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Green and low-cost synthesis of CIGSe nanoparticles using ethanol as a solvent by a sonochemical method - A new approach

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HIGHLIGHTS

- $CuIn_{0.7}Ga_{0.3}Se_2$ nanoparticles were synthesized by a sonochemical method.
- The as-synthesized product's properties were characterized.
- Neither additional heating nor toxic solvents during the synthesis were necessary.
- The products show chalcopyrite structure without being annealed at 500 °C.

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ABSTRACT

A sonochemical method was utilized to synthesize $Cu(In_xGa_{1-x})Se_2$ (CIGSe) nanoparticles using $NaBH_4$ with ethanol as a solvent. The effect of the ultrasonification time intervals on the synthesis was investigated in the range of 2–5 h, 5 h was found to be the most suitable time to obtain the expected $CuIn_{0.7}Ga_{0.3}Se_2$ compounds. The as-synthesized CIGSe nanoparticles possessed a tetragonal structure with quasi-spherical shape, band gap of ~1.25 eV, and targeted $Cu(In_xGa_{1-x})Se_2$ composition. A new reaction scheme is proposed to explain the role of $NaBH_4$ in the plausible reaction paths. The non-toxic solvent used in the synthesis with no additional heating makes the developed method cheaper and "greener" than the previously reported methods.

1. Introduction

CIGSe compounds are effective light-absorbing materials for thin film solar cells, possessing a direct band gap in the range of 1.0–1.7 eV [1,2]. Thin films of CIGSe compounds have been prepared on surfaces of various substrates for applications to solar cells [3–11]. For example solar cells prepared from CIGSe thin films deposited by thermal evaporation showed high energy conversion efficiency of around 22.6% [6]. Although the CIGSe solar cells fabricated by thermal evaporation show high conversion efficiency, the deposition of these elements is very expensive due to the requirement of sophisticated equipment. In addition, the fabricated solar cells are affected by the impurities from the substrates due to the high temperature demand of vacuum-based techniques. To minimize these problems, efforts have been made to develop low-cost and environment-friendly synthesis of CIGSe nanoparticles (NPs).

Recently, CIGSe nanoparticles synthesized by solution processes have been reported [12–16]. In such approaches, Cu, In, Ga, Se elements [13,14] or their salts [14,15] are dissolved in organic solvents and react with each other to form precipitates of CIGSe. These solution processes typically involve toxic organic solvents, such as hydrazine, ethylenediamine, and polyetheramine, as well as reaction temperatures of up to 280 °C. Many of these methods also rely on complex reaction set-ups and procedures incorporating autoclaves or glove-boxes. The drawbacks of the reported solution methods are apparent, which can be eliminated by applying ultrasonic irradiation to the methods. Acoustic cavitation, i.e. the formation, growth, and implosive collapse of a vast amount of vapor cavities in a liquid under ultrasonic irradiation leads to the formation of localized hot spots, where the reaction could take place.

The sonochemical method is considered suitable for the preparation of nanoparticles with a range of functional characteristics

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[17]. A CIGSe nanoparticle synthesis by sonochemistry has been reported with a reaction time of 4 h [18], in which a mixture of ethylene glycol and hydrazine (very toxic) need to be applied to completely dissolve the precursors at 110 °C. The as-synthesized NPs showed a chalcopyrite structure only after annealing at 500 °C. From a sonochemistry point of view, ethylene glycol is unsuitable solvent because of its relatively high viscosity (~16.1 mPa at 20 °C), which does not favor the development of vapor cavities to their full sizes [19,20]. This was probably the reason why the reaction temperature in Ref. [18] needs to be set to 110 °C. Compared to ethylene glycol, ethanol would be a more suitable solvent in sonochemical processes because of its substantially lower viscosity (~1.2 mPa at 20 °C), so that the number of full-size-developed cavities would be sufficient to facilitate reactions at moderate temperatures. In addition, ethanol is a readily available low-cost, environment-friendly solvent, because it could be generated from renewable sources. Sodium borohydride ($NaBH_4$) helps dissolve and reduce Se powders in ethanol with minimal impact on the environment.

In this work, a slightly modified sonochemical procedure for CIGSe nanoparticle synthesis using ethanol as the only solvent was investigated to develop a cheaper and eco-friendlier nanoparticle synthesis process for commercial applications. Although a reduction agent ($NaBH_4$) must be added to the solvent, this approach is substantially less toxic than the previously reported methods.

From the literature survey [5] it is evident that the CIGSe thin film solar cell exhibits the best efficiency when the atomic ratio of Ga/(In+Ga) is around 0.3. Therefore, in the present work, we targeted to synthesize the CIGSe nanoparticles with a composition of $CuIn_{0.7}Ga_{0.3}Se_2$.

2. Experiment details

All chemicals were used as-received. Copper (I) chloride (CuCl, Aldrich 99.995%), indium (III) chloride ($InCl_3$, Aldrich 98%), gallium (III) nitrate hydrate ($Ga(NO_3)_3.xH_2O$, Aldrich 99.999%), selenium (Se, Aldrich 99.99%), ethyl alcohol (C_2H_5OH 99.9%, Fisher Scientific), and sodium borohydride ($NaBH_4$, Aldrich 99.99%) were used as chemicals for the synthesis, and a VCX 750 Sonics & Materials ultrasonic processor was incorporated.

The elemental selenium was first dissolved in two beakers containing solutions of $NaBH_4$ in ethanol until these solutions became transparent (it took about 15 min). Subsequently, $InCl_3$ and $Ga(NO_3)_3.xH_2O$ were added to each beaker separately. The transparent solutions changed to turbid colloidal suspensions with yellow precipitates. These two suspensions were mixed with each other, and finally CuCl was added, the yellow precipitates changed quickly to deep black precipitates. The mixture was ultrasonicated (f = 20 kHz, P = 300 W) at room temperature for different time intervals of 2 h, 3.5 h, 4.5 h, and 5 h, respectively. The precipitates were filtered, washed twice with ethanol and once with deionized water, and vacuum evaporated at 40 °C for 8 h.

The as-synthesized samples were characterized using a range of techniques. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was performed using Al Kα X-rays as the excitation source. The relevant core levels (Cu 2p, In 3d, Ga 2p, and Se 3d) were used to quantify the elemental atomic composition using the sensitivity factors from the database. The crystal structure of the as-synthesized products was characterized by powder X-ray diffraction (XRD, PANalytical, X'Pert-PRO MPD) and Raman spectroscopy (XploRA Plus Horiba). The XRD patterns of the powder samples were measured using Cu/Kα radiation. The Raman spectra were obtained from $100\ cm^{-1}$ to $600\ cm^{-1}$ at room temperature. The chemical compositions of the CIGSe nanoparticles were measured by inductively coupled plasma emission spectroscopy (ICPS, ICPS 8100 Shimadzu system) with standard HCl/HNO_3 digestion.

The size and morphology of the nanoparticles were characterized by transmission electron microscopy (TEM, Philips CM-200), and scanning electron microscopy (SEM, Hitachi S-4800). The optical properties of as-synthesized CIGSe nanoparticles were measured by ultraviolet-visible-near infrared (UV-Vis-NIR, Cary 5000, Varian) over the range 300–1800 nm.

3. Results and discussion

3.1. Reaction scheme

The experimental procedures described above were designed (and later verified by the results obtained) based on the following tentatively proposed reaction pathways:

$$Se + NaBH_4 + 3C_2H_5OH \rightarrow NaHSe + (C_2H_5O)_3B + 3H_2 \quad (1)$$

$$4\,Ga^{3+} + 6HSe^- \rightarrow 2Ga_2Se_3 + 6H^+ \quad (2)$$

$$4In^{3+} + 6HSe^- \rightarrow 2In_2Se_3 + 6H^+ \quad (3)$$

$$2Cu^+ + HSe^- \xrightarrow{\text{ultrasonification}} Cu_2Se + H^+ \quad (4)$$

$$Cu_2Se + xIn_2Se_3 + (1-x)Ga_2Se_3 \xrightarrow{\text{ultrasonification}} 2CuIn_xGa_{1-x}Se_2 \quad (5)$$

The first reaction clearly shows that the role of $NaBH_4$ is to completely reduce Se to HSe^-, which is soluble in ethanol. The second and third reactions took place parallel in separate beakers to form Ga_2Se_3 and In_2Se_3. Finally, the fourth and fifth reactions took place simultaneously when these two beakers were mixed together and CuCl was added, so that the freshly forming Cu_2Se could not be aged to its stable structure. Although details about the effects of ultrasonification on these two reactions are unclear, they are supported by the XRD results. In fact, the XRD results shown in the next section revealed that trace amounts of Cu_2Se compound as impurities in the products with 2–4.5 h ultrasonic irradiation, which seem to disappear prolonging the ultrasonic irradiation to 5 h (see Fig. 1). These results suggest that the ultrasonic effect, beside other effects, favors the decomposition of Cu_2Se to promote reaction (5).

3.2. Effect of the ultrasound time interval

Fig. 1 presents XRD patterns of the as-synthesized products with ultrasonification times of 2 h, 3.5 h, 4.5 h, and 5 h, respectively. We could easily observe that the ultrasonification time of 2 h was not enough to form the typical crystal structure of the $Cu(In_xGa_{1-x})Se_2$ compound. Prolonging the ultrasonification time to 3.5 h and 4.5 h resulted in much better crystallinity with the expected structure, but small amounts of Cu_2Se crystals also appeared. Prolonging the ultrasonification time further to 5 h yielded single-phase tetragonal $CuIn_{0.7}Ga_{0.3}Se_2$ nanocrystals with five main index planes of (112), (220), (312), (400) and (332) without any signs of Cu_2Se. Therefore, under the conditions investigated in this work, an ultrasonification time of 5 h is the most suitable time interval to form the $Cu(In_xGa_{1-x})Se_2$ compounds with the expected crystalline structure.

It is worthwhile to note that SEM images did not indicate any effects of the ultrasonification time intervals on the spherical shape of the as-synthesized nanocrystals between 2 and 5 h (see Fig. 2). Similarly, this ultrasonification time range had an insignificant effect on the reaction temperatures, which were between 61 and 64 °C.