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SURFACTANT ASSISTED GROWTH OF $CuInS_2$ NANOCRYSTALS

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Abstract
In this paper we present a novel surfactant assisted hydrothermal method for the one step synthesis and crystallization of $CuInS_2$ semiconductor nanocrystals. CuCl, $InCl_3$ and thiourea were used as precursors, CTAB and PVA as surfactants and distilled water as solvent. The autoclaving temperature was varied between 150-220^oC and the autoclaving time between 5-15 hours. The obtained powders were investigated by XRD and TEM. The influences of autoclaving temperature and time and of surfactant nature on the crystallinity, phase purity and morphology of the final products are discussed.
Keywords: $CuInS_2$, nanocrystals, hydrothermal, surfactant

1. Introduction

Nanoscale one-dimensional materials, such as nanotubes, nanowires, nanorods, have stimulated great interest in recent years. The fact that the properties of nanocrystals depend on their geometrical shape, configuration, and structure [1] has importance in both basic scientific research and potential technological applications.

The ternary compound semiconductor $CuInS_2$ belongs to the I-III-VI_2 group and crystallizes into the chalcopyrite structure (space group I42d-D_{2d}^{12}). It has a direct band gap near 1.5 eV and high absorption coefficient and photoconductivity [2]. This material can be made both n- and p-type conductive [2, 3]. Its type of conductivity depends on the defect chemistry determined by the stoichiometric ([S]/[Cu]) and molecularity ([Cu]/[In]) ratios [4], which can be varied by synthesis. All these properties make $CuInS_2$ particularly attractive for application in solar energy conversion. Some recent works report on the use of $CuInS_2$ nanocrystals in organic or inorganic matrices for developing more efficient and cheap nanostructured solar cells [5, 6]. Also, it has been demonstrated that the morphology of the

inorganic semiconductor nanocrystals used in solar cells greatly influence the solar cell efficiency [7].

The study of $CuInS_2$ nanocrystal's size and shape benefits on the solar cells efficiencies requires the synthesis of $CuInS_2$ nanocrystals with different morphologies and sizes under controlled stoichiometry and molecularity, which represent a challenge for the materials scientists. Our previous results [8, 9] showed that hydrothermal technique is an appropriate way to the one step synthesis and crystallization of $CuInS_2$ nanocrystals. We report here on some of our results in the attempt to develop a surfactant assisted hydrothermal method for the synthesis of $CuInS_2$ nanocrystals with controlled crystallinity, phase purity and morphology.

2. Experimental

In our experiments, for the hydrothermal synthesis of $CuInS_2$ nanocrystals a stainless steel autoclave with a Teflon liner was used. The controlled heating of the autoclave was performed in a very homogeneous temperature environment provided by a Heraeus UT 6060 drying oven. Analytical grade (Merck) CuCl, $InCl_3$ and thiourea as precursors, cetyltrimethylammonium bromide (CTAB) and polyvinyl alcohol (PVA 72,000) as surfactants and distilled water as solvent were used.

Appropriate amounts of precursors in stoechiometric proportions (thiourea slightly in excess), depending on desired concentration, 0.03M CTAB or PVA, and a corresponding amount of distilled water were mixed by ultrasonic and magnetic stearing, respectively, then the mixture was put into the autoclave. The autoclave was than sealed and introduced in the drying oven and heated to the desired temperature for the prescribed time, then was allowed to cool to room temperature.

The autoclaving temperature was varied between 150-220^{o}C and the autoclaving time between 5-15 hours, the filling rate being maintained at 80%. The synthesis products were filtered off, washed sequentially with distilled water and ethanol and dried in air at 50^{o}C for 1-2 hours. The as obtained black powders were characterized by XRD and TEM.

Powder X-ray diffraction measurements were made at room temperature on a BRUKER D8 ADVANCE X-ray diffractometer using Cu Kα radiation (λ = 1.54184 Å, Ni filter) in a θ:2θ configuration. The peaks of the XRD patterns were identified using the PCPDFWIN Database of JCPDS, version 2.02 (1999).

TEM images were made in a PHILIPS CM-10 transmission electron microscope with an accelerating voltage of 100 kV. Aliquots of the ethanol suspensions of the samples were

dropped on copper grids (2mm diameter) covered with Formwar foil, which were then left to stand until dried and transferred into the microscope.

3. Results and Discussions

Phase analysis made on the basis of powder XRD patterns show that for all the synthesis parameters in the range used in our hydrothermal experiments, tetragonal $CuInS_2$ (roquesite; a = 5.523 Å, c = 11.141 Å, card no. 27-0159) can be obtained.

Further, the aim was to reach the mildest synthesis conditions that yet ensure phase pure and well crystallized yields. When the autoclaving temperature is 150^{o}C, the phase purity and crystallization degree of the samples increases with reaction time (Fig. 1), well crystallized phase pure $CuInS_2$ nanocrystalline samples being obtained for an autoclaving time of 12 h with CTAB as surfactant..

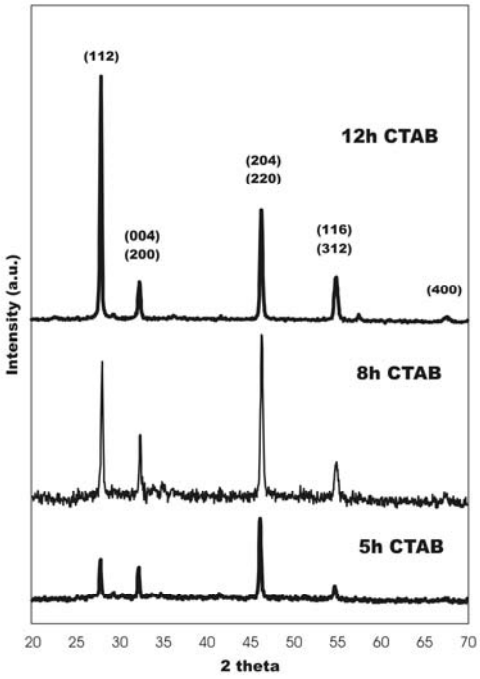

Fig. 1. XRD spectra of a samples obtained with surfactant CTAB at 150^{o}C for a) 5 hours, b) 8 hours and c) 12 hours

Also, as can be seen from Fig. 2, at low autoclaving temperature and time, the other synthesis conditions being the same, phase purity is better with surfactant than without it. This fact demonstrates that surfactant has a favourable effect on the rapid formation of $CuInS_2$ phase.

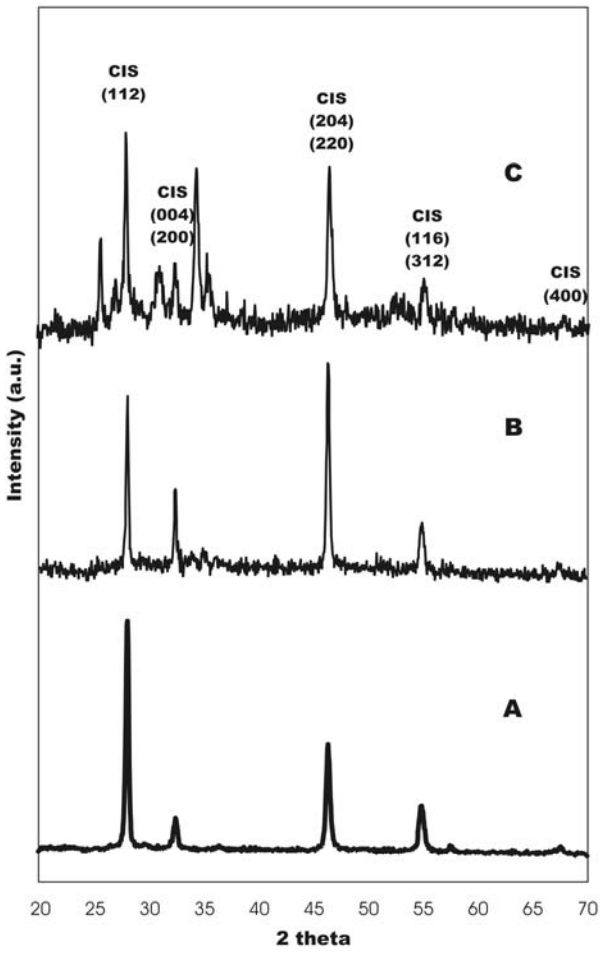

Fig. 2 XRD spectra of samples obtained at 150^{o}C for 5 hours a) with PVA, b) with CTAB and c) without surfactant

With respect to the morphology of the nanocrystals, TEM images (Fig. 3a, b) show that for the same mild synthesis conditions, there are great differences between samples obtained with CTAB and PVA, respectively. Surfactant CTAB is favorable for elongated morphologies (Fig. 3a). This is probably due to its micelle formation capability which can promote oriented growth of nanocrystals [10].

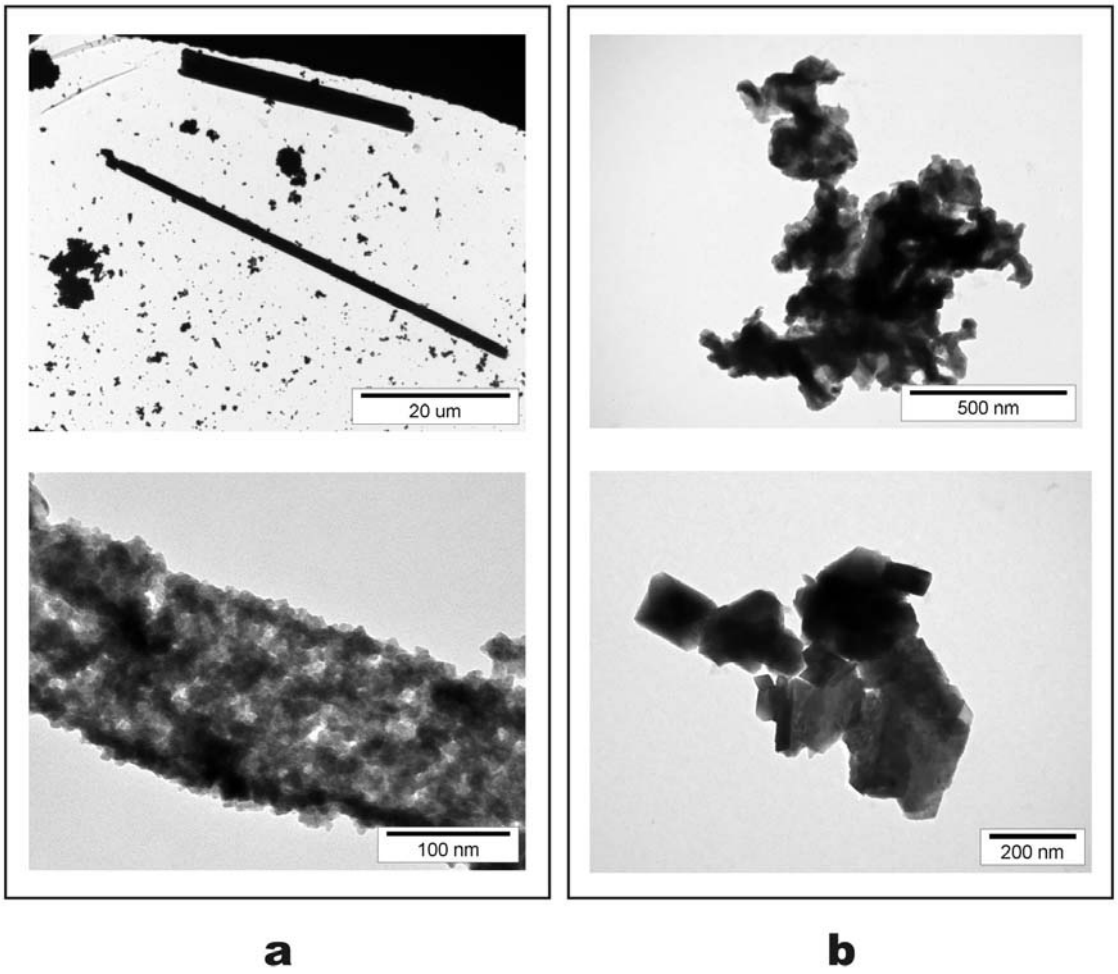

Fig. 3 TEM images of samples obtained with surfactant a) CTAB and b) PVA

4. Conclusions

In summary, a novel surfactant assisted hydrothermal method for the one step synthesis and crystallization of $CuInS_2$ semiconductor nanocrystals has been developed. The mildest synthesis conditions for obtaining well crystallized phase pure $CuInS_2$ nanocrystalline samples with CTAB are 150^oC/12 hours. Phase purity is better with surfactant than without it, in the same synthesis conditions. The morphology of the nanocrystals is influenced by the type of surfactant used: CTAB is favorable for growth of elongated shapes. The possibility to control the yield, size and aspect ratios of the elongated morphologies with surfactant concentration is the subject of further research.

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References

[1] Alivisatos A. P., Science, 271 (1996) 933

[2] Shay J.L., Wernick J.H., Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications, Pergamon Press, New York, 1975

[3] D.C. Look and J.C. Manthuruthil, J. Phys. Chem. Solids 37 (1976) 173.

[4] J.A. Groenink, PH. Janse, Z. Phys. Chem. N.F. 110 (1978) 17

[5] Arici E. et al., Adv. Funct. Mater., 13 (2003) 165

[6] Lenzmann F. et al., Thin Solid Films 451 –452 (2004) 639–643

[7] Huynh W. U., Dittmer J. J., Alivisatos A. P., Science, 295 (2002) 2425

[8] T. Nyari, R. Băieş, P. Vlăzan, I. Grozescu, Sz. Papp, I. Dékány, P. Barvinschi, Analele Universitatii de Vest din Timisoara - Seria Fizica, 44 (2003) 224-227

[9] T. Nyari, P. Barvinschi, R. Baies, P. Vlazan, F. Barvinschi, I. Dékány, Journal of Crystal Growth, 275 (1-2) (2005) e2383-e2387

[10] Changhua An, Qiangchun Liu, Kaibin Tang, Qing Yang, Xiangying Chen, Jianwei Liu, Yitai Qian, Journal of Crystal Growth 256 (2003)128 –133