Retraction for Journal of Materials Chemistry A:

In-situ formed ternary-based hybrid ink for the fabrication of $\rm Cu_2ZnSn(S,Se)_4$ solar cell absorbers

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We, the named authors, hereby wholly retract this *Journal of Materials Chemistry A* article due to data fabrication in Figures 3 and 6. The Raman spectra reported as a CZTSe film in Figure 3b is identical to the Raman spectra reported as CZTSe nanocrystals in Figure 4 of "The synthesis of $Cu_2Zn(Ge_xSn_{1-x})Se_4$ nanocrystals with tunable band gaps", *CrystEngComm*, 2013, **15**, 6942 [DOI: 10.1039/c3ce40953h]. The UV-vis absorption spectra curves in Figure 6b of films of varying S/Se content are the same curve that has been copied, shifted and pasted within the figure: the purple curve is the copy of the blue curve. An investigation by Dr Yongping Lei (Professor and Chairman of College Council of the College of Materials Science and Engineering, Beijing University of Technology, China) determined that Kai Zong was responsible for these instances of data fabrication. Hao Wang, as his tutor and also corresponding author, is responsible for the duty of supervision and management. Other co-authors accept joint responsibility for the preparation of article. Please allow us to sincerely apologise to all readers and the Editorial Office.

Signed: Kai Zong, Yuxiu Sun, Yongzheng Zhang, Hao Wang, Jingbing Liu and Hui Yan, November 2013.

Retraction endorsed by Liz Dunn, Managing Editor, Journal of Materials Chemistry A.

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In-situ Formed Ternary-based Hybrid Ink for the Fabrication of Cu₂ZnSn(S,Se)₄ Solar Cell Absorbers

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ABSTRACT Cu₂ZnSn(S,Se)₄ (CZTSSe) is a promising material for use as the low cost absorber for thin film solar cells, because it is only composed of abundant and economical elements. Herein we outline an alternative strategy to fabricate kesterite CZTSSe absorbers from an easily scalable hybrid ink based on propylmercaptan (PM) solution. The ink comprises a Zn-PM solution, with the in-situ formed readily dispersible particle-based Cu₂SnS₃ ternary precursor. The pre-formed Cu₂SnS₃ precursor would simplify the reaction pathway for the synthesis of CZTSSe thin films, and reduce the formation of detrimental secondary phases. CZTSSe solar cells fabricated by this approach exhibit an average power conversion efficiency up to 7.4 %.

KEYWORDS: Cu₂ZnSn(S,Se)₄, ink, solar cells, thin films

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Introduction

Exploring a safe and scalable route to fabricate low-cost and high-efficiency photovoltaics is one of the most active research fields in the area of solar cells. Kesterite, copper zinc tin sulfide selenide (Cu₂ZnSn(S,Se)₄ or CZTSSe), is considered as a potential substitute to traditional Copper-based quaternary semiconductors, Cu(In,Ga)(S,Se)₂ (CIGSe), due to its direct band gap energy (1.0-1.5 eV), relatively low toxicity, high optical absorption coefficient in the visible range (>10⁴ cm⁻¹), and earth abundant content of elements. ¹⁻³ To date, Guha *et al.* reported the fabrication of CZTSSe thin film solar cells with 8.4 % power conversion efficiency (PCE) using a vacuum-based approach. ⁴ However, such process typically suffers from relatively high cost, low material utilization, difficulty in composition control and difficulties associated with large-scale production.⁵

Recently, thin film processes using solution-based inks have attracted intense attentions, because the precursor film can be deposited on the substrate via a variety of facile techniques, such as dip-coating, slip casting, and screen printing etc., thereby enabling the development of low-cost, high-throughput roll-to-roll processes. ^{6,7} Guo *et al.* ⁸ demonstrated the fabrication of CZTSSe solar cells with 7.2 % power conversion efficiency using copper zinc tin sulfide (CZTS) nanocrystal inks synthesized by hot injection method with the subsequent selenization. However, the quaternary nanocrystal-based synthetic routes do not offer a simple method by which the final film composition can be controlled. Furthermore, the synthesis of nanocrystals by this additional step with controlled size is not compatible with the large-scale production. ⁸⁻¹⁰ Mitzi et al. demonstrated the fabrication of CZTSSe thin film solar cells with higher efficiency over 9.6 %, which is further improved up to 11.1 % by spin-casting precursor inks based on a hybrid solution-particle

hydrazine-based inks.¹¹⁻¹³ However, the corrosivity, explosibility, and toxicity of hydrazine limit its further investigation and large-scale application in industry. ^{14, 15} Furthermore, all processing for precursor solution and film preparations must be performed in the closed environment, such as glove box, due to the corrosivity nature of this solvent, and thus hydrazine would not be easily adaptable for large-scale solar cell fabrication. Therefore, a facile and easily scalable solution-based process for the fabrication of high quality CZTSSe absorber layers is still highly demanded.

In this work, we demonstrate a facile strategy to process CZTSSe absorbers, which features the preparation of hybrid ink using propylmercaptan (PM) solution. The hybrid ink employed for deposition comprises a Zn-PM solution, with the in-situ formed readily dispersible particle-based Cu₂SnS₃ ternary precursors. The concept is similar to that of the hybrid hydrazine-based ink adopted by Mitzi et al, ¹¹⁻¹³ however, which is composed of Cu–Sn chalcogenide (S or S–Se) solution and particle-based Zn-chalcogenide precursors, ZnSe(N₂H₄) or ZnS(N₂H₄). In this hybrid ink system, the solid particles act as stress-relief and crack-deflection centers allowing the deposition of thicker layers than pure solution processes. And the dissolved components can act as an efficient binding media for the particles, removing the need of other organic binders. ¹¹ The film composition can be easily controlled by simply adjusting the ratio of starting materials. Solar cells fabricated with the CZTSSe absorbers by this approach exhibit an average PCE up to 7.4 %.

Experimental section

Chemicals

Copper (II) chlorid dehydrate (CuCl₂·2H₂O, 99.99%), zinc (II) chloride (ZnCl₂, 99.99%), tin (II) chloride dehydrate (SnCl₂·2H₂O, 99%), sulfur powder (S, 99.5%), and propylmercaptan (C₃H₇SH, 98%) were purchased from Aladdin. All chemical reagents were used as received without further purification.

Synthesis of hybrid ink

The synthesis of the hybrid ink and fabrication of CZTSSe thin films are performed in the fume cupboard. In a typical synthesis of Cu₂SnS₃ nanoparticles, 0.18 mmol of CuCl₂·2H₂O and 0.1 mmol of SnCl₂·2H₂O were dissolved in 5 mL of propylmercaptan (PM) under magnetic stirring at room temperature, leading to a clear yellow Cu-Sn-PM solution. Then a certain amount of sulfur powder was adding into the above Cu-Sn-PM solution, the color of the system gradually changed from transparent yellow to deep black. Meanwhile, the Zn-PM solution was prepared in another separate vessel, by mixing 0.12 mmol of ZnCl₂ and 5 mL of PM, yielding a clear and colorless solution. Finally, the hybrid ink was prepared by mixing the Cu₂SnS₃ nanoparticles and Zn-PM solution, targeting final composition [Cu : (Zn+Sn) : S] = 0.8 : 1 : 3, and Zn : Sn = 1.2. The Cu₂SnS₃ nanoparticles used for further characterization were centrifuged at 8000-10000 rpm for 10 min and washed by the solution mixed with amount of hexane and isopropanol for several times, then the Cu₂SnS₃ nanoparticles were dried at 100 °C on a hot plate. All PM-based precursor solutions were prepared in the air condition, and the hybrid ink was stored in a sealed glass vial and can be stable for at least six months.

Synthesis of CZTSSe thin films

The CZTSSe thin films were deposited on Mo-coated glasses via spin-coating from the precursor ink in the fume cupboard. To reach the targeted thickness of the absorption layer, several successive layers were coated following an intermediate heat treatment between 130-230 °C as a pre-heated treatment. A final annealing treatment was conducted in a graphite box at 450-550 °C for 60 min under different chalcogen vapor supply including pure selenium vapor, pure sulfur vapor, combined sulfur and selenium vapor treatment. After the heat treatment, the samples were cooled naturally to room temperature under inert atmosphere. The detailed process of the experiment is shown Fig. S2† in the ESI.

Device fabrication and characterization

The CZTSSe absorber films were then processed into photovoltaic devices by chemical bath deposition of CdS (50 nm), RF magnetron sputtering of i-ZnO (50 nm), and indium-doped tin oxide (250 nm). A 110 nm thick MgF_2 antireflection coating was deposited on top of the device by electron beam evaporation, and thermal evaporation of the patterned Al grid as a current collector. The area of CZTSSe-based

solar cell was 0.093 cm². Photovoltaic devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. *J-V* data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter. External quantum efficiency (EQE) was collected by an EQE Measurement System (Continuous Solar Simulator for PV Cells, Hong-ming Technology Co., Ltd.).

Materials characterization

The mercaptan-based precursor solutions with inorganic salts and sulfur powder were studied by using a Fourier transform infrared spectrophotometer (FT-IR) (Thermo, Nicolet 6700). The hybrid ink dispersed in hexane were dropped on carbon supported Cu grids for transmission electron microscopy (TEM) observation, which was performed on JEM-2100 with an acceleration voltage of 200 KV. The X-ray diffraction (XRD) profiles were measured with a German Bruker AXS D8 ADVANCE diffractometer (Cu K α radiation, λ =1.5405 Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The Raman spectra were obtained by LabRam HR800, the wavelength of laser excitation for Raman measurements was 488 nm, and the laser power was~100 mW. The X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 XPS using an Al K_{α} (1486.6 eV) X-ray source. To exclude the influence from surface-absorbed oxygen and carbon, Ar⁺ ion (3 keV) etching for 3 min was performed before collecting the X-ray generated electrons. The morphologies and microstructures of the films were observed using a Hitach S4800 field emission scanning electron microscope (SEM). The optical properties of thin films were characterized using a Shimadzu UV-3101PC spectrophotometer at room temperature. The electrical properties were analyzed using van der Pauw geometry and Hall effect measurement (HMS-3000/0.55T) at room temperature using indium ohmic contacts.

Results and discussion

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Mercaptan is usually adopted as sulfur source, ligand, and solvent in the synthesis of binary and ternary sulfides (e.g. Cu_xS, CuInS₂),^{16, 17} which is a short-alkyl thiol with strong volatility. Mercaptan could react with metal cations to produce metal thiolates, which would decompose into corresponding sulfides at certain conditions. Furthermore, as a strong ligand for Cu, Zn, and Sn, mercaptan could cap the generated nanoparticles to reduce the surface energy and make the system kept stable for a long time. ¹⁸ The interaction between PM and different metal cations is carried out by the Fourier transform infrared spectrophotometer (FT-IR) analysis (Fig. S1[†] is available in the ESI). It is worth noting that, similar to hydrazine solvent, PM can dissolve a certain amount of sulfur powder, which is the most critical step for the synthesis of hybrid ink in this study, and also a more stable sulfur source in precursor solution, compared with thioacetamide or thiourea usually adopted by non-hydrazine solution system. ¹⁹⁻²¹

Readily dispersible Cu_2SnS_3 nanoparticles were formed in situ by the addition of certain amount of sulfur powder directly to the transparent Cu-Sn-PM solution. Fig. 1 (a) shows a representative TEM image of the obtained Cu_2SnS_3 nanoparticles, which are monodispersed with the diameter of around 20 nm. XRD pattern of the nanoparticles is corresponding well with the standard pattern of Cu_2SnS_3 (JCPDS no. 89-4714), which have tetragonal structure with three major diffraction peaks (112), (204), and (312) planes (Fig. 1 (b)). Fig. 1 (c) reveals the Raman spectra of the Cu_2SnS_3 nanoparticles. The obvious peaks locate at 290, 319, and 354 cm⁻¹ are observed, which matches well with those generally observed in the Raman spectra of tetragonal structured Cu_2SnS_3 . ^{22, 23} No secondary phase, such as CuS_x or SnS_x , are detected.

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Fig. 1 (a) TEM image of the Cu_2SnS_3 nanoparticles, (b) and (c) XRD pattern and Raman spectrum of Cu_2SnS_3 nanoparticles.

The formation mechanism of Cu₂SnS₃ nanoparticles was ascertained by several parallel experiments. Firstly, when sulfur powder was added into the transparent

colorless Cu-PM solution, the color of the system remains unchanged, which indicates that there's no Cu_xS phase forms at present condition. Secondly, $SnCl_2$ cannot be individually dissolved in PM solvent, unless at the presence of $CuCl_2$, forming transparent yellow Cu-Sn-PM solution. It means that Cu^{2+} could oxide Sn^{2+} into Sn^{4+} , leading to well solubility of $SnCl_2$ at the presence of $CuCl_2$ in PM solvent (shown in equation (1)).

$$2Cu(SC_{3}H_{7})_{2} + SnCl_{2} + 2HSC_{3}H_{7} \rightarrow 2Cu(SC_{3}H_{7}) + Sn(SC_{3}H_{7})_{4} + 2HCl \qquad (1)$$

Thirdly, after adding certain amount of sulfur powder into the transparent Cu-Sn-PM solution, the color of the system changed slowly from clear yellow to deep dark, which proves Cu-Sn-S ternary sulfide phase formed at present condition. We suppose that when sulfur powder dissolved in PM, a variety of valence of sulfur ions will generate by the reducing reaction shown in equation (2), here x value is from 0 to 2. After that, S^{x-} can attack the central metal cation of copper and tin thiolates in PM, leading to the final formation of Cu₂SnS₃ nanoparticles (shown in equation (3)). Therefore, during the synthesis of Cu₂SnS₃ ternary phase, the resolution of sulfur powder in PM plays an important role. The related preparation schematic and photographs are shown as Fig. 2:

$$S + 2HSC_3H_7 \rightarrow S^{x-} + C_3H_7SSC_3H_7 + 2H^+$$
 (x=0~2) (2)

$$\operatorname{Cu}(\operatorname{SC}_{3}\operatorname{H}_{7}) + \operatorname{Sn}(\operatorname{SC}_{3}\operatorname{H}_{7})_{4} + 3\operatorname{S}^{\text{x}^{-}} + 5\operatorname{H}^{+} \to \operatorname{Cu}_{2}\operatorname{Sn}\operatorname{S}_{3} \downarrow + 5\operatorname{HSC}_{3}\operatorname{H}_{7}$$
(3)



Fig. 2 The preparation schematic and photographs of the parallel experiments.

As is well known, Cu_2SnS_3 is an indispensible intermediate phase during the formation of CZTSSe phase.²⁴ In the vacuum-based deposition, the complete conversion of elemental metals, alloys, or binary chalcogenides to Cu₂SnS₃ generally takes several hours at higher annealing temperature (>500 °C). It would bring about irreversible loss of Sn due to the evaporation of SnS and the formation of detrimental Cu-rich secondary phases. ^{25, 26} Cao et al. ¹⁰ obtained the high-efficiency solution-processed CZTSSe thin-film solar cells using binary (ZnS) and ternary (Cu_2SnS_3) nanoparticles. Cu_2SnS_3 nanoparticles were obtained by hot-injection method at around 260 °C. However, the nucleation and growth of nanoparticles by hot-injection are cumbersome, and the yield is limited. Bypassing limitations of vacuum-based approach and hot-injection method, since the Cu_2SnS_3 particles have already existed in the precursor ink at room temperature, the present method would simplify the reaction pathway for the resulting CZTSSe solar cell: the formation of secondary phases such as CuS_x and SnS_x is no longer necessary to produce the final CZTSSe phase, and the phase conversion is presumably more thorough as the kinetic obstacles of the reaction route are less severe. ²⁴ The hybrid ink contained Cu₂SnS₃ nanoparticles can be stable for at least six months, because the nanoparticles are capped by PM molecules which make them dispersed well in PM solution.

The XRD data of CZTSSe thin films under different chalcogen vapor supply are displayed in Fig. 3 (a). The XRD patterns of sulfide and selenide films correspond well with the standard patterns of Cu₂ZnSnS₄ (JCPDS no. 26-0575) and Cu₂ZnSnSe4 (JCPDS no. 52-0868), respectively. The diffraction peaks shift to smaller 20 values as the selenium content increases, indicating an increase in lattice constant due to the replacement of sulfur with selenium. No unidentified peaks are observed in the XRD data, demonstrating well-crystallized and single phase films. Fig. 3 (b) shows the same trend of Raman spectra with different chalcogen vapor supply on the thin films. For the sulfide film, the major peaks appear at 334, 287, and 367 cm⁻¹; while for selenide film, the main peaks locate at 196, 172, and 235 cm⁻¹. Both spectra agree well with the reported values for CZTS and CZTSe, respectively. ^{27, 28} For film with

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intermediate S/Se content, the main peaks from both sulfide and selenide are present, following the same trend as previously reported for CZTS with an intermediate S/Se ratio. ²⁹⁻³¹ No evidence of other possible secondary phases such as CuS_x , $CuSe_x$, ZnS, ZnSe, and Cu_2SnS_3 appear in the Raman spectra of each film.



Fig. 3 (a) XRD analysis of CZTSSe films under different chalcogen vapor supply including pure selenium vapor, pure sulfur vapor, combined sulfur and selenium vapor,(b) Raman spectra of CZTSSe films under different chalcogen vapor supply.

Electronic states of each element in the CZTSSe film are determined by X-ray photoelectron spectroscopy (XPS), giving the respective chemical valence: Cu: +1;

Zn: +2; Sn: +4; S: -2; Se: -2 (Fig. S2†). A high-resolution scan (in Fig. 4) around the O (1s) peak detected no trace of oxygen (the detection limit of XPS is < 0.1%), while the intensity of Cl (2p) and C (1s) is about two orders lower than that of Cu (2p3/2), suggesting a low concentration of chlorine and carbon. However, it must be admitted that the Cl residue is hard to avoid, even though the effect of Cl residue in the absorber film on the device performance is not clear today.



Fig. 4 XPS analysis of possible impurities (Cl/C/O) compared with signal from a main element (Cu) obtained from a high-resolution scan.

Figure 5 illustrates representative top-view and cross-section field emission scanning electron microscopy (SEM) images of a typical CZTSSe thin film. The top-view image (Fig. 5 (a)) reveals that the film surface is extremely dense and compact. The cross-sectional image (Fig. 5 (b)) shows that the thickness is approximately 1.52 μ m, and the film consists of large crystallites, with no obvious voids. The larger grain size is an indispensable factor that can affect device performance. Room-temperature electrical property of a typical CZTSSe thin film is determined in a magnetic field strength of 0.51 T at room temperature by Van der Pauw method. The CZTSSe film is found to be p-type conductivity, with the resistivity of 0.54 Ω cm, the carrier concentration of 8.3×10¹⁸ cm⁻³, and the Hall mobility of 13.4 cm²V⁻¹S⁻¹. These results provide further evidence that the CZTSSe

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thin films are favorable to be used as the thin film solar cell absorbers.

Fig. 5 SEM images of CZTSSe thin film (a) top view, (b) cross-sectional view.

Figure 6 (a) displays the UV-vis spectra for CZTSSe thin films under different chalcogen vapor supply. It indicates that the band gap edge absorption of the CZTSSe thin films exhibit an obviously red shift toward a longer wavelength in comparison with the absorption value of the CZTS thin films. The optical band gap is determined by extrapolating the linear region of the plot $(\alpha h v)^2$ versus hv by equation (4) and taking the intercept on the hv-axis.

$$(\alpha h v)^2 = A (h v - E_g) \tag{4}$$

The band gap values calculated from the UV-vis absorption spectra (Figure S4) of CZTSe, CZTSSe, and CZTS films are 1.03, 1.23, and 1.50 eV, respectively, as shown in Fig. 6 (b). These results demonstrate that by adjusting the chalcogen vapor supply during post-annealing, the resulting band-gap values can be judiciously tuned.



Fig. 6 (a) UV-vis spectra for CZTSSe thin films under different chalcogen vapor supply, (b) Band gap values calculated from UV-vis absorption spectra of films with the varying S/Se content.

The annealed CZTSSe absorber layer was intergrated into a photovoltaic device following standard procedures, including the chemical bath deposition of CdS (50 nm), RF magnetron sputtering of i-ZnO (50 nm), and indium-doped tin oxide (250 nm). A 110 nm thick MgF₂ antireflection coating was deposited on top of the device by electron beam evaporation, and thermal evaporation of the patterned Al grid as a current collector. The current-voltage (*J-V*) characteristics of a typical CZTSSe solar cell measured in the dark and under AM 1.5 illumination are presented in Fig. 7 (a).

The device performance parameters are reported based on the active area of 0.093 cm^2 , excluding the area of the Al grid current collector (~11 % of total device area). The as-fabricated device shows a PCE of 7.34 % (V_{OC} = 440 mV, J_{SC} = 32.1 mA cm⁻², FF = 51.9 %), with a best value of 7.52 %. The mean PCE is 7.4 % by averaging the 8 best cells. The present CZTSSe cell has relatively low V_{OC} and high J_{SC} , which is expected from its relatively low band gap (1.23 eV). Fig. 7 (b) shows the external quantum efficiency (EQE) of the corresponding solar cell as a function of photon wavelength. The maximum quantum efficiency of 80 % is obtained for a photon wavelength of 540 nm. The band gap of the absorber layer is determined to be 1.25 eV by fitting a plot of $[E \ln(1-EQE)]^2$ vs. E near the band edge, as shown in the inset of Fig. 7 (b), agreeing well with the band gap value calculated by plotting $(\alpha h v)^2 vs$. hv. The incomplete current collection in the IR region, especially beyond 800 nm, indicates the need for a thicker absorber with enhanced minority-carrier transport. Although the initial efficiency of the CZTSSe thin film is lower than those produced by the hydrazine-based ink (11.1 %), improvements in device performance are expected with further studies by optimization of absorber processes and device components.





Fig. 7 (a) J-V curvers of a typical CZTSSe solar cell measured in the dark and under AM 1.5 illumination, (b) EQE spectrum of the corresponding CZTSSe solar cell; inset: band gap of the absorber was calculated to be \sim 1.25 eV by extrapolation.

Conclusions

In conclusion, we have demonstrated that CZTSSe films with well crystallinity and grain size can be fabricated through using a newly developed hybrid ink based on mercaptan solution. Particular significances are given to the following three facts: 1) We obtained the indispensible intermediate phase, Cu₂SnS₃ nanoparticles, at room temperature by an in-situ forming process. Taking advantage of pre-formed Cu₂SnS₃ particle precursor, it shortens the reaction pathway for the fabrication of CZTSSe films, and reduces the formation of detrimental secondary phases; 2) The ink is formed by simply mixing Zn-PM solution and in-situ formed Cu₂SnS₃ particle precursor at a mild condition, without the involvement of complex nanocrystal synthesis, which is easy for large-scale production; 3) Our readily achievable stable precursor ink, facilitates a convenient method to fabricate CZTSSe films. This easily scalable process can be adapted to numerous ultrahigh throughput printing (e.g., flexographic, screen, ink-jet) and coating (e.g., spin, spray, roll-to-roll) techniques. The resulting CZTSSe absorber layers are implemented into thin-film solar cells and the devices show an initial average PCE up to 7.4 %. Further optimization of CZTSSe

process and device fabrication should lead to enhanced efficiency and an environmentally responsible route to earth abundant element, stable, low-cost, thin-film solar cells.

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Graphical abstract

In-situ Formed Ternary-based Hybrid Ink for the Fabrication of Cu₂ZnSn(S,Se)₄ Solar Cell Absorbers

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We demonstrate a facile strategy to process CZTSSe absorbers using a hybrid ink with the in-situ formed Cu_2SnS_3 nanoparticles.