A new sonochemical method for preparation of different morphologies of CuInS₂ nanostructures

OMID AMIRI^a, MASOUD SALAVATI-NIASARI^{b,*}, MEHDI MOUSAVI-KAMAZANI^a,
DAVOOD GHANBARI^c MOHAMMAD SABET^b and KAMAL SABERYAN^d

^aYoung Researchers Club, Kashan Branch, Islamic Azad University, Kashan, Iran

^bInstitute of Nano Science and Nano Technology, University of Kashan, P.O. Box 87317-51167, Kashan, Iran

^cYoung Researchers Club, Arak Branch, Islamic Azad University, Arak, Iran

^dFuel Cycle Research School, NSTRI, P.O. Box 11365-8486, Tehran, Iran

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Abstract. CuInS₂ nanostructures were synthesized by sonochemical route using (*bis*(salicylate)copper(II)) as a new copper precursor. The effects of different parameters such as sulphur source, solvent, power of irradiation and reaction time on the morphology of the products were investigated. Nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL) and Fourier transform infrared (FT-IR) spectroscopy. CuInS₂ nanostructures paste was prepared by doctor's blade technique on the transparent conductive oxide (TCO). The fill factor (FF), open circuit voltage (V_{oc}), and short circuit current (I_{sc}) were obtained by I–V characterization.

Keywords. CuInS₂; solar cells; ultrasonic; semiconductors.

1. Introduction

I–III–IV₂ ternary chalcopyrite semiconductors have great potential for photovoltaic, non-linear optic and other optoelectronic applications (Shay *et al* 1975; Yamamoto *et al* 1997). CuInS₂ with chalcopyrite structures has attracted considerable attention as a suitable material for fabricating low-cost and efficient solar cells. CuInS₂ (CIS) with its band gap (1.53 eV) at room temperature is an ideal solar absorber material (Moller *et al* 1998; Nekamp *et al* 2000; Kaiser *et al* 2001; Emst *et al* 2003; Klaer *et al* 2007). Therefore, many investigations have been employed for this substance and various CuInS₂ nanostructures such as nanoparticles (Castro *et al* 2003; Dutta *et al* 2006), hollow nanospheres (Zhang *et al* 2003) and nanorods (Jiang *et al* 2000, Xiao *et al* 2001) were prepared. Different chemical methods, such as solvothermal reactions (Du *et al* 2007; Long *et al* 2010), and microwave irradiation (Gardner *et al* 2008) have been used to prepare this material. Jiang *et al* (2008) synthesized colloidal CuInS₂ nanocrystals from a single-source molecular precursor (PPh₃)₂CuIn(SEt)₄. Nairn *et al* (2006) synthesized CuInS₂ nanoparticles by decomposing a molecular precursor using ultra-violet irradiation.

Sonochemical method is a facile route operated under ambient conditions. Ultrasonic irradiation caused cavitation

in a liquid medium, where formation, growth and implosive collapse of bubbles occurred. The collapse of bubbles with short lifetimes produces intense local heating and high pressure. These localized hot spots can generate temperature of about 5000 °C and pressure of over 1800 kPa that these spots are appropriate for many chemical reactions (Salavati-Niasari *et al* 2011; Esmaeili-Zare *et al* 2012). In this work, CuInS₂ nanostructures were synthesized by a simple sonochemical method using a new inorganic precursor. Salicylate as ligand with high steric hindrance is a suitable capping agent for preparation of nanostructures. The effect of various sulphur sources on the morphology of the product has also been investigated.

2. Experimental

2.1 Physical measurements and materials

All the chemical reagents were used as received without further purification. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 100 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered CuK α radiation. Scanning electron microscopy (SEM) images

*Author for correspondence (salavati@kashanu.ac.ir)

were obtained from LEO instrument model 1455VP. Prior to taking images, all samples were coated with a very thin layer of Pt to make the sample surface conductive and to prevent charge accumulation. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Room temperature photoluminescence (PL) was studied by an F-4500 fluorescence spectrophotometer. Transmission electron microscopy images were obtained on a Philips EM208 microscope with an accelerating voltage of 100 kV.

2.2 Preparation of CuInS₂ nanostructures

The copper salicylate [Cu(Hsal)₂] precursor was prepared from the reaction of 1 mmol of copper sulphate pentahydrate and 2 mmol of sodium salicylate. CuInS₂ nanoparticles were prepared by the reaction of Cu(Hsal)₂ and InCl₃ with a sulphur source in propylene glycol (PG) as solvent. 50 mg of Cu(Hsal)₂, 20 mg of InCl₃ and 5 mg of SDS were dissolved in 60 mL of PG and was irradiated under ultrasound waves. Different sulphur sources (2 mmol) such as sodium sulphite (Na₂S₂O₃), thiourea (TU), thioacetamide (TAA), thiosemicarbazide (TSC), L-cysteine (L-Cyst) and carbon disulfide (CS₂) were added dropwise to the solution. The black precipitate was washed with ethanol and deionized water. The product was dried at 60 °C for 3 h under vacuum. The precipitates were annealed under argon atmosphere at 450 °C for 2 h. The annealing converted the mixture of In₂S₃ and CuS into CuInS₂. More details of experiment are given in table 1.

2.3 Preparation of CuInS₂ electrodes

The transparent conductive oxide (TCO) glass used as current collector (solar 4 mm thickness, Pilkington, Tec 7, Japan). CIS electrode was prepared by Dr-blading of CuInS₂ paste on TCO. The electrode configuration was a

transparent layer of nanocrystalline CuInS₂ with an average size of 24 nm and a microcrystalline scattering layer. The as-prepared electrodes were sintered at 450 °C for 30 min. CdS QDs are deposited on the CuInS₂ film by chemical bath deposition method (Zhu *et al* 2010). CuInS₂ film was dipped into a solution containing Cd(NO₃)₂ (0.25 M in ethanol) and CH₃N₂S (0.25 M in methanol), respectively. The procedure was repeated for several cycles and each cycle prolongs by 20 s.

Figure 1. Schematic diagram of (a) formation of nanostructures and (b) effect of salicylate on the particle size.

Figure 2. SEM image of the CuInS₂ synthesized using copper acetate (without using salicylate).

Table 1. Experimental conditions for preparation of CuInS₂.

Sample no.	Solvent	Sulphur source	Time (min)	Power (W)
1	PG	Na ₂ S ₂ O ₃	40	70
2	PG	Tu	40	70
3	PG	TGA	40	70
4	PG	TAA	40	70
5	PG	TSC	40	70
6	PG	L-Cyst	40	70
7	PG	CS ₂	40	70
8	PG	L-Cyst	30	70
9	PG	L-Cyst	50	70
10	H ₂ O	L-Cyst	40	70
11	Gly	L-Cyst	40	70
12	PG	L-Cyst	40	50
13	PG	L-Cyst	40	60

Figure 3. XRD pattern of (a) copper salicylate and (b) CuInS₂ nanoparticles (sample no. 4).

Figure 4. FT-IR spectrum of as-synthesized (a) Cu(Hsal)₂ and (b) CuInS₂ (sample no. 4).

3. Results and discussion

Schematic of nanostructures formation is depicted in figure 1(a). SEM image of synthesized product using pure copper acetate is shown in figure 2 results show that without using salicylate, bulk product is obtained. Salicylate with high steric hindrance is a suitable capping agent for preparation of nanostructures. Ligand group that exist in the surroundings of copper causes less availability of metal, so nucleation occurs over the growth (figure 1b).

Figure 3(a) shows XRD pattern of Cu(Hsal)₂ precursor and figure 3(b) depicts pattern of the CuInS₂ obtained after annealing at 450 °C. The strong and sharp diffraction peaks confirm good crystallinity of the product. Pattern of the CuInS₂ show a pure tetragonal structure with suitable agreement to literature value (JCPDS card no. 75-0106, Space group: 1-42d, lattice constants: $a = 5.5170$, $b = 5.5170$ and $c = 11.0600$). The crystallite size (D_c) of the as-prepared CuInS₂ was calculated to be 26 nm using the Debye–Scherrer equation:

$$D_c = \frac{K\lambda}{\beta \cos \theta},$$

where β is the breadth of the observed diffraction line at its half intensity maximum, K the shape factor, which usually takes a value of about 0.9 and λ (0.154 nm) is the wavelength of the X-ray source used in XRD.

FT-IR spectrum of as-synthesized Cu(Hsal)₂ is illustrated in figure 4(a). Absorption at 1602 cm⁻¹ is related to C=O bond and absorptions at 1245 and 1150 cm⁻¹ are attributed to C–O bonds. Peaks at 1457 and 1567 cm⁻¹ are responsible for stretching vibrations of aromatic ring. Absorption at 3419 is related to O–H bonds. FT-IR spectrum of CuInS₂ nanostructures is depicted in figure 4(b), since pure CuInS₂ has no absorption peaks in the range of 4000–400 cm⁻¹; the result shows that the product did not have major IR-active impurity.

Synthesis of CuInS₂ at 70 W for 40 min has been selected as a basic reaction in this work and the effect of different parameters on the morphology of the products has been investigated. SEM images of the CuInS₂ nanoparticles prepared by different sulphur source are illustrated in figures 5(a–f). SEM images of the products with thiosemicarbazide, thiourea and thioacetamide are depicted in figure 5(a–c), respectively. Ultrasonic irradiation creates bubbles that produce high temperature and energy after decomposition. This process provides appropriate amounts of energy for formation of nanoparticles. L-cysteine was used as a sulphur source and capping agent simultaneously for forming nanoflowers (figure 5d). Figures 5(e and f) show SEM images of synthesized products by thioglycolic acid and sodium sulphite. By using ultrasound irradiation, the formed bubbles collapse, resulting in the generation of high-speed microjets that can generate nanoparticles.

Figure 5. SEM images of the CuInS_2 nanostructure with (a) TSC (sample no. 5), (b) Tu (sample no. 2), (c) TAA (sample no. 4), (d) L-cyst (sample no. 6), (e) TGA (sample no. 3) and (f) $\text{Na}_2\text{S}_2\text{O}_3$ (sample no. 1).

For investigating the effect of sonication time on the morphology of the products, the reaction was carried out in 30, 40 and 50 min. According to the figure 6(a), spherical nanoparticles were achieved; it seems that at 30 min, nanoparticles do not have time to agglomerate. By increasing time from 30 to 40 min (figure 5d), nano-flowers were synthesized. With enhancement time to 50 min, the rod-like structures start to degrade and eventually generate various nanoparticles (figure 6b).

Different solvents with various surface tensions were used. Figure 7 shows SEM image of CuInS_2 nanorods with an average diameter of 90 nm that is synthesized in water. Rod-like morphology is due to the presence of

solvent with lower surface tension. Glycerol has high surface tension, so this power was not able to produce bubbles in solvent, and CuInS_2 was not obtained.

Power effect on the morphology of products was examined. At power of 50 W, nanoparticles were aggregated (figure 8a). By increasing power, more energetic bubbles produce nanoparticles with better distribution (figure 8b). At higher power, particles have more kinetic energy that shows preferential growth, resulting in the formation of nano-flowers (figure 5d).

Figure 9 shows TEM image of CuInS_2 nanoparticles with an average diameter of 50 nm. Photoluminescence (PL) measurement of CuInS_2 nanoparticles (no. 4) was

carried out at room temperature with excitation wavelength at 418 nm that is shown in figure 10. The PL spectrum consists of one strong peak at 554 nm that can be

Figure 6. SEM images of the CuInS₂ nanostructure with (a) 30 min (sample no. 8), (b) 40 min (sample no. 6) and (c) 50 min (sample no. 9).

Figure 7. SEM image of the CuInS₂ nanostructure in the water as solvent (sample no. 10).

ascribed to a high-level transition in CuInS₂ semiconductor crystallites. It is reported that this kind of band-edge luminescence arises from recombining shallowly and exactions trapped electron-hole pairs.

The In³⁺ and Cu²⁺ ions reacted with the S²⁻ ions to form the sulphide compounds of CuS and In₂S₃ according to (1) and (2). The reaction for forming stoichiometric CuInS₂ during annealing process might be given in (3).

CuInS₂ thin film was prepared by doctor's blade technique. Figure 11 shows SEM image of CuInS₂ thin film surface. The particles are homogeneously distributed in film but many spaces exist between particles in the layer. These voids can trap electron and decrease current short circuit current.

J–V curves give key parameters to explain solar cell characterization such as short-circuit current (J_{sc}),

Figure 8. SEM images of the CuInS₂ nanostructure at different power (a) 50 W (sample no. 12) and (b) 60 W (sample no. 13).

Figure 9. TEM image of the CuInS₂ nanostructure (sample no. 4).

Figure 10. Room temperature photoluminescence spectrum of CuInS₂ (sample no. 4).

Figure 11. SEM image of thin film CuInS₂.

Figure 12. A representative I–V curve of a CuInS₂ nanoparticle (a) 100 μm , (b) 120 μm and (c) 220 μm .

open-circuit voltage (V_{oc}) and fill factor. The effect of thin film thickness on these parameters was investigated. When thickness was about $\sim 10 \mu\text{m}$, V_{oc} , J_{sc} and fill factor were obtained as 129 mV, 0.112 mA/cm² and 28%, respectively. A representative J–V curve of a CuInS₂ nanoparticles device is shown in figure 12(a). By increasing the thickness to $\sim 12 \mu\text{m}$, V_{oc} , J_{sc} and FF were achieved 270 mV, 1.47 mA/cm² and 0.32%, respectively (figure 12(b)). With further enhancement of the thickness to 22 μm , V_{oc} , J_{sc} and FF were obtained as 70 mV, 0.81 mA/cm² and 0.24%, respectively (figure 12c).

As shown in the curves, it was found that by increasing the thickness from 10 to 12 μm , short circuit current, open-circuit voltage and fill factor have been increased. Also with further increase to 22 μm , these parameters have been decreased in respect to 12 μm . The main reason for this deterioration is increase in electron recombination by increasing the thickness. So, it is concluded that the optimum thin-film thickness is 12 μm .

4. Conclusions

Copper indium sulphide nanostructures were successfully synthesized from Cu(Hsal)₂ precursor by a facile sonochemical method. The effects of different parameters such as sulphur source, solvent, power of irradiation and reaction time on the morphology of the products were investigated. CuInS₂ thin film was deposited on the glass substrates by Dr-blading and it is applied into solar cell and measured V_{oc} , J_{sc} and FF.

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