



Preparation of Stoichiometric Cu₂S Nanoparticles by Ultrasonic Method

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This study reports on the synthesis of Cu₂S nanoparticles via an ultrasonic method by employing Na₂SO₃ as a reducing agent. This method is novel, simple and can be easily controlled. Effects of power and time of sonication were investigated. Morphology, structure, and composition of the obtained products were characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), scanning electron microscope (SEM) and photoluminescence (PL) spectroscopy. The effects of time and power of irradiation were studied. XRD calculations show that the average crystallite diameter of Cu₂S nanoparticle is about 25 nm. The calculated band gap of Cu₂S nanoparticle (2.24 eV) shows obvious blue shift

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1. INTRODUCTION

Copper sulfides have attracted interest due to their special property and potential application [1, 2]. Among these materials Cu₂S (chalcocite) is of great interest because of its unique optical and electronic properties [3]. It has a direct band gap of around 1.2 eV and can be used in solar cells [4], optoelectronic devices [5], photocatalyst [3], etc. Therefore many investigations have been paid to this substance and various Cu₂S nanostructures such as nanoparticles [6], nanorods and nanowires [7] were prepared. Different chemical methods such as solvothermal reactions [8] and microwave irradiation [9] have been used to synthesize this material. The main feature of current investigation is synthesis of pure Cu₂S nanostructures without other phases and impurities including CuS, Cu_{1.8}S, Cu₇S₄, and Cu₃₁S₁, so employing a facile and suite procedure for synthesis of pure Cu₂S nanostructures are important subject and received considerable attention. In this paper we report a simple, novel and surfactant free synthetic procedure for preparation of Cu₂S nanostructures by employing Na₂SO₃ as a weak reducing agent. Nanostructures were synthesized from reaction between [Cu(en)₂]SO₄ and thiosemicarbazide. The effects of power and time of ultrasonic irradiation were also studied.

2. SYNTHESIS AND CHARACTERIZATION

2.1 The Method of Sample Manufacturing and Analysis

[Cu(en)₂]SO₄, was synthesized according to this procedure: 0.01 mol of CuSO₄ was dissolved in 20 ml of distilled water. 0.02 mol of ethylenediamin was dissolved in 20 ml of distilled water and was then added to the first solution slowly. The mixture was stirred and heated (80 °C) for 5 h. The blue obtained precipitate was centrifuged, washed with ethanol and distilled water and dried at 50 °C.

Preparation of copper sulfide nanoparticle:

Copper precursor (0.3 mmol) was dissolved in 40 ml of propylene glycol. Na₂SO₃ (0.15 mmol) and HCl (0.1 ml) were then added to the solution. 0.15 mmol thiosemicarbazide (TSC) was then added to the solution. Afterward, the solution was exposed by ultrasonic irradiation with different power at 100 °C for appropriate time. The black obtained precipitates were centrifuged, washed with ethanol and distilled water several times and dried at 50 °C at vacuum oven for 10 h. The summarized parameters of different conditions are listed in Table 1.

Table 2 – Reaction conditions

Sample No.	Time (min)	Power (W)	Product
1	30	55	CuS
2	30	55	Cu ₂ S
3	15	55	Cu ₂ S
4	60	55	Cu ₂ S
5	30	35	Cu ₂ S
6	30	75	Cu ₂ S

3. RESULTS AND DISCUSSION

The XRD results for samples no. 1 and 2 are presented in Fig. 1. By using [Cu(en)₂]SO₄ (without Na₂SO₃) pure CuS nanoparticles (JCPDS no. 03-1090) obtained (Fig. 1a) while pure Cu₂S nanoparticles obtained when both [Cu(en)₂]SO₄ and Na₂SO₃ were used (Fig. 1b). All of the diffraction peaks in Fig. 1b can be indexed to the tetragonal structure of Cu₂S (space group P43212) which is very close to the values in the literature (JCPDS No. 72-1071 with lattice parameters $a = b = 3.9962 \text{ \AA}$, $c = 11.2870 \text{ \AA}$). From broaden peaks in XRD it can be concluded that the particle size of the product is small. The average crystallite diameter of the obtained product was estimated by Debye-Scherrer equation:

$$D_c = \frac{k\lambda}{\beta \cos \theta}$$

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Where β is the breadth of the observed diffraction line at its half-intensity maximum, K is the so-called shape factor, and λ is the wavelength of X-ray source used in XRD. The average crystallite diameter of the obtained products was about 25 nm.

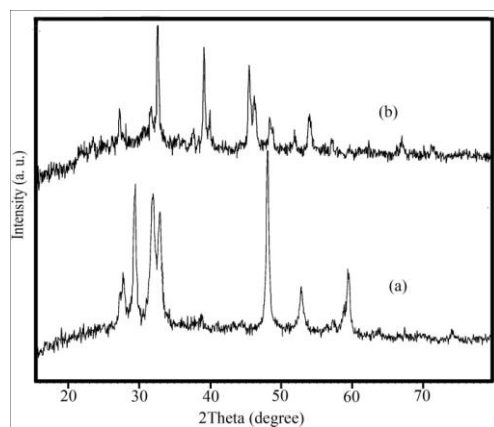


Fig. 1– XRD pattern of as synthesized sample (a) sample no. 1 (CuS) and (b) sample no. 2 (Cu₂S)

The EDX spectrum of the Cu₂S crystals is shown in Fig. 2. The L_{α} , L_{β} , K_{α} and K_{β} lines of Cu and K_{α} of S are obviously observed. Based on the calculation of the peak areas, the ratio of copper to sulfide was found to be approximately 2 : 1 as expected. Therefore, both XRD and EDX analyses revealed that pure Cu₂S were successfully synthesized by the current synthetic route.

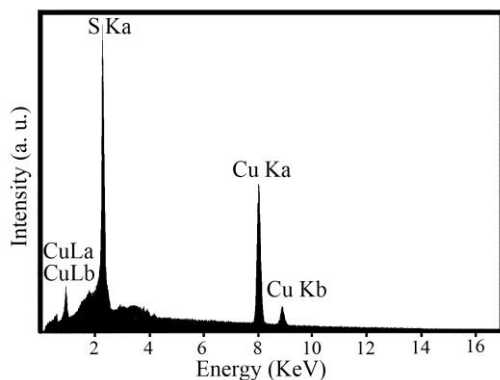


Fig. 2 – EDX spectrum of the as synthesized Cu₂S nanoparticles

The morphology of the samples was revealed by scanning electron microscopy (SEM). Fig. 3a shows SEM image of pure CuS nanoparticles obtained at 55 W for 30 min without Na₂SO₃ addition. Fig. 3b shows SEM images of pure Cu₂S nanoparticles prepared in the presence Na₂SO₃ for 30 min at 55 W.

For investigating the effect of sonication time on the morphology of the Cu₂S nanostructures, the reaction carried out in 15 and 60 min. Fig. 4a-b confirmed, with decreasing of aging time to 15 min (sample no. 3), the obtained particles were bigger in comparison with those particles of sample no. 2 with the aging time of 30 min. Particles size decreased with increasing irradi-

ation time. When the time is close to 60 min (sample no. 4), conglomerate effects are observed (Fig. 4b). At this condition, small nuclei obtained but when particles become small consumedly, they are unstable and to reach more fixity stick together. Therefore, to achieve an appropriate and uniform size and morphology, the optimal time is necessary. optimum time is 30 min for current experiment.

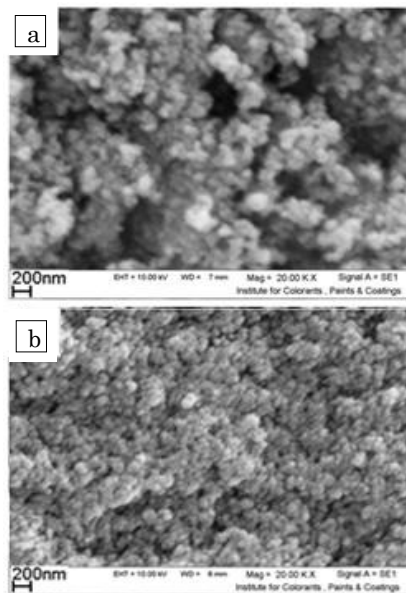
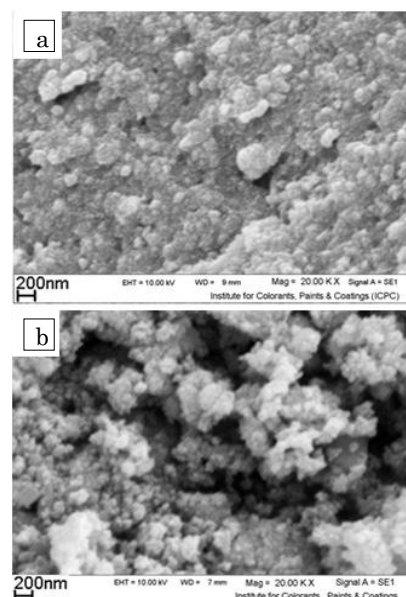


Fig. 3 – SEM images of the products at 55 W and 30 min (a) sample no. 1 (CuS) and (b) sample no. 2 (Cu₂S)

Fig. 4c-d shows the SEM images of samples 5 and 6 that were obtained in different power 35 and 75 W, respectively. In the powers of fewer than 35 W micro-particle are observed because they are not separated well and this power is not enough for them to be separated (Fig. 4c). With increasing power, the particles are smaller. When power reached to 75 W, agglomeration effects were observed (Fig. 4d). Particles produced at 55 W are uniform (Fig. 3b). Thus optimum power is 55 W for current experiment.



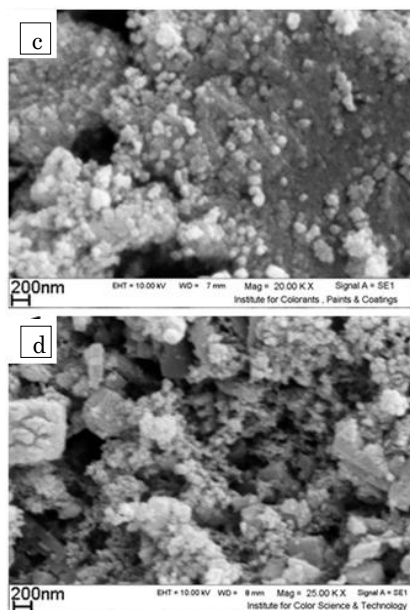


Fig. 4 – SEM images of samples 3 (a), 4 (b), 5 (c), 6 (d)

Fig. 5 displays the photoluminescence behavior of as-prepared Cu_2S nanostructure dispersed in an ethanol solution. It shows a sharp and strong peak centered at a wavelength of 552 nm (excitation at 482.5 nm). As compared to the band gap of bulk Cu_2S which is 1.2 eV [4] the absorption spectrum of as-prepared samples exhibits a blue-shift (2.24 eV, 552 nm).

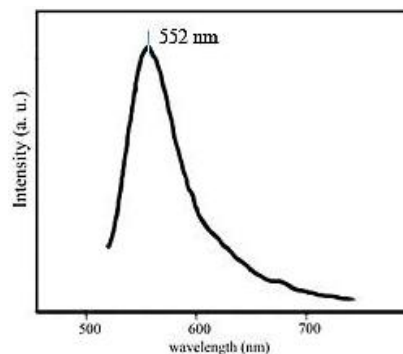


Fig. 5 – PL spectrum of the as synthesized Cu_2S nanoparticles

4. CONCLUSIONS

In summary, Cu_2S nanoparticles were successfully prepared using Na_2SO_3 as a weak reducing agent. It was found that the Cu_2S nanoparticles were formed by non- Na_2SO_3 -assisted method. According to this mechanism, the Na_2SO_3 acted as a soft reducing agent leading to formation of the Cu_2S nanocrystals. Effects of power and time of sonication were investigated. The XRD, EDX, SEM and PL were used to characterize the products.

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