PREPARATION OF NANOPARTICLES OF CZTSe BY MICROWAVE-ASSISTED CHEMICAL SYNTHESIS

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Abstract

In this study we present the synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanoparticles by microwave-assisted chemical synthesis employing organic solvents. The effect of reaction time, reactant concentration, solvent and additives (inorganic material) was studied on the structural and optical properties of the nanomaterials. The powder samples were analyzed by X-ray diffraction (XRD), Raman spectroscopy, X-ray energy dispersive spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). The results show that the synthesis performed with triethanolamine and deionized water is better than others solvents, producing nanocrystals of quaternary phase (CZTSe) with stoichiometric relations similar to the reported research in the literature, which falls in the range of $\text{Cu}/(\text{Zn}+\text{Sn})$: 0.8 - 1.0, Zn/Sn : 1.0 - 1.20. The nanoparticles of CZTSe synthesized in this study present desirable properties in order to use them in solar cell and photoelectrochemical cell applications.

Key words: CZTSe, nanoparticles, microwave-assisted chemical synthesis.

INTRODUCTION

Semiconductors with photovoltaic properties are considered to be one of the most important green energy sources for harnessing solar energy. During the past few decades, a wide variety of absorber materials with excellent optical and electrical properties have been investigated including CuInGaSe_2 (CIGS) and CdTe [1-6] which are already employed in commercialized thin film solar cells with module efficiencies around 13% and 16% respectively [7], while at laboratory it has been reached higher efficiencies than 22% in both cases [8]. However, the limited supply of In, Ga and Te coupled with the toxicity issue of Cd discourage the use of these materials on large scale [9]. In the search for appropriate

absorber materials which overcome the aforementioned issues, research has been focused on the kesterite-related family of thin-film chalcogenide materials such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{(4-x)}$ (CZTSSe) [10-13]. Wadia et al [14] estimated the electricity contribution and cost impact of material extraction to a finished solar module by calculating the maximum TWh and minimum ¢/W of 23 inorganic compounds. This study shows a cost of 0.005 ¢/W for (CZTS), which is one of the lowest values obtained. Besides, they present outstanding electrical and optical properties, p-type conductivity, large absorption coefficient ($>10^4 \text{ cm}^{-1}$) and a tunable band gap of 0.85 to 1.7 eV which is close to the optimal value for single-junction solar cells as predicted theoretically [15-19].

CZTS-based semiconductors have proved to be potential candidates for thin film solar cells reaching maximum efficiency of 12.6% [20]. These materials have been synthesized by physical techniques like evaporation [21] and sputtering [22], as well as chemical techniques like solvothermal synthesis [23], spin coating [24], chemical bath deposition [25], doctor blade [26], electrodeposition [27], and solid state reaction [28]. Although physical methods produce high quality thin films, they generally suffer from slow throughput, low material utilization, and high energy consumption. In particular, for the deposition of CZTS/CZTSe films the vacuum-based approaches encounter significant challenges to maintain phase purity and compositional stoichiometry due to element volatility and re-evaporation from deposited films [13,29]. On the other hand, chemical techniques don't use vacuum and high temperatures; they are cheaper than physical methods, and provide better opportunity to control phase purity. Therefore, a lot of investigations have been focused on chemical techniques, achieving similar or superior efficiencies to physical techniques [30]. The highest power conversion efficiency for CZTSSe based solar cell has been reached up to 12.6% where CZTSSe layer was deposited using hydrazine based precursor solution followed by selenization process. However, hydrazine is an explosive, hepatotoxic and carcinogenic solvent [31].

In order to develop an environmental friendly process, it's not only enough to use absorber materials constituted of non-toxic elements but also solvents for solution processing step. Amines are substances which are non-toxic and have been used for solvothermal synthesis of kesterites. Some non-toxic solvents or mixture of solvents have been tested, as: isophorondiamine [32], triethylene glycol [33], triethylenetriamine [34], ethylenediamine and polyvinylpyrrolidone [23], oleylamine [35], isophorondiamine and trioctylphosphine [36] and triethanolamine [37].

Among a rich variety of chemical methods including solvothermal, hot-injection or arrested precipitation, sol-gel and wet chemical route [23-25], microwave-assisted chemical

synthesis (MACS) is a method not frequently used for synthesis of inorganic materials; there are few publications regarding the synthesis of this kind of metal chalcogenides, such as CZTS, CuInSe_2 , CuInTe_2 , CuInS_2 , ZnSe , Cu_2S , CdS , CdSe , ZnS , ZnSe and CdTe [38-44]. Microwave-assisted chemical synthesis has several advantages over typical solvothermal process; reactions take place in minutes or hours which by solvothermal would take place in hours or days [45-46].

EXPERIMENTAL

We performed a systematic study on the synthesis of CZTSe by MACS, analyzing the effect of precursor concentration, reaction time and solvents on the crystalline structure and chemical composition of CZTSe nanocrystals. The precursor solution was prepared by adding 2.0 mmol of copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 1.0 mmol of tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), 1.0 mmol of zinc nitrate hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$) and 4.0 mmol of elemental selenium powder (Se) into triethanolamine (TEA). The solution was stirred at 100 °C for 30 mins in order to dissolve the reactants. Then reactions were performed in a microwave reactor (Anton Paar Synthos 3000 operating at 2.45 GHz), which was programmed at 240 °C for different time periods using a 5 min ramp, and it was set a security limit of maximum pressure of 60 psi. In the first set of experiments 40 ml of TEA was used as solvent and the effect of reaction time was inspected by selecting 3 different reaction times: 0.5, 1.0 and 1.5 h. In the second set of synthesis, the effect of precursor concentration on stoichiometry and crystallinity of the products was analyzed by employing 20 ml of TEA instead of 40 ml so that the molar concentration of precursor salts would be double. Further test using lower volume of TEA (<20 ml) was not done due to the incomplete dissolution of the precursors. During the second set of synthesis the reaction was set at 240 °C for 1 h. Finally, the effect of solvent was tested, by diluting TEA with 10, 20, 30, 32 and 35% of deionized water, however, only 10 ml of the mixture (TEA-deionized water) was used, keeping the reactant proportion, but reducing the reactants by half. The microwave assisted reaction was set as 240 °C for 1 h.

At the end of the reaction a black precipitate was obtained which was separated by centrifugation and washed several times with deionized water and ethanol. Then the product was dried in an oven for 3 to 5 h at 60 °C to obtain dry powder which was used for further characterization.

The crystal structure of the nanoparticles obtained were characterized by powder X-ray diffraction (XRD), using a Rigaku diffractometer, using Cu K α radiation, $\lambda=1.5406$ Å, in the 2θ range of 10–100° at a grazing incidence angle of 0.5°. Raman spectroscopy was used in

order to confirm the formation of the quaternary CZTSe phase and discard the presence of other secondary phases. Raman spectra of the samples were recorded on a JobinYvon RAM HR800 Raman spectrometer equipped with an Olympus BX41 microscope and a charge-coupled device detector. The 632.8 nm emission of a He-Ne laser was used as the excitation source. Elemental composition was analyzed by X-ray energy dispersive spectroscopy (Oxford Instruments) attached to a Hitachi SU1510 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) was performed on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos 150 MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. The binding energy (BE) values were referred to the C 1s peak at 284.8 eV.

RESULTS AND DISCUSSION

Figure 1 presents the X-ray diffraction patterns of the nanocrystals obtained at 0.5 h, 1.0 h and 1.5 h using 40 ml TEA as solvent. It is important to mention that the vapors produced during the synthesis increased the pressure up to its limiting value of 60 psi, reaching a final temperature of 226 °C instead of 240 °C. The reference patterns of the tetragonal CZTSe (PDF# 052-0868) and the CuSe phase (PDF-01-0728417) are also included in the figure. Samples obtained at 1.0 and 1.5 h reaction time (Figure 1 b and c) coincide well with the pattern (PDF-00-052-0868), the major diffraction peaks at 2 theta values of 27.13, 45.05 and 53.34°, which corresponds to (112), (204) and (312) planes along with other peaks of relatively low intensity, which corresponds to (400), (008), (316), (424), (228), (512) and (1110) planes. While at 0.5 h (Figure 1a) there is presence of the secondary phase CuSe (PDF-01-0728417) at 2 theta values of 28.01, 31.10 and 46.02°, corresponding to (102), (006) and (110) planes. The tendency to form copper selenide phase is explained by Ahmadi et al. [47] taking into account the Pearson classification of ions as hard or soft acids/bases according to their polarizability, oxidation state and electronegativity. Cu ions are considered as soft acids, while Sn and Zn ions are considered between soft and hard acids. Se ions are considered as soft bases. According to this theory, soft acids react faster and form stronger bonds with soft bases than hard acids with soft bases, which explains the tendency to form Copper selenide phases [32]. Besides, the higher reactivity and relatively high mobility of copper ions with respect to zinc and tin ions, helps the reaction between copper and selenide ions [48]. The presence of binary CuSe phase at shorter reaction period suggests that 0.5 h is not enough to crystallize in quaternary phase.

Figure 1: XRD patterns of synthesized nanocrystals in TEA at 240 °C for a) 0.5 h, b) 1.0 h and c) 1.5 h. The principal peaks of CuSe pattern are indicated in a), while the peaks of CZTSe are indicated in c).

To confirm the CZTSe phase, samples were analyzed by Raman spectroscopy (Figure 2). Previous studies have shown that the Raman spectrum of tetragonal CZTSe contains the most intense peak at 192 cm^{-1} along with two sub peaks of low intensity at 170 and 232 cm^{-1} [36, 49-52]. Figure 2 shows the Raman spectra of CZTSe powder samples prepared at different reaction times for all the three samples. Characteristic peaks of CZTSe were observed at 173, 192 and 232 cm^{-1} except for the sample obtained at 0.5 h (Figure 2a), where an additional peak corresponding to the secondary CuSe phase was detected at 260 cm^{-1} [53] which is in agreement with the XRD analysis. There is no significant difference between the samples at 1.0 h and 1.5 h, so 1.0 h is considered to be more appropriate because of saving energy and time.

Figure 2: Raman spectra of synthesized nanocrystals in TEA at 240 °C for a) 0.5 h, b) 1.0 h and c) 1.5 h.

EDS analysis was carried out in order to analyze the chemical composition of the samples. Table 1 shows the results obtained from the CZTSe nanoparticles prepared at 0.5 h, 1.0 h and 1.5 h. Previous results indicate that the CZTSe-based best efficiency solar cells have

slightly Cu-deficient and Zn-rich composition with Cu/Zn+Sn ratio oscillating between 0.8 to 1.0 and Zn/ Sn from 1.0 to 1.2 [54-56]. From the table 1 we can observe that the most desired stoichiometric ratio was obtained when reaction took place at 1 h, however the values are not within range desired.

Sample	Cu/(Zn+Sn)	Zn/Sn
a	0.54	0.59
b	0.79	0.62
c	0.67	0.57

Table 1.- EDS analysis of synthesized nanocrystals in TEA at 240° C for a) 0.5 h, b) 1.0 h and c) 1.5 h.

Figure 3 shows the XRD pattern of CZTSe samples synthesized at two different precursor concentrations. There is no significant difference in XRD peaks position results as can be seen, however synthesis with higher concentration produces more intense and narrower peaks, which can be attributed to better formation and higher crystallinity. In both cases no impurity phases corresponding to binary or ternary system can be detected.

Figure 3: XRD patterns of synthesized nanocrystals in TEA at 240 °C for 1.0 h using a) single concentration and b) double concentration.

The calculated crystallite size using the Scherrer equation varies between 35 and 40 nm, which is in agreement with those obtained by solvothermal methods [16, 32, 35].

The estimated lattice parameters are found to be $a=5.69$ and 5.71 Å, $c=11.32$ and 11.35 Å on using 40 ml and 20 ml TEA, respectively. The estimated values are in good agreement with the standard values ($a= 5.693$ and $c= 11.333$ Å) reported in JCPDS file 052-0868.

The average crystallite size estimated using the Scherrer equation was similar in both cases, and was found to be around 40 nm. Lattice constants were similar also, values calculated were $a=5.70$ and $c=11.31$ Å. The improved crystalline structure in the case of samples using 20 ml TEA can be attributed to the higher reaction temperature (240°C; closer to temperatures reported in many solvothermal studies [16, 32, 35]) achieved during microwave treatment of the precursor solution with respect to the sample prepared using 40 ml of TEA.

In Raman spectra (figure 4) it is possible to observe the presence of the well-defined peak at 173 cm^{-1} in the case of concentrated precursor compared to the diluted solution. The peaks at 192 and 232 cm^{-1} are similar in both cases. So we can infer that a concentrated precursor solution helps to produce well crystalline products in microwave assisted synthesis. However, we could not try higher concentration as the reactants can't be dissolved at TEA. Therefore higher concentrations were not tested.

Figure 4: Raman spectra of synthesized nanocrystals in TEA at 240 °C for 1.0 h using a) single concentration and b) double concentration

Table 2 shows the EDS composition analysis of the powder samples obtained at different precursor concentrations. The sample showed a better stoichiometric coefficients when 20 ml of TEA is used, but it's not really significant as can be seen in table 2.

Sample	Cu/(Zn+Sn)	Zn/Sn
SC	0.79	0.62
DC	0.75	0.80

Table 2.- EDS analysis of synthesized nanocrystals in TEA at 240° C for 1.0 h with a) single (SC) and b) double reactants concentration (DC).

In order to study the effect of solvent on the crystalline phase and chemical composition of CZTSe, a series of samples was prepared in a mixed solvent of TEA and deionized water containing different volume percent of TEA. The molar proportion of metal precursors and Se remain unchanged, but reducing the quantity reactants by half. In this batch of experiments we are looking for a stoichiometry in which the atomic percent ratios of the constituent elements should be in the optimal range reported. TEA was partially substituted by deionized water in order to get the goal. Substitutions were of 10, 20, 30, 32 and 35 % of TEA by deionized water. Only 10 ml of the mixture (TEA-deionized water) was used, this was in order to reduce vapors consequently reaching higher synthesis temperatures (close to 240 °C).

XRD analysis (Figure 5) shows no-significant difference up to 32% TEA solution; at 35% substitution there is the presence of secondary phase Cu₂Se (PDF 01-0714843) at 2 theta values of 44.80, 52.49 °, corresponding to (220) and (311) planes.

Figure 5: XRD patterns of synthesized nanocrystals for 1.0 h, when TEA was partially replaced for deionized water at a) 10%, b) 20%, c) 30%, d) 32% and e) 35%. Miller indices of Cu₂Se are indicated in blue, while CZTSe are in black.

To optimize the quantity of water in the mixed water-TEA solvent we have plotted the position of the principal diffraction peaks corresponding to (112), (204) and (312) against the percentage of water (Figure 6). As can be seen in all the three cases the plots follow an exponential tendency of the peak shift towards the larger 2θ values with respect to the standard ones (JCPDS #00-052-0868). The intersection of the line corresponding to the standard 2θ values with the fit exponential of the plot can provide the optimized water

content in order to coincide the crystalline structure of the products with the JCPDS file. In the three cases theoretically predicted percentage of water is around 30.5 to 31.5 %. This value is in agreement with lattice constants and most importantly with the stoichiometric coefficients found in EDS study.

Figure 6: Analysis of XRD peaks displacement because of water percentage used. Plane a)(204), b) (312) and c) (112).

Raman spectra (Figure 7) confirm the formation of quaternary CZTSe phase at different water substitutions. When substitution of water is less than 35% pure CZTSe phase was achieved while when substitution reaches 35%, the peak corresponding to Cu_2Se phase appears at 258 cm^{-1} [57]. Samples with a substitution less than 35 % presents characteristic peaks of quaternary phase at 170 (172), 190 (192) and 232 cm^{-1} .

Figure 7: Raman spectra of synthesized nanocrystals for 1.0 h, when TEA was partially replaced for deionized water at a) 10%, b) 20%, c) 30%, d) 32% and e) 35%.

EDS analysis was carried out in order to check if composition was improved. Table 3 shows the atomic percentage and the stoichiometric ratios of the constituent elements for different CZTSe samples. From the table it can be seen that when water content is beyond 30%, zinc concentration in the product increases while tin decreases; stoichiometric coefficients are also in the optimum range when 32% of water is used. Nevertheless, it is important to observe that selenium content is less than expected; it was expected to be 50% of selenium in the final product and only 40% was obtained, this might be due to a strong bonding between selenium and TEA during the quelation process. In addition, zinc reactants are more soluble in water than tin reactants

Sample	Cu/(Zn+Sn)	Zn/Sn	Cu%mol	Zn%mol	Sn %mol	Se%mol
M10%H ₂ O	0.86	0.57	27.79	11.51	20.09	41.11
M20%H ₂ O	0.77	0.69	26.19	13.75	19.99	40.07
M30%H ₂ O	0.75	0.71	25.08	13.83	19.49	41.59
M32%H ₂ O	0.92	1.10	27.98	16.03	14.52	41.48
M35%H ₂ O	1.0	1.45	29.90	17.73	12.21	40.16

Table 3.- EDS analysis of synthesized nanocrystals for 1h at 240 °C, when TEA was partially replaced by deionized water at a) 10, b) 20, c)30, d)32 and e) 35%.

Lattice constants and crystal size are reported in table 4. As we can see the final reaction temperature decreases with increasing the amount of water. This is because of the boiling point of water is less than TEA, consequently when more water is used more vapors are produced and the pressure limit is reached at lower temperatures. The crystal size and lattice constants are similar to previous studies which are very proximate to the standard values when water used is around 30 to 32%.

Sample	Water (%)	Temperature (°C)	Crystal size (nm)	a=b	c
M10%H ₂ O	10	238	54	5.701	11.365
M20%H ₂ O	20	237	52	5.657	11.447
M30%H ₂ O	30	236	41	5.701	11.343
M32%H ₂ O	32	235	41	5.683	11.365
M35%H ₂ O	35	234	24	5.675	11.314
PDF-052-0868				5.693	11.333

Table 4.- Lattice constants and crystal size analysis of synthesized nanocrystals for 1h at 240 °C, when TEA was partially replaced by deionized water at a) 10, b) 20, c)30, d)32 and e) 35%.

XPS analysis were carried out for CZTSe nanoparticles synthesized for 1.0 h at 240° C, in a mixture of 68% TEA and 32% of deionized water, in order to investigate the oxidation states of the constituent elements. Figures 8a-8d show the binding energies obtained from the high resolution core level spectra. The peak of Cu 2p was split into 931.8 eV ($2p_{3/2}$) and 951.4 eV ($2p_{1/2}$), the separation of 2p doublet by 19.8 eV, is indicative of the presence of oxidized copper (Fig. 8a). The peak of Zn 2p was split into 1021.6 eV ($2p_{3/2}$) and 1044.6 eV ($2p_{1/2}$), the separation of 2p doublet by 23 eV can be attributed to Zn^{+2} (Fig. 8b). Sn 3d showed 2 peaks at 486.1 eV ($3d_{5/2}$) and 494.5 eV ($3d_{3/2}$), the separation of 3d doublet by 8.4 eV can be attributed to Sn^{+4} (Fig. 8c). Two peaks located at 53.51 eV ($3d_{5/2}$) and 54.57 eV ($3d_{3/2}$) were assigned to Se with oxidation state of -2 (Fig. 8d). Therefore XPS analysis is in accordance to the expected oxidation states of these elements in CZTSe [58,59].

Figure 8: XPS spectra of synthesized CZTSe nanocrystals for 1.0 h in a solution of 68% of TEA and 32% of deionized water.

CONCLUSIONS:

We have developed an easy, economic, fast and environmentally friendly method to synthesize CZTSe nanocrystals. This is the fastest method reported so far to synthesize CZTSe; the chemical process takes only 1 h. In addition it is economic as the precursors and TEA are cheaper than others solvents, such as oleylamine, and more important it is not toxic. Besides, the use of water makes the method cheaper and follows the green chemistry principles. Work involving thin films fabrication in which the selenization process will take place in order to optimize composition and deposition of the powders to the substrate, is in progress.

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