

# Synthesis of $\text{Cu}_2\text{SnSe}_3$ Nanocrystals for Solution Processable Photovoltaic Cells

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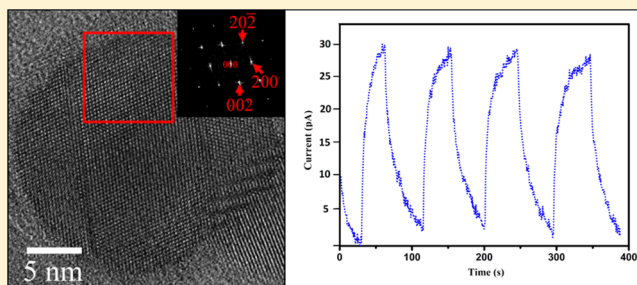
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## Supporting Information

**ABSTRACT:** This paper describes the synthesis of ternary chalcogenide  $\text{Cu}_2\text{SnSe}_3$  nanocrystals as an alternative solar absorber material to conventional quaternary  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ . We used the hot coordination solvent method with hexadecylamine as the capping ligand for the first time for this material system. Using a variety of characterization techniques, such as X-ray diffraction, selected area electron diffraction, convergent beam electron diffraction, and Raman spectroscopy, the nanocrystals were found to be monoclinic  $\text{Cu}_2\text{SnSe}_3$  with an optical energy band gap of 1.3 eV and have a narrow size distribution. These nanocrystals are shown to be photo-sensitive in the range of wavelengths corresponding to the solar spectrum, which makes them highly promising as alternative photon absorber materials for photovoltaic applications.



## INTRODUCTION

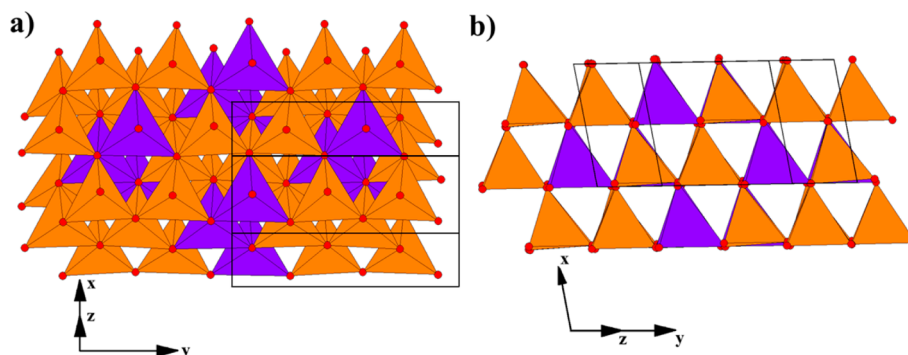
Multicomponent chalcogenide semiconductors, such as  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  (CIGS), are promising candidates for solar energy harvesting, and to-date, the highest efficiency achieved for this type of solar cell is 20.3%.<sup>1</sup> However, due to the limited supply and increasing price of indium and gallium, there is a strong drive to find alternative materials with high abundance and low cost. Recently, there is a growing interest in two such chalcogenide semiconductor compounds,  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) and  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe). The highest efficiency achieved for these types of solar cell is 11.1%.<sup>2–8</sup> When In is replaced by Sn and Ga by Zn in quaternary CZTSe, the reduction in the cost of the active material can be substantial for large-scale production. This group of semiconductors has similar electrical and optical properties to CIGS,<sup>9–11</sup> although, at present, the efficiency is still lower, so solar cells made using these materials still required some optimization.

In general, the more components there are in a material system, the more difficult is the composition and phase control. Complex quaternary CIGS compounds required precise control of the growth conditions, and the same goes for CZTS and CZTSe compounds. Hence, simpler ternary compound systems, such as  $\text{Cu}_2\text{SnS}_3$  and  $\text{Cu}_2\text{SnSe}_3$ , are highly attractive, and nanocrystals of these materials are highly applicable for the fabrication of low-cost thin-film solar cells because of their

solution processability. Bulk  $\text{Cu}_2\text{SnSe}_3$  is a p-type semiconductor with a direct band gap of 0.8–1.1 eV and a high absorption coefficient ( $>10^4 \text{ cm}^{-1}$ ).<sup>12–16</sup>  $\text{Cu}_2\text{SnSe}_3$  can have the following crystal structures:  $F\bar{4}3m$  cubic ( $a = 5.696 \text{ \AA}$ ),<sup>17</sup>  $I\bar{4}2d$  tetragonal ( $a = 5.689 \text{ \AA}$ ,  $c = 11.37 \text{ \AA}$ ),<sup>18</sup>  $C1c1$  monoclinic ( $a = 6.9670(3) \text{ \AA}$ ,  $b = 12.0493(7) \text{ \AA}$ ,  $c = 6.9453(3) \text{ \AA}$ ,  $\beta = 109.19(1)^\circ$ ),<sup>19</sup> or  $C1c1$  monoclinic superstructure ( $a = 6.9612(14) \text{ \AA}$ ,  $b = 12.043(2) \text{ \AA}$ ,  $c = 26.481(5) \text{ \AA}$ ,  $\beta = 94.97(3)^\circ$ ).<sup>20</sup> For cubic  $\text{Cu}_2\text{SnSe}_3$ , Cu and Sn share the same atomic positions with an occupancy of 0.67 and 0.33, respectively, whereas in tetragonal  $\text{Cu}_2\text{SnSe}_3$ , Cu and Sn only share the  $4b$  Wyckoff site (0, 0, 0.5) with an occupancy of 0.33 and 0.67, respectively, and with full occupancy of Cu at the  $4a$  site (0, 0, 0). However, for the monoclinic structure, both Cu and Sn are ordered over the cation positions and do not share the same atomic positions. There is also a slight distortion in both the  $\text{CuSe}_4$  and the  $\text{SnSe}_4$  tetrahedra as compared to the cubic structure (Figure 1). Interestingly, this material was also reported to be a good candidate in various optoelectronic applications, such as highly efficient acoustic-optic and thermoelectric devices,<sup>12,21</sup> and a precursor material for the

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**Figure 1.** Representation of the crystal structure of C1c1  $\text{Cu}_2\text{SnSe}_3$  projected (a) along and (b) perpendicular to the closed packed direction, where  $\text{CuSe}_4$  and  $\text{SnSe}_4$  tetrahedra are drawn in orange and purple, respectively.

growth of the promising solar cell absorber, CZTSe, via a reaction of  $\text{Cu}_2\text{SnSe}_3$  and  $\text{ZnSe}$ .<sup>22</sup>

The syntheses of bulk and thin films of  $\text{Cu}_2\text{SnSe}_3$  have been reported,<sup>12–15,23</sup> and some of this work focuses on the synthesis of nanocrystals, for example, the colloidal synthesis of cubic nanocrystals of  $\text{Cu}_2\text{SnSe}_3$  using oleylamine (OLA) as the coordinating solvent.<sup>24</sup> Most recently, nanocrystals of the wurtzite phase of  $\text{Cu}_2\text{SnSe}_3$  were prepared using dodecylamine and 1-odecanethiol as the coordinating solvents and di-*tert*-butyl diselenide ( $t\text{Bu}_2\text{Se}_2$ ) as the selenium source.<sup>25</sup> These recent developments on the colloidal synthesis of high-quality nanostructure materials have opened up new routes for the fabrication of solution processable, low-cost, and high-efficiency printable solar cells using the nanoink concept.<sup>26</sup> Though some work has been done on synthesis, the understanding of the relationship between the crystal structure of  $\text{Cu}_2\text{SnSe}_3$  nanocrystals and their optoelectronic properties is lacking. Therefore, the aim of this study is to synthesize the ternary chalcogenide  $\text{Cu}_2\text{SnSe}_3$  nanocrystals by the hot coordination method and evaluate the potential of this compound as the photon absorber in photovoltaic cells by understanding its structural, optical, and electrical properties.

## EXPERIMENTAL DETAILS

**Materials.** Copper(I) chloride (>99.995%), copper(II) acetate (97%), tin(IV) chloride (98%), tin(II) acetate (99%), and hexadecylamine (HDA) (98%) were purchased from Sigma-Aldrich, and selenium (Se) powder (<325 mesh, 99.7%) was obtained from Acros Organics. Acetonitrile (HPLC grade, 99.7%) was purchased from Fluka, while methanol, chloroform, and toluene are technical grade (95%).

**Characterization Techniques.** Ultraviolet–visible/near-infrared (UV–vis/NIR) absorption spectra of the as-synthesized nanocrystals dispersed in toluene were obtained at room temperature and under ambient conditions using a UV–vis/NIR PerkinElmer Lambda 900 spectrophotometer ( $300 < \lambda < 2000$  nm, step size of 0.5 nm). The size, morphology, and crystal structure of the nanocrystals were characterized using transmission electron microscopy (TEM), selected area electron diffraction (SAED), and convergent beam electron diffraction (CBED). The samples for TEM (JEOL 2100F, with an accelerating voltage of 200 kV) were prepared by dropping nanocrystals dispersed in toluene onto lacey carbon-coated copper or nickel grids. The composition and elemental distribution of the as-prepared  $\text{Cu}_2\text{SnSe}_3$  nanoparticles were determined semiquantitatively using energy-dispersive X-ray spectroscopy (EDX) in the TEM. Electron energy loss spectra (EELS) were collected with a Gatan imaging filter (GIF) in a Philips CM 300 TEM. The phase and crystallographic structure of the nanocrystals were characterized by grazing incidence X-ray diffraction (GIXRD) patterns, which were recorded using a Bruker D8 Advance X-ray diffractometer with  $\text{Cu K}\alpha$

radiation ( $\lambda_{\text{ave}} = 1.54 \text{ \AA}$ ) operating at 40 kV and 40 mA. The scanning was conducted with a fixed  $\theta$  of  $0.5^\circ$ , a scanning rate of  $0.2^\circ \text{ min}^{-1}$ , a step size of  $0.02^\circ$ , and a  $2\theta$  range from  $10^\circ$  to  $80^\circ$ . Rietveld refinement was done using cubic, tetragonal, and monoclinic  $\text{Cu}_2\text{SnSe}_3$  models.<sup>17–20</sup> The fundamental parameters peak-shape profile was used; a five-coefficient Chebyshev polynomial and  $1/x$  background, zero error, scale factors, unit cell parameters, and crystal size were sequentially refined using the TOPAS V4 program. Fractional coordinates, occupancies, and the atomic displacement factors were fixed to the values obtained from the database. To determine how reliable the fit is in TOPAS, several criteria are used, and they are the following:  $R_{\text{wp}}$ ,  $R$  weighted pattern;  $R_{\text{exp}}$ ,  $R$  expected;  $R_{\text{B}}$ ,  $R$  Bragg; and  $\chi^2$  (goodness of fit) =  $(R_{\text{wp}})/(R_{\text{exp}})$ .

$$R_{\text{exp}} = \sqrt{\frac{\sum M - P}{\sum w_m Y_{o,m}^2}} \quad (1)$$

$$R_{\text{wp}} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m Y_{o,m}}} \quad (2)$$

$$R_{\text{B}} = \frac{\sum |I_{o,k} - I_{c,k}|}{\sum I_{o,k}} \quad (3)$$

$$\text{GOF} = \chi^2 = \frac{R_{\text{wp}}}{R_{\text{exp}}} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{M - P}} \quad (4)$$

$Y_{o,m}$  and  $Y_{c,m}$  are the observed and calculated data, respectively, at data point  $m$ ,  $M$  is the number of data points,  $P$  is the number of parameters,  $w_m$  is the weighting given to data point  $m$ , and  $I_{o,k}$  and  $I_{c,k}$  are the observed and calculated intensities of the  $k$ th reflection.

Further evidence for composition and valence state of the product was acquired using the ESCALABMK II X-ray photoelectron spectroscopy (XPS), with  $\text{Mg K}\alpha$  X-ray as the excitation source. The binding energies obtained from the XPS analysis were corrected with C 1s to 284.60 eV. The micro-Raman spectra were recorded from 50 to  $600 \text{ cm}^{-1}$  by using an XY Dilor-JobinYvon-Spex spectrometer attached to an Olympus microscope, equipped with a double monochromator and a multichannel detection system. The 633.8 nm He–Ne laser line was used as an irradiator source with a power irradiance of 20 mW. Cyclic voltammetry (CV) measurements were performed on an Autolab PG302N electrochemical workstation. Carbon and gold electrodes were used as working and counter electrodes, respectively. The reference electrode was a  $\text{Ag/AgCl}$  electrode with 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) dissolved in acetonitrile as the supporting electrolyte. The ferrocene/ferrocenium couple was utilized as an internal standard.<sup>27</sup> A few drops of diluted nanocrystals in chloroform were deposited onto the surface of the working electrode to form a nanocrystal film. The scan rate was set at  $100 \text{ mV/s}$ , and during all the measurements, the electrolyte solution was deoxygenated by bubbling

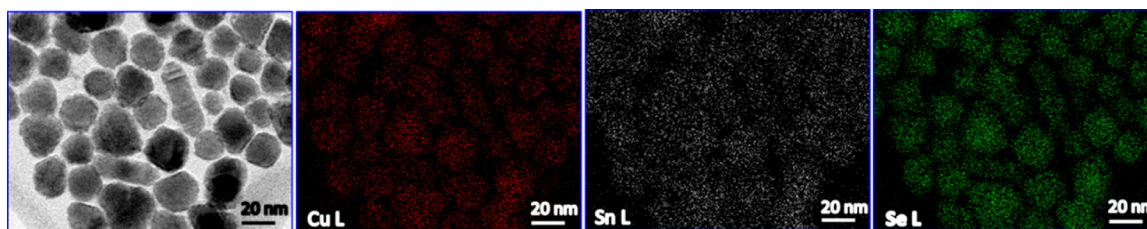


Figure 2. Bright-field TEM image of  $\text{Cu}_2\text{SnSe}_3$  nanocrystals and corresponding EDX elemental maps.

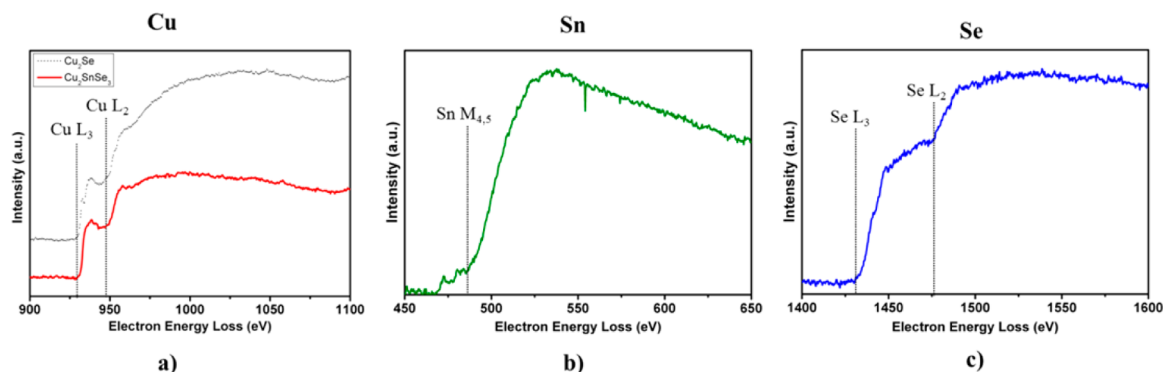


Figure 3. EELS spectra obtained from the  $\text{Cu}_2\text{SnSe}_3$  nanocrystals and shown after background subtraction: (a) Cu L with the Cu L edge from  $\text{Cu}_2\text{Se}$  shown dotted, (b) Sn M, and (c) Se L edges. The original EELS spectra before background subtraction are shown in Figure S6 (Supporting Information).

$\text{N}_2$  gas through it for 10 min. The photosensitivity of the nanocrystal film was recorded using a Keithley 4200 parametric analyzer in a TTP-6 (Lakeshore Cryogenic) probe station at ambient condition. A halogen light source was used as the white-light source for the irradiation of the film.

**Synthesis of  $\text{Cu}_2\text{SnSe}_3$  Nanocrystals.**  $\text{Cu}_2\text{SnSe}_3$  nanocrystals were synthesized using the hot coordination solvent method since this method has been shown to give very good control over composition and morphology for a wide range of semiconducting chalcogenide nanocrystals.<sup>28–31</sup> The reaction was started by heating a stoichiometric mixture of  $\text{SnCl}_4$  (0.1 mmol),  $\text{CuCl}$  (0.2 mmol), and 6.5 g of HDA in a 50 mL three-neck flask in an oxygen-free environment to 80 °C and degassing for 1 h. The complete dissolution of the cation precursors at around 140 °C was confirmed by a change of color of the solution to yellow. A mixture of 0.3 mmol of selenium powder in 4 g of HDA was heated to 50 °C in order to melt the HDA and form a suspension. This was then injected into the reaction flask at 140 °C under constant stirring and a nitrogen flow. The mixture was further heated to 240 °C and held for an hour. After the reaction was complete, the mixture was cooled down to 60 °C. Toluene and methanol were added to the solution, and the mixture was sonicated for 10 min to remove all the free ligands and also the unreacted precursors. The solution was then centrifuged at 9000 rpm for 20 min, followed by 7000 rpm for 10 min. The supernatant was discarded for each cycle in the centrifuge, and the nanocrystals were redispersed in toluene before the next cycle. The purified precipitates were subsequently redissolved in toluene or chloroform for further characterization.

## RESULTS AND DISCUSSION

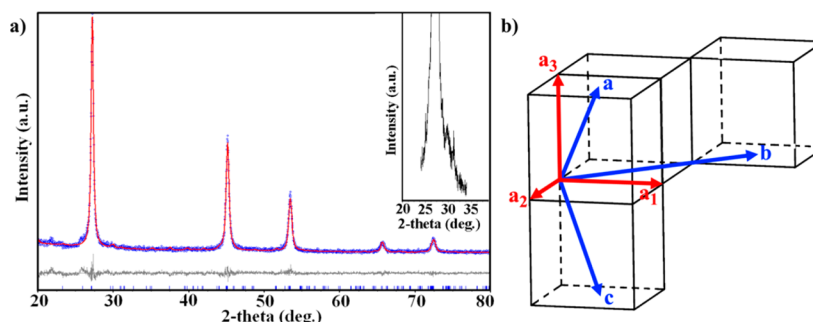
Both reaction parameters and precursors determine the phase and morphology of the desired product (Figures S1–S3, Supporting Information). Among the potential capping ligands reported, hexadecylamine (HDA) was chosen as it has been shown to be an effective capping ligand for the synthesis of CIGS nanocrystals, resulting in a narrow size distribution,<sup>32</sup> and generally, amines facilitate the formation of nanoparticles at lower temperatures.<sup>33</sup> The injection temperature for the hot coordination method controls the size and morphology of the

nanocrystals formed (Figure S3, Supporting Information). The optimum reaction temperature was found to be 240 °C, and this temperature is similar to that previously reported for the synthesis of CIGS nanocrystals.<sup>32</sup> In this paper, monodisperse nanocrystals of  $\text{Cu}_2\text{SnSe}_3$  with uniform shapes and sizes were successfully synthesized by injecting Se at 140 °C using hexadecylamine (HDA) as the capping ligand and then increasing the reaction temperature to 240 °C.

**Compositional and Structural Analysis.** A semiquantitative energy-dispersive X-ray spectroscopy (EDX) analysis revealed that the Cu/Sn/Se ratio was 2.1:0.9:3, close to the nominal composition (Figure S4, Supporting Information). The elements were homogeneously distributed within the nanocrystals, and there was no considerable compositional variation among the nanocrystals (see the EDS maps in Figure 2). In addition, from the X-ray photoelectron spectra (XPS) (Figure S5, Supporting Information), it is possible to deduce that the valence states of Cu, Sn, and Se are +1, +4, and –2, respectively, which confirms the formation of  $\text{Cu}_2\text{SnSe}_3$ .<sup>34–36</sup>

To determine the bonding state and the local electronic state of the elements in the synthesized nanocrystals, EELS spectra were collected. The Cu, Sn, and Se EELS edges are shown in Figure 3, confirming the presence of these three elements. The shape of an EELS edge is characteristic of the oxidation state and local bonding around each atom. Thus, to determine the oxidation state of Cu, we initially compared the Cu edge (Figure 3a) with edges from Cu oxides with oxidation states of  $\text{Cu}^0$ ,  $\text{Cu}^{\text{I}}$ , and  $\text{Cu}^{\text{II}}$  but found a poor match. This is because the electronic environment of Cu bonded to O is different from that for Cu bonded to Se. When compared with the Cu edge from  $\text{Cu}_2\text{Se}$ , a better match was found (dotted line in Figure 3a), consistent with Cu in  $\text{Cu}_2\text{SnSe}_3$  having an oxidation state of  $\text{Cu}^{\text{I}}$ . The Cu edge shape is also close to that reported for  $\text{Cu}_2^{\text{I}}\text{ZnSnSe}_4$ <sup>37</sup> and  $\text{Cu}^{\text{I}}\text{InSe}_2$  nanocrystals.<sup>38</sup>

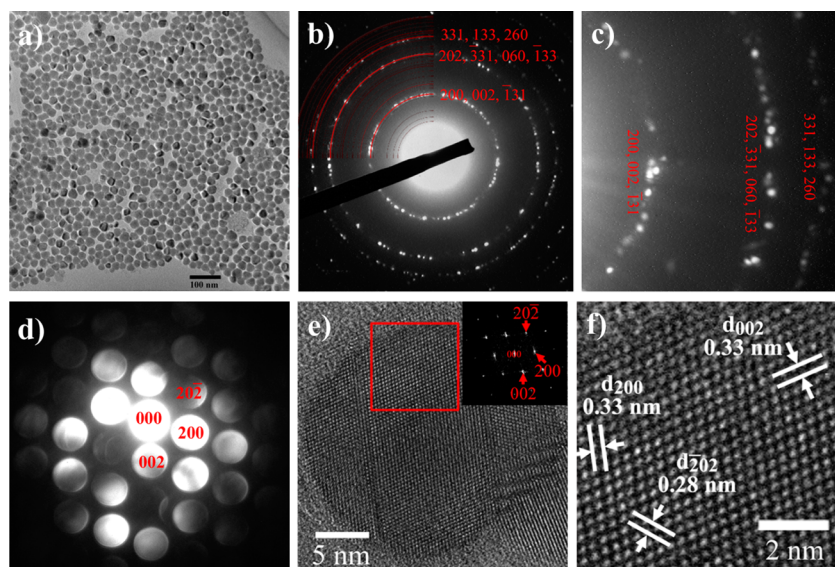




**Figure 4.** (a) X-ray diffraction pattern and Rietveld refinement of phase-pure monoclinic  $\text{Cu}_2\text{SnSe}_3$  nanocrystals. The blue circles are the experimental plot, and the red line is the calculated plot of the Rietveld refinement. The gray line is the difference between the calculated and experimental intensities, and the vertical lines show the positions of Bragg peaks corresponding to monoclinic  $\text{Cu}_2\text{SnSe}_3$ . The inset shows the low-intensity reflection acquired with a longer scanning time (60 s/step) with a step size of  $0.02^\circ$  over the  $2\theta$  angular range from  $24^\circ$  to  $30^\circ$ . (b) The relationship between the monoclinic and pseudocubic subcells.<sup>38</sup>

**Table 1.** Refined Crystallite Size, Unit Cell Parameters, and Reliability Factors from Rietveld Refinement of the X-ray Powder Diffraction Pattern

unit cell parameters					reliability factors			crystallite size
$a$	$b$	$c$	$V$	$\beta$	$R_{\text{wp}}$	$R_{\text{B}}$	$\chi^2$	
$6.981 \pm 0.002 \text{ \AA}$	$12.072 \pm 0.004 \text{ \AA}$	$6.952 \pm 0.002 \text{ \AA}$	$553.6 \pm 0.3 \text{ \AA}^3$	$109.12 \pm 0.02^\circ$	9.4	3.03	1.26	20 nm



**Figure 5.** (a) Low-magnification TEM image of synthesized  $\text{Cu}_2\text{SnSe}_3$  nanocrystals showing the nanocrystals' size distribution. (b) SAED pattern from an area of nanocrystals. (c) Enlarged SAED pattern showing the presence of a number of extra weak reflections next to the stronger  $\text{Cu}_2\text{SnSe}_3$  rings. (d) CBED pattern of a single nanocrystal taken along the  $[010]$  zone axis. (e) HRTEM image of a single  $\text{Cu}_2\text{SnSe}_3$  nanocrystal taken along  $[010]$  with inset diffractogram. (f) Enlarged HRTEM image with the plane spacings marked.

Because  $\text{Cu}_2\text{SnSe}_3$  has been known to crystallize in different space groups,<sup>17–20</sup> X-ray powder diffraction studies was used to determine the structure of  $\text{Cu}_2\text{SnSe}_3$ . The starting Rietveld refinement model used the highest symmetry cubic, resulting in  $R_{\text{wp}} = 10.3$ ,  $R_{\text{B}} = 4.96$ , and  $\text{GOF} = 1.32$ . As the major intense XRD peaks for cubic, tetragonal, and monoclinic crystal structures are common (Figure S7, Supporting Information), high-resolution analysis involving a longer scanning time (60 s/step) with a step size of  $0.02^\circ$  over a  $2\theta$  angular range from  $24^\circ$  to  $30^\circ$  was required to distinguish the lower symmetry structures. As a result, a minor reflection at  $2\theta = 29.72$  (inset of Figure 4a) was seen, which is attributed to the monoclinic structure. From the Rietveld refinement of the pattern using the monoclinic model, values of  $R_{\text{wp}} = 9.4$ ,  $R_{\text{B}} = 3.03$ , and  $\text{GOF} =$

1.26 were obtained (Figure 4a and Table 1). The improvement in the residuals suggests that the nanocrystals have the monoclinic  $C1c1$  structure.  $\text{Cu}_2\text{SnSe}_3$  nanoparticles reported by Sharma et al. and Jeong et al. were found to have cubic and wurtzite structures.<sup>23,24</sup> The relationship between the monoclinic and pseudocubic subcells is given by<sup>39</sup>

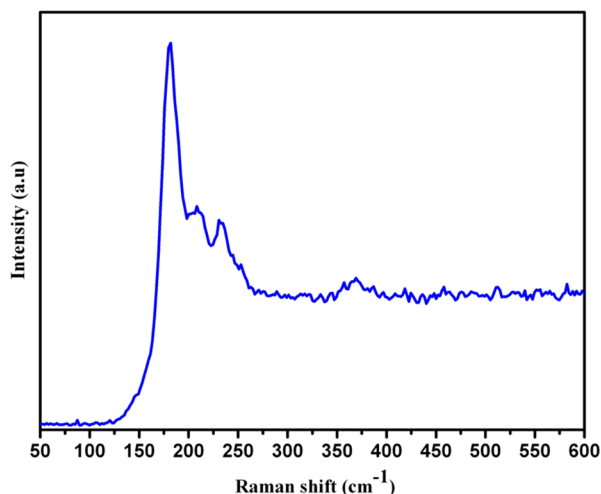
$$\begin{aligned} a &= a_1/2 + a_2/2 + a_3, \\ b &= 3a_1/2 - 3a_2/2, \text{ and} \\ c &= a_1/2 + a_2/2 - a_3 \end{aligned} \quad (5)$$

where  $a$ ,  $b$ , and  $c$  are the monoclinic lattice vectors, and  $a_1$ ,  $a_2$ , and  $a_3$  are pseudocubic vectors (Figure 4b). There is also a

monoclinic  $C1c1$   $Cu_2SnSe_3$  phase with a larger unit cell whose presence cannot be discounted. This superstructure is a low-temperature crystal structure that has a volume 4 times larger than that of the parent monoclinic structure.<sup>20</sup> However, at present, it is not possible to conclusively prove the existence of this phase due to the limitations of powder XRD.

High-resolution transmission electron microscopy (HRTEM), convergent beam electron diffraction (CBED), and select area electron diffraction (SAED) of the nanocrystals provide further structural confirmation (Figure 5b–f). The strong reflections in the diffraction pattern (Figure 5d) correspond to the monoclinic structure of  $Cu_2SnSe_3$ . Interestingly, SAED showed the presence of a number of extra weak reflections in the intense reflection rings (Figure 5c). These extra spots may suggest the lower symmetry of the  $Cu_2SnSe_3$  structure. CBED patterns and HRTEM images were taken along the  $[010]$  zone axis, and the  $d$ -spacings were found to be  $d_1 = 0.28$  nm,  $d_2 = 0.33$  nm, and  $d_3 = 0.33$  nm, corresponding to the  $(20\bar{2})$ ,  $(200)$ , and  $(002)$  crystal planes, which are consistent with the XRD results obtained for monoclinic  $Cu_2SnSe_3$  (Figure 5d–f) (see Table S1 (Supporting Information) for the refined structure factors for  $C1c1$   $Cu_2SnSe_3$ ). The diameter of the nanocrystals estimated from the TEM image in Figure 5a is about 20 nm, consistent with the value calculated from the XRD pattern based on the volume-weighted column length (Table 1) with a narrow size distribution. Figure S8 (Supporting Information) shows the nanocrystal size distribution obtained by measuring 220 individual nanoparticles with the average size of 20 nm.

Raman spectroscopy, where direct information about the vibrational properties of crystalline materials can be obtained, has shown to be a useful tool for the characterization of semiconductors, where direct information about the vibrational properties of crystalline materials can be obtained. Figure 6



**Figure 6.** Raman spectrum from  $Cu_2SnSe_3$  nanocrystals.

shows the unpolarized room-temperature Raman spectrum of the as-synthesized  $Cu_2SnSe_3$  nanocrystals. Four peaks listed in Table S2 (Supporting Information), an intense peak at  $180\text{ cm}^{-1}$  and a broad peak at  $200$  and  $230\text{ cm}^{-1}$ , are attributed to the  $Cu_2SnSe_3$  phase, and this is in agreement with work reported earlier.<sup>40</sup> The most intense peak at around  $180\text{ cm}^{-1}$  can be attributed to the strongest  $\bar{A}$  mode and resembles the vibration of an anion atom with cations at rest. The Raman

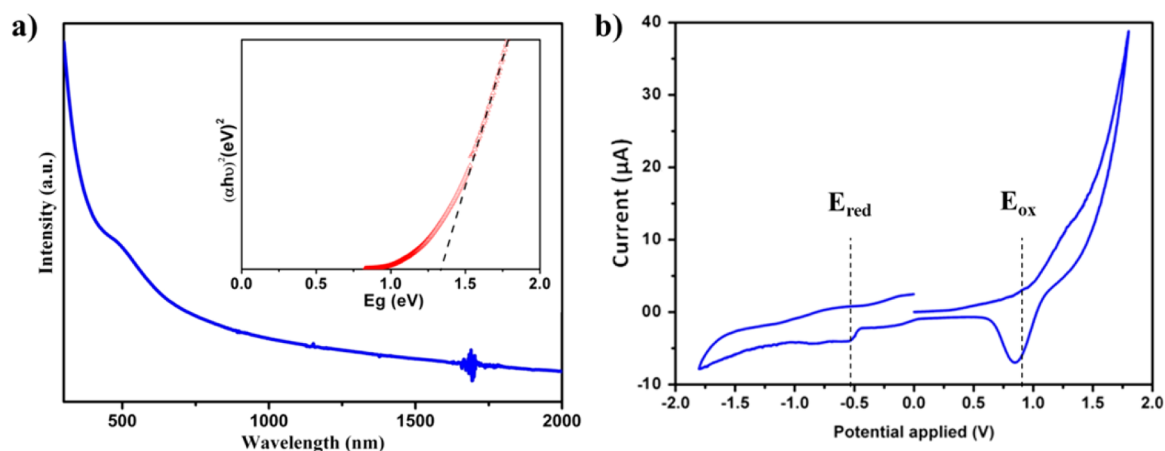
shifts for monoclinic  $Cu_2SnSe_3$  ( $C1c1$  space group and 2 Cu, 1 Sn, and 3 Se atoms in  $4a$  Wyckoff positions) have been calculated and correspond very well to previously reported data and to our observation (see Table S2, Supporting Information), confirming that our  $Cu_2SnSe_3$  has the monoclinic structure.<sup>41,42</sup> Together with the XRD data, it provides strong proof that the nanocrystals are monoclinic. We also collected Raman spectra from above  $500\text{ cm}^{-1}$  in order to determine whether the secondary phase,  $Cu_{2-x}Se$ , is present. No evidence of any secondary phase, particularly the  $Cu_{2-x}Se$  phase (which has a peak at around  $520\text{ cm}^{-1}$ ), was found.<sup>43</sup>

**Optical and Electrical Analysis.** The absorption properties of  $Cu_2SnSe_3$  nanocrystals were evaluated using UV–vis spectroscopy. The absorption spectrum of the  $Cu_2SnSe_3$  nanocrystals shown in Figure 7a exhibits a broad absorption band in the visible range with a tail extending to the infrared regime. The band gap of the synthesized  $Cu_2SnSe_3$  nanocrystals is estimated to be around 1.3 eV, as shown in the inset of Figure 7a. The estimated band gap is consistent with that obtained from the PL spectrum of a single  $Cu_2SnSe_3$  grain reported by Altosaar et al.<sup>42</sup> There is a wide range of band-gap energies reported for this compound. For bulk  $Cu_2SnSe_3$  synthesized by the vertical Bridgman–Stockbarger technique and sputtered thin films, the band gap was found to be 0.84 eV.<sup>12,14</sup> Thin-film  $Cu_2SnSe_3$  prepared by coevaporation onto a glass substrate with an average grain size of 600 nm was found to have two direct transitions at 0.74 and 1.12 eV.<sup>13</sup> On the other hand, the energy band gap of thin-film  $Cu_2SnSe_3$  prepared by coevaporation onto a soda lime glass substrate and then annealed at 573 K was found to be 0.9 eV.<sup>44</sup> These observations show that the band gap of nanocrystals generally shifts to a higher energy from bulk and thin-film  $Cu_2SnSe_3$ , and this is most probably related to the quantum size effect. The most recently reported optical and electrochemical energy band gaps for cubic and wurtzite  $Cu_2SnSe_3$  nanocrystals are 1.5 and 1.7 eV, respectively.<sup>25</sup> In general, it is not easy to elucidate the reason for the discrepancies in the energy band gap due to the wide range of different sample preparation and characterization techniques. Our observed optical band gap is in the range of reported values for nanocrystalline  $Cu_2SnSe_3$ .

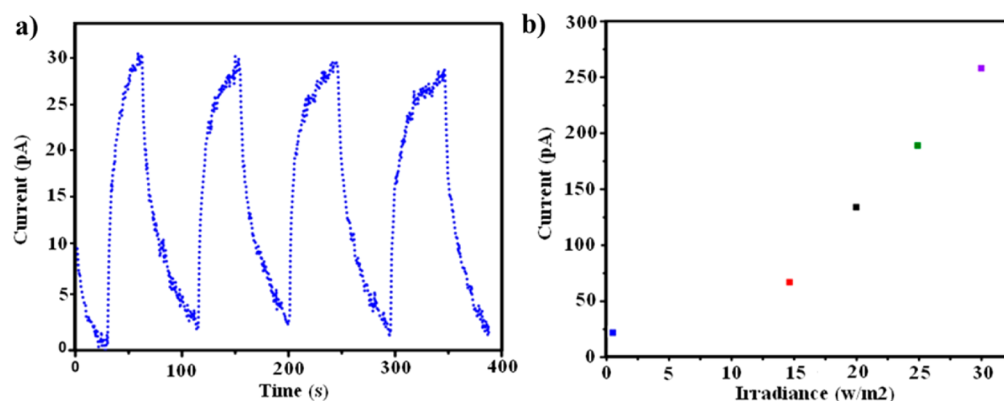
Another way to determine the band gap as well as the energy levels of the valence band and conduction band of inorganic semiconductor nanocrystals is through the use of cyclic voltammetry (CV) to electrochemically measure the reduction and oxidation potentials.<sup>45–47</sup> The as-deposited  $Cu_2SnSe_3$  nanocrystals were first dipped into a 0.1 M solution of hydrazine in acetonitrile for 30 s to remove the capping ligands. The valence and conduction bands of the inorganic semiconductors can be calculated based on the known HOMO/LUMO levels of ferrocene using the following equation (where  $E_{FC}$  is the oxidation onset of ferrocene):<sup>27</sup>

$$E_{\text{HOMO/LUMO}} = [(E_{\text{ox/red}} - E_{FC}) + 4.7] \text{ eV} \quad (6)$$

The oxidation process is related to the injection of a hole into the HOMO level of organic molecules or valence band of inorganic semiconductors, and the reduction process is related to the injection of an electron into the LUMO level or conduction band of inorganic semiconductors. The CV scan for  $Cu_2SnSe_3$  is shown in Figure 7b. The calculated valence and conduction bands from the CV results are  $-5.4$  and  $-3.9$  eV, respectively, and the electrochemical band gap of  $Cu_2SnSe_3$  nanocrystals was found to be 1.5 eV, which is a little higher than the estimated optical band gap. Similar differences were



**Figure 7.** (a) Room-temperature UV–vis absorption spectra of monoclinic  $\text{Cu}_2\text{SnSe}_3$  nanocrystals, and the inset shows how the band gap is determined for these nanocrystals. (b) Cyclic voltammetry measurement from monoclinic  $\text{Cu}_2\text{SnSe}_3$  nanocrystals treated with hydrazine.



**Figure 8.** (a) Photoresponsiveness of the nanocrystal film at an incident light intensity of  $30 \text{ W/m}^2$  and a bias voltage of  $0.05 \text{ V}$ . (b) Dark current and photocurrents as a function of light intensity at a bias voltage of  $0.1 \text{ V}$ .

also seen for band-gap measurement of  $\text{CdSe}$ ,  $\text{CdSe}_x\text{Te}_{1-x}$  and  $\text{CdTe}$  tetrapods.<sup>46</sup>

The energy band gap of  $\text{Cu}_2\text{SnSe}_3$  calculated from the optical and electrochemical measurements was found to range from 1.3 to 1.5 eV, and this is essentially very close to the optimum band gap of 1.4 eV for photovoltaic devices. This suggests that this material may be a good alternative candidate for solution processable solar cells.

To evaluate the potential of this material for solar cell applications, the photoresponsiveness of these nanocrystals was also measured. Both the photocurrent stability and the photosensitivity of the as-prepared nanocrystal film were measured under alternating light and dark conditions. The incident light intensity used was  $30 \text{ W/m}^2$ , and a bias voltage of  $50 \text{ mV}$  was applied. The photoresponse from the  $\text{Cu}_2\text{SnSe}_3$  nanocrystals is shown in Figure 8a. In the dark, the current was only  $0.15 \text{ pA}$ . However, with an incident light intensity of  $30 \text{ W/m}^2$ , the current could reach up to  $30 \text{ pA}$ , giving a photosensitivity of about 200. The photosensitivity of the nanocrystal film was further confirmed using photocurrent measurements of the sample at different incident light intensities. As shown in Figure 8b, when the intensity of the light was increased, the photocurrent of the nanocrystals increased accordingly. The photosensitivity of the  $\text{Cu}_2\text{SnSe}_3$  nanocrystals has not been studied in detail by others, but our calculated value from the photoreponse measurement is in good agreement with the composite system of related

materials.<sup>36,48</sup> Therefore, these results demonstrate the potential of  $\text{Cu}_2\text{SnSe}_3$  nanocrystals as a photon absorber material in solution processable solar cells.

## CONCLUSIONS

In conclusion, we have synthesized highly crystalline  $\text{Cu}_2\text{SnSe}_3$  nanocrystals with a narrow size distribution using the hot coordination solvent method. A crystallochemical study using XRD, SAED, CBED, electron energy loss, X-ray photoelectron, and Raman spectroscopies revealed that the  $\text{Cu}_2\text{SnSe}_3$  nanocrystals have the monoclinic  $\text{C1c1}$  space group with lattice parameters  $a = 6.981 \pm 0.002 \text{ \AA}$ ,  $b = 12.072 \pm 0.004 \text{ \AA}$ ,  $c = 6.952 \pm 0.002 \text{ \AA}$ , and  $\beta = 109.12 \pm 0.02^\circ$ . The nanocrystal film shows a photoresponse of 200 under illumination. The band gap of the synthesized nanocrystals was deduced from UV–vis spectroscopy and cyclic voltammetry and corresponded very well to the optimum band gap for solar energy absorption. Hence, this makes them suitable as potential candidates for the development of solution processable low-cost photovoltaic devices.

## ASSOCIATED CONTENT

### Supporting Information

TEM images and XRD spectra of as-synthesized nanocrystals using different precursors, TEM images of as-synthesized nanocrystals in different Se injection temperatures, EDX spectrum of  $\text{Cu}_2\text{SnSe}_3$  nanocrystals, XPS analysis of as-



synthesized  $\text{Cu}_2\text{SnSe}_3$  nanocrystals, XRD pattern of synthesized  $\text{Cu}_2\text{SnSe}_3$  nanocrystals and the simulated XRD patterns of monoclinic and cubic  $\text{Cu}_2\text{SnSe}_3$ , representative size distribution histogram of as-synthesized  $\text{Cu}_2\text{SnSe}_3$  nanocrystals, refined structure factors for different  $hkl$  of  $\text{Cu}_2\text{SnSe}_3$ , and calculated Raman data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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