Ligand exchange in $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles and its effect on counter electrode performance in dye-sensitized solar cells

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MS received 15 October 2018; accepted 26 March 2019

Abstract. Ligand-exchanged $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanoparticles (NPs) were successfully synthesized from colloidal NPs by replacing the long chain organic ligand from the surface of NPs *via* a bi-phasic method. It was found that ammonium sulphide salt $(\text{NH}_4)_2\text{S}$ plays a key role in changing the surface of the NPs from hydrophobic to hydrophilic. The efficacy of the ligand exchange process over the surface of the CZTS NPs was analysed using X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy and scanning electron microscopy with energy dispersive X-ray. The ligand-exchanged CZTS NP-based counter electrodes (CEs) were fabricated by drop casting the inorganic ligand (ammonium sulphide)-capped CZTS nanoink onto the conducting substrate. Our result indicates that dye-sensitized solar cells (DSSCs) with inexpensive CZTS NP-based CEs show 2.42% efficiency. The present result indicates that CZTS CEs will be helpful as an alternative CE to a Pt CE in DSSC application.

Keywords. DSSC; CZTS CEs; Pt CEs; bi-phasic ligand exchange; colloidal NPs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have enormous advantages viz. low-production cost, ease of fabrication and tunable aesthetic features. Recently, porphyrin-based dye in conjunction with a cobalt-based electrolyte achieved the world certified efficiency of 13% [1]. A typical DSSC consists of three primary components: a photoanode with a sensitizer, an electrolyte containing a redox mediator and a counter electrode (CE). An ideal CE consists of Pt. It should show high-electrocatalytic activity for the reduction of charge carriers in the electrolyte as well as high conductivity. However, as a noble metal, Pt is expensive and large-scale manufacturing is restricted [2]. In addition, the platinum CE interacts with a traditional iodide-based electrolyte and can decompose to PtI_4 which affects the long-time stability of DSSCs [3]. Hence, to address these problems, several materials such as carbon-based materials, conducting polymers, sulphides and nitrides have been utilized to replace Pt [4–7]. Among them, the inorganic quaternary chalcogenides such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ have attracted prominent attention due to their optical and electrical properties in thin film solar cells. They possess a direct band gap with high-absorption co-efficient ($>10^4 \text{ cm}^{-1}$) [8]. CZTS-based CEs have excellent stability towards the iodide-based electrolytes [9]. The performance of the CZTS-based CE has potential to replace Pt in DSSCs [10]. So far, several approaches have been applied to fabricate CZTS CEs, such as thermal evaporation, sputtering, hot injection methods and facile one-pot synthesis methods [11–14]. However, the size- and shape-controlled

CZTS NPs were achieved *via* a hot injection method. Nevertheless, the alkyl long chain ligands have been utilized to yield colloidal NPs with a controlled size and shape. But they act as insulating barriers over the surface of NPs that impede effective charge transfer properties and lead to poor conductivity, and also hinder the performance of NPs in electrical and photoelectric devices [15]. So far, the high-temperature annealing process was carried out to remove the organic ligands, but it leaves the carbon residue during the annealing process on the surface of NPs, which hinders the device performance [16]. So, efforts were made to prepare hydrophilic CZTS NPs *via* a bi-phasic method. As compared with other ligand exchange processes, the ammonium sulphide-based bi-phasic ligand process has electrostatic stabilization between the polar solvents and the NPs [17]. The simple, cost effective ligand exchange process was performed to exchange the NPs (hydrophobic to hydrophilic) *via* ultrasonication. During the process, the colloidal NPs switched from the toluene phase to the formamide (FA) phase thereby yielding the hydrophilic CZTS NPs. Furthermore, the drop-casting method has been used to produce CZTS and Pt-based CEs. The as-prepared CEs were used in DSSCs and the efficiency of the device was measured.

2. Experimental

2.1 Hydrophilic nanoparticle preparation

The CZTS NPs were prepared following the procedure detailed in our previous report [18]. In a typical synthesis

Figure 1. Ligand exchange process from hydrophobic to hydrophilic CZTS NPs.

Figure 2. Schematic illustration of the preparation of the CZTS-based CE.

process: copper chloride, zinc acetate and tin chloride with oleylamine (OAm) were taken in a three-neck flask to form a metal complex and the elemental sulphur with OAm forms polysulphide (H_2S^-) in another three-neck flask. Polysulphide was injected into the metal complex at the elevated temperature to produce the CZTS NPs. The ligand exchange process was applied according to the previous reports with some modification [22]. The following procedure can be used to prepare hydrophilic CZTS NPs: herein, 1:10 ratios of ammonium sulphide ($(\text{NH}_4)_2\text{S}$) solution in FA (CH_3NO) with 5 ml solution of CZTS NPs in toluene were mixed together. It forms the bi-phasic solution and is shown in figure 1. Then the solution was ultrasonicated until the nanoparticles were transferred from toluene to the FA phase. After the ligand exchange, the solution was washed with toluene several times to remove the excess organic ligands. Further, acetonitrile was added to remove the excess FA and to precipitate NPs. The precipitated NPs were redispersed in ethanol/water to form

a nanoink. The phase transformation process can be easily examined by the naked eye (hydrophobic to hydrophilic) as shown in figure 1.

2.2 CE preparation

The hydrophilic CZTS NPs were drop cast on the cleaned fluorine-doped tin oxide (FTO) substrate as shown in figure 2. The FTO substrates were first cleaned in a soap solution using an ultrasonication bath and in DI water, ethanol and isopropanol. Then the cleaned FTO substrates were air dried before deposition. The CE material was prepared by the drop casting method using the hydrophobic and hydrophilic nanoink (concentration 5 mg ml^{-1}). The FTO substrate was heated to 100°C and the CZTS nanoink was dropwise added onto the FTO substrate, further, the substrate temperature was increased to 150°C and maintained for 10 min. This process was repeated five times to increase the thickness. Finally, the

prepared CZTS film was annealed at 200°C for 30 min to remove the excess ligands on the material.

2.2a Device fabrication: Commercially available TiO₂ paste (Sigma-Aldrich) was used to produce the photoanode according to the previous reports [19]. The resultant TiO₂ films were sensitized by immersing it in 0.5 mM ethanol and *tert*-butyl alcohol solution of N749 black dye tris(*N,N,N*-tributyl-1-butanaminium)[[2,2'',6,2''-terpyridine]-4,4',4''-tricarboxylato(3-)-*N*1,*N*1',*N*1'']tris(thiocyanato-*N*) hydrogen ruthenate(4-) for 12 h and air dried to prepare the photoanode. The electrolyte consists of 0.05 M of LiI, 0.03 M of I, 0.5 M of TBT and 0.6 M of BMII in acetonitrile and injected into the assembled DSSC. The Pt CE was prepared using hydrochloroplatinic acid (H₂PtCl₆) via a thermal decomposition method. The Pt ink (a mixture of 0.7 mol H₂PtCl₆ + isopropanol) was drop cast on the FTO substrate and annealed at 420°C for 20 min to prepare the Pt CE [20]. The active area of the cell is 0.16 cm⁻².

2.2b Characterization: Structural analysis was characterized using a Bruker D8 advance (copper K α = 1.54 eV, θ = 20–80°). Fourier transform infrared (FTIR) spectra were recorded using attenuated total reflection (ATR)-FTIR mode on a Jasco FTIR 6300. The surface morphology and elemental analysis were carried out using a Carl Zeiss MA15/EVO18 scanning electron microscope equipped with energy dispersive X-ray (EDX) spectral analysis. The optical studies were performed using a Jasco UV-650 spectrophotometer. Cyclic voltammetry (CV) measurement was performed in the CH instrument using three electrode systems (Pt—CE and Ag/AgCl as a reference electrode). The photocurrent–voltage measurement was carried out using a Sol3A Class AAA solar simulator.

3. Results

3.1 Structural analysis

The X-ray diffraction (XRD) pattern of the as-synthesized CZTS NPs is shown in figure 3. In the as-synthesized CZTS NPs, three major diffraction peaks were observed in the range of 28, 47 and 56° corresponding to (112), (220) and (312) planes, respectively. However, the long chain alkyl ligand OAm was used in the synthesis process to control the growth of the nanoparticles. It acts as a surface-passivated layer over the nanoparticles and affects the performance of the device. So, scientific efforts were devoted to the elimination of the ligand without producing the carbon residue which also affects the device quality. The complete removal of ligands produces a cluster of the nanoparticles which is also not suitable for device application. To stabilize the NPs, the bi-phasic ligand exchange process was applied to switch the CZTS NPs from a long chain ligand to a short chain ligand, which increases the conductivity of the material and produces electrostatic

Figure 3. XRD spectra of OAm-mediated CZTS NPs and S²⁻ ligand-exchanged CZTS NPs.

Figure 4. FTIR spectra of hydrophobic (before ligand exchange) and hydrophilic (after ligand exchange) CZTS NPs.

stabilization in the polar solvents [21]. Herein, the NPs are transferred from the OAm phase to the sulphide phase (S²⁻) using FA as a solvent and inorganic salt (ammonium sulphide) as a phase transfer reagent. The surface modification process has not changed the crystalline nature of the material, which is confirmed by the XRD results. The XRD pattern of the ligand-exchanged NPs reveals three major peaks which are present at 28, 47 and 56° corresponding to (112), (220) and (312) planes, respectively. Both these peaks match well with JCPDS card no. 260575. The XRD results indicate that the surface-modified process did not affect the crystalline nature of the material and the removal of large organic molecules will improve the crystallinity of the materials [22].

3.2 FTIR spectral analysis

The ligand exchange process was confirmed using the ATR-FTIR method. Figure 4 shows the FTIR spectra of both the samples (OAm-CZTS and CZTS-(NH₄)₂S nanoparticles). The CZTS-OAm showed a sharp methyl (C–H) band in the

higher range ($2800\text{--}3000\text{ cm}^{-1}$). This feature disappeared in the ligand-exchanged (CZTS- $(\text{NH}_4)_2\text{S}$) nanoparticles [22]. The band peaks present at 1632 cm^{-1} and the sharp peak at 1400 cm^{-1} correspond to the FA phase. Nevertheless, the annealing process leaves a significant carbon residue on the surface of NPs, which was not observed in the FTIR spectra of CZTS NPs in the FA phase [23].

3.3 Ultraviolet–visible (UV–Vis) analysis

The UV absorption spectra of the as-synthesized CZTS NPs are shown in figure 5. The optical band gap of hydrophilic

Figure 5. The optical absorption spectra of the as-synthesized CZTS NPs. The inset shows the optical band gap of hydrophilic CZTS.

CZTS NPs was calculated using the Tauc plot ($\alpha h\nu$ vs. $h\nu$, α —absorption co-efficient, h —Planck's constant and ν —frequency). The band gap (E_g) value is estimated to be 1.51 eV by extrapolating a line in the x -axis. These values match well with the previous report on kesterite CZTS (1.4–1.6 eV) [10–15]. This band gap value is the optimum value for photovoltaic application.

3.4 Surface morphological studies

The morphology of the as-synthesized CZTS NPs was demonstrated using the scanning electron microscopy (SEM) image. Figure 6a and b shows the hydrophobic CZTS NPs with different magnifications. The NPs could be seen as a nanosphere with agglomeration. After the ligand exchange the homogenous nanospheres were observed. The surface modification process cannot affect the surface morphology of the materials as confirmed by SEM images. Elemental analysis was carried out for hydrophobic and hydrophilic CZTS NPs. All four constituents were present in both the samples. Both the samples show non-stoichiometric ratios, CZTS-OAm (2.14:0.93:0.92:4.1) and CZTS- $(\text{NH}_4)_2\text{S}_2$ (2.01:0.92:0.91:4.3). It may be due to the different ionic nature of the elements. In addition, a slight compositional variation was observed on the surface-treated NP, which may be due to the surface treatment of ammonium sulphide salt. The final composition tuning in the NPs leads to an effective performance in the device application [18,23].

Figure 6. Surface morphological image and EDX spectra of (a–c) hydrophobic CZTS NPs and (d–f) hydrophilic CZTS NPs.

Figure 7. CV measurements of three different CEs.

Figure 8. Photovoltaic performance of DSSCs with different CEs.

3.5 CV measurements

The electrocatalytic activity of CZTS and Pt CEs was evaluated using CV measurements. The CZTS CE exhibits an electrocatalytic activity similar to that of the Pt CE in the reduction of the electrolyte (I_3^- to I^-) in DSSCs. The higher peak current and lower peak to peak separation indicate the excellent electrocatalytic activity. Figure 7 shows the electrocatalytic activity of the as-synthesized materials. The

ligand-exchanged CZTS CE shows superior electrocatalytic performance as compared with the OAm-capped CZTS CE. The peak to peak separation was higher for S^{2-} -CZTS as compared to that of Pt (0.54 V). The current density of S^{2-} -CZTS is higher when compared with that of OAm-CZTS. So S^{2-} -CZTS is an effective CE material and it is capable of replacing Pt. Yang *et al* already reported the conduction band (-3.85) and valance band (-5.40) values of CZTS using CV measurements. The following equation is used to calculate the electrochemical band gap of the material:

$$E_{CB}/E_{VB} = [(E_{red/ox} - E_{ferrocene}) + 4.7] \text{ eV} \quad (1)$$

The reduction and oxidation value (E_{ox} (V) = -0.58 and E_{red} (V) = 0.76) of the as-synthesized S^{2-} -CZTS was calculated from the CV measurements. On the basis of the results, the valence band energy level of -3.9 eV and the conduction band of -5.5 eV were determined. The energy levels of the CZTS CE matched with previous reports. The estimated electrical band gap is $E_g = 1.6$ eV. The electrical band gap is slightly higher than the optical band gap. This band gap variation may be due to the interfacial energy barrier between the material and the CE [18,24].

3.6 I-V characteristics of DSSCs

The photovoltaic performance of the device was evaluated using a separate photoanode (FTO/TiO₂/N749 black dye) with various CEs (Pt, S^{2-} -CZTS and OAm-CZTS). The current density and the voltage ($J-V$) measurements of the solar cells are shown in figure 8 under 1 sun illumination. The standard dye/Pt CE shows the $J_{sc} = 8.8 \text{ mA cm}^{-2}$, $V_{oc} = 0.73$ V and fill factor (FF) = 0.61 which yields the power conversion efficiency (PCE) of 3.77%. By replacing the Pt CEs with hydrophilic (S^{2-}) CZTS CEs, the efficiency of the device is slightly lower than that of the Pt CE and higher than that of hydrophobic (OAm) CZTS CEs. The V_{oc} of 0.65 V and J_{sc} of 8.3 mA cm^{-2} are obtained for hydrophilic (S^{2-}) CZTS CEs. The resultant PCE (2.42%) is high as compared with that of the hydrophobic CZTS CE (0.39%). Table 1 represents the summary of the DSSC performance with different CEs. The lower efficiency in the hydrophobic CZTS CEs could be due to the surface passivation layer in CEs. It also hinders the charge transport properties of the CEs and affects the performance of the device. The device with hydrophobic CZTS NPs gives

Table 1. DSSC parameters V_{oc} —open circuit voltage, J_{sc} —short circuit current and FF.

Material	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	Efficiency (%)
Pt-CEs	733 ± 0.09	8.8 ± 0.14	0.61 ± 0.08	3.77 ± 0.2
OAm-CZTS	470 ± 0.03	2.6 ± 0.6	0.32 ± 0.1	0.39 ± 0.14
S^{2-} -CZTS	650 ± 0.01	8.3 ± 0.4	0.45 ± 0.03	2.42 ± 0.35

the $J_{sc} = 2.6 \text{ mA cm}^{-2}$, $V_{oc} = 0.47 \text{ V}$ and $FF = 0.32$ with 0.39% efficiency. However, the above result suggests that the hydrophilic CZTS also serves as an effective CE instead of Pt. The hydrophilic CZTS-based DSSCs show a lower FF as compared with Pt. Further optimization is needed to increase the performance of the devices [11–14,25,26].

4. Conclusion

CZTS NPs were successfully synthesized *via* a hot injection method. The hydrophobic and hydrophilic CZTS nanoink was drop cast onto the FTO substrate to fabricate the CE materials for DSSCs. The surface-passivated organic ligand was exchanged with inorganic salt over the surface of the NPs, which was confirmed from the FTIR results. The resulting ligand-exchanged CZTS NPs enhance the performance of the devices as compared to the OAm-CZTS CE-based DSSCs. CZTS CEs have the potential to replace the Pt CEs in DSSCs.

Acknowledgements

The authors sincerely thank DST (DST-TM/SERI/FR/90(G)) and UGC (F.No. 42-855/2013) for funding the research work. The I – V characteristics were determined using the facility at CeNSE (INUP user program) in IISc, Bengaluru, funded by the Ministry of Electronics and Information Technology (MeitY), and Govt. of India.

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