at 0 V versus RHE using the Bentham PVE300 unit and a TMC300 monochromator-based IPCE with a Xenon arc lamp in the wavelength range 300 to 1200 nm.

3 Result and Discussion

To optimize the structural, morphological, optical, and electrical properties of CZTS films, the initial sulfur content in the precursor solution was varied, and Table 1 shows the initial metal salts and thiourea molar composition used in the synthesis of CZTS nanocrystals. The steps involved in the synthesis of CZTS nanoparticles are described in reactions Eqs. (1)-(3):³⁹

$$\mathbf{M} - \mathbf{X} + \mathbf{T}\mathbf{u} \to [\mathbf{M}(\mathbf{T}\mathbf{u})\mathbf{m}] - \mathbf{X},\tag{1}$$

1

1

1

| Cu | Zn | Sn | S |
|----|--------------|---|--|
| 2 | 1 | 1 | 2 |
| 2 | 1 | 1 | 4 |
| | Cu 2 2 | Cu Zn 2 1 2 1 | Cu Zn Sn 2 1 1 2 1 1 |

1

1

1

2

2

2

Table 1 Initial molar composition of metal salts and thiourea.

6

8

10

S03

S04 S05



Fig. 1 (a) Photoelectrochemical performance of CZTS photocathode fabricated with different *S* ratios in $1M Na_2SO_3$ solution (pH 7) under chopped solar-simulated AM 1.5G light irradiation. (S01, S02, S03, S04, and S05 represent the thiourea concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 M, respectively), (b) Expanded *IV* curves of S01 and S04.

$$[M(Tu)m] - X + C_2H_5OH \rightarrow [M(Tu)m] - OC_2H_5 + H - X, \qquad (2)$$

$$Tu - M1 - \ddot{O} - C_2H_5 + Tu - M2 - \ddot{O} - C_2H_5 + Tu - M3 - \ddot{O} - C_2H_5 \xrightarrow[360^{\circ}C]{} Cu_{1-2}Zn_{1+2}SnS_4$$
(3)

In the first step, a thiourea-metal complex ([M(Tu)m] - X) is formed, and this complex then reacts with alcohols to form thiourea-metal alkoxide $([M(Tu)m] - OC_2H_5)$. CZTS nanocrystals are formed in the final step during the sintering process at 350°C by the thermal decomposition of the thiourea-metal-alkoxide complex according to the reaction Eq. (3). As shown in reactions Eq. (1) to Eq. (3), the formation of CZTS is highly dependent on the initial sulfur concentration, the physical and electrical properties of CZTS can be easily manipulated.

Figures 1(a) and 1(b) show the PEC water splitting performances of CZTS/FTO photocathodes (i.e., S01, S02, S03, S04, and S05) under AM 1.5 illumination and chopped light, and the expanded I - V curves of S01 and S04 photocathodes, respectively. The photoactivity was determined by measuring the photocurrent density produced by illumination, where the current density produced by illumination represents the amount of solar energy converted into electrical energy and stored as chemical energy in the electrochemical cell. The gradual increase of the negative photocurrent when the potential is swept more negatively confirms the p-type PEC behavior and electron injection into the electrolyte at the interface of different CZTS/FTO cathodes, as shown in Fig. 1. Notably, the dark currents observed in various CZTS/FTO electrodes are extremely low. According to the PEC results shown in Fig. 1, there is a clear increase in photocurrent with increasing sulfur precursor concentration, with a maximum photocurrent density of 3.0 mA/cm² observed when the S content was equal to 0.8 M (sample S04) and almost leveling off above 0.8 M. (sample S05). Using the current-potential curves, the HC-STH is calculated to be 0.15, 0.20, 0.25, 0.32, and 0.31% at 0.22 V RHE for S01, S02, S03, S04, and S05 electrodes, respectively.^{40,41} The significantly lower dark current in photocataode S04 than in S01, as shown in Fig. 1(b), indicates a better rectification factor and thus a better charge separation in the CZTS prepared with a S content of 0.8 M.

Figure 2 shows the IPCE measurements of the CZTS/FTO electrodes S01 and S05. The increase in IPCE observed across wavelengths 400 to 900 nm indicates improved charge separation and transport to the electrolyte with an increase in precursor sulfur concentration and is consistent with the observed cathodic photocurrent in the PEC results shown in Fig. 1.



Fig. 2 IPCE spectra of CZTS films (a) S01 and (b) S05 photocathodes in $1M Na_2SO_3$ solution under the bias voltage of -0.5 V.

These findings imply that varying the initial precursor sulfur concentration is an effective way to improve CZTS PEC performance.

It is well understood that the enhancement of the water-splitting reaction of a photocathode is highly related to the increase in diffusion lengths of minority charge carriers that affect the charge collection efficiency. As a result, the observed improvement in PEC performance of CZTS fabricated with higher sulfur concentrations could be attributed to bulk properties of CZTS, such as improved crystallinity, electronic properties, and/or the enhancement of the porous structure.⁴² Hence, the optical and electrical properties of bulk CZTS were investigated to correlate the improvement in PEC performance of CZTS electrodes to the variation of bulk CZTS properties with increasing initial precursor sulfur concentration and are presented in the sections that follow.

The crystalline and material phases in CZTS films fabricated with different sulfur concentrations were identified using low angle x-ray diffraction studies. The presence of the characteristic 2θ diffraction peaks for kesterite CZTS at 28.5 deg (112), 33.0 deg (200), 47.3 deg (220), and 56.3 deg (312), as shown in Fig. 3, is consistent with the JCPDS reference (PDF #260575), as well as other reported values that confirm the formation of kesterite CZTS.^{43,44} Importantly, the presence of intense peaks at 28.0 deg, 33.0 deg, 47.3 deg, and 56.3 deg indicates the



Fig. 3 XRD patterns of CZTS films of S01, S02, S03, S04, and S05 on FTO substrate.

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| Sample | 20 | FWHM | Crystallite size (nm) |
|--------|---------|--------|-----------------------|
| S01 | 28.4947 | 0.8243 | 10.39 |
| S02 | 28.4221 | 0.8012 | 10.69 |
| S03 | 28.4883 | 0.5709 | 15.02 |
| S04 | 28.3525 | 0.5203 | 16.47 |
| S05 | 28.4807 | 0.5123 | 16.79 |

Table 2 Crystallite size of CZTS with different S ratio at (112) planes.

polycrystalline nature of the kesterite structure of CZTS, whereas the dominant diffraction peak at 28.0 deg (112) indicates the preferential crystallite orientation in the (112) direction. Furthermore, as shown in Fig. 3, the increase in peak intensity of the (112) plane of CZTS thin films is greater than that of the (200), (220), and (312) planes, implying preferential formation of CZTS crystallites with the 112 orientation as precursor thiourea concentration increases.

The sizes of CZTS crystallites calculated from the (112) plane using Debye–Scherrer's formula, $D = k\lambda/\beta \cos \theta$, as a function of precursor thiourea concentrations are shown in Table 2. In Debye–Scherrer's formula, D is the crystallite size, k is the Scherrer constant, λ is the wavelength of Cu K α (0.15406 nm), β is the full-width at half-maximum (FWHM) of (112) peak, and θ is the Bragg angle. As given in Table 2, with the increase in sulfur concentration, the FWHM values showed a decreasing tendency and conversely, the crystallite size of CZTS showed an increasing trend. The estimated maximum and minimum crystallite size (D) of CZTS at the highest and lowest thiourea concentrations are 16 and 10 nm, respectively. X-ray diffraction (XRD) analyses revealed the formation of smaller crystallite sizes at lower precursor sulfur concentrations, and as the precursor sulfur concentration increased, the formation of larger and higher density CZTS crystallites with a preferential (112) orientation was clearly visible.

The absence of diffraction peaks at 27.10 deg and 31.88 deg, which correspond to the CuS and SnS phases, respectively, confirms that secondary phase formation was inhibited during CZTS synthesis.^{45,46} Therefore, Raman spectroscopy was used to distinguish ZnS and CTS impure phases from CZTS, due to XRD measurements alone cannot confirm the formation of single-phase kesterite due to overlapping of the diffraction patterns of CZTS, ZnS, and CTS (Cu₂SnS₃), and the results are shown in Fig. 4.⁴⁷ The Raman spectra of CZTS films synthesized with a lower sulfur precursor concentration are overshadowed by strong fluorescence peaks, making the Raman peaks of CZTS films synthesized with a lower sulfur precursor concentration difficult to see. However, as shown in Fig. 4, weak Raman peaks can be identified for



Fig. 4 RAMAN spectra of CZTS films of S05.

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Fig. 5 SEM images of CZTS samples S01, S02, S03, S04, and S05 synthesized by varying the thiourea concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 M, respectively.

CZTS films fabricated with higher sulfur precursor concentrations. While the main Raman peak at 336 cm⁻¹ can be attributed to the kesterite CZTS structure and the presence of shoulder peaks at 316, 348, and 351 cm⁻¹ in the main peak indicated the possibility of forming ternary CTS and binary ZnS phases.^{20,47} Hence, from XRD and Raman measurements, it is evident that the CZTS thin film fabricated with a higher precursor sulfur content is composed of kesterite CZTS as the major phase and ZnS and CTS as minor phases, with no other secondary phases, such as CuS and SnS.

The morphological differences of CZTS nanostructures formed with varying precursor sulfur concentrations were studied using SEM and TEM. The SEM images in Fig. 5 show the formation of agglomerated nanoscale particulate clusters of CZTS particles, resulting in a very rough surface with varying precursor sulfur concentrations. A closer look at these images reveals that the surface roughness of the CZTS films prepared with higher sulfur concentrations. Dense and larger nanoclusters with larger CZTS nanoparticles were observed at higher sulfur concentrations sulfur concentrations. TEM and HRTEM images of the corresponding CZTS NCs synthesized with various sulfur concentrations are shown in Fig. 6 for further evaluation of the size and morphology of CZTS nanoparticles fabricated with various sulfur initial concentrations.

The TEM micrographs clearly show the dispersion of particles with a size of 15 nm at lower sulfur concentrations. However, as the sulfur concentration increased, some of the smaller nanoparticles began to grow into larger particles, and the presence of 20- to 25-nm size CZTS particles was observed at the highest sulfur concentration. The major lattice spacing in highresolution TEM images of CZTS nanoparticles synthesized at different sulfur concentrations was found to be 0.31 nm, which can be attributed to the lattice spacing of (112) planes for kesterite CZTS NCs and is completely consistent with XRD measurements.²⁴ Furthermore, the lattice spacing of 0.19 nm, which corresponds to the (220) plan of the CZTS structure, can be seen in all images. Hence, the formation of highly crystalline CZTS nanoparticles is evident by the observation of clear lattice fringes throughout the entire CZTS nanoparticles synthesized at higher sulfur concentrations.⁴⁸ The absence of 0.33 nm lattice fringes, which corresponds to the (100) plane of CuS, confirms the absence of CuS as the secondary phase in CZTS nanostructures synthesized at higher sulfur concentrations. However, the presence of a few ZnS particles with a lattice spacing of 0.29 nm, which corresponds to the (011) plane of ZnS in CZTS nanocrystals, is clearly visible as a secondary phase. According to the XRD, Raman, and TEM analyses, the suppression of the formation of CuS and SnS phases with increasing sulfur concentration can be noted, and thus the absence of these secondary phases is beneficial in minimizing charge recombination in the CZTS photocathode. Furthermore, it is possible to conclude that increasing precursor sulfur concentrations promotes the formation of well-crystalline CZTS crystallites Abeykoon et al.: Significant role of the initial precursor sulfur concentration in the photoelectrochemical...



Fig. 6 TEM and HETEM images of CZTS samples S01, S02, S03, S04, and S05 synthesized by varying the thiourea concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 M, respectively.

with large grain sizes. As the grain size of the CZTS films plays an important role in determining the PEC performance, in which a large CZTS grain size is preferred due to improved charge transport properties over small grain-sized film, enhanced PEC performance can be expected with larger CZTS grains.⁴⁹ Furthermore, the large grains in the film help to reduce charge carrier recombination at grain boundaries, resulting in increased charge carrier lifetime.

To analyze the composition of the CZTS film, a certain area of the film was mapped by EDS, and the element distributions are shown in Fig. 7. It is clear that copper, tin, and sulfur were homogeneously distributed in the entire area of the films of different CZTS fabricated with different sulfur concentrations. However, the Zn distribution is found to be inhomogeneous, with higher Zn distributions observed as sulfur concentration increased, which could be due to the formation of secondary ZnS phases, which is completely consistent with Raman measurements.

The absorbance's of CZTS thin films were measured using a UV–VIS spectrophotometer to investigate the variation of optical properties of CZTS films with sulfur concentrations and the results are shown in Fig. 8. The optical energy band gaps of CZTS thin films were evaluated using the Tauc relation, $\epsilon h\nu = C(h\nu - E_g)^n$, where ϵ is the absorption coefficient in (cm⁻¹), *h* is the Planck constant in (Js), ν is the frequency of radiation (Hz), *C* is the proportionality factor called Tauc parameter, E_g is the optical energy band gap (eV), *n* is the parameter connected with the distribution of density of states, and its value is ½ for allowed direct energy band gap.^{39,46} The calculated onsets of absorption of S01, S02, S03, S04, and S5 by UV–VIS spectroscopy measurements are 1.55, 1.6, 1.65, 1.7, and 1.77 eV, respectively, indicating that the onset of



Fig. 7 EDEX analysis of CZTS samples S01, S02, S03, S04, and S05 synthesized by varying the thiourea concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 M, respectively.



Fig. 8 UV–VIS diffuse reflectance spectra of CZTS samples S01, S02, S03, S04, and S05 synthesized by varying the thiourea concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 M, respectively. Inset shows the Tauc plot showing band gap energy of the same samples.

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Fig. 9 Mott–Schottky plots of the CZTS samples S01, S02, S03, S04, and S05 synthesized by varying the thiourea concentrations.

absorption increases with sulfur concentrations. The increase in bandgap may be due to a decrease in average particle size as sulfur concentration increases. Because XRD analyses revealed an increase in particle size from 10 to 16 nm with increasing sulfur concentration, and hence, the observed increase in bandgap with increasing sulfur concentration cannot be attributed to the quantum size effect.

Flat band (FB) potentials and charge carrier density are important factors influencing PEC performance. The Mott–Schottky (M–S) analysis was used to investigate the FB potentials and charge carrier density, and Fig. 9 shows a typical M–S plot of $1/C^2$ versus V(RHE) of different CZTS nanostructures fabricated with different *S* concentrations.⁴⁷ The observed negative slopes of M–S plots of CZTS films indicate that CZTS NSs fabricated in sulfur concentrations ranging from 0.2 to 1.0 M are p-type. FB potentials and acceptor concentrations of various CZTS NSs synthesized were calculated by intercepting the M–S curve with the *x* axis and calculating the slope of the M–S plot, respectively, and are shown in Table 3. The majority charge carrier concentrations (acceptor density) of different CZTS were estimated by Mott–Schottky curves using the following equation:^{50,51}

$$\frac{1}{C^2} = \frac{2}{qN_{\rm SC}\kappa\varepsilon_0 A^2} \left(V - V_{\rm fb} - \frac{\kappa T}{q} \right)$$

where C is the capacitance, ε is the relative permittivity, ε_o is the permittivity of free space, q is the electric charge, N_{sc} is the doping density, V is the applied voltage, V_{fb} is the FB potential, k is the Boltzmann constant, A is the area of the electrode, and T is the temperature.

| Sample | FB potential (V) | CB (eV) | Charge carrier concentration (cm ⁻³) | Bandgap energy (eV) | | |
|--------|------------------|---------|--|---------------------|--|--|
| S01 | 0.187 | -1.36 | 3.53×10^{19} | 1.55 | | |
| S02 | 0.159 | -1.42 | 4.82×10^{19} | 1.58 | | |

 6.86×10^{19}

 7.03×10^{19}

 7.73×10^{19}

Table 3 FB potential, charge carrier concentration, and bandgap energy of CZTS films with different *S* ratio.

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S03

S04

S05

1.65

1.71

1.76

0.094

0.062

0.030

-1.55

-1.64

-1.73



Fig. 10 EIS of the CZTS samples S01, S02, S03, S04, and S05 synthesized by varying the thiourea concentrations. Dotted points are experimental values and the fitted results are shown by straight lines.

The calculated band energy positions for CZTS NSs in Table 3 show that CZTS synthesized with different sulfur concentrations can effectively drive the hydrogen generation reaction because the bottom of the CZTS nanostructures' conduction band (CB) is located above the hydrogen reduction energy (-1.2 eV versus RHE).⁵² Importantly, the observed onset potentials for S01 (0.60 V RHE) to S05 (0.60 V RHE) in the respective photocurrent-potential profiles shown in Fig. 1 are consistent with the measured FB potentials of S01 (0.70 V RHE) to S05 (0.58 V RHE) by capacitance measurements. As shown in Table 3, increasing the precursor S concentration increases free charge carrier densities while decreasing the FB potentials of CZTS NSs. Consequently, the charge carrier analysis results strongly support the improved PEC performances of CZTS films fabricated with a higher initial S concentration, i.e., because the negative shift of the CB position of CZTS nanostructures favors the charge transfer kinetics for the hydrogen generation reactions, and thus enhanced hydrogen production with CZTS nanocrystals fabricated with a higher sulfur concentration can be justified. Furthermore, because higher donor concentrations can improve charge separation and transport by increasing charge carrier transfer at the electrode-electrolyte interface, the PEC performance of CZTS electrodes with higher donor concentration is expected to be better.^{53,54} In addition, increased charge carrier concentration causes increased band bending, which may provide a driving force for charge separation, but the narrow depletion region effectively prevents charge carrier separation.⁵⁵

EIS analyses were used to investigate the charge transport and recombination at the heterostructural interface in different CZTS photocathodes, and the Nyquist plots of different CZTS photocathodes fabricated with varying sulfur concentrations are shown in Fig. 10. The equivalent electronic circuit used to fit the impedance spectra is shown in the inset of Fig. 10. In the equivalent circuit, R_s , R_{ct} , R_{rc} , C_1 , and W are the ohmic series resistance of the electrode system, electrons transport resistance in CZTS, charge transfer resistance of the charge recombination process at the photoelectrode/electrolyte interface, the double layer capacitance at the electrode– electrolyte interface, and Warburg function, respectively.⁵⁶ Table 4 shows the fitted R_s , R_{ct} , and R_{rc} values, and it can be seen that the R_{ct} of the CZTS films increases slightly while the R_{rc} increases significantly as the sulfur concentration increases.

According to EIS analysis, the R_{rc} is inversely proportional to the charge recombination rate of the device, whereas the R_{ct} is proportional to electrical conductivity and a device with a higher R_{rc} and a lower R_{ct} should provide better PEC performance. Accordingly, a better PEC performance of CZTS films fabricated with higher sulfur concentrations can be justified further dueto high R_{rc} values. According to EIS analyses, the improved PEC performance of CZTS films fabricated with higher sulfur concentrations can be attributed primarily to easier electron transfer to the electrolyte, thereby enhancing water splitting reactions, and this behavior can be linked to Abeykoon et al.: Significant role of the initial precursor sulfur concentration in the photoelectrochemical...

| Sample | R_s (Ω) | R _{ct} (kΩ) | R _{rc} (kΩ) | τ (μS) |
|--------|--------------------|----------------------|----------------------|--------|
| S01 | 43.10 | 5.42 | 7.05 | 1.06 |
| S02 | 37.12 | 6.31 | 11.02 | 1.04 |
| S03 | 36.86 | 7.86 | 37.17 | 1.05 |
| S04 | 28.72 | 10.04 | 40.38 | 0.82 |
| S05 | 27.96 | 10.55 | 79.74 | 0.82 |

Table 4 Equivalent circuit parameters by best fitting impedance data with different S ratio.

an increase in grain size and a decrease in grain boundaries, which is consistent with structural and morphological studies.

Therefore, based on the surface morphology and charge carrier dynamics analyses, the PEC performance of CZTS films fabricated with different sulfur concentrations could be attributed to several factors. In comparison to small grain-sized films formed at lower sulfur concentrations, larger CZTS crystallites with larger grain sizes formed at higher sulfur precursor concentrations may result in improved charge transport properties. In addition, the presence of large CZTS grains in the film reduces photogenerated carrier recombination at grain boundaries, resulting in increased charge carrier lifetime. Moreover, the increase in crystallinity and crystallite size of CZTS nanoparticles with higher donor concentrations formed at higher *S* concentrations may contribute to improved PEC performance by shifting the CB negatively and easing charge carrier transfer at the electrode–electrolyte interface.

4 Conclusion

In this investigation, CZTS nanostructures with different optical and electrical properties were synthesized by varying the initial precursor sulfur concentrations, and the corresponding CZTS thin films were grown on FTO substrates via thermal evaporation. By varying the initial precursor sulfur concentration, crystallite size, bandgap as well as valence band edge position, charge carrier concentrations as well as charge transport properties, etc. of CZTS can be manipulated to improve PEC performance and hydrogen generation by water splitting. The improved PEC performance of CZTS fabricated with higher sulfur concentrations is due primarily to improvements in crystallinity, crystallite size, donor concentrations, and a negative shift in CB energy, which facilitates charge carrier transfer at the electrode–electrolyte interface. Furthermore, the large grains in the film help in reducing photogenerated carrier recombination at grain boundaries, resulting in increased charge carrier lifetime. As a result, it was demonstrated that by simply varying the initial precursor sulfur concentration, the optical and electrical properties of CZTS can be optimized for the fabrication of efficient photocathodes.

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Lahiru K. Abeykoon is currently an MPhil research assistant in the energy and advanced material chemistry research group in the National Institute of Fundamental Studies (NIFS). He received his BSc degree (applied sciences) special degree in applied physics from Sabaragamuwa University of Sri Lanka (SUSL) in 2015. His research interests include the synthesis, characterization, and applications of various nanostructured materials for energy conversion.

Hong-Yi Tan is currently a research fellow of the Hydrogen Production and Utilization Lab in Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. He received his PhD in material science from the University of Chinese Academy of Sciences in 2016. His current research interests include nanostructured materials, electrocatalysis, and reforming catalyst for hydrogen production and utilization.

Chang-Feng Yan works as the head of the Hydrogen Production and Utilization Lab in Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. He received his PhD from the University of Science and Technology of China in 2005. He has been working on electrocatalysis and photoelectrochemical technologies for hydrogen production and utilization. His recent research focuses on electrocatalyst and electrochemical cell design and architecture for water splitting and fuel cells.

Jayasundera Bandara has been a senior research professorin the National Institute of Fundamental Studies, Sri Lanka, since 1999. He received his PhD from Swiss Federal Institute of Technology in Lausanne (EPFL) in 1998. His research is focused on novel materials and nanostructures for application in dye/q-dot sensitized solar cells, conversion of solar energy into chemical fuels (water splitting and reduction of carbon dioxide) and environmental remediation.