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Using Simple Microwave Approach for Synthesize of $CuInS_2$ Nanostructures and Investigation of their Performance in Solar Cells

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This study focuses on the preparation and characterization of single phase $CuInS_2$ nanoparticles with a copper complex as precursor via microwave technique. The effect of sulfur sources on product size and morphology was investigated. The products were characterized by X-ray diffraction, scanning electron microscopy, ultraviolet-visible spectroscopy, and photoluminescence spectroscopy. Thin films $CuInS_2$ were prepared by doctor's blade method and then studied via I-V characterization.

Keywords: $CuInS_2$, Microwave, Nanoparticles, Solar cell.

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1. INTRODUCTION

Semiconductor nanocrystals (NCs), and luminescent NCs have attracted considerable interest during the past decades because of their numerous applications in photoelectronic devices and biotechnology [1]. Among ternary semiconductor compounds belonging to the I-IIIVI$_2$ series, CuInX$_2$ (X = Se, Te, S) are promising materials for photovoltaic applications because of the suitability of their electrical and optical properties [2]. Qian's group reported the preparation of CIS nanocrystals (NCs) via solvo / hydrothermal routes from dual multiple sources [3]. Castro et al. synthesized ultrafine CIS NCs by thermal decomposition of the single-source precursor, [(PPh$_3$)$_2$CuIn(SEt)$_4$] [4]. several deposition methods have been developed for preparing $CuInS_2$ thin films, such as single source evaporation [5], co-evaporation [6], sulfurization of metallic precursors [7], chemical vapor deposition [8], electro-deposition [9], spray pyrolysis [10], sputtering [11] and rapid thermal process [12] etc. Up to now, different morphologies of $CuInS_2$ thin film and powders have been obtained, such as nanoparticles [13], nanorods [14], nanotubes [15], nanowires [16], foamlike $CuInS_2$ nanocrystallites [17], and porous microspheres [18]. Microwave irradiation plays an important role in chemical reactions in aqueous media [19], reducing the time [20] and the cost, decreasing particle size with narrow size distribution, increasing the product yield rate, and producing high purity products in comparison with conventional methods [21]. Microwave irradiation suggests great advantages as the simplest and fastest technique since selective dielectric heating, due to the difference in the solvent and reactant dielectric constants, can provide significant improvement in reaction rates [22]. In this experiment $CuInS_2$ nanoparticles were synthesized and characterized with different physical measurement. The effects of sulfur sources, solvents, microwave heating time and irradiation power were investigated. Thin film of $CuInS_2$ was fabricated by doctor's blade and I-V characterization was used for calculating solar cell characteristic.

2. SYNTHESIS AND CHARACTERIZATION

2.1 Method of Sample Manufacturing and Anaysis

To synthesize $CuInS_2$ nanoparticles, 0.02 mol of [Cu(Hsal)$_2$] and 0.02 mole of indium chloride (InCl$_3$) were solublized in 30 ml propylene glycol separately and stirred for 10 min. Subsequently two solutions mixed together. This mixture was then combined with sulfur (0.04 mole in 50 ml propylene glycol) sources. Final compound was stirred for 10 min and left for the reaction to proceed by cyclic microwave radiation at 750 powers in propylene glycol as solvent for 6 min. Each cycle was 90 s long, and composed of 30 and 60 s for the on and off periods, respectively. The precipitates were washed with water and ethanol, dried at 80 °C for 24 h and were characterized by SEM, PL, UV-Vis, and XRD analyses. $CuInS_2$ films were prepared by Doctor's blade coating using slurry of 0.05 g $CuInS_2$ powders dispersed in 5 ml ethanol, 0.05 g ethyl cellulose and 0.05 ml Triton X-100 mixture on Indium Tin Oxide (ITO)-coated glass substrate. Then, the glass substrate was maintained at 300 °C for 30 min to remove the organic compounds. With a chemical bath deposition (CBD), CdS thin film have coated on $CuInS_2$ electrode. CBD was performed with a solution consisting of 0.01M Cd(NO$_3$)$_2$, and 0.08M thiourea. The bath was heated to 80 °C then the sample was immersed. The counter-electrode was prepared by chemical deposition of a platinum solution above an ITO electrode. This electrode was placed over the CdS / $CuInS_2$ electrode. The redox electrolyte consisted of 0.05 M LiI, 0.05 M I_2 and 0.5 M 4-tert-butylpyridine at acetonitrile as a solvent. The photocurrent–voltage (I-V) curves were used to calculate short-circuit current (I_{sc}), open-circuit voltage (V_{oc}) and fillfactor (FF) of the DSSCs. I-V mesurement was made under simulated Air Mass 1.5 global illumination.

3. RESULT AND DISCUSSION

In this work, influence of sulfur sources on morphology and particle size of as-prepared $CuInS_2$ nanoparticles was

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studied. As shown in Fig. 1, two different sulfur sources were used for preparation of $CuInS_2$ crystals. When thiourea was used as sulfur source, nanoparticles with smallest size were obtained (Fig. 1a). When Carbon disulfide was used instead of thiourea, aggregated spheres with about 200 nm diameters were achieved (Fig. 1b).

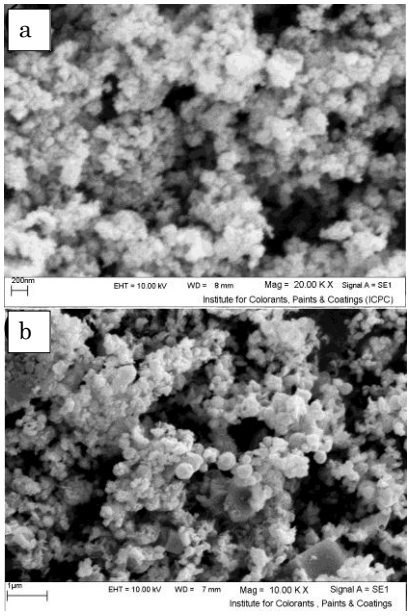

Fig. 1 – SEM image of $CuInS_2$ prepared by (a) Thiourea and (b) Carbon disulfide as sulfur source

Optical properties of the $CuInS_2$ nanocrystals were investigated by UV-vis spectroscopy and photoluminescence (PL) spectroscopy at room temperature. Fig. 2 (a, b) shows UV-Vis spectra and plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$. The band gap of $CuInS_2$ nanoparticles could be obtained by extrapolating the slope of curves to the x-axis in a plot of $(\alpha h\nu)^2$ against hv on the basis of the absorbance of UV-visible measurement. From above information, estimated bangap for as-synthesized nanoparticles was 2.2 eV which showed about 0.7 eV blue shift in comparison with bulk sample with 1.53 eV bandgap. This is due to smaller particle size of synthesized product compared with the bulk one. Fig. 2c illustrates room-temperature photoluminescence (PL) spectra of $CuInS_2$ nanoparticles. A broad PL band can be observed at 2.07 eV that has 130 meV red shift in comparison to UV-vis result. It was found that this red shift value is due to presence of defect levels in $CuInS_2$ structure [23]. Thus a stokes shift at PL spectrum can be seen.

Fig. 3 shows the diffractograms of $CuInS_2$ nanoparticles. As shown in this Fig, the main diffraction peaks were observed at 28.38°, 32.9°, 46.67°, 55.23° in the XRD pattern of the $CuInS_2$ which confirm that the formed material is $CuInS_2$ with tetragonal structure. (JCPDS No. 15-0681, $a = 5.511$ and $c = 11.05$). There is no peak from impurity compared with the standard diffraction pattern of $CuInS_2$ which indicates the products have high purity. The crystal size of the $CuInS_2$ nanoparticles was estimated by Debye-Scherrer equation ($d = 0.9\ k\ /\ \beta\ \cos\theta$) and it was about 4.7 nm, which is in agreement with the other observation results. The diffraction peaks are clearly broadened, which can be the result of the reduced particle size.

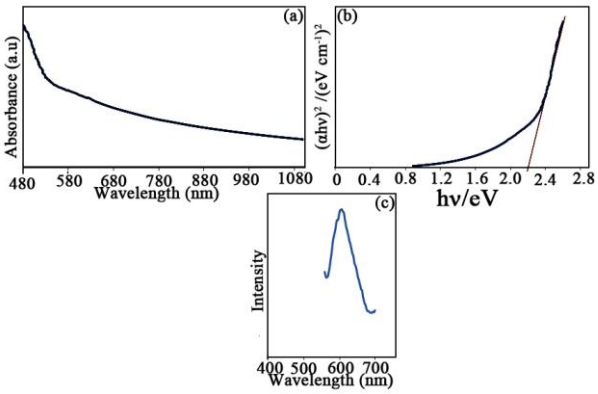

Fig. 2 – (a) UV-Vis spectra, (b) plot of $(\alpha h\nu)^2$ versus $(h\nu)$, and PL spectra of $CuInS_2$ nanostructure

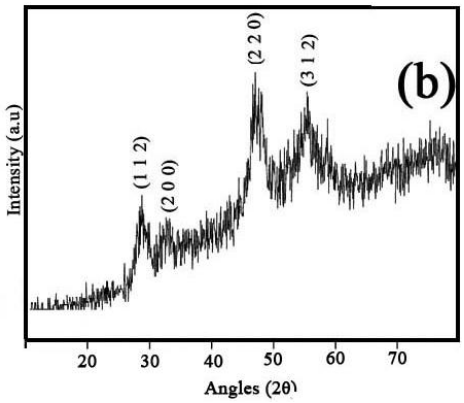

Fig. 3 – XRD pattern of $CuInS_2$ nanostructure

The current-voltage measurement for a $CuInS_2$ solar cell is shown in Fig. 4. The fill factor (FF) and open-circuit voltage (V_{oc}) were 34 % and 140 mV, respectively. Short-circuit current density, *Jsc*, was 0.066 mA/cm^2, which is very low value. Because of presence of the large number of boundaries grain, the high levels of carrier recombination were achieved and therefore electron transfer becomes low. These boundaries grain generally have a higher number of deep trap states and therefore, act as efficient recombination centers. Another reason for low short circuit current is high bangap of synthesized nanoparticles. A low bandgap absorbing material has high absorption, high current and low open-circuit voltage and a high band gap absorbing material has low absorption, low current, and high open-circuit voltage. Also by increasing bandgap, trap states that lie within the bandgap has increased, so the short circuit current value has decreased.

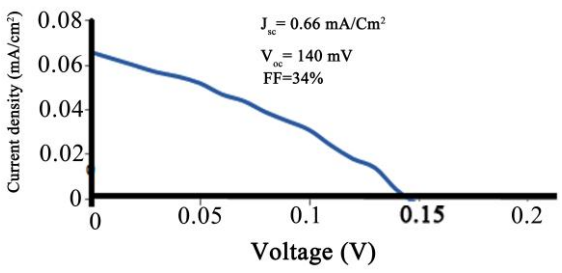

Fig. 4 – I-V characterization of solar cell

4. CONCLUSION

In this work $CuInS_2$ nanoparticles were synthesized from a new metallic complex as copper precursor. $CuInS_2$ nanoparticles were obtained via microwave approach at very short time. It was found that the best sulfur source for $CuInS_2$ nanoparticles formation was thiourea. The bandgap of nanoparticles that were obtained by UV-vis was 2.2 eV. The value of 0.7 eV blue shift at bandgap is mainly due to smaller of particle size respect to the bulk one. Thin film of $CuInS_2$ was prepared by doctor's blade technique and solar cell was made from ITO / $CuInS_2$ / CdS / Pt-ITO layers. I-V characterization was obtained from this cell. Calculated fill factor (FF), open circuit voltage (V_{oc}) and short circuit current (I_{sc}) were achieved from I-V curve. The small value of I_{sc} is mainly due to very small particles, presence of some space between particles in thin film and high bandgap of product.

REFERENCES

1. H. Chander, *Matter. Sci. Eng*. **49**, 113 (2005).
2. J.L. Shay, J.H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, (Pergamon, Oxford: 1975).
3. Q. Lu, J. Hu, K. Tang, Y. Qian, G. Zhou, X. Liu, *Inorg. Chem*, **39**, 1606 (2000).
4. S.L. Castro, S.G. Bailey, R.P. Raffaelle, K.K. Banger, A.F. Hepp, *Chem. Mater*. **15**, 3142 (2003).
5. L.L. Kazmerski, G.A. Sanborn, *J. Appl. Phys.* **48**, 3178 (1977).
6. R. Scheer, T. Walter, H.W. Schock, M.L. Fearheiley, H.J. Lewerenz, *Appl. Phys. Lett*. **63**, 3294 (1993).
7. Y. Ogawa, A. Jager-Waldau, Y. Hashimoto, K. Ito, *Jpn. J. Appl. Phys.* **33**, L1775 (1994).
8. H.L. Hwang, C.Y. Sun, C.S. Fang, S.D. Chang, C.H. Cheng, M.H. Yang, H.H. Lin, H. Tuwan-Mu, *J. Cryst. Growth* **55**, 116 (1981).
9. G. Hodes, T. Engelhard, D. Cahen, L.L. Kazmerski, C.R. Herrington, *Thin Solid Films* **128**, 93 (1985).
10. H. Onnagawa, K. Miyashita, *Jpn. J. Appl. Phys.* **23**, 965 (1984).
11. H.L. Hwang, C.L. Cheng, L.M. Liu, Y.C Liu, C.Y. Sun, *Thin Solid Films* **67**, 83 (1980).
12. K. Siemer, J. Klaer, I. Luck, J. Bruns, R. Klenk, D. Bräunig, *Sol. Energ. Mater. Sol. C.* **67**, 159 (2001).
13. T. Nyari, P. Barvinschi, R. Băies, P. Vlăzan, F. Barvinschi, I. Dékány, *J. Crystal Growth* **275** e2383 (2005).
14. Y. Jiang, Y. Wu, X. Mo, W. Yu, Y. Xie, Y. Qian, *Inorg. Chem*. **39**, 2964 (2000).
15. Y. Jiang, Y. Wu, S. Yuan, B. Xie, S. Zhang, Y. Qian, *J. Mater. Res*. **16**, 2805 (2001).
16. K. Wakita, M. Iwai, Y. Miyoshi, H. Fujibuchi, A. Ashida, *Compos. Sci. Technol*. **65**, 765 (2005).
17. G. Shen, D. Chen, K. Tang, Z. Fang, J. Sheng, Y. Qian, *J. Crystal Growth* **254**, 75 (2003).
18. H. Hu, B. Yang, X. Liu, R. Zhang, Y. Qian, *Inorg. Chem. Commun*. **7**, 563 (2004).
19. K.J. Rao, B. Vaidhyanathan, M. Ganguli, P.A. Ramakrishnan, *Chem. Mater*. **11**, 882 (1999).
20. B.D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley: Reading, MA: 1978).
21. H.M. Kingston, S.J. Haswell (Eds.) *Microwave-enhanced Chemistry* (Washington, DC: 1997**)**.
22. A.B. Panda, G. Glaspell, M.S. El-Shall, *J. Am. Chem. Soc*. **128**, 2790 (2006).
23. K. Nose, Y. Soma, T. Omata, S. Otsuka-Yao-Matsuo, *Chem. Mater*. **21**, 2607 (2009).