Controlling $\text{Cu}_2\text{ZnSnS}_4$ photocatalytic ability through alterations in sulfur availability[†]

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[†] Dedicated to Prof. Dr Gerhard Ertl for his pioneer research on modern surface chemistry.

Abstract

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanocrystals (NCs) were made via a one-pot solvothermal method with various amounts of available free-sulfur and a fixed amount of sulfur bound to 2-mercapto-5-n-propylpyrimidine (MPP). Varying the sulfur availability yields CZTS NCs of different stoichiometry, from which five distinct samples were analyzed for consistency both microscopically and macroscopically. As revealed by X-ray absorption fine structure investigation, samples fabricated in the presence of decreased free-sulfur showed decreased CZTS character, with sporadic compositions and no long term order; however, when fabricated in the presence of no free-sulfur, sulfur from the degraded MPP was found incorporated into the CZTS structure. These NCs showed improved long-term order over standard synthetic procedure. The catalysis of methyl viologen (MV) from MV^{2+} to MV^+ state by CZTS under light irradiation was used as the probe to test the photovoltaic nature. The photocatalysis was enhanced in the films made from NCs fabricated without available free-sulfur. This enhancement is consistent with the measured band gaps, with more ordered NCs showing a band gap that better matches the most intense regions of the solar spectrum.

Keywords: $\text{Cu}_2\text{ZnSnS}_4$ (CZTS); Synchrotron spectroscopy; X-ray absorption fine structure; Photocatalysis; X-ray diffraction; Optical band gap

1. Introduction

Semiconductor nanocrystals (NCs) for use in thin film photovoltaics have shown great promise as a source for renewable solar energy, especially those such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) that contain only cost-effective and non-toxic elements [1-4]. These materials are comprised of elements abundant around the globe, making them prime candidates for marketable high-efficiency solar cells [5-7]. CZTS is a p-type semiconductor with a tunable direct energy band gap of 1.4-1.5 eV and a high absorption coefficient $> 10^4 \text{ cm}^{-2}$, with device efficiencies greater than 10% [8, 9]. Unfortunately, the methods for making these high efficiency CZTS cells are in themselves energy intensive, and high-cost, severely limiting the usefulness of these cells [3, 5-7, 10]. The whole purpose for moving to CZTS from other alternatives like $\text{CuIn}_x\text{Ga}_{(1-x)}\text{S}_2$ (CIGS), or CdTe [11] will be compromised if it involves high-cost, energy intensive processes. Therefore, one has to devise a method for regulating NC growth without the use of such energy intensive processes [12].

Our solvothermal process for CZTS production has been shown to be an effective way of fabricating the NCs at low-cost [5, 13, 14]. The resultant NCs show a high consistency in composition and structure, producing predominantly the ideal kesterite structure with few secondary phases, though the relationship of the starting materials ratio against final compositions is not clear [14, 15]. Systematic improvements to the NC quality, the NC films, and ultimately the device efficiency require correlation between the changes made in starting material and the final NC outcome.

Ideal CZTS NCs are of kesterite crystal structure – of the space group $I\bar{4}$ – with a relatively Cu-poor and Zn-rich composition [5, 16, 17]; however, fabricated CZTS can form an alternate stannite structure – of the space group $I4_2m$ – and both crystal structures can form in Cu-rich, Zn-poor compositions. The fabrication of the desired crystal structures requires careful control of the conditions and the starting ratios; this becomes a challenge when using solution phase synthesis as the final compositions do not correspond directly to the initial starting ratios [16-18]. Present work has focused on exploring this trend, and determining the effects of changes in starting conditions on the final NCs. Particular attention is paid to the delivery of sulfur to the system.

Crystal structure and related photoactivity have been previously reported with respect to the effects of Cu-poor, Cu-stoichiometric, and Cu-rich NCs fabricated solvothermally. The effects of these changes were studied on the photocatalytic conversion of methyl viologen (MV) from the oxidized MV^{2+} to the reduced MV^+ [5, 14]. While promising, tighter control over NC formation would result in long term improved order, and thus tighter films. To achieve this, alterations in sulfur content were investigated with respect to sulfur presence in both free and organic capping-ligand-bound forms as a method for controlling the fabrication environment. Sulfur-containing precursors are known to aid in producing more uniform films [1], which is suggestive of highly conserved NC structure. By changing the sulfur content, and the method by which sulfur is supplied, it is anticipated that long-term NC order can be achieved.

CZTS composition was studied using energy dispersive X-ray spectroscopy (EDX), and compared against precursor sulfur-content to determine the relationship between sulfur availability and NC composition. Distinct samples were selected for analysis by powder X-ray diffraction (XRD), and X-ray absorption fine structure (XAFS), to determine local and long-range crystal structure, and to elucidate the effect of sulfur addition on the final NC structures. NCs were then deposited in a thin-film. The films were tested by measuring the catalytic conversion of MV^{2+} to MV^+ in the format of photoelectrochemical measurements (PECMs). Higher catalytic conversion is indicative of higher photovoltaic response and thus allows for the determination of improvements in the absorber layer for use in solar cell devices. Band gap analysis using ultraviolet-visible (UV-vis) spectroscopy was performed to ensure the top-performing NCs having ideal band gap for future devices. XAFS is another powerful tool in addition to other synchrotron spectroscopy techniques [19, 20] for energy materials.

2. Experimental

2.1. Synthesis and film formation

CZTS NCs were synthesized in a modified one-pot solvothermal process as published elsewhere [14]. Metal precursor salts of copper(II) acetylacetonate (acac) (Sigma-Aldrich 97%), and tin(II) chloride (Alfa Aesar 98%), with zinc(II) acetylacetonate (Sigma-Aldrich 95%) substituted for zinc (II) chloride (Sigma-Aldrich 98%), were briefly dissolved in benzyl alcohol (BA) (Sigma-Aldrich 99.8%) at 160 °C. 2-mercapto-5-n-propylpyrimidine (MPP) was added to the solution along with 0.2 M thiourea (TU) (Fluka 99.0%) in BA. The MPP and TU

concentrations were varied specifically in this work to alternate the free-S and S in ligand form. The reaction vial was then heated at 180 °C for 10 minutes to decompose TU and allow S to react with the metal precursors, and to facilitate ligand-S association to the metals precursors. The resulting dispersed CZTS NCs were cooled down, and then transferred into centrifuge tubes for separation using a Thermo Scientific Sorveall Legend Micro 21 centrifuge at 12.0×10^3 times gravity for 6 minutes. The liquid was removed and the particles were washed and dispersed in solvents such as acetone, isopropanol, and ethanol using a 1510 Branson Sonicator at 40 kHz for a minimum of 5 minutes. The washed NCs were then allowed to air dry for no less than 30 minutes. For NC compositional studies, the dried crystals were stored under normal atmospheric conditions in a dry environment for additional 24 hours to remove trace amounts of solvent prior to analyzing. For dropcasting, NCs were redispersed in acetone before being dropcast in a predetermined surface area of 10 mm^2 on molybdenum-coated glass. The glass functions as the back contact (BCs), which were pretreated by immersing in 2% Hellmanex for 2 min and rinsing with ethanol, isopropanol, and deionized water prior to use.

2.2. Characterization

Structural and compositional analyses were performed using EDX with scanning electron microscopy (SEM), XRD, and XAFS using synchrotron radiation. A Hitachi S-4500 field emission microscope with a 100 kV EDX system was used for EDX/SEM. An Inel CPS Powder Diffractometer with an Inel XRG 3000 Cu X-ray generator with an Intel CPS 120 detector provided the XRD data. Sn K-edge EXAFS measurements were performed at the PNC/XSD 20-BM beamline of the Advanced Photon Source (APS) at Argonne National Laboratory, Argonne, IL. Thin uniform NC samples were prepared on Kapton tape, and the tape was folded to a thickness of about 1-2 absorption lengths ($1/\mu$ where μ is the absorption coefficient). A Si (111) monochromator and a 400 μm vertical slit was used over a 29.0 to 30.1 keV range. The detection mode was fluorescence X-ray yield recorded using a 13-element Canberra detector. The samples were placed at 45° with respect to the incident photons, and the fluorescence detector was placed at 90° with respect to the incident photons. The detector count rate was kept below 50,000 counts to prevent detector saturation. All spectra were normalized to the incident photon flux, I_0 . Reference Sn foil (EXAFS Materials Inc.) with a thickness of 50 μm , used for energy calibration, was measured in transmission mode downstream of the sample between two ion chambers filled with an 85:20 sccm N_2/Ar mixture. With a software package of Athena and

Artemis, fluorescence yield was plotted over the corrected energy range by normalizing the pre-edge to zero and the post-edge to unity. Normalized spectra were converted using the Fourier Transform with k^2 weighting from $k = 1.0$ to $6.5 \text{ \AA}^{-1}$ to obtain the peaks in R space [21].

CZTS NCs were analyzed for current density generated by its photocatalytical conversion of MV^{2+} to MV^+ by PECMs, Scheme 1[5, 13-15, 22, 23]. NCs were dispersed in acetone or isopropanol at a concentration of 20 g/L and dropcast onto a 10 mm^2 area of the above cleaned BC. The BC was connected to the electrode, standardizing contact area to ensure reproducibility between samples. The cast CZTS films were then immersed in an electrolyte solution of 0.05 M MV^{2+} (Sigma-Aldrich 98%) and 0.1 M potassium chloride (Sigma-Aldrich 99.0%). Using a three-electrode system, potential was measured via the film electrode and a saturated calomel electrode, while current was measured via the film electrode and a platinum counter electrode to obtain PECMs. Light from a 150 W Newport Xe lamp with an AM 1.5 filter was used as a sun simulator and was shone periodically at 0.33 Hz on the sample in controlled sequence using a ThorLabs SC10 shutter. The photocatalytic current was collected using a CHI 832a electrochemical analyzer over a linear potential sweep from 0.0 to -0.4 V at a scan rate of 5 mV/s.

CZTS band gaps were determined through UV-vis absorption by means of a Varian Cary 50 spectrometer using 20 mM CZTS dispersions in acetone. The scans were carried out at a rate of 1 nm/s from 1100 to 400 nm, and the resulting absorption converted to generate a plot relating the absorption coefficient to the wavelength energy, known as a Tauc plot.

3. Results and Discussion

3.1. Structural Properties

Fabricated NCs were characterized to determine their crystal phase and electronic properties for optimization prior to their photocatalysis measurements. Initial optimization was focused on the composition to obtain a correlation between reactant ratios and the resultant NC composition with respect to the sulfur content. Contributions to the sulfur content came from both thiourea and MPP capping ligand, though the extent of the contribution from the capping ligand is not well known. Table 1 outlines the effects of decreasing thiourea content on the final NC stoichiometries by focusing on specific permutations of the reduction.

Table 1. Sulfur Content Associated with TU and MPP and its Effects on Final NC Composition

Sample	Initial Element Ratio	Final Element Ratio in
	Cu:Zn:Sn:TU:MPP (mol)	CZTS Cu:Zn:Sn:S
M1	1.7 : 1.6 : 1.0 : 3.3 : 7.7	2.1 : 1.3 : 1.0 : 4.2
M2	1.7 : 1.6 : 1.0 : 2.5 : 7.7	2.2 : 0.8 : 1.0 : 4.7
M3	1.7 : 1.6 : 1.0 : 1.6 : 7.7	2.1 : 0.7 : 1.0 : 5.5
M4	1.7 : 1.6 : 1.0 : 0.8 : 7.7	1.7 : 1.6 : 1.0 : 4.0
M5	1.7 : 1.6 : 1.0 : 0.0 : 7.7	1.9 : 1.1 : 1.0 : 4.0

Initial reductions in TU from sample M1 to M3 showed an inverse relationship with final sulfur, with a 50% decrease in TU resulted in an increase in sulfur content by 30%, which can be attributed to more complexation between metal precursors and sulfur in MPP, similar to sulfurisation of co-sputtered metallic and sulfur-containing precursor films [1]. With decreased availability of free S from TU, the number of metal-sulfur complexes associated with free S will be decreased due to decreasing sulfur presence, reducing the available CZTS nucleation sites. This again appears similar to that in sulfurisation process of co-sputtered metallic and sulfur-containing precursor films [1]. The above S reduction also allows for additional complexation between the metal and the capping ligand to occur. This in turn leads to additional capping ligand presence within the final product as a result of increased MPP-metal bonds, and thus an increase in sulfur content is observed in the final NCs [24]. The resultant decrease in Zn content is likely an effect of additional Cu-on-Zn type antisite defects (Cu_{Zn}) [4, 25, 26]. The fact that Zn being the most chalcogenide-reactive of the metal precursors, followed by Sn, increases the chance for free sulfur to quickly bind in place of MPP-sulfur, which limits the availability of Zn and Sn for incorporation within the crystal lattice, leading to the respective relative increased Cu and S content observed. The incorporation of the Cu_{Zn} defect is of low enough energy that it seems favorable over the dissociation of the other metals from the capping ligand. This trend holds until the free sulfur available from thiourea drops below the stoichiometric sulfur in the final CZTS NCs. All metal precursors are expected to predominantly be bound to the sulfur of the capping ligand. The ratio between Sn and S is particularly significant because the Sn position remains relatively constant between different crystal structures of CZTS in comparison to the S position.

A series of samples were tested to determine the compositional relationship between Cu/Zn and sulfur source, normalized based on the Sn content (Fig. 1.). Low TU leads to the formation of Zn-rich and Cu-poor NCs, while high TU leads Zn-poor and Cu-rich NCs to form. This holds true up to the TU/MPP ratio of 0.18, where an inflection is observed. This inflection point shows a wide range of Cu/Zn ratios, from as low as 1.2 to as high as 2.9, but does not show intermediate ratios – the recognized ideal for CZTS. This inflection is consistent with reduced TU, to the point where TU alone no longer can supply enough S to account for all produced CZTS. Given the known production of CZTS with only MPP-sulfur present, in the absence of thiourea, the MPP must be a viable source of sulfur. Further, the reaction visually occurs slower, taking twice the time to observe the black color indicative of CZTS formation. This occurs due to the higher decomposition temperature of MPP, which begins around 200°C [23]. Though the reaction is never heated to temperatures above which MPP decomposes, we clearly see some decomposition in the absence of free-S. This suggests that the formation of CZTS using MPP-sulfur does occur, though at a significantly slower rate when compared to that using free sulfur from thiourea. This leads to the increase in Zn and Sn availability for incorporation in the final NCs, yielding a more controllable synthetic process.

The resultant NC crystal structure was examined using powder XRD, Fig. 2. Patterns were taken for compositionally different samples to understand the effect on long term crystal order. Despite the various compositional differences, the XRD patterns in Fig. 2 show remarkably similar structural details. The XRD diffraction peaks at the (112), (220), and (312) planes correspond to the expected kesterite CZTS planes (JCPDS 26-0575) for all samples, and show a tetragonal unit cell with parameters $a = b = 5.40 \text{ \AA}$, and $c = 10.7 \text{ \AA}$, with 90° internal angles. These correspond well with literature values of $a = b = 5.40 \text{ \AA}$, and $c = 10.8 \text{ \AA}$ [27]. This suggests a lack of secondary phase formation during synthesis, the confirmation of which can be seen in Fig. 2. The peaks characterizing common secondary phases are not present to the extent of detection of the instrument [12, 16, 28]. When coupled to the observed peak broadness, NC compositional changes are more likely indicative of small local structure deviations and defects rather than whole structural changes to the NCs. These deviations are commonly attributed to Cu and Zn defects [25].

3.2. Extended X-ray absorption fine structure (EXAFS)

The extended and local structure of the NCs were examined using synchrotron EXAFS (Fig. 3), which allows for the examination of the NCs for local structural abnormalities and reconcile the described structural properties with the crystal structure [5]. Cu and Zn occupy lattice positions where the second shell nearest neighbors are various due to antisite defects, whereas the Sn environment is relatively constant. The Sn K-edge EXAFS (Fig. 3a) are identical in all samples, with little deviation in the threshold energy (E_0), which indicates a singular oxidation state (Sn^{4+} according to the XRD result in Fig. 1) and chemical environment of Sn across all the samples. This confirms that the long range order of the NCs is maintained, and that the Sn local environment is invariant, as expected. This suggests that each Sn site experiences equal scattering from nearest neighbors, indicating a high degree of similarity among neighboring S atoms. This suggests that any defects are aperiodic. These defects would thus be unobserved in diffraction patterns due to the symmetric constraints imposed, which is consistent with the presented XRD data. The Sn radial distance (Fig. 3b) provides explanation for the local structure deviations.

Due to the unresolved positional nature of the Cu and Zn as describe above, the Sn sites were selected for EXAFS analysis to help correlate changes in the spectra with the associated variations in the sulfur content. The radial distribution maximum corresponds to the average Sn-S inter atomic distance plus a phase correction factor (an identical negative value for constant absorber, Sn and back scattered S). Thus to the first approximation, the difference in the radial distribution represents the difference in the Sn-S bond between samples. Relative to samples made in the presence of high TU content – which corresponds to the M1 sample – there is a small increase in Sn radial distance in the samples with little-to-no TU content – which corresponds to the M3 through M5 samples. This suggests a correlation between Sn radial distance and the reduction in free sulfur during synthesis. This further corresponds to the inclusion of additional MPP-bound S in the lattice, as is suggested compositional changes (Table 1). This is further suggested by the peak intensity, which is proportional to coordination number and the Debye-Waller factor (a measure of the root mean square displacement due to thermal motion; the smaller the DW factor, the more order the environment). Since the coordination number is supposed to be constant in all samples, the peak intensity then correlates to better long-range order [29, 30]. A larger amplitude also indicates fewer defects, with more consistent NC packing. The increased bond strength is consistent with the removal of excess free-S, which

would contribute to additional negative charge carriers on the metals, and thus a weaker initial association between individual CZTS components. This allows for additional point defects and local deformation [31] between metals, resulting in the long term disorder observed in M1 through M3. The long term radial distance between M4 and M5 are highly consistent to each other; this is particularly noticeable in the peaks at 4 and 7.2Å. Where high free-S samples show highly inconsistent long term radial distance, M4 and M5 deviate from each other only around the 5.5Å region, likely indicative of a Cu_{Zn} defect [27]. This data corresponds well to the observed trends associated with changes to the TU:MPP ratio. Initial decreases in TU show similar peak positions, but contain a small shoulder peak, indicative of the non-equal Sn bond in M2. Given that Sn is known to be bonded solely to S [22], this shoulder peak is indicative of a secondary S bond. This could be attributed to MPP-bound S rather than free S, or to the presence of lattice distortions that incorporate extra additional sulfur in the tetrahedral holes. Compositional data suggests the former to be more likely given that the overall S content increase in M2 is relatively small. This indicates the S environments are dissimilar, confirming presence of MPP-bound S and free-S in the NCs. Additionally, stronger bonds between Sn and S are due to some Cu_{Zn} antisite defects [27]. The continued reduction of TU from starting material causes a small increase in radial distance relative to the M1, indicating a small relaxation in the Sn-S bond. This is consistent with the increased sulfur content of M3, as more sulfur fills the unused tetrahedral holes, resulting in a 1.0:5.5 ratio of Sn:S. In the transition to the second relationship, the increase in peak height is indicative of stronger bonds and more uniform crystal structure [27]. The enhanced peak suggests an increased uniformity within the second shell, which leads to the sharper and more defined secondary peaks in the spectra. Both M4 and M5 show a high degree of similarity through several shells, which indicates a level of control in the crystal structure formation as a result of the predominant sulfur source being MPP-bound. The slower release of sulfur into the reaction appears to favor the formation of Zn-rich Cu-poor stoichiometry in highly conserved crystal structures. This is outlined in the Cu / (Zn + Sn) ratio. The ratios determined for M1 through M3 are all >1, yielding the expected Cu rich films[14]. Observation of NCs synthesized via MPP-decomposition controlled S release show a drastic decrease in the ratio, from 0.65 for M4 to 0.90 for M5. This Zn-rich and Cu-poor configuration is known to be ideal for fabrication of high efficiency solar cells, suggesting that a slow sulfur release mechanism could be advantageous in the synthesis of this material.[3, 32, 33]

3.3. Photocatalysis

It is plausible that the changes in composition and crystal structure have a profound impact on the effectiveness of the NCs as photoabsorbing layers. By measuring the photoinduced catalytic abilities of the individual absorbing layers, the changes in composition can be reconciled with photo-absorbing ability [22, 34]. Fig. 4 demonstrates a typical PECM.

Fig. 4 inset outlines the photocatalytic reduction of MV^{2+} to MV^+ , which serves as a measure of the current density associated with a layer of NCs. The greater the difference between the current density in light-on and light-off scenarios, the better the CZTS layer for photoconversion and thus for potential use in photovoltaics. On exposure to light, the creation of a photogenerated electron-hole pair occurs, with the electron transfer to the methyl viologen solution via the scheme outlined herein.

Ideal films require good absorption via equation 1, with limited to no decay through equation 2, with preferential electron transfer through equation 3. Films that show enhanced product separation – equation 5 – and limited recombination of charges – equation 4 – will maximize photocatalysis. These were measured via PECMs as illustrated in Scheme 1. On excitation, the electron transfer to MV^{2+} occurs at the surface, indicated by the sharp rise in the current density. The surface composition is thus of great importance to the catalytic response, with more uniformity resulting in increased performance [34], with less electron scavengers present to drive equations 2 and 4 [35]. This is of note in the initial spike, followed by the small decay in current density seen in the light on scenario of Fig. 4, as outlined by Khoshmashrab et al [5]. Increased product separation increases the photocatalysis of MV^{2+} to MV^+ . Using M1 as a standard, alternate compositions were tested to compare the compositional trends to their resultant current densities, and thus form optimized absorber layers for use in fabricating CZTS-based solar cells. Fig. 5 outlines these effects.

Initial decreases in the free-S content reduce the effective photocatalysis of MV^{2+} to the point of completely diminishing any photo-response by M3, therefore the photocurrent density. This is consistent with published literature, suggesting that increasing defects to a large degree, leads to an increase in “traps” for the electron that leads to increased recombination. This means in the presence of excess sulfur, any photogenerated electrons are unable to escape the film to participate in the catalysis. This suggests that the increase in S:Sn of 0.5 from M1 to M2 affects an increases in decomposition and in electron-hole recombination (equations 2 and 4), reducing the desired electron transfer (equation 3). This is seen by the decrease in effective current density from 0.045 mA/cm² in M1 to 0.035 mA/cm² in M2. The films made predominantly with MPP-bound S show good photoresponse, consistent with highly ordered CZTS films, but only the film made in the absence of free-S show enhancement of the photocatalysis process. Measures of the current density associated with M4 are equivalent to M1 at 0.045 mA/cm², whereas M5 consistently reaches 0.055 mA/cm². This improved photocatalysis associated with the films fabricated from little-to-no free sulfur suggests that there is a detrimental effect of excess free-S on the final NCs. Unfortunately, the excess free-S is required, as indicated by the poor performance of the M2 and M3 samples grown in more stoichiometric free-S quantities. This can be attributed to the instability of the CZTS precursor solution [4]. Initial decreases in TU reduce the free-S content, leading to a destabilization of the precursor solution and resulting in some secondary phase formation. As the free-S decreases, the MPP-bound S begins to play a more prominent role in the formation of CZTS, which appears to reduce this instability and leads to more regular films, likely the result of decreased secondary phase formation. Similar trends have been reported in conjunction with TU in studies involving annealing or film structure, suggesting that TU is indeed adversely affecting the observed photoresponse here [4, 36]. This is corroborated by the enhancements seen in the photocatalysis from the films produced with only MPP-bound S. The MPP-bound S appears to offer similar benefits to those seen when using long-chain organic capping ligands to control the synthesis[2], but without requiring high temperature annealing to remove the unwanted carbon residue, thus avoiding any adverse Sn loss associated with SnS loss at high temperature[10]. Controlling the rate of S-infusion to the metal precursors yields improved catalytic results consistent with the improved NC composition and

local defect structure. This can also be associated with the band gap of the NCs. Fig. 6 outlines the changes in optical band gap resulting from the changed composition and structure.

It is ideal for the band gap to be 1.45 – 1.51 eV corresponding to the most intense region of the solar spectrum [3]. The reference films made with excess free-S show a lower than ideal band gap, potentially indicating a more stannite structure [14, 37]. Initial decreases in available free-S lead to higher than ideal band gaps, which could be attributed to the additional S within the structure and thus a decrease in the p-type character [4]. This is difficult to probe, given techniques such as XRD lack the ability to probe local structure, and a soft X-ray synchrotron source is required to probe the S k-edge; however, the presence of additional S has been shown through EDX, and the additional negative charge content is contrary to the formation of local positive charge required for p-type formation. This adverse effect is reversed as free-S content is decreased further. As the available free-S decreases to lower levels and eventually removed from synthesis, the band gap gradually shifts back to lower regions, though higher than that of the M1 film, and within the desired absorbance region. This correlates well with the observed stoichiometry changes, with the Cu-poor and Zn-rich films showing ideal band gaps, while Cu-rich films show lower than ideal band gaps. This makes sense, given the propensity for increases to the band gap as a result of decreases in copper [38]. The samples without any free-S showed decreased band gaps associated with lower Cu, while maintaining a higher crystallinity and thus a greater photogenerated catalysis due to the lack of compounding factors resulting from the presence of excess sulfur.

4. Conclusions

CZTS NCs growth through solution phase, one-pot, solvothermal synthesis shows dependence on different sulfur environments. Altering the free-S availability shows initial reductions in CZTS formation, with large deviations from stoichiometric in the final NC composition; however, on further reduction below Sn concentration in solution, MPP-bound S begins to play a role, mitigating any loss of stability in the precursor solution and resulting in highly conserved CZTS NCs. This trend continues, even in the presence of no free-S. The catalytic conversion of MV^{2+} to MV^{+} also follows a similar trend, with large decreases in catalytic conversion observed in decreasing free-S availability, with increased and even enhanced conversion in films made in the presence of very little free-S, or exclusively MPP-

bound S. This suggests that the slow-release of S through MPP degradation offers enhanced control over the NC formation, and thus greater control over final stoichiometry and long-term crystallinity. Both of these conditions are desired characteristics for eventual CZTS solar cell device fabrication.

The sulfur source and availability also contribute to the band gap of the fabricated CZTS. Initial decreases in free-S were inversely proportional with the increased band gap, which is consistent with the decreased catalytic conversion. The high band gap achieves less photo-excitation, converting less of the solar spectrum and thus converts less MV^{2+} . As MPP-bound S begins to play more of a role, the band gap begins declining back towards the optimal gap, with the NCs fabricated solely based on MPP-bound S corresponding better with the most intense portion of the solar spectrum than any other combination. The slow-release mechanism offered through MPP-degradation appears favorable to free-S association of metal ions for solution-phase synthesis of CZTS NCs.

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References

- [1] C. Platzer-Björkman, J. Scragg, H. Flammersberger, T. Kubart, M. Edoff, *Sol. Energy Mater. Sol. Cells*, 98 (2012) 110-117.
- [2] Y. Kim, K. Woo, I. Kim, Y.S. Cho, S. Jeong, J. Moon, *Nanoscale*, 5 (2013) 10183-10188.
- [3] Q. Guo, G.M. Ford, W.-C. Yang, B.C. Walker, E.A. Stach, H.W. Hillhouse, R. Agrawal, *J. Am. Chem. Soc.*, 132 (2010) 17384-17386.
- [4] S.-N. Park, S.-J. Sung, D.-H. Son, D.-H. Kim, M. Gansukh, H. Cheong, J.-K. Kang, *RSC Adv.*, 4 (2014) 9118-9125.
- [5] S. Khoshmashrab, M.J. Turnbull, D. Vaccarello, Y. Nie, S. Martin, D.A. Love, P.K. Lau, X. Sun, Z. Ding, *Electrochim. Acta*, 162 (2015) 176-184.
- [6] A. Shavel, D. Cadavid, M. Ibáñez, A. Carrete, A. Cabot, *J. Am. Chem. Soc.*, 134 (2012) 1438-1441.
- [7] M. He, D. Zheng, M. Wang, C. Lin, Z. Lin, *J. Mater. Chem. A*, (2014).
- [8] T. Kato, N. Sakai, H. Sugimoto, *Photovoltaic Specialist Conference (PVSC)*, 2014, pp. 0844-0846.
- [9] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, *Adv. Energy Mater.*, 4 (2014) 1301465_1-1301465_5.
- [10] J.J. Scragg, T. Ericson, T. Kubart, M. Edoff, C. Platzer-Björkman, *Chem. Mater.*, 23 (2011) 4625-4633.
- [11] M.G. Panthani, V. Akhavan, B. Goodfellow, J.P. Schmidtke, L. Dunn, A. Dodabalapur, P.F. Barbara, B.A. Korgel, *J. Am. Chem. Soc.*, 130 (2008) 16770-16777.
- [12] H. Yang, L.A. Jauregui, G. Zhang, Y.P. Chen, Y. Wu, *Nano Lett.*, 12 (2012) 540-545.
- [13] D. Vaccarello, J. Hedges, A. Tapley, D.A. Love, Z. Ding, *J. Electroanal. Chem.*, 738 (2015) 35-39.
- [14] D. Vaccarello, A. Tapley, Z. Ding, *RSC Adv.*, 3 (2013) 3512-3515.
- [15] A. Tapley, D. Vaccarello, J. Hedges, F. Jia, D.A. Love, Z. Ding, *Phys. Chem. Chem. Phys.*, 15 (2013) 1431-1436.
- [16] H. Zhou, W.C. Hsu, H.S. Duan, B. Bob, W. Yang, T.B. Song, C.J. Hsu, Y. Yang, *Energ. Environ. Sci.*, 6 (2013) 2822-2838.
- [17] D.B. Mitzi, O. Gunawan, T.K. Todorov, K. Wang, S. Guha, *Sol. Energy Mater. Sol. Cells*, 95 (2011) 1421-1436.
- [18] H. Katagiri, K. Jimbo, W.S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, *Thin Solid Films*, 517 (2009) 2455-2460.
- [19] X. Liu, W. Yang, Z. Liu, *Adv. Mater.*, 26 (2014) 7710-7729.
- [20] T.-K. Sham, *Adv. Mater.*, 26 (2014) 7896-7901.
- [21] B. Ravel, M. Newville, *J. Synchrotron Rad.*, 12 537-541.
- [22] H. Ye, H.S. Park, V.A. Akhavan, B.W. Goodfellow, M.G. Panthani, B.A. Korgel, A.J. Bard, *J. Phys. Chem. C*, 115 (2010) 234-240.
- [23] A. Tapley, C. Hart, D. Vaccarello, D.A. Love, Z. Ding, *J. Electrochem. Soc.*, 161 (2014) H725-H729.
- [24] W. Huang, Q. Li, Y. Chen, Y. Xia, H. Huang, C. Dun, Y. Li, D.L. Carroll, *Sol. Energy Mater. Sol. Cells*, 127 (2014) 188-192.
- [25] S. Chen, J.H. Yang, X.G. Gong, A. Walsh, S.H. Wei, *Phys. Rev. B*, 81 (2010) 245204_1-245204_10.
- [26] S. Schorr, *Sol. Energy Mater. Sol. Cells*, 95 (2011) 1482-1488.

- [27] F.J. Espinosa-Faller, D.R. Conradson, S.C. Riha, M.B. Martucci, S.J. Fredrick, S. Vogel, A.L. Prieto, S.D. Conradson, *J. Phys. Chem. C*, 118 (2014) 26292-26303.
- [28] A. Redinger, D.M. Berg, P.J. Dale, S. Siebentritt, *J. Am. Chem. Soc.*, 133 (2011) 3320-3323.
- [29] M.M. Koza, A. Leithe-Jasper, H. Rosner, W. Schnelle, H. Mutka, M.R. Johnson, Y. Grin, *Phys. Rev. B*, 89 (2014) 014302_1-014302_8.
- [30] A.A. Maradudin, P.A. Flinn, *Phys. Rev.*, 129 (1963) 2529-2547.
- [31] P.T. Erslev, M.R. Young, J.V. Li, S.C. Siah, R. Chakraborty, H. Du, R.J. Lad, T. Buonassisi, G. Teeter, *Sol. Energy Mater. Sol. Cells*, 129 (2014) 124-131.
- [32] R. Haight, X. Shao, W. Wang, D.B. Mitzi, *Appl. Phys. Lett.*, 104 (2014) 033902_1-033902_5.
- [33] P. Xu, S. Chen, B. Huang, H.J. Xiang, X.G. Gong, S.H. Wei, *Phys. Rev. B*, 88 (2013) 045427_1-045427_8.
- [34] A. Amara, A. Ferdi, A. Drici, J.C. Bernède, M. Morsli, M. Guerioune, *Catal. Today*, 113 (2006) 251-256.
- [35] N. Todorova, T. Giannakopoulou, K. Pomoni, J. Yu, T. Vaimakis, C. Trapalis, *Catal. Today*, (<http://dx.doi.org/10.1016/j.cattod.2014.11.008>).
- [36] X. Wen, W. Luo, Z. Zou, *J. Mater. Chem. A*, 1 (2013) 15479-15485.
- [37] C. Malerba, F. Biccari, C.L.A. Ricardo, M. Valentini, R. Chierchia, M. Müller, A. Santoni, E. Esposito, P. Mangiapane, P. Scardi, A. Mittiga, *J. Alloys Compd.*, 582 (2014) 528-534.
- [38] R. Caballero, I. Victorov, R. Serna, J.M. Cano-Torres, C. Maffiotte, E. Garcia-Llamas, J.M. Merino, M. Valakh, I. Bodnar, M. León, *Acta Mater.*, 79 (2014) 181-187.

Scheme 1. A schematic of PECM set-up for measuring photocatalysis of MV²⁺.

Fig. 1. Effects of changing sulfur-source on Cu / Zn stoichiometry. The grey region indicates compositions that was extrapolated.

Fig. 2. Powder XRD comparisons of three distinct stoichiometries.

Fig. 3. a) Normalized Sn K-edge EXAFS spectra of the CZTS NCs in fluorescence yield and b) radial distances.

Fig. 4. Photocatalysis of MV^{2+} to MV^+ resulting from photon absorbance observed in M1. Control measures were taken in the dark, as indicated by the dotted line.

Fig. 5. PECM comparison of each of the four altered stoichiometries. M2 and M3 show high resistivity, while M4 and M5 show little resistivity, as denoted by the decreased slope of the line and low current density in light off conditions.

Fig. 6. Changes to the optical band gap induced by stoichiometric changes, ± 0.03 eV.

Graphical abstract