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Synthesis and characterization of nano-structured materials CuS (Covellite) for their applications

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Abstract- Nano structured materials pure forms of CuS (Covellite) were synthesized by the reaction of copper acetate and thiourea with the addition of sodium hydroxide, by simple chemical precipitation technique at room temperature for their applications. Synthesized CuS nanocrystals were characterized by powder X-Ray diffraction for finding particle size, optical properties of the product and band gap energy were studied by UV- visible absorption spectroscopy and morphology was determined by Scanning Electron Microscope (SEM). CuS nanocrystals thus prepared were of 21nm-30nm size. It was found that the particle size and yield depends on reaction time, amount of reactants, temperature and also on the amount of reducing agent used.
Key Words: nanocrystal, semiconductor, CuS, SEM

Introduction

Crystals of size in the order of a few nanometers (ranging 1 – 100nm) in at least one dimension are nanocrystals. It has been proved that as particle becomes smaller in size, they may take on different chemical and physical properties. The nanocrystals exhibit higher chemical reactivity than conventionally prepared samples [1-3]. Recently, much attention has been paid to the application of nanoparticles [4, 5]. Copper sulphide is an important p-type semiconductor which belongs to wurtzite structure [6] with copper vacancies within the lattice [7]. Various morphologies of CuS have been prepared such as nanoparticles, nanodisks [8], nanorods [9-11], nanotubes [12] and nanowires [13]. CuS is extensively used in solar cells [14], optical filters, photo electric transformers, sensors and as super ionic materials [15].It shows metallic conductivity and transform into a super conductor at 1.6K [16].Many approaches have been proposed to synthesize CuS in various methods including thermolysis [11], microwave irradiation, hydrothermal or solvothermal method [17]. In this paper, a new route Chemical precipitation method is reported for preparing CuS nanocrystals at room temperature.

2 Experimental

2.1. Materials

Copper acetate, thiourea, were copper and sulphur precursors. NaOH is used to adjust pH value. All chemicals were analytical reagents and were purchased from Chenchems Company. All the reagents used in our experiment were analytically pure and used without further purification.

2.2. Experimentation

9.965gm of copper acetate was dissolved in 250ml of water with constant stirring. 7.612 gm of thiourea was dissolved in 50ml 5 wt% of sodium hydroxide was dissolved in 10ml of deionized water. First $Cu(ac)_2$ solution and thiourea solutions were mixed together slowly with constant stirring. Blue colour copper acetate solution turned green by the addition of thiourea solution. Then NaOH solution was added to the original solution. The colour of the solution turned golden brown as the first drop of NaOH solution was added

and the colour deepened with more of addition. The solution was left without disturbance for 2 hours at room temperature,(30°C). The precipitate formed was filtered and rinsed with deionised water several times and repeatedly washed with acetone. Pure CuS nanocrystals were thus synthesized and dried at room temperature. This procedure was again repeated for 4hours, 6hours and 8hours. To improve the ordering the samples were annealed at 60°C for 30 minutes. When the amount reducing agent (NaOH) added was reduced, the yield also reduced.

The synthesis process can be described as follows.

$$CH_3COOCu + H_2NCS\text{-}NH_2 \xrightarrow{NaOH} CuS + CH_3COOH + NH_3 + H_2O$$

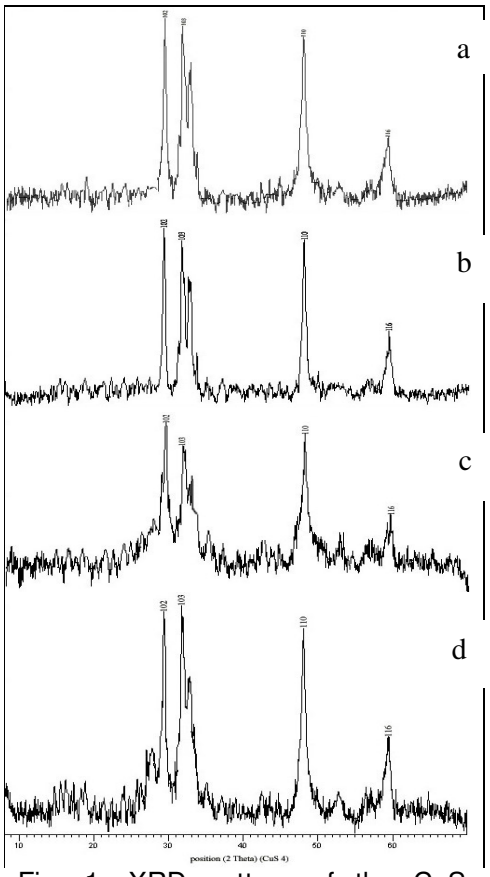

Fig. 1- XRD pattern of the CuS samples synthesized for reaction times (a) 2 hrs, (b) 3 hrs, (c) 6 hrs and (d) 8 hrs at room temperature.

Copper acetate reacts with thiourea in the presence of sodium hydroxide gives Copper sulphide precipitate in a pure form with other impurities, which are removed by rinsing with water and acetone.

3. Results and discussion

3.1. X-Ray diffraction

An x-Ray diffraction (XRD) pattern of CuS for different reaction time is being compared in Fig (1). The pattern contains peaks of (100), (102), (103) and (110) planes at 27.05°, 29.39°, 31.74° and 48.05° respectively, which corresponds to typical CuS (covellite) with hexagonal structure having lattice constant of a=3.792 A° and c16.344A°.The grain sizes were determined for the samples and are presented in table 1.

Table 1- The crystal sizes of the synthesized samples are given below

Sr. No	Samples	Reaction Time (hours)	Average Size (nanometers)
1	CuS 1	2 hrs	34.28
2	CuS 2	3 hrs	28.48
3	CuS 3	6 hrs	21.39
4	CuS 4	8 hrs	26.22

3.2 Scanning electron Microscope SEM

The morphology of the products has been studied by scanning electron microscope. The SEM images show great correlation with the nanocrystal size values calculated using Scherrer Formula from XRD Data's. SEM images of CuS nanocrystals at different reaction time are given in Fig. 2. Aglomeration of nanocrystals could be seen in SEM images that could be removed by reducing the concentration of the precursor solutions or by adding any surfactant.

3.3. UV- visible absorption spectroscopy

The absorption peaks of CuS in UV indicates that the as prepared CuS nanocrystals are promising in the development of photo electric devices. Fig.3 represents the UV-Visible absorption spectra obtained for synthesized CuS for different reaction times 2hrs - CuS 1, 3hrs - CuS 2, 6hrs - CuS 3 and 8hrs - CuS 4 at room temperature in the range of 200-1000nm. The absorption spectra show that all the samples of CuS nanocrystals have optical absorption in the region 300nm and above.

4. Conclusion

By the reaction of copper acetate and thiourea with sodium hydroxide at room temperature (30℃), we obtained CuS nanocrystals of grain size 21-34 nanometers. The method of preparation is inexpensive, easy and environmental friendly. This novel method may open a new door for the synthesis of nanostructures of various materials by selecting suitable complex precursors at room temperature.

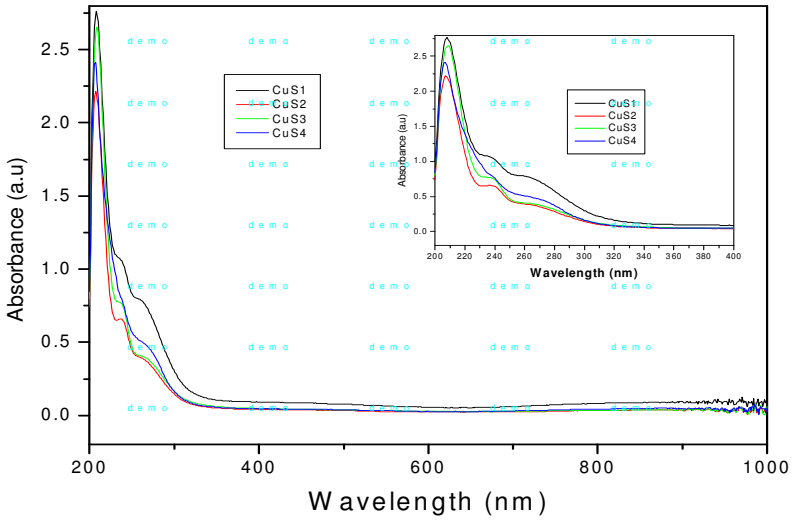

Fig. 3- UV-Visible absorption spectra obtained for reaction times 2hrs - CuS 1, 3hrs - CuS 2, 6hrs - CuS 3 and 8hrs - CuS 4 at room temperature

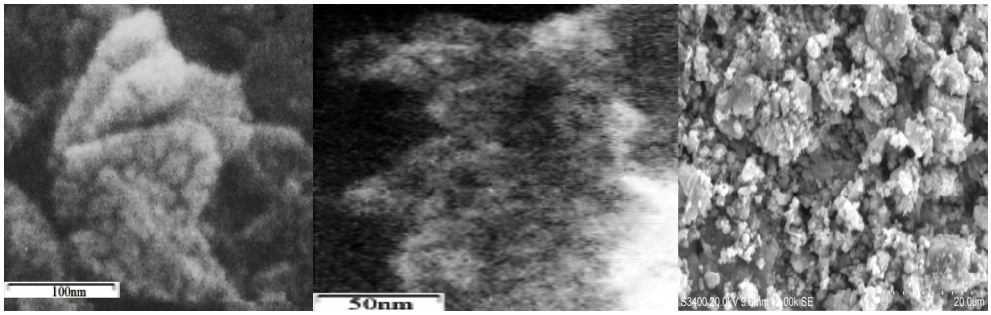

Fig 2- SEM images of CuS nanocrystals at reaction time 3hrs, 6hrs and 8hrs.

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