

EFFECT OF CAPPING AGENT ON TIN SULPHIDE ($\text{Sn}_x\text{S}_{1-x}$) NANOPARTICLES BY COST EFFECTIVE CHEMICAL ROUTE

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Tin sulfide ($\text{Sn}_x\text{S}_{1-x}$) nanoparticles were synthesized by chemical bath precipitation method using acetic acid as a complexing as well as capping agent. The growth of $\text{Sn}_x\text{S}_{1-x}$ was mainly influenced by the acetic acid concentration. The synthesized nanoparticles were subjected for X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence analysis to investigate its structural, surface and its luminescence properties. A noticeable result was obtained from the photoluminescence of the synthesized $\text{Sn}_x\text{S}_{1-x}$ nanoparticles which strongly evidences the $\text{Sn}_x\text{S}_{1-x}$ nanoparticles property mainly influenced by capping agent.

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1. Introduction

Nanomaterials have been extensively studied due to their unique physical and chemical properties and also its potential applications in diverse areas [1]. These properties and potential applications have stimulated the search for new synthetic methods for these materials. In recent years, great resources have been devoted to the preparation of nanocrystals using a wide variety of methods including electrodeposition [2], solvothermal route [3, 4], thermal decomposition [5] and chemical reduction [6]. These efforts have led to the successful synthesis of many nanocrystals including metals [7,8] oxides [9], as well as sulfides [10,11] which have already been used as optoelectronic materials in sensors, laser materials, solar cells and other devices.

IV-VI semiconductor compounds such as PbSe, SnSe and SnS have been important role in different areas of materials science for several decades [12]. Several binary sulphides of tin such as SnS (orthorhombic), SnS_2 (hexagonal), Sn_2S_3 (rhombic) and Sn_3S_4 (tetragonal) were studied for their respective properties [13]. Mixed phases of the compound Sn_xS was also studied in detail [14]. Among them SnS_2 is a semiconducting material exhibiting n-type conductivity [15] Tin disulphide (SnS_2) is an important CdI_2 -type IV-VI group layered semiconductor with an optical band gap of 2.2 – 2.35 eV [16-17], which is little smaller than that of CdS. Tunable band gap of SnS_2 is the potential candidate for efficient solar cell [18] and in recent years industrial scale p-type tin sulfide fabrication by physical as well as chemical route is one of the challenging task and many researchers are involved in this task. It has the potential to be a good visible light-sensitive photocatalyst. In this paper we mainly focused the role of capping agent concentration on the morphologically tunable growth probability of tin sulphide nanoparticles.

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2. Experimental procedure

In the present experimental 0.2 M of Tin Chloride di-hydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), 0.5 M of Acetic acid were mixed together for several seconds to get a clear and homogenous solution and 0.8 M of thiourea ($(\text{NH}_2)_2\text{CS}$) were mixed and 50 ml water was added to make the final chemical bath volume of 100 ml. Prior to the precipitation reaction the chemical bath temperature was set at 80 °C. Duration of deposition was 3 hours and the final product was washed by using distilled water several time to remove the other impurities and dried in air atmosphere.

Seven samples were prepared by varying only the capping agent concentration as 0.75 M, 1.0 M, 1.25 M, 1.50M, 1.75 M and 2.0M and all other experimental conditions are identical.

3.Result and discussion

3.1 Photoluminescence Studies

Photoluminescence measurements were carried out at room temperature at the excitation wavelength of 313nm. Fig.1 shows the synthesized tin sulfide nanoparticles with various acetic acid (complexing agent) concentrations. In all the samples, it is observed that a strong and sharp peak of ~ 11nm width centered at 495 nm corresponds to green emission and its energy gap of ~2.51 eV which is good agreement with the reported literature [19] and green shifted compared to the other reported value of 2.35 eV [16-17]. This intense strong peak evident for the crystallinity and surface quality of the fabricated nanoparticles. It may due to radiated recombination of excitons lying at higher energy levels [20]. The PL emission peak intensity increases with respect to the gradual increment of the acetic acid concentration.

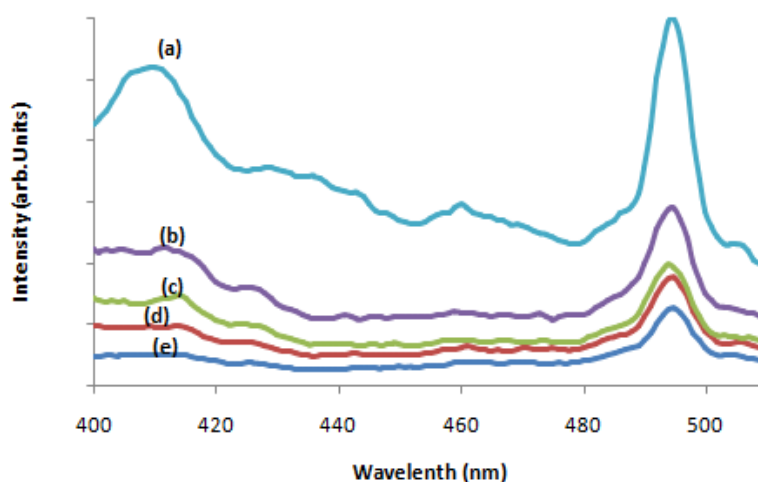


Fig. 1. PL spectra of Tin Sulfide nano particle of (a) 2.0 M (b) 1.75 M (c) 1.25 M (d) 0.75 M and (e) 0.5 M acetic acid concentrations.

3.2 Structural Properties

The structural properties of synthesized nanoparticles were investigated using powder X-ray diffraction (XRD) analysis with minimum scan steps of 0.001 ° per minute. The wavelength of the X-ray source utilized for XRD measurement was Cu-K α : 1.5406 Å. Fig.2 shows the XRD pattern of tin sulphide nanoparticles with 2.0 M acetic acid concentration. The pattern shows good crystalline property compared to lower acetic acid concentration mean that the acetic acid plays a vital role in improving the structural property and exhibit mixed phase of hexagonal and orthorhombic. Characteristic peak for other impurity has not found in the XRD pattern resembles the purity of the particle.

The grain size was calculated using Scherrer's formula is given by

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where, λ wavelength of X-rays, β is the full width half maximum (FWHM), θ -is the diffraction angle.

The grain size is found that $\sim 103\text{nm}$. The higher acetic acid concentration will capture more Sn ions and it will release the Sn ions slow and steadily which probably leads the formation of good quality $\text{Sn}_x\text{S}_{1-x}$ nanoparticles.

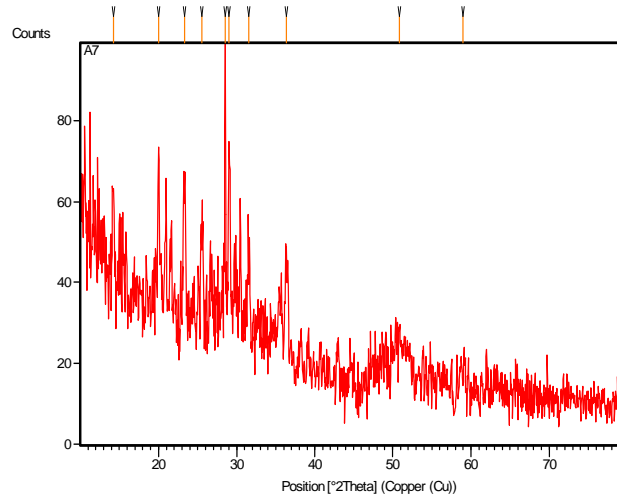


Fig. 2. XRD pattern of mixed phase tin sulphide nano particle for 2.0 M acetic acid concentration.

3.3 SEM studies

Fig.3 (a & b) shows the SEM micrograph for lower capping agent concentrations (0.5 M and 0.75 M) shows powdery morphology. For the higher acetic acid concentration (1.75 M and 2 M) rod like morphology observed (Fig 3(d) & 3(e)). In Fig 3(e) (2 M acetic acid) more number of rods have been observed compared to Fig 3(d) (1.75 M acetic acid), this may be result of acetic acid improves the $\text{Sn}_x\text{S}_{1-x}$ growth in one predominant axis which lights the result of intense PL emission. At the higher concentration of acetic acid there is the possibility of growth in C-axis direction increases may the reason for the rod like morphology [21]. Most of the rods are less than 1micro meter width. All the micrograph results show defect free, less voids with very less pin holes.

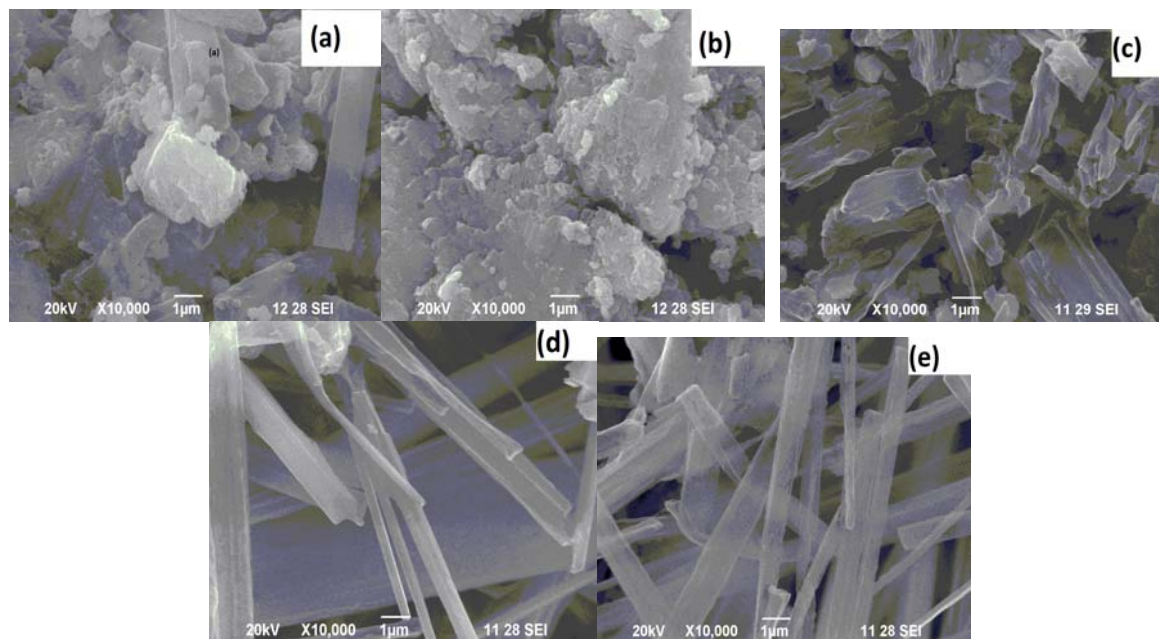


Fig. 3. SEM images of mixed phase tin sulphide nano particles of (a) 0.5 M, (b) 0.75 M, (c) 1.25 M, (d) 1.75 M (e) 2 M acetic acid concentration.

4. Conclusion

Based on the above investigation, we conclude that the higher concentration of capping agent enhances the structural, optical and morphological property of tin sulphide nanoparticles, confirmed by XRD, Photoluminescence and SEM characterizations. The obtained nano particle has mixed phase. A strong and sharp emission peak of green emission observed from PL spectrum obtained from the higher acetic acid concentration. Improvement of growth in one direction results rod like morphology also observed from the higher acetic acid concentration. The lower acetic acid concentration reveals the powdery morphology.

References

- [1] U. Simon, R. Flesch, H. Wiggers, G. Schon, G. Schmid, J. Mater. Chem. **8**, 517(1998).
- [2] H. Natter, M. Schmelzer, R. Hempelmann, J. Mater. Res. **13**, 1186 (1998).
- [3] P. Zhang, L. Gao, Langmuir **19**, 208 (2003).
- [4] S. Schlecht, L. Kienle, Inorg. Chem. **40**, 5719 (2001).
- [5] C. Nayral, T. Ould-Ely, A. Maisonnat, B. Chaudret, P. Fau, L. Lescouzeres, A. Peyre-Lavigne, Adv. Mater. **11**, 61 (1999).
- [6] C.S. Yang, Q. Liu, S.M. Kauzlarich, Chem. Mater. **12**, 983 (2000).
- [7] K.V.P.M. Shafi, A. Gedanken, R. Prozorov, J. Mater. Chem. **8**, 769 (1998).
- [8] K.W. Park, J.H. Choi, B.K. Kwon, S.A. Lee, Y.E. Sung, H.Y. Ha, S.A. Hong, H. Kim, A. Wieckowski, J. Phys. Chem. B **106**, 1869 (2002).
- [9] Y. Liu, C. Zheng, W. Wang, C. Yin, G. Wang, Adv. Mater. **13**, 1883 (2001).
- [10] S. Haubold, M. Haase, A. Kornowski, H. Weller, Chem. Phys. Chem. **2**, 331 (2001).
- [11] L.S. Price, I.P. Parkin, M.N. Field, A.M.E. Hardy, R.J.H. Clark, T.G. Hibbert, K.C. Molloy, J. Mater. Chem. **10** 527 (2000).
- [12] K. Unger, Verbindungshalbleiter, Akademische Verlagsanstalt, Leipzig, 339 (1986).
- [13] L. Amalraj, C. Sanjeeviraja, M. Jayachandran, Journal of Crystal Growth **234**, 683(2002).
- [14] R.D. Engelken, H.E. Mc Claud, Chuan Lee, Mike Slayton, Hossein Ghoreishi, J. Electrochem. Soc. **134**, 2696 (1987).

- [15] B. Thangaraju, P. Kaliannan, J. Phys. D: Appl. Phys. **33**, 1054 (2000).
- [16] Yang C et al., J Solid State Chem. **182**, 807 (2009).
- [17] Zang YC et al., Appl. Catal. B **95**, 153 (2010).
- [18] Loferski JJ, J. Appl. Phys. **27**, 777 (1956).
- [19] Yanbao Zhao, Zhijun Zhang, Hongxin Dang, Weimin Liu, Materials Science and Engineering B **113**, 175 (2004).
- [20] Furui Tan et al., Nanoscale Research Letters **6**, 298 (2011).
- [21] H. Wang et al., Advanced Powder Technology **24**, 599 (2013).