

Synthesis of quaternary chalcogenide CZTS nanoparticles by a hydrothermal route

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Abstract: $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has emerged as a potential absorber towards inorganic photovoltaic device application for its outstanding properties like non toxicity, earth abundancy nature, optimal band gap matched with solar spectrum (1.45- 1.65eV), high absorption coefficient (10^4cm^{-1}). Here, a low cost, environment friendly facile hydrothermal route to synthesize phase pure CZTS nanoparticles using Cu (II), Zn (II), Sn (II) inorganic metal salts and thiourea as Sulphur source in distilled water solution as precursor is reported. The as synthesized samples characterized by X-Ray diffraction (XRD) and RAMAN confirmed structure and phase of CZTS nanocrystals. The morphology of the prepared CZTS have been characterized by scanning electron microscopy (SEM). The particle size is found in the range 4-5 nm with crystalline nature have been characterized by transmission electron microscope (TEM). The optical band gap of the as prepared samples is calculated to be 1.65eV from UV-Visible analysis which proves it can be used towards photovoltaic applications.

1. Introduction

Increasing in worldwide clean energy crisis calls for the development of harvesting the renewable solar energy through photovoltaic cell (PVC). Thin film solar cells (TFSCs) belong to second generation PV, in which active absorber layer attracts the attention of research community due to large versatility in deposition techniques, device fabrication process and tuning the photo conversion efficiency (PCE). Mostly, TFSCs include the high efficient absorber materials like cadmium telluride (CdTe), copper indium gallium selenium (CIGS), copper indium selenium (CIS) [1, 2]. The highly toxicity of elements like indium, gallium, selenium urgently calls for the non- toxic, earth abundant, low cost absorber materials towards PVC application [3]. Being a P- type semiconductor, $\text{Cu}_2\text{ZnSnS}_4$ referred as CZTS has emerged as a potential absorber to overcome the existing glitches along with its outstanding specifications like high absorption coefficient ($>10^4\text{cm}^{-1}$) and the tunable optical band gap of 1.45-1.65eV which has favorably match with the solar spectrum [4]. According to physical limitation of Shockley Queisser (SQ) photon balance the PCE for a single – junction CZTS solar cells should be 32.2% [5]. On the other hand, in practical the efficiency has reached to the level of 12.6% by Todorov et al. [6] which is noticeably less in comparison to the predicted theoretical value. To enhance the PCE of CZTS based solar cells there are continuous research effort to optimize the material properties and device architecture. There has been lot of research focus on the methods of preparation of CZTS which controls the phase and sizes. Since the Vacuum as well as non- vacuum methods are utilized to deposit and fabricate CZTS based TFSCs. Vacuum routes consists of atomic beam sputtering, RF magnetron sputtering, thermal evaporation, and pulse laser deposition (PLD), chemical vapor deposition (CVD) etc. Vacuum based deposition methods suffer certain drawbacks like high input capita (like high vacuum, high temperature, expensive chemicals etc. sophisticated experimental set up), low output and difficulties during deposition into large area based devices. These shortcomings are the limitations for achieving the ultimate goal of maximal PCE of low cost, environmentally sustainable TFSCs. Thus non vacuum deposition technique such as electrochemical deposition, spray pyrolysis, SILAR method, sol gel method, direct liquid coating are promising methods for synthesis of CZTS. The high performance direct liquid coating deposition routes for deposition of CZTS either utilize binary metal sulphides solution based inks or sulfurization of metal precursor [7]. The maximal efficiency of 12.6% was obtained for CZT(S,Se) nanocrystals based solar



cells fabricated by Todorov et al. [6] through a hydrazine hydrate-based solution approach. The hydrazine-based process suffers from major drawback i.e hydrazine is massively explosive, hepatotoxic, and carcinogenic. Zinc sulphides typically have negligible solubility in hydrazine hydrate solvent under ambient conditions. One way to prefabricate the photovoltaic absorber material by using nanocrystal ink and these inks could be ideally deposited under mild conditions by screen paint, knife coating, roll to roll, dip coat and spin coating etc. for large scale production. Guo et al. [8] reported that the PCE of CZTS based photovoltaic device up to 7.2% by simply coating colloidal CZTS nanoparticle ink with subsequent annealing and post selenization steps. As material synthesis procedure greatly affects the device performance, it should be cost effective, environment friendly, easily hand able. On the other hand, nanocrystals seek tremendous attention over bulk materials as they are solution processible, tunable band gap with respect to nanocrystal size which realizes multi junction with multiple carrier generation. Various methods are employed to synthesize CZTS nanocrystals such as hot injection [9], sol-gel [10], microwave assisted method [11], solvothermal [12] etc. Among them one pot facile solvothermal wet chemical approach provides the uniform precursor formation with controlled phase and growth nanocrystal size. Mostly CZTS nanoparticles were prepared via amine group solvents as surfactant, capping agent and stabilizer which are quite expensive. To overcome this, synthesis of size controlled CZTS nanoparticles via a simple, environment friendly, low cost method should employed.

Chunrui Wang et al. [13] synthesized CZTS nanocrystals by hydrothermal route using distilled water as solvent and they have found ~7nm range particles confirmed through transmission electron microscopy. Here we report, a low cost green hydrothermal synthesis approach of CZTS nanocrystals using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ metal salts and thiourea as reacting agent. As for our concern there is only one paper on this context is reported. Further improvement in physical properties and sized of the prepared CZTS could be optimized correlating with the preparation conditions.

2. Materials and methods

In an environment friendly synthesis process, Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Zinc chloride (ZnCl_2) and Stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) were all of analytical grade and used as received. All distilled water used throughout synthesis was procured from Milli-Q purification system. Copper chloride dihydrate, Zinc chloride, stannous chloride dihydrate and thiourea as Sulphur source (with molar ratio 2:1:1:4) are dissolved in adequate amount of distilled water to make precursor solution. The precursor has been stirred for 45 mins till the color of the solution turns clear, slightly yellowish. Then the precursor solution was transferred into a 100ml stainless steel with Teflon liner autoclave kept inside in a muffle furnace for 20 hours at 200°C temperature. After the hydrothermal reaction the autoclave is allowed to cool to ambient conditions naturally. The obtained precipitate was washed 4 times with ethyl alcohol and dried at 80°C under vacuum condition. Then the obtained black powder was collected for further characterizations. The schematic diagram of the synthesis procedure is given in Figure 1.

The synthesized CZTS powder has been characterized through various characterization techniques. The crucial factors like crystallinity and the phase of the synthesized sample was confirmed by XRD, RAMAN (Renishaw Raman microscope) and the particle size and the information regarding the nano crystal distribution was revealed by the microscopy study Technai G220 (transmission electron microscopy (TEM), Nano nova scanning electron microscopy (SEM)). Structural characteristics of powder were determined by XRD analysis carried out using a diffractometer (Philips X'pert) with a scan rate of 5° per minute with step size 0.05 in the 2θ range from 10° to 80°. The analytical diffractometer (Rigaku Japan, Ultima-IV) operating in Bragg configuration is equipped with graphite-monochromitized with Cu Kα radiation ($\lambda = 1.54184 \text{ \AA}$). The morphology, size and shape of the derived particles were examined by TEM and from its selected area electron diffraction (SAED) and high resolution TEM (HRTEM) results the crystal structure of the samples can be further identified. Morphological view made by TEM displays of nano-sized crystals well dispersed ($c = 0.03 \text{ mg/mL}$) in N, N dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$) as a dispersant medium. Specimens for transmission

electron microscopy were obtained by taking CZTS sample-DMF dispersion onto a 300-mesh Cu grid, coated with a lacey carbon film and subsequent evaporation of the solvent. For optical analysis $c=0.01\text{mg/ml}$ was prepared in 15ml valve. The band gap was extracted from the data obtained by the analysis of UV-Visible spectroscopy.

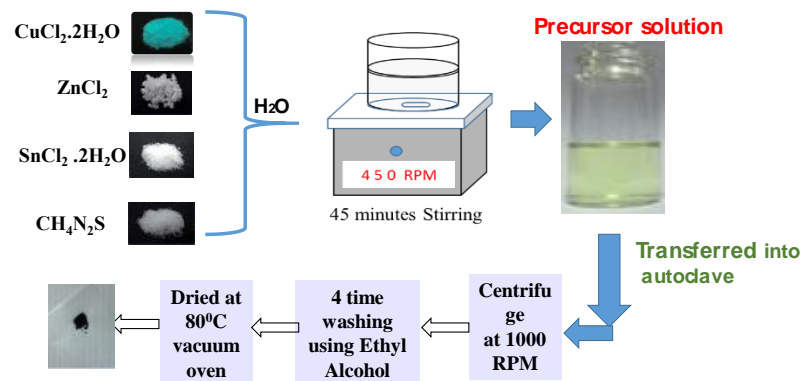


Figure 1. Schematic diagram of CZTS nanocrystal synthesis

3. Result and Discussion

Figure 2(a) shows the diffraction pattern of CZTS nanocrystals prepared at low temperature 200°C for 24 hours. It exhibits prominent peaks at the positions $2\theta = 27.98^{\circ}, 31.75^{\circ}, 38.23^{\circ}, 45.65^{\circ}, 54.73^{\circ}, 74.13^{\circ}$ assigned to the orientation of (112), (200), (211), (220), (312) and (332) diffraction planes corresponds to the kesterite phase of CZTS (JCPDS card no-26 0575) respectively. From the Debye-Scherrer formula:

$$d = 0.89\lambda/\beta \cos\theta$$

(Where, 0.89 is a constant called shape factor, λ is X-ray wavelength, θ is Bragg angle, β is full width half maximum (FWHM) of significant diffraction peak and d is the crystallite size) the nanocrystallite size of as synthesized CZTS sample is calculated to be 4.95 nm from the strongest. The lattice constant of quaternary kesterite CZTS is quite close to binary phase β ZnS and Cu_3SnS_4 structure [14, 15]. The tetragonal CZTS unit cell inside which each sulfur anion is bonded to four cations and each cation is bonded to four sulfur anions has lattice parameters $a=b= 5.4270\text{\AA}$, $c = 10.8480\text{\AA}$. The kesterite CZTS has a tetragonal unit cell with S atoms located at face - centered - cubic sub lattice and Cu, Zn, Sn atoms occupy the half the tetrahedral interstitial site within S sub-lattice. The lattice parameters for tetragonal unit cell were calculated by using the expression (h, k , and l are the miller indices of the plane):

$$\frac{4\sin^2\theta_{hkl}}{\lambda^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

Raman scattering gives a more definitive structure analysis. The information regarding the electronic state excitations of lattice in a material providing the information of detecting secondary phases can be

obtained by extremely useful tool Raman Spectroscopy (RS) analysis. The decrease in the particle dimensions can cause a wavenumber shift and Raman peak broadening as a result of phonon confinement observed in nanometer scale. Raman spectra of the nanocrystals shown in Figure 2(b) have a peak around 334 cm^{-1} which correspond to kesterite phase of CZTS. Figure 3 (a) shows the SEM photograph of as prepared CZTS nanocrystals of $5\mu\text{m}$ scale. The uniform distribution of CZTS nanocrystals is confirmed from SEM photograph. The CZTS agglomeration consists of several small nanocrystals is shown in Figure.

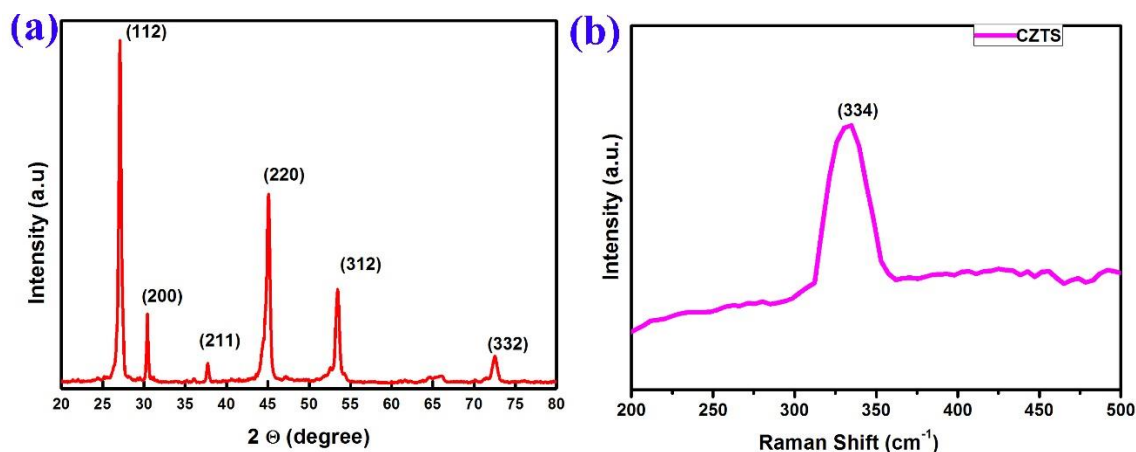


Figure 2. (a) X-Ray diffraction pattern and **(b)** Raman spectra of CZTS nanocrystals synthesized at 200°C for 20h

The low resolution TEM (LRTEM), shown in Figure 3 (b) gives a clear cut picture of the distribution of CZTS nanoparticles. The HRTEM (high resolution TEM) figure given in Figure 3 (c) gives the information regarding crystallinity, size and shape of the synthesized CZTS nanocrystals. From TEM photograph it is clear that the synthesized CZTS nanocrystals are spherical in shape with average nanocrystal size $\sim 4.23\text{nm}$, which is in agreement with obtained value from XRD data. Figure 3 (d) is the selected area electron diffraction (SAED) pattern of CZTS. The SAED pattern reveals the polycrystallinity nature of sample. The HRTEM images show inter planar spacing of 3.13\AA of kesterite CZTS.

The optical properties of colloidal nanoparticles have quite vital significance for their further use in optoelectronics. Figure 4(a) shows the absorption spectra of as synthesized CZTS QDs as a function of nanocrystal size which features a broad shoulder with a trail towards long wavelength direction. The band gap of the CZTS nano particles stably dispersed in DMF was obtained by plotting $(\alpha h\nu)^2$ as a function of $h\nu$ also depicted in the Figure 4(b). The band gap of the synthesized sample is estimated from the absorbance plot. The absorbance graph shows a strong absorbance in visible range and a long tail extending to longer wavelengths. From the long wavelength extrapolation of the band edge of the absorption spectra, the optical band gap of the synthesized sample is calculated to be 1.65eV Figure 4 (b). The good absorption in visible range makes the material suitable for the absorber layer towards photovoltaic device application.

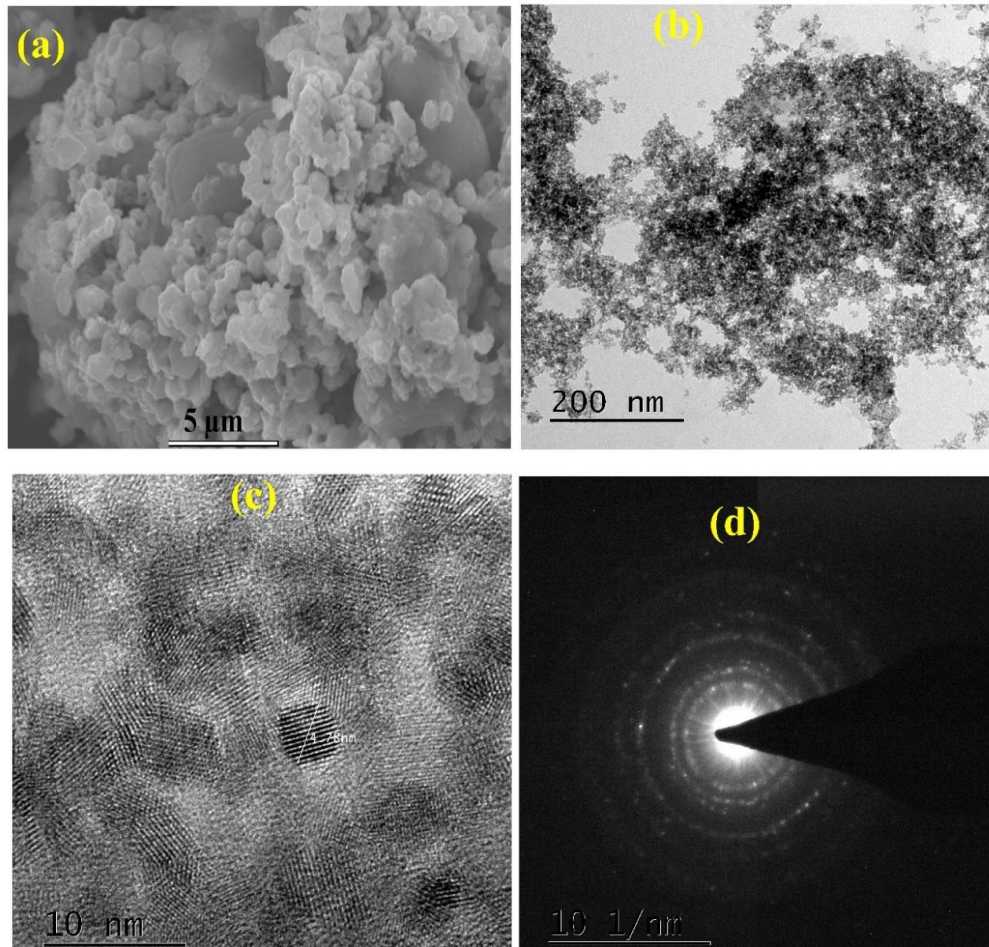


Figure 3. (a) SEM (b) LRTEM (c) HRTEM (d) SAED pattern of the synthesized CZTS nanocrystals

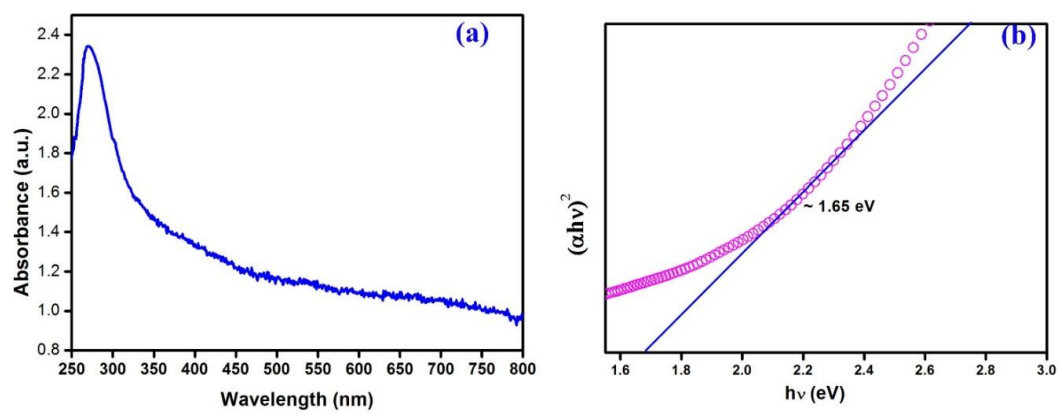


Figure 4. (a) UV-Visible absorbance spectra (b) band gap of CZTS nanocrystals

4. Conclusion

In conclusion, kesterite CZTS nanocrystals are synthesized by a simple hydrothermal environmental friendly approach using thiourea as Sulphur source. XRD, SEM, LRTEM, HRTEM characterizations have confirmed the structure, phase, morphology of synthesized CZTS nanocrystals. X-ray diffraction study confirmations about the crystalline phase of synthesized CZTS. From the HRTEM analysis the average size of CZTS nanocrystal is found to be around 4nm. The band gap of synthesized sample is calculated to be 1.65eV which indicates that the synthesized material has good applicability in visible range. The synthesized CZTS nanocrystals could be used as absorber layer material in photovoltaic device for various applications.

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