

A facile chemical route to copper sulfide CuS nanocrystallites – pH effect of the morphology and the shape of them

C. M. SIMONESCU^{*}, L. PATRON^a, V. S. TEODORESCU^b, M. BREZEANU, C. CAPATINA^c

Department of Inorganic Technology and Environmental Protection, Faculty of Applied Chemistry and Materials Science, University "Politehnica" of Bucharest, Polizu Street, no. 1-7, RO-011061, Bucharest, Romania

^aRomanian Academy, Physical and Chemical Institute I. G. Murgulescu, Splaiul Independentei Street, No.202, Bucharest, Romania

^bNational Institute R&D for Materials Physics, P.O.Box. Mg-7, Bucharest-Magurele, Ro-77125, Romania

^cDepartment of Environmental Engineering, University "Constantin Brancusi", Genova Street, no. 3, RO-210152, Targu-Jiu, Gorj, Romania

A facile chemical route for the synthesis of copper sulfide (CuS) nanocrystallites consists of the reaction between $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. In this reaction the influence of the following factors was pursued: pH value, reaction time, molar ratios, temperature and others. In this article we tried to establish the evolution of the morphology and the shape of the CuS nanocrystallites with the pH value. The CuS nanocrystallites obtained were studied by X ray diffraction, IR spectrometry, TEM – transmission electron microscopy and SAED selected area electron diffraction. The CuS crystallites are formed in spherical or "discoidal" particles which are bonded in bigger aggregates. The reaction pH value was varied from a slightly acid value to an alkali value. In case of alkali medium the crystallites dimensions were smaller than their value in slightly acid medium.

(Received January 18, 2006; accepted March 23, 2006)

Keywords: Copper sulfide nanocrystallites, pH effect, XRD, IR, TEM

1. Introduction

In the past several years, synthesis and physical characterization of nanocrystalline sulfide semiconductors have attracted significant interest and it is still the subject of many researches owing to their important physical and chemical properties [1-5]. Among these materials CuS is a useful semiconductive material. CuS is an important material which possesses nearly ideal solar control characteristics [6].

For the obtaining of copper monosulfide many methods were applied such as: direct reaction of the elements at high temperature, chemical deposition, hydro- and solvothermal synthesis. Traditionally copper sulfides have been prepared by solid-state reactions [7,8] and self-propagating high temperature synthesis [9-11]. Molecular precursors have also been used to prepare copper sulfides. Paul *et al.* [12] synthesized CuS by decomposition of the complex $\text{Cu}(\text{S}_6)(\text{solv})_2$ (solv = solvent) at 500 °C, Grijavala *et al.* [13] synthesized CuS from system $[\text{Cu}(\text{en})_2]^{2+}$ (en = ethylenediamine) and thiourea. Wang and coworkers [14] used sonochemical method to obtain copper monosulfide (CuS) nanoparticles. Xie Yi *et al.* [15] obtained CuS in aqueous ammonia at 60 °C in proper redox atmosphere and Zhao Dongyuan *et al.* [16] synthesized CuS nanocrystals with different shapes using thiourea as the sulfur source and triethylenediamine

(TEMA) or di-n-butylamine (DBA) as surfactant under hydrothermal condition.

Through the reaction between copper acetate and sodium thiosulphate in molar ratio 1:6 at 90 ± 5 °C CuS was obtained as main product. Reaction pH was modified by using cheap and nontoxic aqueous ammonia. Compared with the other methods mentioned above, this route is relatively mild, nontoxic, convenient and safe.

2. Experimental

The copper sulfides were prepared by reacting copper acetate with sodium thiosulphate in molar ratio 1:6, in aqueous solution, at 90 ± 5 °C. Sodium thiosulphate was selected as the sulfur source to control the slow release of S^{2-} ions, and aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, the concentration of NH_3 is about 25%) as the supplementary ligand and the Cu^{2+} from $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ as complexing agent. All of these were purchased from Merck Chemistry Co. Ltd.

Reactions were conducted at the medium pH (5,5- a weak acidic pH) and at the alkali pH (11,5 - a medium basic pH).

In case of the medium pH (5,5) the 0.1 mmol of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was mixed with 0.6 mmols of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 200 mL distilled water. After continuous stirring for 5 minutes the solid compounds were dissolved and a yellow solution was obtained. The

initial pH of the solution was 5.5. After 10 minutes of stirring the yellow solution obtained changed into a brown-yellow solution which then was modified in a green solution and a green-black precipitate was obtained. This mixture was heated at 90 ± 5 °C, and maintained at this temperature by continuously heating and stirring for two hours. At the end, this mixture was cooled at room temperature and precipitate was filtered and washed with distilled water. The final product was dried at room temperature.

At the medium basic pH (11.5), the 0.1 mmol of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was mixed with 0.6 mmols of $\text{Na}_2\text{S}_2\text{O}_3$ in 200 mL distilled water, and by continuously stirring for 5 minutes the solid compounds were dissolved 20 mL of aqueous ammonia was titrated into the mixture, resulting in the formation of a blue solution of copper ammonia complex. The solution pH was 11.5 and temperature 17 °C. This mixture was heated and stirred for two hours at 90 ± 5 °C, whereupon the black-violet solution and a black precipitate were formed. Then the solution with precipitate was cooled to room temperature. After filtering and washing with distilled water, the final product was dried at room temperature.

The samples obtained from these two systems were characterized by IR Spectroscopy, X-ray powder diffraction (XRD), TEM – transmission electron microscopy, and SAED selected area electron diffraction. The elemental chemical analyses were performed by an Electronics SPD 1200A ICP emission analyzer with a pump flow of $1.85 \text{ mL} \cdot \text{min}^{-1}$ and a flow rate of the auxiliary gas (Ar 99.99%) of $0.5 \text{ L} \cdot \text{min}^{-1}$. The IR Spectra were recorded on a FT-IR 620 (Jasco, Japan) Spectrophotometer in the $400\text{-}4000 \text{ cm}^{-1}$ range using KBr pellets. Powder X-ray diffraction (XRD) was used to characterize the sample. Data were collected on a X-ray diffraction-Diffractometer Shimadzu XRD6000. Transmission electron microscopy (TEM) was applied to determine the morphology of the prepared products by specific methods for crystalline powders study. These powders were dispersed in alcohol and then they were deposited on a TEM grid with carbon support. The images of selected area electron diffraction (SAED) were realized on polycrystalline particles aggregates. TEM study was performed using a Jeol 200CX electron microscope.

3. Results and discussion

At the weak acidic pH, near CuS yarrowite - Cu_9S_8 , CuS_2 , and antlerite - $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ were obtained. The presence of these species was determined by IR spectroscopy, X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

The presence of small peaks in IR spectrum (Fig. 1) at 1623 cm^{-1} , 1101 cm^{-1} and 3425 cm^{-1} which are characteristic SO_4^{2-} and H_2O molecules showed that there

is a low quantity of $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ near the copper sulfides.

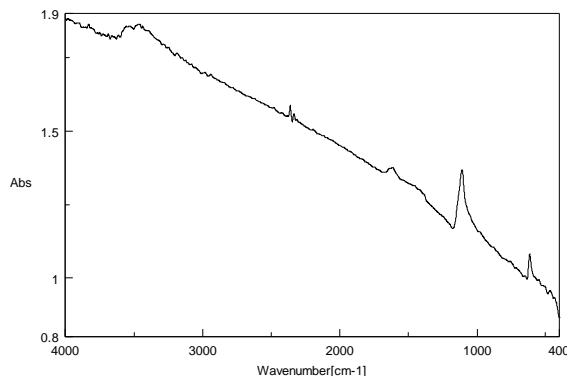


Fig. 1. IR spectrum of product obtained from system $\text{Cu}^{2+}:\text{S}_2\text{O}_3^{2-}$ (1:6) at 5.5 pH.

The XRD pattern of a typical sample as prepared is shown in Fig. 2. The pattern indicates that the prepared product is crystalline. All peaks in the pattern correspond to the reflections of hexagonal phases CuS (ASTM File No. 79-2321 [17]), hexagonal phase Cu_9S_8 (ASTM File No. 36-0379 [18]), cubic CuS_2 (ASTM File No.33-0492 [19]), and orthorhombic antlerite $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ (ASTM File No. 84-2037 [20]). All their reflection peaks were indexed.

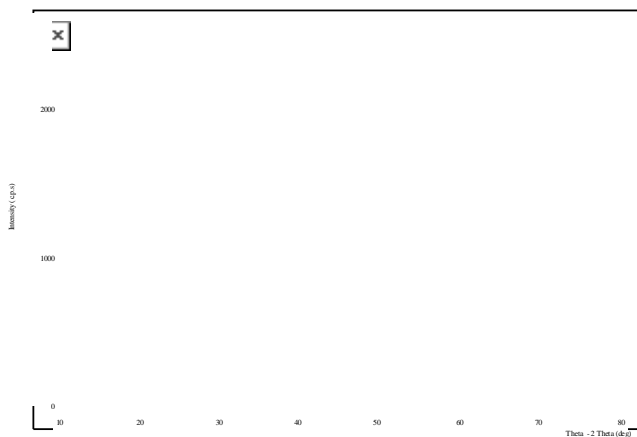


Fig. 2. XRD pattern of the mixture of copper sulfide and copper sulfate.

The results are in good agreement with the observations from TEM images (Figs. 3 and 4).

Fig. 3 shows the TEM images of prepared nanocrystalline copper sulfides. This image reveals that the morphologies of the particles were hexagonal in shape which are similar to those of copper monosulfide, Cu_9S_8 and and cuboidal characteristic to copper disulfide and $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ prepared by other methods.

The mixture of copper sulfides consists of aggregate of small particles with an average diameter of 70-150 nm, and bigger particles with an average diameter > 500 nm. This mixture consists of particle units with double

morphology. The small particles have a cuboidal or paralelipipedic shape and are bound like in row aggregate. The bigger crystallites are facetates showing an hexagonal plate morphology.

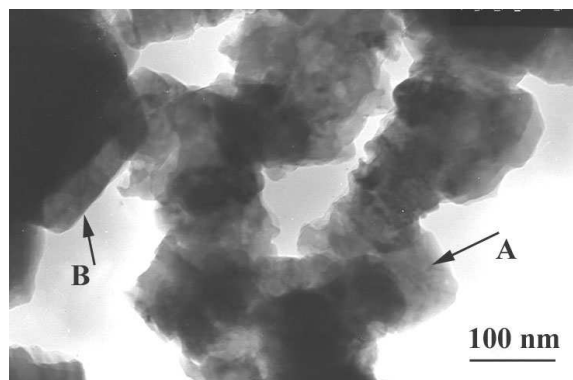


Fig. 3. Transmission electron microscope of mixture of copper sulfide and copper sulfate sample obtained from copper acetate and sodium thiosulphate system.

From this picture an internal porosity it can be observed with 10-15 nm dimension of pores.

In Fig. 4 a diffraction image of this mixture is presented, and the presence of cubic CuS_2 phase it can be observed.

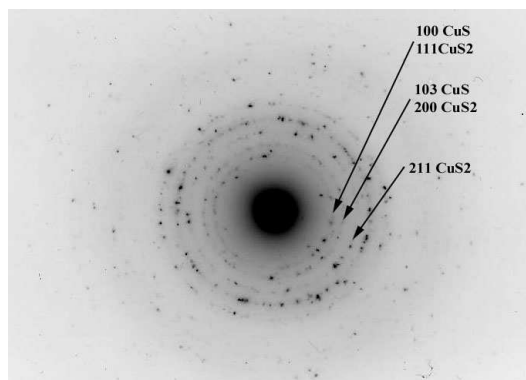


Fig. 4. Diffraction image of copper sulfides mixture. Near the hexagonal phases CuS and Cu_9S_8 the phase CuS_2 is presented which is responsible for the cuboidal morphology of crystallites.

Thus by reaction between copper acetate and sodium thiosulfate in molar ratio 1:6 at $90 \pm 5^\circ\text{C}$, and 5.5 pH value it was obtained a mixture consisting of hexagonal CuS and Cu_9S_8 crystallites with an average diameter > 500 nm, cubic CuS_2 with an average diameter of 70-150 nm and orthorhombic phase $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$.

By reaction between copper acetate and sodium thiosulfate in molar ratio 1:6 at $90 \pm 5^\circ\text{C}$, and 11.5 pH value only CuS was obtained. It can be seen in Fig. 5 (IR spectrum) that in this case there are no impurities, e.g., thiosulphate, acetate, or other impurities, which could be

detected in the samples, indicating that the level of impurities is low.

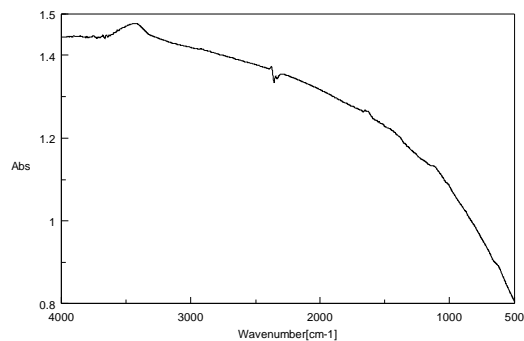


Fig. 5. IR spectrum of copper sulfide obtained from system $\text{Cu}^{2+}:\text{S}_2\text{O}_3^{2-}$ (1:6) at 11.5 pH.

This result is confirmed by XRD pattern (Fig. 6) obtained from X-ray powder diffraction. In this case all peaks which are presented in the spectrum are characteristic to the hexagonal phase CuS (ASTM File No. 79-2321 [17]).

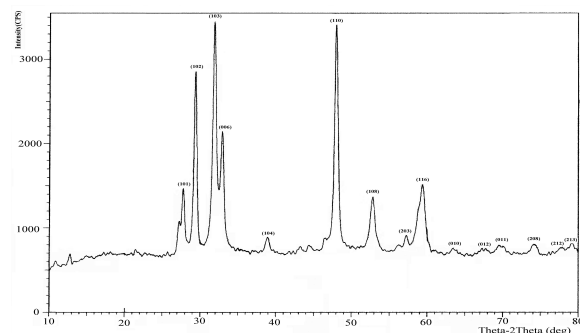


Fig. 6. XRD pattern of the copper monosulfide obtained from a system of copper acetate and sodium thiosulphate (1:6) at $90 \pm 5^\circ\text{C}$ and 11.5 pH value.

The TEM images presented in Figs. 7 and 8 confirmed the presence of the hexagonal phase CuS and it can be seen from this figure that in this case the dimension of CuS crystallites is much lower than in the absence of an alkaline medium.

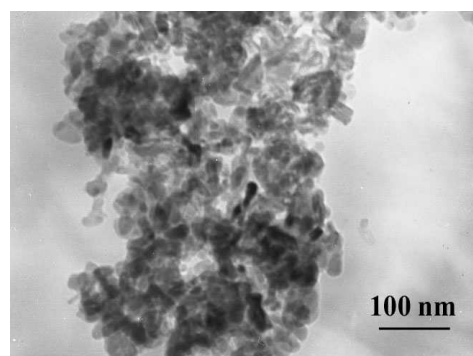


Fig. 7. Transmission electron microscope of copper sulfide CuS .

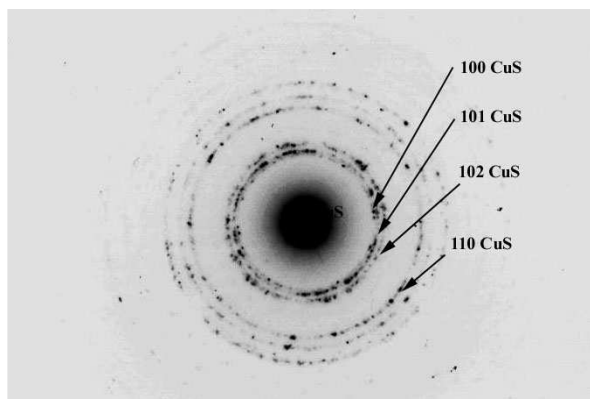


Fig. 8. Diffraction image of copper sulfide CuS.

4. Conclusions

In this study the pH influence of the copper sulfides obtained from the $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ system was analysed. The molar ratio of 1:6 was used, the pH values varied from the medium pH (5,5) to the alkali pH value (11.5) which was realized with a NH_4OH 25% solution. In case of medium pH it was obtained a mixture formed by hexagonal CuS and Cu_9S_8 crystallites with an average diameter > 500 nm, cubic CuS_2 with an average diameter of 70-150 nm, and orthorhombic $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$. At the alkali pH value only CuS was obtained. IR spectrum confirmed presence of CuS, and TEM images showed that the CuS particles have an average diameter of about 20-30 nm. Thus by changing medium pH in the $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ system different phases with different dimensions of crystallites were obtained, and an alkali value of pH influences positively the process of nanocrystallite formation.

References

- [1] Q. Y. Lu, J. Q. Hu, K. B. Tang, Y. T. Qian, X. M. Liu, G. E. Zhou, *J. Solid State Chem.* **146**, 484(1999).
- [2] K. Sooklal, B. S. Cullum, S. M. Angel, C. J. Murphy, *J. Phys. Chem.* **100**, 4551(1996).
- [3] S. W. Chen, L. A. Truax, J.M. Sommers, *Chem. Mater.* **12**, 3864(2000).
- [4] P. Boundjouk, B. R. Jarabek, D. L. Simonson, D. J. Seidler, D. G. Grier, G. J. McCarthy, L. P. Keller, *Chem. Mater.* **10**, 2358(1998).
- [5] C. Wang, X. Mo, Y. Zhu, H. Liu, Z. Chen, *J. Mater. Chem.* **10**, 607(2000).
- [6] R. S. Mane, C. D. Lokhande, *Mater. Chem. Phys.* **65**, 1(2000).
- [7] R. J. Coustal, *Chim. Phys.* **238**, 277(1958).
- [8] I. P. Parkin, *Chem. Soc. Rev.* **25**, 199(1996).
- [9] J. Yi, J. J. Moore, *J. Mater. Sci.* **25**, 1159(1990).
- [10] D. M. P. Mingos, D. R. Baghurst, *Chem. Soc. Rev.* **20**, 1(1991).
- [11] T. Ohtani, M. Motoki, K. Koh, K. Ohshima, *Mater. Res. Bull.* **30**, 1495(1995).
- [12] P. P. Paul, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc.* **115**, 3316(1993).
- [13] H. Grijvala, M. Inoue, S. Buggavarapu, S. Calvert, *J. Mater. Chem.* **6**, 1157(1996).
- [14] H. Wang, Jian-Rong Zhang, Xiao-Ning Zhao, S. Xu, Jun-Jie Zhu, *Mater. Lett.* **55**, 253(2002).
- [15] X. Jiang, Y. Xie, J. Lu, W. He, L. Zhu, Y. Qian, *J. Mater. Chem.* **10**, 2193(2000).
- [16] Q. Lu, F. Gao, D. Zhao, *Nanotechnology* **13**, 741(2002).
- [17] H. J. Gotsis, A. C. Barnes, P. Strange, *J. Phys.: Condens. Matter.* **4**, 10461(1992).
- [18] R. Goble, *Can. Mineral.* **18**, 511(1980).
- [19] E. Hinze, Will, *Neues Jahrbuch. Mineral., Monatsh.* **11**, 481(1980).
- [20] F. C. Hawthorne, L. E. Groat, R. K. Eby, *Can. Mineral.* **27**, 205(1989).

*Corresponding author: clausimo2003@yahoo.co.uk