

Effect of different polyol solvents on the synthesis of CuInS₂ nanoparticles by cyclic microwave irradiation

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CuInS₂ nanoparticles were synthesized by a cyclic microwave irradiation method at 600 W for 75 cycles. The effect of different polyol solvents (ethylene glycol, glycerol, and propylene glycol) on the synthesis of the CuInS₂ nanoparticles was investigated. Characterized by XRD, the powders synthesized using ethylene glycol and glycerol were pure CuInS₂ with tetragonal structure. However, CuInS₂ with the existence of CuS was obtained when using propylene glycol due to the lower resulting reaction temperature. FTIR spectra of the residual solvents after the synthesis process were determined and this revealed that ethylene glycol and glycerol were the solvents with good reducing capability. FESEM images revealed that the synthesized CuInS₂ powders were composed of nanoparticles with diameters in the range of 20-100 nm. The CuInS₂ nanoparticles synthesized using glycerol were smaller than those synthesized using ethylene glycol, due to the higher viscosity of glycerol.

Key words: CuInS₂, Microwave radiation, Semiconductors, Nanocrystalline materials.

Introduction

CuInS₂ has been extensively used as an absorber material for photovoltaic applications due to its direct band gap of 1.5 eV [1, 2]. Several synthesis methods, such as colloidal [1], hydrothermal [2] and microwave [3], have been recently used to prepare CuInS₂ nanostructures. Of these, microwave synthesis has attracted considerable attention because it is an efficient, energy saving and environmentally benign method for synthesizing nanocrystalline metal oxides and sulfides with various sizes and morphologies [4, 5]. In microwave synthesis, the microwave radiation interacts with polar molecules or conducting ions in solution to create rapid volumetric heating, resulting in shorter reaction time and higher reaction rate [5]. Polyol or polyalcohol is usually employed as a solvent for microwave synthesis to prepare inorganic nanomaterials due to its high boiling point, high dielectric loss constant, and good reducing capability [6-8].

Different polyol solvents have different physical and chemical properties which differentially affect the microwave synthesis of nanomaterials. This study synthesized CuInS₂ nanoparticles by a cyclic microwave irradiation method using three different

polyol solvents- ethylene glycol (EG), glycerol (Gly), and propylene glycol (PG) -to investigate their effects on the characteristics of the synthesized powders. The characteristics of the synthesized powders were examined by XRD and FESEM techniques. In addition, the reducing capability of each solvent was determined by FTIR technique.

Experimental Procedure

In a typical procedure, CuCl₂·2H₂O (2 mmol), InCl₃·4H₂O (2 mmol), and CH₃CSNH₃ (4 mmol) were separately dissolved in 10.0 mL of the polyol solvent. The solutions were mixed together for 30 min, and then the mixed solution was irradiated using 2.45 GHz microwave radiation at 600 W for 75 cycles. For each cycle, the microwave power was turned on for 30 s of every 60 s (50% power). The resulting powder was collected and washed with deionized water and then ethanol. Finally, the powder was dried at 80 °C overnight and then characterized using XRD, FTIR, and FESEM techniques.

The purity, crystallinity, and crystal structure of the synthesized powders were characterized by XRD (Rigaku MiniFlex II) with a CuK α radiation (1.5406 Å). Vibration modes of the powders were investigated by FTIR (Bruker TENSOR27) using the KBr pellet technique. Particle size and morphology of the powders were determined by FESEM (JEOL JSM-6335F), operated at 15 kV of accelerating voltage. UV-Vis

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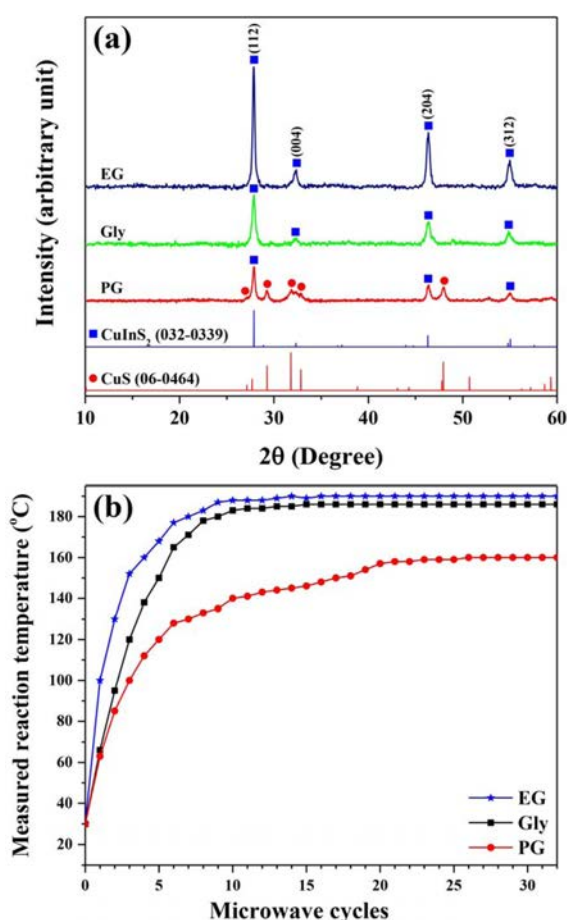


Fig. 1. (a) XRD pattern of the powders synthesized using different solvents and (b) measured reaction temperatures of the different solvents irradiated at 600 W with the prolonged reaction time.

diffuse reflectance spectra (DRS) were recorded on the samples diluted in BaSO₄ by a UV-Vis-NIR spectrophotometer (UV-3101PC, Shimadzu) equipped with an ISR-3100 integrating sphere attachment.

Results and Discussion

The XRD spectra of the powders synthesized using different solvents are shown in Fig. 1(a). In all powders, the diffraction peaks at 2θ of 27.86°, 32.24°, 46.32°, and 54.87° were indexed to the (112), (004), (204), and (312) planes of a tetragonal CuInS₂ structure (JCPDS no. 032-0339). However, in the XRD spectrum of the powder synthesized using PG, the diffraction peaks of a hexagonal CuS structure (JCPDS no. 06-0464) were also found, implying that pure CuInS₂ did not completely form at the given microwave heating power. In addition, the intensity of the diffraction peaks of the CuInS₂ powder synthesized using EG were higher than those synthesized using Gly and PG, suggesting higher crystallinity. These results could be explained by the reaction temperature of the solvents. The ability of a conductive media to convert electromagnetic energy into heat at a given frequency and microwave power is

Table 1. Some properties of the solvents used [5, 10-12].

Solvents	Ethylene glycol	Glycerol	Propylene glycol
Structure	<chem>OCCO</chem>	<chem>OCC(O)CO</chem>	<chem>CC(O)CO</chem>
Boiling point (°C)	197	290	187
Dielectric loss tangent (at 2.45 GHz)	1.35 (at 20 °C)	0.54 (at 20 °C)	~0.23 (at 25 °C)
Viscosity (mPa·s at 25 °C)	16.2	934	11.3

determined by the dielectric loss tangent ($\tan \delta = \delta''/\delta'$), where δ'' is the dielectric loss and δ' is the dielectric constant [5-7]. A solvent with high $\tan \delta$ more effectively convert microwave energy to thermal energy; as a result, high reaction temperature can be achieved. The $\tan \delta$ of the solvents used in this research are shown in Table 1. In Fig. 1(b), the measured reaction temperatures of EG, Gly and PG irradiated at 600 W were 190 °C, 186 °C, and 157 °C, respectively. The higher crystallinity of the CuInS₂ powder synthesized using EG could be due to the higher reaction temperature of the solution, relating to its higher $\tan \delta$ [5]. On the other hand, the lowest $\tan \delta$ of PG corresponded to the lowest reaction temperature of the solution. This could be the reason that the CuS phase still remained in the CuInS₂ powder synthesized using PG at given microwave power. This result was consistent with the previous study reporting the remaining of CuS when the temperature was lower than 160 °C [9].

The formation of CuInS₂ nanostructures was related to the reduction of Cu²⁺ to Cu⁺ in solvent under microwave radiation [13]. After the reduction, the H₂S released from CH₃CSNH₃ reacted with Cu⁺ and In³⁺ to yield CuInS₂. Since each polyol solvent possesses different oxidation potentials, a solvent with stronger reducing capability is a more effective reducing agent. During the synthesis process, the hydroxyl groups in polyol solvent can be oxidized by the metallic precursor. To investigate the reducing capability of the polyol solvents, pure solvents, residual solvents after the synthesis, and pure solvents irradiated at 600 W for 75 cycles were further analyzed by FTIR (Fig. 2). Vibration peaks of the pure solvents (EG, Gly and PG) exhibited at 3384-3385 cm⁻¹, 2933-2946 cm⁻¹, 2879-2883 cm⁻¹, 1652-1654 cm⁻¹, 1414-1457 cm⁻¹, and 1079-1110 cm⁻¹ are attributed to O-H stretching, C-H asymmetric stretching, C-H symmetric stretching, O-H bending, C-H bending, and C-O stretching, respectively [14].

The FTIR spectrum of the residual EG after the synthesis showed a strong vibration peak of C=O stretching at 1758 cm⁻¹, contributed to the ketone

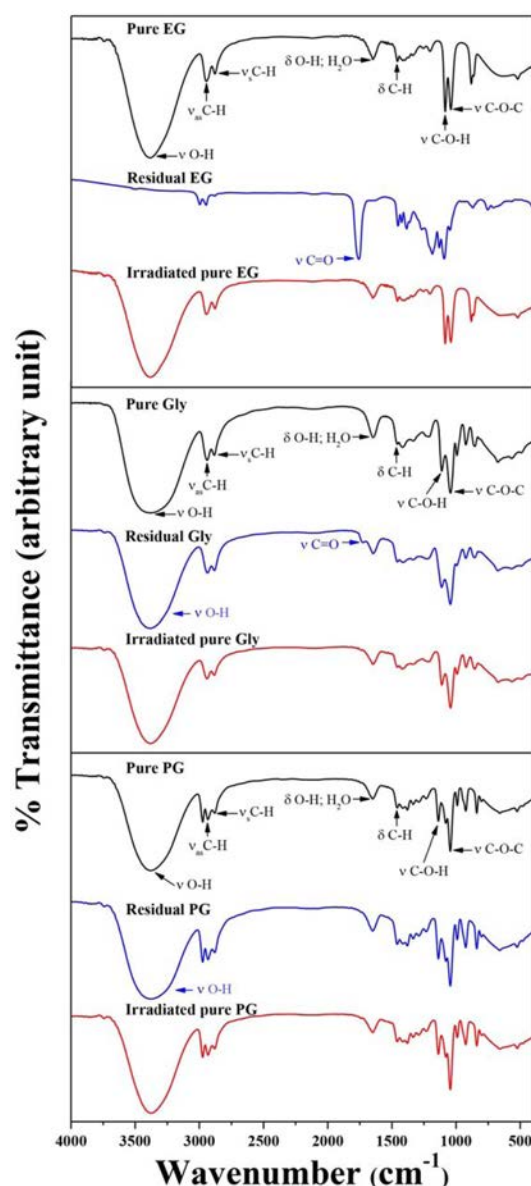


Fig. 2. FTIR spectra of pure solvents, residual solvents after the synthesis process and pure solvents irradiated at 600 W for 75 cycles.

carbonyl group of diacetyl [15]. In addition, the O-H stretching band of the hydroxyl group was disappeared, implying that EG was completely oxidized to diacetyl during the microwave reaction. The FTIR spectrum of the residual Gly showed a weak vibration peak of C=O stretching at 1725 cm^{-1} , contributed to the aldehyde group of glyceraldehyde or ketone carbonyl group of dihydroxyacetone, and the remaining of the O-H stretching band could be the hydroxyl groups of the oxidation products [16]. Generally, PG can also reduce the metallic precursor resulting in acetone, propanal, and allyl alcohol [17]. But, these product compounds can evaporate and/or decompose during the microwave synthesis, due to their relatively low boiling points (56°C , 48°C , and 97°C for acetone, propanal, and allyl

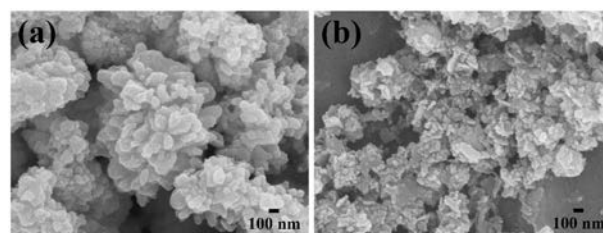


Fig. 3. FESEM images of the CuInS_2 nanoparticles synthesized using (a) EG and (b) Gly.

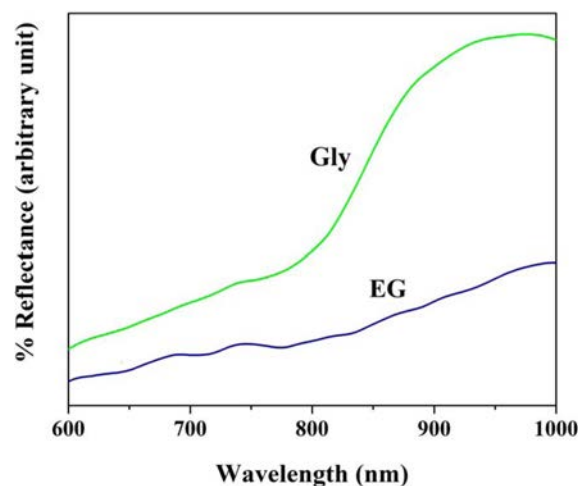


Fig. 4. UV-Vis diffuse reflectance spectrum of the CuInS_2 nanoparticles.

alcohol, respectively [18]). For this reason, the vibration peaks of the C=O stretching of these products were not observed in the FTIR spectrum of the residual PG. However, the remaining of O-H stretching band implied that PG was not completely reduced Cu^{2+} ions during the microwave synthesis in according to the XRD result (Fig. 1(a)). It is noted that the FTIR spectra of the EG, Gly, and PG irradiated at 600 W for 75 cycles (Fig. 2) were the same as the respective pure solvents, confirming that the microwave irradiation did not decompose the pure solvents. These results suggested that microwave radiation enhanced the reducing capability of EG and Gly. As a result, the CuS was not found in the CuInS_2 powders synthesized using EG and Gly as revealed in their XRD spectra (Fig. 1(a)). Based on the XRD and the FTIR results, EG was the most favorable solvent for the microwave synthesis where the CuInS_2 powder synthesized using EG had the highest crystallinity.

FESEM images (Fig. 3) of the CuInS_2 powders synthesized using EG and Gly were composed of CuInS_2 nanoparticles with diameters in the range of 20–100 nm. The nanoparticles synthesized using Gly were smaller than those synthesized using EG. This difference could be due to the different solvent viscosities (Table 1). The viscosity of Gly is significantly higher than EG; the solubility and diffusion rate of ions in the Gly solution is, therefore, lower. This suppresses crystalline growth, resulting in the smaller size of the synthesized CuInS_2

nanoparticles. The optical properties of the CuInS₂ powders synthesized using EG and Gly were investigated by UV-Vis diffuse reflectance spectrum (Fig. 4). The spectrum exhibited light absorption in the visible light region, extending into the near-infrared region. The CuInS₂ nanoparticles synthesized using Gly exhibited stronger absorption compared to those synthesized using EG. The CuInS₂ nanoparticles with smaller in size have a greater ability to reflect and scatter light. Thus, we obtained different results of light absorption ability.

Conclusions

In summary, we reported the effect of different polyol solvents (ethylene glycol, glycerol, and propylene glycol) on the cyclic microwave irradiation synthesis of the CuInS₂ nanoparticles. The purity and crystallinity of the CuInS₂ nanoparticles depended on the resulting reaction temperature and the reducing capability of the polyol solvents used. The size of the CuInS₂ nanoparticles was also influenced by the viscosity of the polyol solvents. In addition, the size affected the light absorption ability. The results of this research could be useful in the microwave irradiation synthesis of other related inorganic nanomaterials.

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