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Sphere-like $CuSbS_2$ Nanoparticles Synthesized by Solvothermal Method for Photovoltaic Applications

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Abstract

$CuSbS_2$ nanoparticles with orthorhombic crystal phase and sphere like morphology were synthesized using solvothermal method. The obtained $CuSbS_2$ nanoparticles were characterized by means of suitable analytical technique such as X-ray powder diffraction (XRD), Dynamic light scattering (DLS), Field Emission Scanning Electron Microscope (FESEM), Photoluminescence spectroscopy (PL), Cyclic Voltammetry and Impedance spectroscopy respectively. The XRD results showed that the obtained sample as orthorhombic crystallinity with (310), (111), (410), (301), (620) and (521) planes of the $CuSbS_2$ nanoparticles. The dynamic light scattering results provided a hydrodynamic average diameter of 7 nm and the morphological investigation given by the FESEM showed the uniform sphere like particles. PL shows that the emission is near IR region and the impedance analysis depicts a semicircular pattern with a diagonal line of 45° angle. These results indicate that $CuSbS_2$ nanomaterials are a promising absorber material for photovoltaic application.

Keywords: $CuSbS_2$, Solvothermal, Nanomaterials, Photovoltaic.

1. Introduction

Ternary $CuSbS_2$ is considered as one of the most suitable absorber material for solar cell applications owing to its abundance, less toxicity, large absorption coefficient of 10^4- 10^5 cm^{-1} in the visible region of the solar spectra, charge carrier concentration that can be tuned in wide range from 10^{16} to 10^{20} cm^{-1} and acting as a platinum-free potential counter electrode material for dye-sensitized solar cells [1–5]. High optical absorption and optimum band gap energy in the range of 1.4-1.6 eV are the most important parameters that are strongly influencing on the cell efficiency [6,7]. Besides, the maximum conversion efficiency achieved so far based on $CuSbS_2$ phase is 3.1% [8]. Various deposition techniques such as, chemical vapor deposition [9], sputtering [10], thermal evaporation [3], spray pyrolysis [11], precursor-based routes [12], solvothermal [13] and hot injection [6] methods have been carried out for fabrication of thin film photovoltaic cell.

Recently, the development of simple and low cost methods such as solvothermal and drop casting are carried out for the synthesis and deposition of $CuSbS_2$ nanomaterials. In this approach, ethylenediamine together with 0.5 g of PVP as surfactant for different reaction temperatures is analyzed. Herein, the work is carried out to synthesize $CuSbS_2$ nanoparticles with the addition of 0.5 g of PVP along with other precursor and investigated the structural, morphological, optical and electrical properties.

2. Experimental Procedure

Synthesis of $CuSbS_2$ nanoparticles were synthesized utilizing solvothermal method. In a typical reaction, 2.5 mM copper (II) acetate monohydrate, 2.5 mM antimony (III) chloride and 7.5 mM thiourea were dissolved in ethylenediamine under constant stirring for 30 min. Later 0.5 g Polyvinylpyrrolidone (PVP) was added to the above mixture, inorder to stabilize the growth and allow the formation of well defined structure. When the chemicals were completely dissolved, the precursor solution was transferred into a Teflon lined stainless steel autoclave, placed it in a hot air oven and maintained at 180˚C for 24 h. Once the reaction was over the oven was cooled down to reach the ambient temperature. The nanoparticles were collected using centrifuge at 3000 rpm for 10 min. Centrifugation process was carried out several times using deionized water and ethanol inorder to obtain final product. The obtained product was gray in color and kept for drying overnight.

The synthesized $CuSbS_2$ nanoparticles were characterized by powder X-ray diffraction (XRD, Rigaku) equipped with Cu-K β (λ=1.39220 Å, 40 kV, 30 mA and step width 0.02 degree). The hydrodynamic size of the $CuSbS_2$ nanoparticles was characterized using a Nano Plus Zeta / Nanoparticle analyzer instrument. The particle size and morphology of the sample were determined by field emission scanning electron microscope (FE-SEM, ZEISS at accelerating voltage 5 KV). To study the optical properties, the room temperature photoluminescence spectroscopy was taken with a Perkin Elmer (Model Lambda 45). The electrical characterizations such as Cyclic Voltammetry and Impedance of the $CuSbS_2$ nanoparticles were recorded using Princeton Applied Research.

3. Results and Discussion

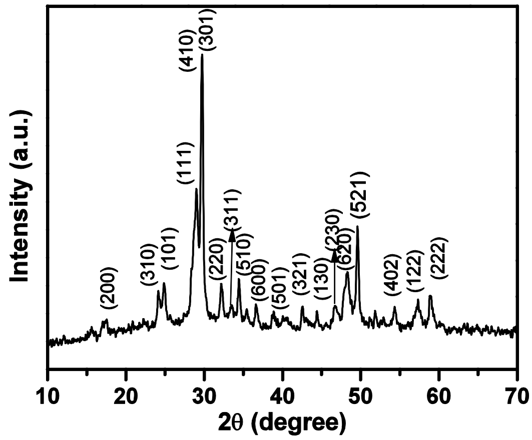

Figure 1. XRD pattern of the synthesized $CuSbS_2$ Nanoparticle

The XRD pattern of $CuSbS_2$ nanoparticles that are shown in Fig. 1 shows the major peaks at 2θ = 23.58º, 28.44º, 28.72˚, 29.91˚, 48.23˚ and 49.78º that are attributed to the planes of (310), (111), (410), (301), (620) and (521). These planes are perfectly indexed as $CuSbS_2$ nanoparticles with orthorhombic crystal structure which is matching well with that of the standard JCPDS, card no. 44-1417 [14]. The average crystallite size of $CuSbS_2$ nanoparticles is determined using Debye-Scherrer formula and is found to be 7.2 nm.

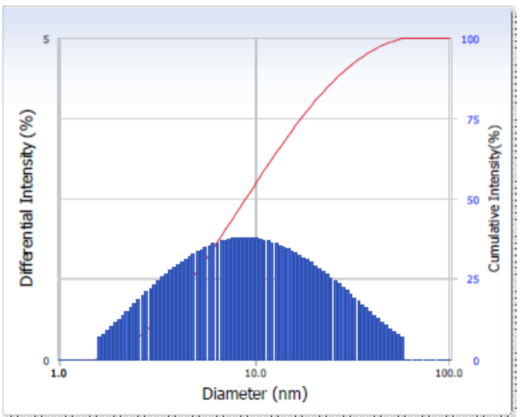

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Figure 2. The size distribution of $CuSbS_2$ nanoparticles using dynamic light scattering measurement

Fig. 2 shows the size distribution of the synthesized $CuSbS_2$ nanoparticles using dynamic light scattering measurement. Here the size distribution profile of small $CuSbS_2$ nanoparticles in dispersion are carried out and the obtained result gives a hydrodynamic average diameter of 7 nm and a Polydispersity Index of 0.006.

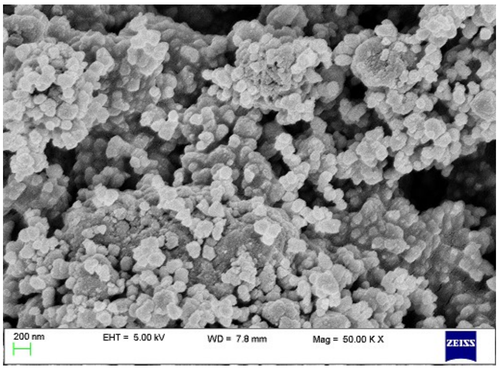

Figure 3. FESEM images of the synthesized $CuSbS_2$ Nanoparticles

The surface morphology of the synthesized $CuSbS_2$ nanoparticles analyzed using the field emission scanning electron microscope and the images are shown in Fig. 3. From the images it is clear that the ethylenediamine together with PVP influences the final morphology of the particles and the obtained $CuSbS_2$ nanoparticles are composed of a large number of homogenous and uniform spheres like particles.

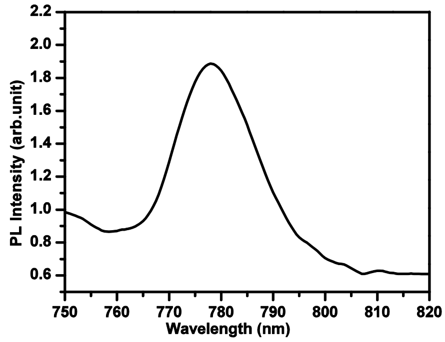

Figure 4. Photoluminescence spectra of the synthesized $CuSbS_2$ nanoparticles

The Photoluminescence spectra that are recorded with an excitation wavelength of 520 nm are as shown in Fig.4. The pattern in the PL spectra illustrates that the emission is near IR region with a band edge emission of 778 nm.

The electrochemical behavior of the material is studied using the impedance analysis and Cyclic Voltammetry is shown in Fig.5. Here a small amount of tetrabutylammonium perchlorate is added as an electrolyte. The three electrodes used for the impedance analysis such as $CuSbS_2$ as working electrode, Calomel the reference electrode and platinum as the counter electrode. The aim of impedance measurement is to understand the materials performance based on the transport resistance.

The obtained Nyquist plot is shown in Fig. 5 (a) which depicts a semicircular pattern with a diagonal line of 45° angle. This semi circle arc is small suggesting the small value of charge transfer resistance of $CuSbS_2$ nanoparticles based photo electrode and is found to be 5 KΩ. The diagonal line of 45° angle shows the diffusion process of the material. Hence it can be concluded that the materials small charge transfer resistance and the long electron life time leads to have an excellent performance in solar cell applications [15]. To understand the electrochemical reaction of the $CuSbS_2$ nanoparticles cyclic Voltammetry analysis is carried out and the obtained pattern is shown in Fig. 5(b). The peaks suggest that the ternary $CuSbS_2$ nanoparticles involve two electrochemical reactions that are having two electron transfer system. These peaks are at 1.25 V and -0.68 V.

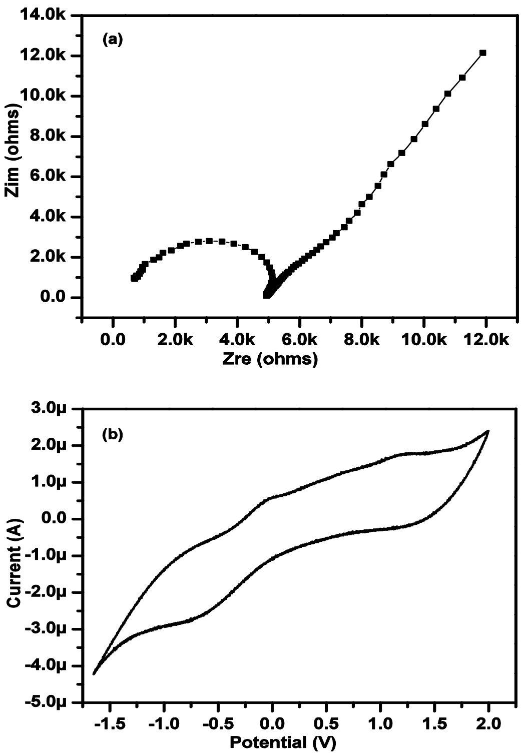

Figure 5. (a) Nyquist plot measured from Electrochemical Impedance Spectroscopy and (b) Cyclic Voltammetry profile of the obtained $CuSbS_2$ nanoparticles

4. Conclusions

$CuSbS_2$ nanoparticles were synthesized by facile solvothermal method. Here ethylenediamine and PVP played major role for the production of well defined sphere like $CuSbS_2$ nanoparticle without agglomeration. The average crystallite size of the obtained $CuSbS_2$ nanoparticle was found to be 7.2 nm. The orthorhombic crystal structure of the synthesized nano powder was confirmed by XRD. From FESEM analysis it was clear that obtained $CuSbS_2$ nanoparticles are homogenous sphere like particles and the DLS analysis gave the hydrodynamic average size of 7 nm. PL emission spectrum shows that the emission was near IR region. Electrical studies based on CV analysis revealed that the material was having two electron transfers. The above mentioned results highlight $CuSbS_2$ nanoparticle are promising p-type absorber material for photovoltaic applications.

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