

A Facile Solvothermal Method for Synthesis of CuInS₂ Nanostructures

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Abstract

CuInS₂ nanostructures were synthesized via a simple surfactant-free solvothermal route. In this synthesis, thiosemicarbazide and thioglycolic acid were used as sulfur sources. The effects of different parameters such as type of precursor and time on the morphology and particle size of the samples have been investigated. The nanostructures were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), Fourier transform infrared (FT-IR) and photoluminescence (PL) spectroscopy. The fill factor (FF), open circuit voltage (V_{oc}), and short circuit current (I_{sc}) were obtained by I-V characterization.

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1. Introduction

CuInS₂ is an appropriate candidate as photovoltaic absorber for thin film solar cells since it has well-adapted direct band gaps energy of approximately 1.54 eV. It is in the optimum range for solar-energy conversion, possibility of n-type and p-type doping, suite lattice and electron affinity, extremely good stability and high absorption coefficients [1-4]. Therefore many investigations have been employed for it and various CuInS₂ nanostructures such as nanoparticles, hollow nanospheres and nanorods were prepared. Different chemical methods such as solvothermal reactions, microwave irradiation have

been used to prepare this material [5-10]. It is well known that the unique feature of semiconductors is controlled by their size and shape, so employing a facile and suite procedure for synthesis of semiconductors with different size and morphologies are important subject and received considerable interest. We have been interested in the synthesis of CuInS₂ nanostructures via for a few years [11-14]. In this work we report a simple solvothermal method for preparation of CuInS₂ nanostructures. Nanostructures were synthesized from reaction between copper salicylate (Cu(Hsal)₂) as a new precursor and thiosemicarbazide (TSC). The effects of time on the particle size of products were studied.

2. Experimental

2. 1. Materials and characterization

All the chemical reagents were of analytical grade and were used without further purification. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu K_{α} radiation. Fourier transform infrared (FT-IR) spectrum was recorded by a Nicolet Magna-550 spectrometer in KBr pellets. The electronic spectrum of the sample was taken on Perkin-Elmer LS-55 luminescence spectrometer. Scanning electron microscopy (SEM) images were obtained on LEO instrument. Prior to taking images, the samples were coated by a very thin layer of Au to make the sample surface conductor and prevent charge accumulation.

2. 2. Synthesis of CuInS_2 nanostructures

The copper salicylate ($\text{Cu}(\text{Hsal})_2$) precursor was prepared from reaction of 1 mmol of copper sulfate penta hydrate and 2mmol of sodium salicylate.

In a typical synthesis procedure $\text{Cu}(\text{Hsal})_2$, InCl_3 , thiosemicarbazid or thioglycolic acid (TGA) were dissolved in 40ml of propylene glycol (PG) with the molar ratio of 1:1:2. The obtained mixture was stirred until black solution obtained. After stirring, the reactants were put into a 250 ml capacity Teflon-lined autoclave. The autoclave was maintained at 180 °C for 6–10 h and then cooled down to room temperature naturally. After reaction in solvothermal the samples were cooled to room temperature naturally. Black precipitates were washed with deionized water and ethanol, and air-dried at room temperature.

3. Results and discussion

XRD pattern of the synthesized product is shown in Fig. 1. Pattern of the sample was indexed as a tetragonal phase (space group 1-

42d) which is very close to the values in the literature (JCPDS No. 38-0777 with cell constant $a = b = 5.5200 \text{ \AA}$ and $c = 11.1200 \text{ \AA}$). The strong and sharp reflection peaks in the XRD pattern indicated that CuInS_2 products were well-crystallized. No peaks from any other impurities such as CuS or other compounds are detected.

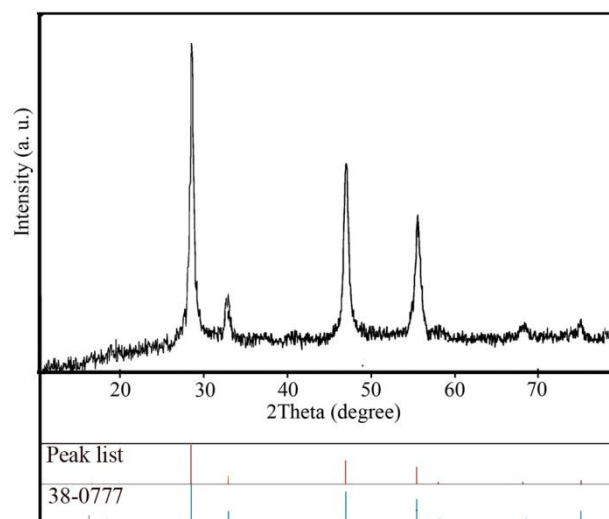


Fig. 1. XRD pattern of the as-synthesized product with TSC at 8h.

Fig. 2 shows SEM image of CuInS_2 powder obtained with thiosemicarbazid at 6h that is consist of particles with diameters about 50-150 nm. The effect of time on the morphology and particle size of the products was investigated. SEM images of the obtained products at 8 h are shown in Fig 3. As shown in Fig. 3 when the time was increased from 6 to 8 nanoparticles with smaller sizes (30-60nm) were obtained. Results show in higher time nucleation stage overcome to growth stage and smaller particles were achieved. SEM images of obtained products at 10 h are shown in Fig 4 that shows nanoparticles with average sizes 60 nm were achieved.

SEM images of the as-synthesized products with thioglycolic acid at 8 h are illustrated in Fig 5. By using thioglycolic acid, rice-like nanostructures were obtained. TGA has a role of sulfur source and capping agent simultaneously.

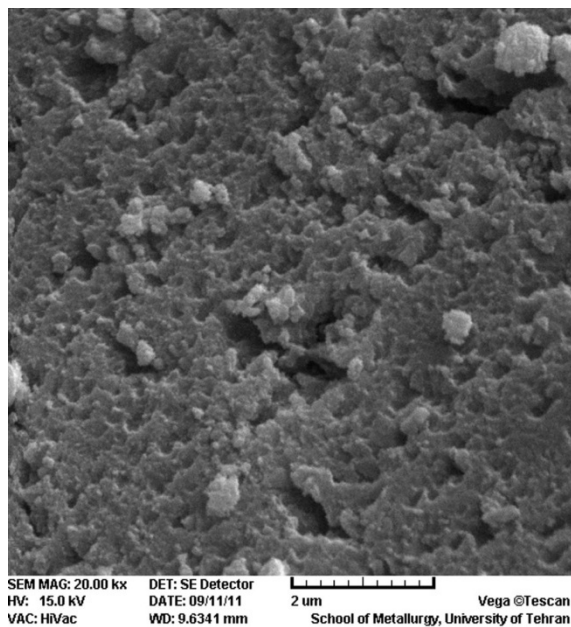


Fig. 2. SEM image of CuInS_2 achieved with thiosemicarbazide at 6 h.

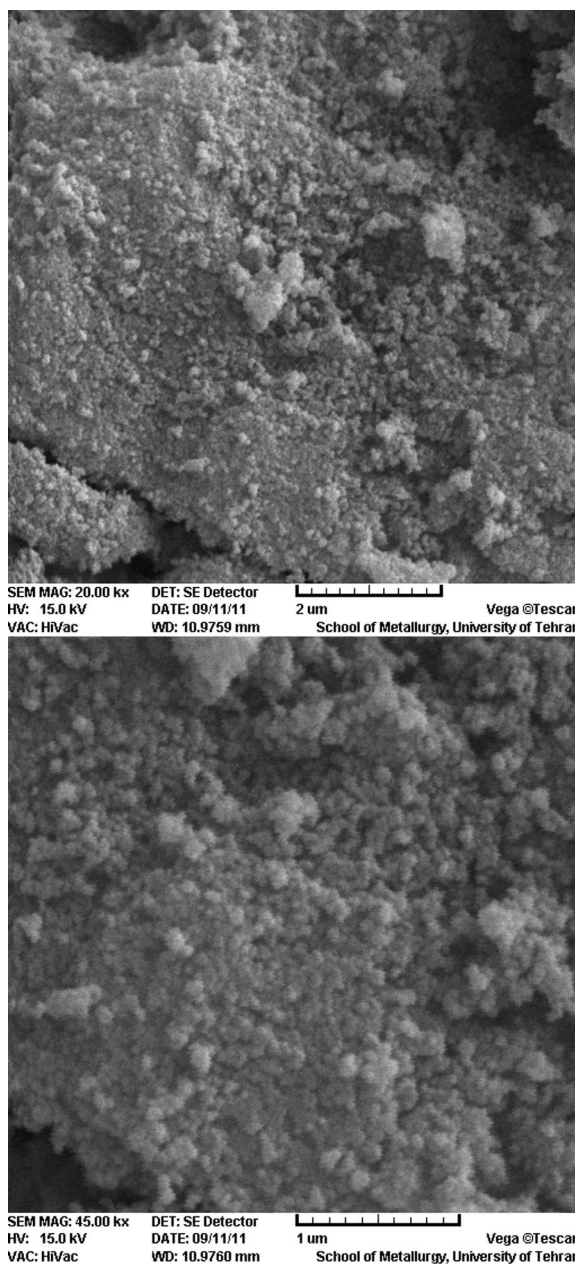


Fig. 3. SEM images of the obtained CuInS_2 with TSC at 8h.

Obviously solvothermal is a unique method for fabricating nanostructures with specific and controlled morphologies. Since the reactivity of different sulfide source is not the same in the coordination reactions, the CuInS_2 nanostructure synthesized using different sulfide source differs in the structure of the nanostructure.

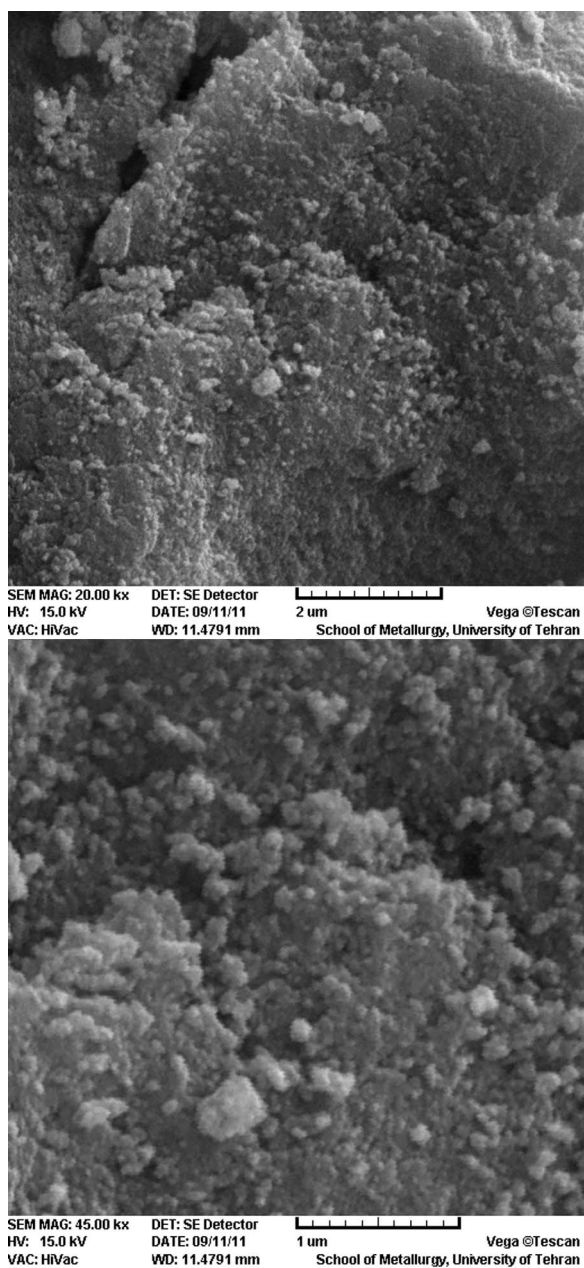


Fig. 4. SEM images of the CuInS₂ with TSC at 10 h.

Based on complex theory, some of them like thioglycolic acid which dissociated and release S²⁻, also behave as a ligand and capping agent. It can be seen that when thiosemicarbazid were used as sulfide source nanoparticles of CuInS₂ obtained and when thioglycolic acid was used, rice-shape nanostructures were synthesized (Fig.5).

Thioglycolic acid as complexing agent has significant effect in morphology of the nanostructures.

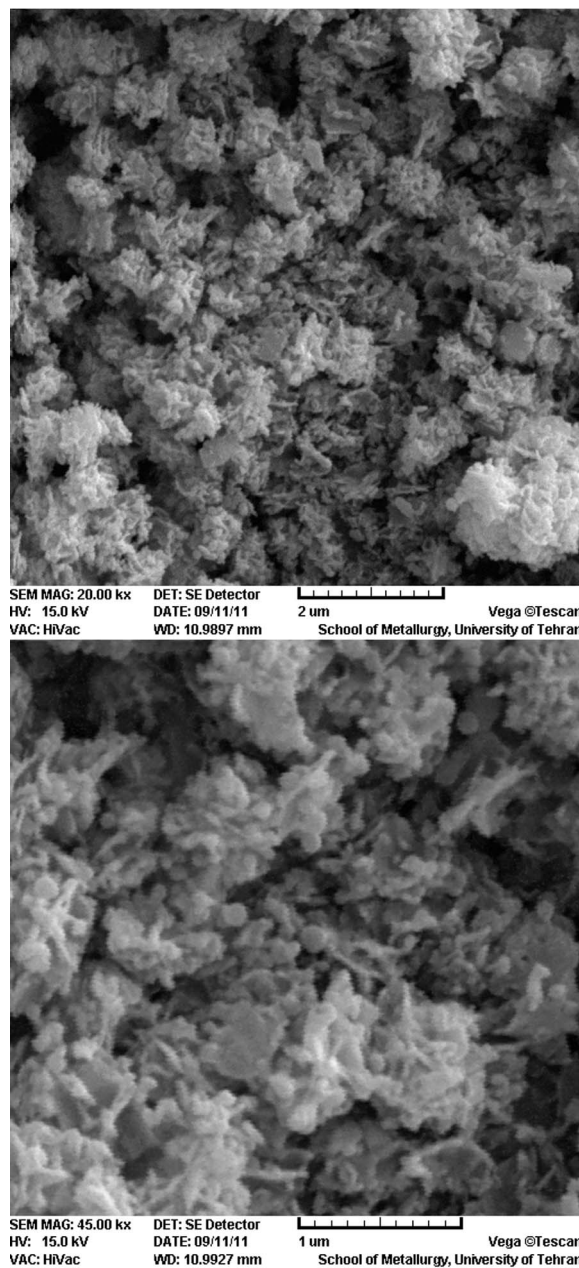


Fig. 5. SEM images of the obtained CuInS₂ with thioglycolic acid at 8 h.

The purity of CuInS₂ nanoparticles was also confirmed by energy-dispersive X-ray (EDX) analysis (Fig 6), the very strong peaks for Cu, In,

and S are found in the spectrum, and no impurity was detected through the EDX spectrum. The molar ratio of Cu to In and S is almost 1:1:2, which is near consistent with stoichiometric CuInS_2 .

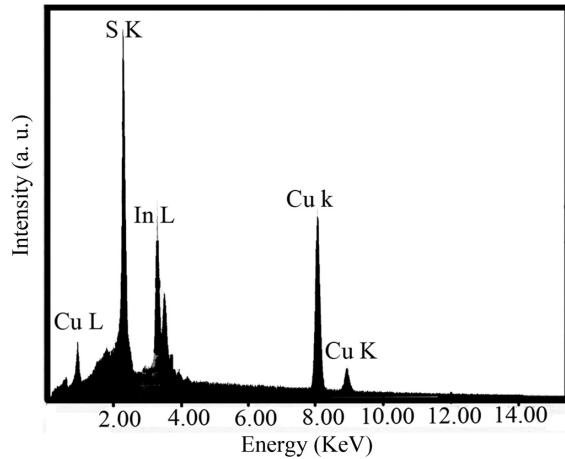


Fig. 6. EDX analysis of CuInS_2 nanoparticles.

Photoluminescence measurement of CuInS_2 was carried out at room temperature with excitation wavelength 532 nm which are laid out in Fig. 7. The PL spectrum was consisted of a strong peak at 598 nm that can be ascribed to a high level transition in CuInS_2 semiconductor crystallites. we are aware, photoluminescence spectroscopy is a useful tool for the investigation of recombination phenomena in semiconductors. By using photoluminescence spectra, band gap can be determined along with the relative energetic position of sub-band gap defect states [15]. The calculated band gap of CuInS_2 nanostructure is about 2.07 eV. This value shows obvious blue shift compared to that of bulk phase (1.54 eV).

Fig. 8 shows the FT-IR spectrum of the achieved CuInS_2 at 8h. Absorptions at 3438 cm^{-1} (attributed to stretching vibrations O-H bond), proved the presence of moisture on the surface of CuInS_2 nanostructures. Since pure doesn't have any

absorption in the $400\text{-}4000\text{ cm}^{-1}$, this spectrum confirms product doesn't have IR-active impurities.

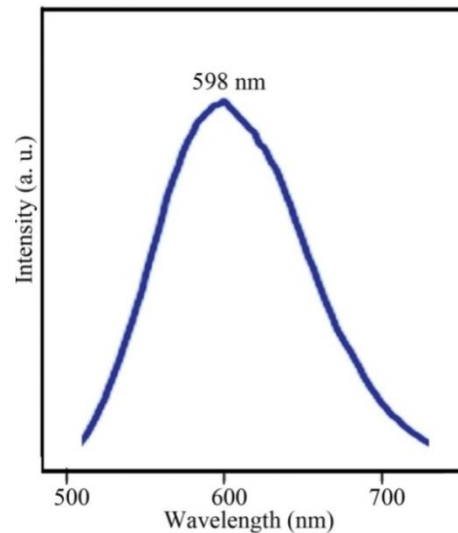


Fig. 7. Room temperature photoluminescence spectrum of the obtained CuInS_2 with TSC at 8 h.

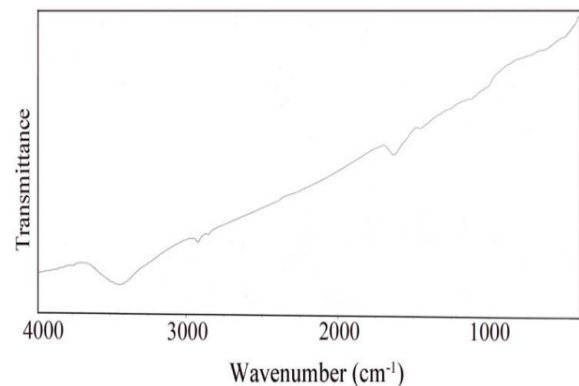


Fig. 8. FT-IR spectrum of CuInS_2 nanoparticles.

CuInS_2 thin film for the solar cell was prepared as mentioned in literature [14]. I-V characterization of a typical solar cell fabricated using in situ approach is shown in Fig. 9. The measurement of the current density-voltage (I-V) curves was carried out under the illumination of AM1.5 ($100\text{ mW}/\text{cm}^2$). Device characteristics are as follows: $V_{oc} = 0.67\text{ V}$, $J_{sc} = 1.24\text{ mA}/\text{cm}^2$, FF = 30%.

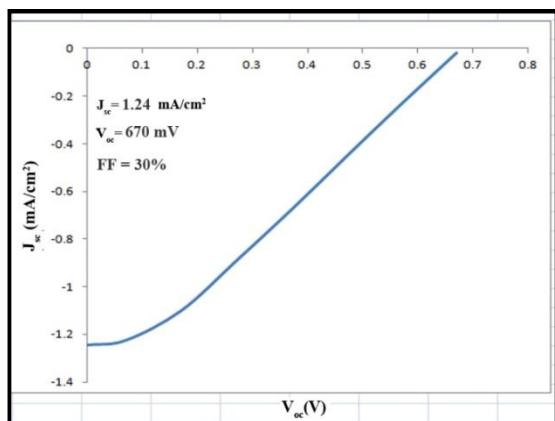


Fig. 9. I–V characterisation of the solar cell of the obtained CuInS₂ with TSC at 8 h.

4. Conclusion

CuInS₂ nanostructures were synthesized via a facile solvothermal method employing thiosemicarbazide and thioglycolic acid as sulfur sources. Copper salicylate was used as a new precursor for synthesis of nanostructures. This method is simple and can be easily controlled. Effects of time on the morphology and particle size of the products were also investigated. The nanostructures were characterized by XRD, EDX, SEM, FT-IR and PL spectroscopy. To examine the application of CuInS₂ nanostructures as an absorption layer, a thin film of CdS was put on the CuInS₂ film by chemical bath in order to make up a solar cell.

References

- [1] T. T. John, M. Mathew, C. SudhaKantha, K. P. Vijayakumar, T. Abe, Y. Kashiwaba, *Sol. Energy. Mater. sol. Cells.* 89 (2005) 27–36.
- [2] Bera, S. IlSeok, *J. Solid. State. Chem.* 183 (2010) 1872–1877.
- [3] A. Antony, A. S. Asha, R. Yoosuf, R. Manoj, M. K. Jayaraj, *Sol. Energy. Mater. sol. Cells.* 81 (2004) 407–417.

- [4] S. Peng, F. Cheng, J. Liang, Z. Tao, J. Chen, J. *Alloys Compd.* 481 (2009) 786–791.
- [5] X. H. Xu, F. Wang, J. J. Liu, K. C. Park, M. Fujishige, *Sol. Energy. Mater. sol. Cells.* 95 (2011) 791–796.
- [6] Y. Jiang, Y. Wu, X. Mo, W.C. Yu, Y. Xie and Y. T. Qian, *Inorg. Chem.* 39 (2000) 2964–2965.
- [7] J.P. Xiao, Y. Xie, R. Tang, Y.T. Qian, *J. Solid. State. Chem.* 161 (2001) 179–183.
- [8] K. Wakita, M. Iwai, Y. Miyoshi, H. Fujibuchi, A. Ashida, *Compos. Sci. Technol.* 65 (2005) 765–767.
- [9] W.M. Du, X.F. Qian, J. Yin, Q. Gong, *Chem. Eur J.* 13 (2007) 8840–8846.
- [10] J.S. Gardner, E. Shurdha, C.M. Wang, L.D. Lau, R.G. Rodriguez and J.J. Pak, *J. Nanopart Res.* 10 (2008), 633–641.
- [11] M. Mousavi-Kamazani, M. Salavati-Niasari, H. Emadi, *Mater. Res. Bull.* 47 (2012), 3983–3990.
- [12] M. Mousavi-Kamazani, M. Salavati-Niasari, H. Emadi, *Micro. Nano. Lett.*, 7 (2012) 896–900
- [13] S. M. Hosseinpour-Mashkani, F. Mohandes, M. Salavati-Niasari, K. Venkateswara-Rao, *Mater. Res. Bull.* 47 (2012) 3148–3159.
- [14] M. Sabet, M. Salavati-Niasari, F. Davar, *Micro. Nano. Lett.*, 11 (2011) 904–908
- [15] T. Schmidt, K. Lischka, W. Zulehner, *Phys. Rev. B*, 45 (1992) 8989–8994.