JOURNAL OF CRITICAL REVIEWS

ISSN- 2394-5125 VOL 7, ISSUE 05, 2020

SOLVOTHERMALLY DERIVED Cu_2FeSnS_4: A POTENTIAL CANDIDATE FOR PHOTOCATALYSIS AND PHOTOVOLTAICS

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Abstract

The present work reveals the morphological and compositional studies of Solvothermally prepared Cu_2FeSnS_4 (CFTS) particles. A pale yellow solution was obtained by mixing suitable amount of $CuCl_2.2H_2O$ for Copper source, $FeCl_2.4H_2O$ for iron source, $SnCl_2.2H_2O$ for tin source and Thiourea (SC(NH2)2 for sulfur source in 50 ml Dimethyl formamide (DMF) solvent. The compositional and morphological studies of the grown material were carried out by using Energy Dispersive X-ray Analysis (EDAX) instrument attached with Scanning electron microscope (SEM). SEM studies shows that the CFTS particles are uniformly distributed with average size of around 0.5 microns whereas the particle size of CFTS was reduced to 0.3 microns when PVP (polyvinylpyrrolidone) added in the precursor solution. It was observed that the CFTS particles are Fe poor whereas the other compositions are within in the range of stoichiometric ratio. On the other side Fe content improves when PVP was used as a capping agent. The physical appearance of material shows that the band gap of obtained material may be close to the energy value suitable for Photovoltaic devices.

Keywords: Cu_2FeSnS_4, Solvothermal synthesis, Scanning electron microscope, EDAX.

1. Introduction

Cu_2FeSnS_4 (CFTS) belongs to the category of quaternary chalcogenides and considered to be very encouraging material due to its wide applications in photocatalysis, thin film solar cells, optoelectronics etc.[1-3]. Due to its high value of absorption coefficient (10^5 cm^{-1}) and direct optical band gap ranging from 1.2 eV to 1.5 eV, CFTS can be used as a absorber material for the fabrication of thin film solar cells [4-5]. CFTS based dye synthesized solar cells (DSSC) [6] were reported with the power conversion efficiency of about 8%. It is observed that the CFTS may show good results in comparison to Cu_2ZnSnS_4 (CZTS) both in photo catalysis and in photovoltaics. Different techniques were used to prepare CFTS nanostructures e.g. ball milling [7], hydrothermal [8], Electro spinning , hot injection etc. For large scale fabrication we can use solvothermal method to obtain good quality material. The solvothermal process is a chemical reaction processed in a closed system in a solvent (non-aqueous or aqueous solution).The reaction in solvothermal is processed at higher temperature than the boiling point of the solvent. In general we can say that it is high pressure process. The chemical parameters and the thermo dynamical parameters are the two parameters involved in solvothermal process. The precursor's concentration seems to play an important role on the control of the shape of Nano crystallites resulting from solvothermal process. The selected solvent plays an important role in the target-material through the chemical mechanism of the reaction. It was found from literature survey that there are very less no of reports available on synthesis of CFTS via solvothermal technique. The photo catalytic efficiency about 62 to 92% can be enhanced by replacing Zn by Fe in CZTS [9-15]. In the present report we have synthesized the Cu_2FeSnS_4 (CFTS) by solvothermal technique using DMF as a solvent and PVP as a capping agent. The morphological and compositional analysis was also reported.

2. Experimental Details

All salts and reagents used for the synthesis of CFTS were analytical grade and no further purification was required. A pale yellow solution was obtained by mixing 1.704 gm of $CuCl_2.2H_2O$, 0.994 gm of $FeCl_2.4H_2O$, 1.128 gm SnCl2.2 H2O and 1.598 gm Thiourea in 50 ml DMF (Dimethylformamide). The stirring of the solution was carried out for about 30 min (Figure 1) using magnetic stirrer. A pale yellow solution thus obtained is transferred to Teflon liner autocalve. The solvothermal reaction was carried out at the elevated constant temperature of 180 °C and reaction time was set for 06 hours. After the completion of reaction autoclave was allowed to cool down naturally to room temperature. The resulting black solution (Figure 2) was centrifuged and washed several times using ethanol, after which it was dried and stored for futher studies. A similar process was repeated for another type of CFTS, where 0.2 gm of PVP (polyvinylpyrrolidone) was used as a capping agent. The morphological and compositional

ISSN- 2394-5125 VOL 7, ISSUE 05, 2020

studies of the grown material were carried out by using Energy Dispersive X-ray (EDAX) instruement attached with Scanning electron microscope(SEM).

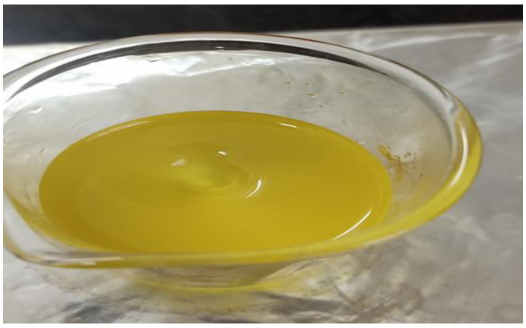	
Figure1: Solution obtained after mixing and stirri reagents	Figure2: CFTS material before and after ce process.

3. Results & Discussion

Figure 3 shows a SEM micrograph of a solvothermally derived Cu_2FeSnS_4. (Sample v1). It can be clearly seen in the micrograph that surface is uniformly covered with the particles of average size approximately 0.5 microns. Figure 4 show the compositional analysis of CFTS. It was found that material grown is Fe poor and copper rich, however sulfur and Tin was found near to the the required ratio. The decrease in the sulfur content was due to washing of the material several times during centrifuge process.

Figure 5 shows micrograph of CFTS prepared by using PVP (Polyvinylpyrrolidone) as a capping agent (Sample v2). It was found that some agglomerates were also formed in the product which may be removed by giving ultrasonic treatment to the solution obtained before centrifuge. SEM image shows that by using PVP the average particle size reduced to approximately 0.3 microns. The compositions of Cu, Fe, Sn and S was also improved as shown in the Figure 6.

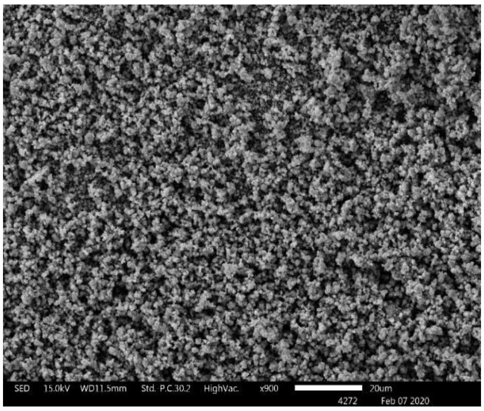

Figure 3: SEM micrograph of Cu_2FeSnS_4 grown at 180^0C for 06 hours

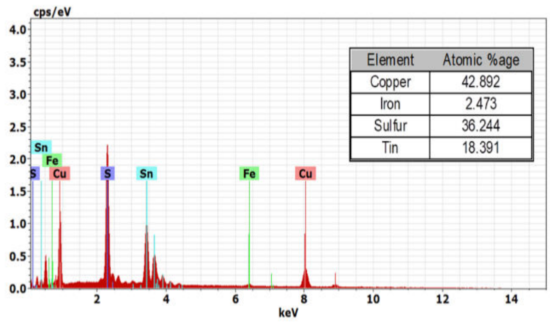

Figure 4: EDAX pattern and data of Cu_2FeSnS_4 grown at 180^0C for 06 hours

It was found from the compositional analysis that CFTS which was grown without using capping agent (Sample v1) was rich in copper and poor in iron content whereas another one (Sample v2) which was prepared using PVP was rich in sulfur and poor in iron. The two parameter i.e. the ratio of Cu/ (Fe+Sn+S) or S/ (Cu+Sn+Fe) may affect the optical properties of nanoparticles. The present study reveals that the ratio of Cu-rich (Cu/Fe+Sn+S) is about 0.75 (Sample v1) and the ratio of Cu-poor Cu/ (Fe+Sn+S) is about 0.69 (Sample v2). The decrease in this ratio probably improves the absorbance in CFTS particles[16].

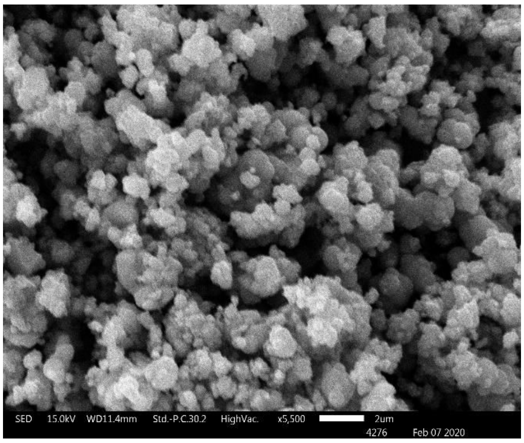

Figure 5: SEM micrograph of Cu_2FeSnS_4 grown at 180^0C for 06 hours with using PVP as a capping agent

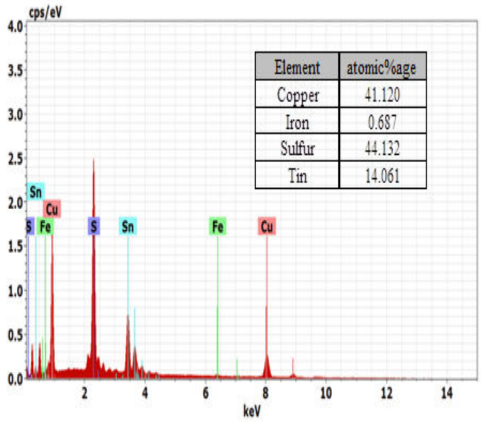

Figure6: EDAX pattern and data of Cu_2FeSnS_4 grown at 180^0C for 06 hours with using PVP as a capping agent

4. CONCLUSION

We can conclude that CFTS particles can be grown by solvothermal technique at short span of time. The use of capping agent helps to reduce the particle size and improves the stoichiometry of the CFTS material. It was also concluded that solvothermally derived Cu_2FeSnS_4 (CFTS) can work as a potential candidate for photocatalysis and photovoltaics.

ACKNOWLEDGEMENTS

The authors are grateful to Nano technology lab, MM(DU) for providing the various facilities. The authors are also thankful to the Department of Biotechnology, MM(DU) for providing a centrifuge facility.

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