International Congress on Nanoscience and Nanotechnology
9-11 November 2010 Shiraz - Iran

SYNTHESIS AND CHARACTERIZATION OF CUINSE$_2$ NANOPOWDER WITH DIFFERENT MORPHOLOGIES

M.Najafi[1*], M.R.Vaezi[2], S.Kh.Sadrnezhad[3]
[1,2]Department of new material, Material and Energy Research Center, Karaj, Iran
[3]Department of Material engineering, Sharif university, Tehran, Iran
** Corresponding Author's E-mail:Maryam.Najafi25@yahoo.com*

KEYWORDS
$CuInSe_2$, nanostructures, solvothermal, semiconductor

ABSTRACT
In this paper, crystalline semiconductor $CuInSe_2$ (CIS) nanostructures as new material for solar cells were prepared using a solvothermal route. For this purpose, cupric chloride, indium chloride, and selenium powder were mixed in amine solvents of ethylenediamine or diethyl amine. The effects of reaction time and solvent type were studied. The obtained results show that through selective processing conditions, the phase, morphology, and dimensions of the synthesized CIS nanostructures can be controlled. X-ray diffraction, XRD patterns of the obtained nanopowder show that the structure of synthesized nanopowder has been mainly formed from chalcopyrite phase. The morphology of $CuInSe_2$ nanopowders analyzed by scanning electron microscope (SEM). The results show that the obtained morphology are rod, plate and particle.

INTRODUCTION

Ternary chalcopyrite semiconductor nanostructures are being intensively investigated for low cost photovoltaic applications. With a direct band gap of 1.02 eV and a high absorption coefficient of more than 10^4 cm^{-1}, $CuInSe_2$ has been regarded as a favorable absorber material for use in thin film solar cells [1-3] .The ternary compound $CuInSe_2$, which belongs to the I-III-VI$_2$ family, has emerged as a leading material for high efficiency and radiation-hard solar cell applications. In fact, in recent years devices based on this material have achieved conversion efficiency up to around 17 % [4].

Using particle size and morphology as control parameters to tailor band gap provides a novel approach to the development of materials for device applications. Nanocrystalline materials have a wide range of optical and electronic properties that are accessible in the nanoscale [5].

Nanocrystals have been prepared with various synthetic methods. Many approaches involve aqueous solution and the classical techniques of colloidal chemistry [6]. We have been interested in the use of a solvothermal route, which is carried out at low temperature and does not require organometallic or toxic precursors; to produce various kinds of nanocrystalline materials[7]. Here we report a solvothermal route to chalcopyrite $CuInSe_2$ nanocrystals using alkylamines as a solvent. In ethylenediamine $CuInSe_2$ was obtained as nanorod, nanoplate and nanoparticles, while diethylamine gave $CuInSe_2$ as irregular nanoparticles.

EXPERIMENTAL

The nanostructures were synthesized using a solvothermal processing. A stoichiometric mixture of selenium powders, $CuCl_2 \cdot 2H_2O$ and $InCl_3.4H_2O$ was first dissolved in an anhydrous solvent. The anhydrous solvents used include ethylenediamine and diethylamine.

The solution was then loaded into an 80-mL Teflon-lined stainless steel autoclave up to 45% of the total volume. For the solvothermal synthesis, the sealed autoclave was heated to a reaction temperature of 180 °C, 210 °C, and 240 °C for 15 h. and then cooled down to room temperature.

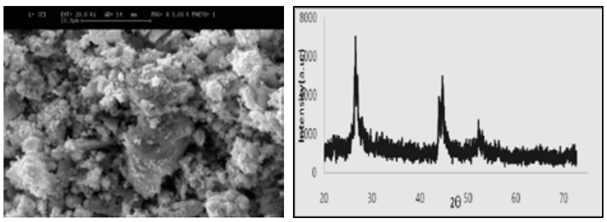
After the synthesis, the precipitates were centrifuged and washed with distilled water and absolute ethanol several times to remove the solvent and by-products. The samples were placed in a 60 °C oven for 6-h to obtained dried powders. The dried powders were analyzed using scanning electron microscopy (SEM) operated at 20 Kv. and X-ray diffraction technique.

RESULTS AND DISCUSSION

$CuInSe_2$ nanopowders having various morphologies, shapes, and dimensions were obtained. The effect of solvent type is first presented, followed by effect of temperature; finally, the crystalline nanostructures are presented and discussed.

EFFECT OF SOLVENT TYPE

Particles having irregular shapes were obtained using diethylamine as the solvent, regardless of the other synthesis conditions. Fig. 1A shows the irregular particles obtained at 210 °C for 15 h. The irregular particles were found to be crystalline $CuInSe_2$ as shown in Fig. 1B. When ethylenediamine was used as the solvent, precipitates having different geometries were obtained under different conditions.



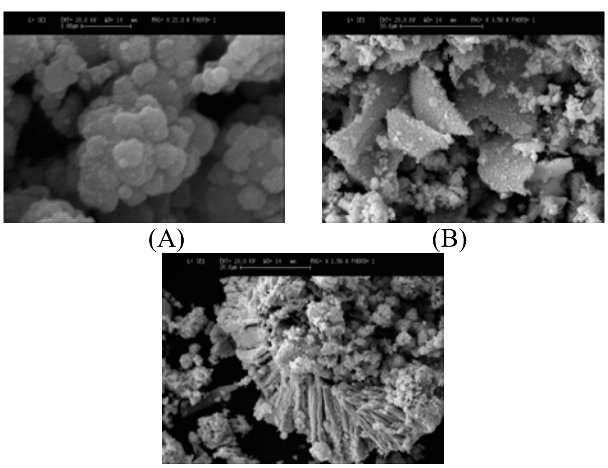
(A) (B)

Fig 1. (A) Irregular particles obtained at 210 °C for 15 h, (B) XRD pattern showing that the irregular particles are crystalline $CuInSe_2$.

EFFECT OF TEMPERATURE

Here, we examine the effects of temperature using ethylenediamine as solvent. particles (Fig. 2A), plates (Fig. 2B), and rods (Fig. 2C) were obtained at 180 °C, 210 °C, and 240 °C, respectively.

Precipitates with different phases were also obtained at different temperatures. At the lower temperatures of 180 °C (Fig. 2A) and 210 °C (Fig. 2B), Se, Se_6, and In_2Se_3 were found as by-products of the desired $CuInSe_2$ as shown in Fig. 3A and B, respectively.



(A) (B)

(C)

Fig2. (A) Particles, (B) plate, and (C) rod morphologies were obtained at 180°C, 210°C, and 240 °C for 15 h., respectively.

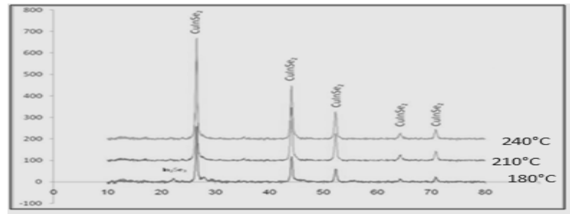


Fig 3. XRD diffractogram of $CuInSe_2$ synthesized at (A) 180 °C and (B) 210 °C, and (C) 240 °C for 15 h. In_2Se_3 was found as by-products in the patterns (A) and (B).

CONCLUSION

In summary, we have successfully synthesized $CuInSe_2$ particles, plate and rods. It was found that the solvent type and reaction temperature influence the morphology, phase, and dimensions of the nanostructures. Particles having irregular shapes were obtained using diethylamine as the solvent, regardless of the other synthesis conditions. When ethylenediamine was used as the solvent, particles, plate and rods were obtained at 150 °C, 180 °C, and 200 °C, respectively.

REFERENCES

[1] Chih-Hui Chang, Jyh-Ming Ting, Phase, morphology, and dimension control of CIS powders prepared using a solvothermal process, Thin Solid Films 517 (2009) 4174–4178

[2] Yi-Han Yang and Yit-Tsong Chen, Solvothermal Preparation and Spectroscopic Characterization of Copper Indium Diselenide Nanorods, J. Phys. Chem. B 2006, 110, 17370-17374

[3] Hailin Peng, David T. Schoen, Stefan Meister, Xiao Feng Zhang, and Yi Cui, Synthesis and Phase Transformation of In2Se3 and CuInSe2 Nanowires, J. AM. CHEM. SOC. 9 VOL. 129, NO. 1, 2007 35.

[4] Yu-Hsiang A. Wang, Changqing Pan, Ningzhong Bao, Arunava Gupta, Synthesis of ternary and quaternary CuInxGa1-xSe2 (0≤x ≤1) semiconductor nanocrystals, Solid State Sciences (2009) 1–4.

[5] Y.-G. Chuna, K.-H. Kimb, K.-H. Yoon,Synthesis of CuInGaSe2 nanoparticles by solvothermal route, Thin Solid Films 480–481 (2005) 46–49

[6] By Bin Li, Yi Xie, Jiaxing Huang, and Yitai Qian,Synthesis by a Solvothermal Route and Characterization of CuInSe2 Nanowhiskers and Nanoparticles, Adv. Mater. 1999, 11, No. 17.

[7] Ge´rard Demazeau, Solvothermal processes: a route to the stabilization of new materials, J. Mater. Chem., 1999, 9, 15–18