A facile route to synthesis of AgInS₂ nanostructures

MEHDI RANJBAR*, MOHAMMAD ALI TAHER[†] and MOHAMMAD SADEGHINIA

Kashan Branch, Islamic Azad University, Kashan, Iran

[†]Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran

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Abstract. AgInS₂ nanoparticles have been synthesized via a facile one-step process using AgNO₃, thiosemicarbazid (TSC) and InCl₃·4H₂O as starting reagents from propylene glycol solution. The effects of concentration of precursors, reaction time and type of sulfur sources on the morphology and particle size were also studied. X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), scanning electron microscope (SEM), transmission electron microscope (TEM), ultraviolet–visible spectroscopy (UV–Vis) and photoluminescence (PL) spectroscopy were used to characterize the obtained products.

Keywords. Nanoparticles; AgInS₂; chalcogenides; semiconductors.

1. Introduction

The I–III–IV₂ ternary chalcopyrite semiconductors have attracted much attention because of their fundamental electronic and optical properties and important applications in linear and nonlinear optical instruments and photovoltaic solar cells (Kale *et al* 2006; Qasrawi *et al* 2008). Because of their outstanding luminescent properties, these compounds also attract lots of interest as an alternative for the more toxic cadmium-containing quantum dots (QDs) (Allen and Bawendi 2008; Omata *et al* 2009). Among these materials, AgInS₂ (AIS) is a direct, narrow bandgap semiconductor (Aissa *et al* 2012) with good chemical stability and high extinction coefficients in the visible to near-infrared region and have been applied in the photovoltaic solar cells and photocatalysis (Aguilera *et al* 2003; Akaki *et al* 2005). Therefore, many investigations have been employed for this substance and various AgInS₂ structures, such as nanoparticles (Zhang *et al* 2011) and nanorods (Cui *et al* 2001) have been successfully fabricated by various techniques such as solvothermal (Cui *et al* 2001), hydrothermal (Hu *et al* 2004), spray pyrolysis (Gorska *et al* 1980), microwave hydrothermal synthesis (Zhang *et al* 2011) and multiple-source methods (Tian and Vittal 2007). Although, AgInS₂ compound indicates the *n*-type electrical conductivity but this characteristic can be changed to *p*-type conductivity via doping with different elements such as Sb (Yoshino *et al* 2003) and Sn (Albor Aguilera *et al* 2007). In this paper, we reported a rapid and simple method to synthesize the nanocrystalline AgInS₂ by refluxing raw materials in

propylene glycol for 1 h. Besides, the effects of precursor concentrations, reaction time and type of sulfur source on the morphology and particle size of products were studied.

2. Experimental

2.1 Physical measurements and materials

All the chemical reagents were used as-received without further purification. XRD patterns were recorded by a Philips X-ray diffractometer using Ni filtered CuK α radiation. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. Scanning electron microscopy (SEM) images 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. UV–Vis spectrum of the sample was taken on a JASCO UV–Vis (Model V-670) scanning spectrometer. 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 AgInS₂ nanostructures

In a typical experimental procedure, AgNO₃ (2 mmol), InCl₃·4H₂O (2 mmol), thiosemicarbazide (TSC) (4 mmol) and 40 mL propylene glycol (PG) were mixed and magnetically stirred for 15 min. The mixture was then heated to reflux (350 °C) at a rate of ~5 °C per min. The mixture

*Author for correspondence (mehdi.ranjbar@outlook.com)

was maintained at refluxing for 60 min before it was cooled down to room temperature by removing the heat source. The brown product was precipitated by adding ethanol and separated via centrifugation. The final product was dried in vacuum at 60 °C for 5 h. Reaction conditions are listed in table 1.

3. Results and discussion

Figure 1 shows XRD patterns of sample 1. All the peaks can be readily indexed to the crystallized AgInS_2 (JCPDS no. 75-0117) with tetragonal phase (space group $I-42d$, and $a = b = 5.8160 \text{ \AA}$ and $c = 11.1700 \text{ \AA}$) and orthorhombic phase of AgInS_2 (JCPDS no. 25-1328 and space group $Pna21$) with lattice parameters ($a = 7.0010 \text{ \AA}$, $b = 8.2780 \text{ \AA}$ and $c = 6.6980 \text{ \AA}$). EDS analysis was employed to investigate the chemical composition and purity of the as-synthesized AgInS_2 nanoparticles. A typical energy-dispersive X-ray spectrum is shown in figure 2, which indicates the presence of Ag, In and S in the products. Based on the calculation of the peak areas, the atomic ratio of Ag to In and S was about 1:1:2, nearly consistent with the stoichiometry of AgInS_2 . Therefore, both XRD and EDX analyses show that pure AgInS_2 nanocrystals are successfully produced via the present synthetic route. Figure 3(a) shows SEM image

of sample 1 which was synthesized in 40 mL PG for 60 min in present TSC as a sulfide source. The product is mainly composed of small particles and, in some areas, agglomerated particles. In the present research, effects of concentration of precursors, reaction time and type of sulfur sources on the morphology and particle size were investigated by SEM. For investigating the effect of concentration on the morphology and particle size, 80 and 120 mL of solvent (samples 2 and 3, respectively) was used instead of 40 mL. As figure 3(a–c) shows, with decreasing concentration of the precursor, particle size is larger and optimum conditions were obtained using 80 mL (sample 2 and figure 3b). Most coarse particles were obtained when 120 mL of PG was used (figure 3c). It is believed that when the reactants concentration increased, the nucleation rate increased, which led to the formation of small nuclei at the same time. Further increasing of this ratio may lead to agglomeration due to the formation of unstable and ultra-fine nuclei that have a strong tendency to be stable by agglomeration (figure 3a). To further investigate the details of morphology, TEM images (sample 2) were taken and are shown in figure 4. Sonication for 20 min was employed in order to disperse it before the sample was deposited on the carboncoated copper grid for the TEM measurement. The product is mainly composed of a large amount of spherical and spheroidal nanoparticles with average size of about 15–40 nm. Figure 5(a and b) shows SEM images of samples 4 and 5 prepared in presence of $\text{Na}_2\text{S}_2\text{O}_3$ and CS_2 as a sulfur source, respectively. From the investigation of these images, it is clear that AgInS_2 nanostructure synthesized using different sulfide source differ in the morphology and particle size of the nanostructure,

Table 1. Reaction conditions for the preparation of AgInS_2 nanostructure.

Sample no.	Volume of solvent	Sulfur source	Time (min)
1	40	TSC	60
2	80	TSC	60
3	120	TSC	60
4	80	$\text{Na}_2\text{S}_2\text{O}_3$	60
5	80	CS_2	60
6	80	TSC	30
7	80	TSC	90

Figure 1. XRD pattern of as-synthesized AgInS_2 (sample 1).

Figure 2. EDX spectrum of as-synthesized AgInS_2 nanoparticles (sample 1).

Figure 3. SEM images of as-synthesized AgInS_2 (a) sample 1, (b) sample 2 and (c) sample 3.

Figure 4. TEM images of as-synthesized AgInS_2 (sample 2).

Figure 5. SEM images of as-synthesized AgInS_2 (a) sample 4 and (b) sample 5.

Figure 6. SEM images of as-synthesized AgInS_2 (a) sample 6 and (b) sample 7.

Figure 7. UV-Vis absorption spectrum of as-synthesized AgInS₂ nanoparticles (sample 2).

Figure 8. PL spectrum of as-synthesized AgInS₂ nanoparticles (sample no. 2).

because the reactivity of different sulfide sources is not the same in the coordination reactions. It can be seen when sodium thiosulfate (Na₂S₂O₃) was used, flower shape nanostructures were formed (figure 5a), but by

using carbon disulfide (CS₂), AIS microstructures were obtained (figure 5b). Influence of time of reaction was investigated on the as prepared AIS samples. Figure 6 shows SEM images of AIS samples prepared at 350 °C for 30 min (sample 6) and for 90 min (sample 7). With decreasing of aging time to 30 min, the obtained particles (figure 6a) were bigger than the particles of sample 1 with the aging time of 60 min. It can be observed that with the increase of reaction time up to 120 min, size of the nanoparticles decreased, but in some areas conglomerate effects were observed (figure 6b). The optical properties of AIS nanoparticles obtained in pure ethanol were investigated at ambient temperature using UV-Vis absorption spectroscopy (figure 7). For AIS nanocrystals, the UV-Vis absorption spectra display an intensive peak located at 451 nm. The absorption spectra show a blue shift compared to that of the bulk AIS (~1.9 eV) (Zhang *et al* 2011). These amounts of blue shift may be attributed to the low dimension of the particles. Photoluminescence (PL) measurement of AIS nanoparticle (sample 1) was carried out at room temperature with excitation wavelength 455 nm which are laid out in figure 8. PL spectrum consisted of a strong peak at 550.5 nm that exhibits a blue shift (2.25 eV) compared to that of bulk phase (1.9 eV) (Zhang *et al* 2011).

4. Conclusions

In summary, we propose a rapid and facile method to synthesize AgInS₂ nanocrystalline by refluxing AgNO₃, InCl₃·4H₂O and sulfur precursors in propylene glycol at 350 °C for 1 h. This method is novel, simple and can be easily controlled. Effects of precursor concentrations, reaction time and type of sulfide source were investigated. The as-prepared AgInS₂ nanostructure was characterized extensively by techniques such as XRD, EDS, SEM, TEM, UV-Vis and PL. Our experimental results indicated the type of sulfur source which plays an important role in the morphology of AgInS₂. XRD studies showed that pure orthorhombic AgInS₂ nanostructure has been produced.

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