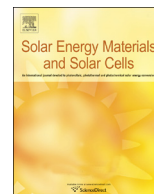




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## Voltammetry investigation on copper zinc tin sulphide /selenide (CZTS<sub>x</sub>Se<sub>1-x</sub>) alloy nanocrystals: Estimation of composition dependent band edge parameters



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## ABSTRACT

Among various light-absorbing materials, Copper Zinc Tin Sulphide (CZTS), Selenide (CZTSe) and their alloy structures (CZTS<sub>x</sub>Se<sub>1-x</sub>) are viewed as important candidates in thin film solar cell applications. Next development in this field could be a band edge engineering using varied composition layer-structure. Such configuration is expected to absorb broad spectrum of light and will also provide additional gradient for the efficient charge separation. For such development, however the prior knowledge of band edge parameters as a function of composition is needed. Herein, we describe the bench top electrochemical approach to estimate conduction and valence band edge positions for CZTS<sub>x</sub>Se<sub>1-x</sub> as a function of 'x'. CZTS<sub>x</sub>Se<sub>1-x</sub> alloy nanocrystals with varied compositions have been prepared by solvothermal method. These were carefully characterized by UV-vis, FTIR-ATR, XRD, Raman, TEM, SEM, and EDAX analysis to confirm the formation of alloys with desired composition. Cyclic voltammetry analysis carried out on them gave distinct cathodic and anodic peaks, which are co-related to the electron transfer mediated through conduction and valence band edges, respectively. The band edge parameters obtained by cyclic voltammetry matched well with the one reported previously by photoelectron spectroscopy method.

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### 1. Introduction

Exceedingly increased in energy demand and at the same time depletion in the fossil fuel reservoirs, force us to seriously consider renewable energy sources, with a prominent attention to the solar energy. Among various photovoltaic devices, Si based solar cells have been extensively investigated for last several decades and commercially available. However, energy intensive single crystal technology to manufacture them is considered to be a major hurdle for the sustainable growth. To overcome this challenge, thin films of other light absorbing direct band gap semiconductors have been tested extensively for the solar cells applications. Among them, copper indium gallium sulfides/selenides (CIGS) [1] and CdTe [2,3] have shown optimum efficiency and stability and thus, views as potential candidates for the commercial applications. However, the use of toxic element like cadmium, tellurium put an additional recycling cost. Moreover, fast depletion of indium reservoir is another concern for the sustainable growth [4–6]. Due to these reasons more attention has been paid in recent years to the

semiconductors, based on less toxic, earth abundant elements such as copper zinc tin sulphide (CZTS) and (CZTSe) [7–16]. This films of CZTS and CZTSe are deposited readily by radio frequency (RF) and diode (DC) magnetron sputtering technology and the corresponding solar cells deliver efficiency better than 10% with a good stability [13,14,16–18]. Lot of efforts have been put to further decrease the manufacturing cost by using low temperature film deposition techniques viz. spin coating, drop casting and knife coating of CZTS nanocrystals slurry on suitable substrates followed by a post annealing and selenization [9,19,20]. The devices made by this method delivered the efficiency close to 7.2%, which further improved to about 9% by modified synthesis procedures and optimized selenization [20]. The record efficiency of 12.6% is achieved by spin coating the hydrazine based hybrid precursors, followed by a post-annealing [21]. This improvement is attributed to the formation of alloy structure with selenium, without compromising charge mobility.

To take the idea of alloy structure to improve the performance of the solar cells to a next level, it would be interesting to prepare CZTS nanocrystals with varied compositions (CZTS<sub>x</sub>Se<sub>1-x</sub> alloy) and deposit their thin films in a tandem fashion. This strategy would not only give a more favorable potential-gradient to help

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better charge separation but also would capture the broader spectrum of sunlight with minimum heat losses. To implement this idea, however valence band ( $E_{VB}$ ) and conduction band ( $E_{CB}$ ) edges of  $CZTS_xSe_{1-x}$  alloy nanocrystals need to be estimated as a function of 'x'. These parameters in case of quantum dots are generally estimated by ultraviolet photoelectron spectroscopy (UPS) [22] and scanning tunneling spectroscopy (STS) [23,24]. Both these techniques involve major instrumentation and tedious sample preparation and thus out of reach to many chemists for the routine applications. Recently, our group [25–29] and many others [30–35] have demonstrated that these parameters can be equally accurately estimated by bench top approach like cyclic voltammetry (CV). Cathodic and anodic peaks in the CV analysis are associated to the electron transfer mediated through conduction and valence band-edges, respectively. In short, electronic states of quantum dots can directly be invoked by these techniques. The band structure parameters of various quantum dots as a function of size [28] (size quantization effect) and composition [25] (band gap bowing effect) have been estimated by CV and matched very well with the independent results obtained by photoelectron spectroscopy in air (PESA) [25,36]. Interaction of graphene with quantum dots also have been studied and the results have been further corroborated by time resolved photoluminescence (PL) spectroscopy [29]. Even though there are lot of convenience to use CV to estimate the band edge parameters, sometimes nature of solvent pose some limitation on the available potential window especially in case of wide band-gap materials. Thus the measurements need to be carried out in the non-aqueous media and under inert atmosphere.

In case of  $CZTS_xSe_{1-x}$  alloys, there is only one report to date which describe the estimation of their band edge parameters by the Ultra Violet Photoelectron Spectroscopy (UPS) [22]. CV measurements have been used in few samples to substantiate the results. Here, authors observed the cathodic peak from which they reported conduction band edge positions as a function of composition. In their measurements, the anodic peak is not seen clearly. Therefore, the valence band edge has been estimated indirectly by supplementing the results from UV-Visible NIR spectroscopy. Optical band-gap however may not be equal to the electrochemical band gap due to the difference in the mechanism in the charge separation [27]. So, independent values of cathodic and anodic peaks are needed for the more complete knowledge of band structure.

With this motivation, we prepared well-characterized  $CZTS_xSe_{1-x}$  alloy nanocrystals with varied composition by solvothermal method and undertook detailed voltammetric investigation. The CV results gave reproducible values of conduction band and valence band edges as a function of composition. The results have shown an excellent agreement with the similar values reported from the UPS data [22].

## 2. Materials and methods

### 2.1. Materials

Copper (II) acetylacetonate, zinc acetylacetonate were purchased from Acros Organics. tin (IV)bis(acetylacetonate) dibromide, oleylamine (OLA) technical grade 70%, tetrabutylammonium per chlorate (TBAP), dichloromethane (DCM) were purchased from Sigma Aldrich. Toluene, propan-2-ol were purchased from SDFCL and used as received.

### 2.2. Synthesis of CZTS nanocrystals ( $x=1$ )

CZTS nanocrystals have been prepared by a hot injection method suggested by Agrawal et al. [9]. For that, copper (II)

acetylacetonate (1.5 mmol), zinc acetylacetonate (0.75 mmol), tin (IV) bis (acetylacetonate) dibromide (0.75 mmol) and 10 mL oleylamine were mixed well in a 100 mL three necked flask, under nitrogen atmosphere. The solution was initially heated to  $\sim 130$  °C under vacuum ( $\sim 0.01$  torr) and degassed for 30 min with  $N_2$  gas. Degassing procedure was repeated for 5 times to insure complete elimination of air from the system. Once the mixture turned into a clear brown transparent solution, the temperature was raised to 225 °C. Into it, freshly prepared, 3 mL sulphur solution in oleylamine (1 M) was swiftly injected which turned solution dark. Sulphur solution was prepared before hand by dissolving 0.128 g in 4 mL oleylamine at room temperature under inert atmosphere. The flask temperature was maintained 225 °C for 30 min. The temperature of the flask was then quickly brought down to  $\sim 80$  °C by lifting the flask from the heating mantle and applying wet towel to the flask from outside. The reaction was further quenched by adding a mixture of 5 mL of toluene and 40 mL of isopropanol. The solid product obtained was separated from mother liquor by centrifugation (10,000RPM for 5 min), followed by a decantation. The product was re-dispersed in 20 mL toluene and again flocculated by adding 10 mL of isopropanol and centrifuged followed by decantation. The final solid product was dried in a vacuum and stored in vacuum desiccators.

### 2.3. Synthesis of $CZTS_xSe_{1-x}$ alloy nanocrystals with $x=0, 0.25, 0.5$ , and $0.75$

The synthesis of  $CZTS_xSe_{1-x}$  alloys nanocrystals with  $x=0, 0.25, 0.5$ , and  $0.75$  was carried out by method suggested by Riha et al. [37]. Unlike sulphur, selenium is insoluble in neat oleylamine. So, to dissolve it, 5 mM  $NABH_4$  was added in 5 mL oleylamine, followed by weighed amount of selenium powder to get desired mole ratios;  $x=0, 0.25, 0.5, 0.75$  M of S/Se. The sulphur solution was prepared as discussed before. Prior to the injection, both the solutions are mixed in a desired ratio and injected to the reaction mixture at 225 °C. The products were extracted by the procedure, described before.

### 2.4. Materials characterization

UV-Visible NIR spectra were recorded on dispersion of  $CZTS_xSe_{1-x}$  alloy nanocrystals in toluene with the help of Agilent 8453 diode array single beam spectrophotometer. The FTIR spectra were recorded using Bruker FTIR Tensor-37 spectrometer, having a diamond ATR attachment. Powder X-ray diffractograms (XRD) were recorded on dry powder samples using a Bruker, D8-Advance, X-ray Diffractometer ( $CuK\alpha$ , 40 kV and 40 mA). Low resolution transmission electron microscopic (TEM) images were recorded using a Philips CM200 transmission electron microscope (200 kV). For the phase characterization, Raman spectra were recorded on the samples using RENISHAW inVia-312c23 at 532 nm operated at 1% (1.5 W) power. Size distribution and elemental compositions were estimated by FEI make Nova NanoSEM 450 FESEM, with EDAX using Bruker XFlash 6I30. AFM images were recorded on Bruker, Multimode 8.0.

### 2.5. Electrochemical Characterization

The Electrochemical characterizations were performed with the help of Metrohm Potentiostat/Galvanostat (Auto lab PGSTAT 100). A commercial Au disk electrode (CHI Instruments, USA, 2-mm diameter), Ag wire, and Pt-wire-loop were used as working, quasi-reference, and counter electrodes, respectively. Prior to the experiment, the working electrode was polished over 0.5  $\mu m$  alumina powder, rinsed with copious amount of Milli-Q water. It was then further electrochemically cleaned by potentiodynamically

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