BRIEF COMMUNICATION

Preparation and Characterization of Cu$_2$S Nanoparticles Via Ultrasonic Method

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Abstract This study reports on the synthesis of Cu$_2$S nanoparticles via an ultrasonic method by employing Na$_2$SO$_3$ as a reducing agent. Morphology, structure, and composition of the obtained products were characterized by X-ray diffraction, energy dispersive X-ray analysis, scanning electron microscope and photoluminescence spectroscopy. The effects of time and power of irradiation were studied.

Keywords Nanoparticles · Cu$_2$S · Ultrasonic · Electron microscopy · Complex

Introduction

Copper sulfides have attracted interest due to their special property and potential application [1–4]. Among these materials Cu$_2$S (chalcocite) is of great interest because of its unique optical and electronic properties [5]. It has a direct band gap of around 1.2 eV and can be used in solar cells [6–8], optoelectronic devices [9, 10], photocatalyst [5], etc. Therefore many investigations have been paid to this substance and various Cu$_2$S nanostructures such as nanoparticles [11], flower-like [12], nanorods [5, 13] and nanowires [13] were prepared. Different chemical methods such as solvothermal reactions [14] and microwave irradiation [15] have been used to synthesize this material. The main feature of current investigation is synthesis of pure Cu$_2$S nanostructures without other phases and impurities including CuS, Cu$_{1.8}$S, Cu$_7$S$_4$, and Cu$_{31}$S$_1$, so employing a facile and suite procedure for

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synthesis of pure Cu_2S nanostructures are important subject and received considerable attention. We have been interested in the synthesis of sulfide nanostructures for a few years [16–22]. In this paper we report a simple, novel and surfactant free synthetic procedure for preparation of Cu_2S nanostructures by employing Na_2SO_3 as a weak reducing agent. Nanostructures were synthesized from reaction between $[Cu(en)_2]SO_4$ and thiosemicarbazide. The effects of power and time of ultrasonic irradiation were also studied.

Experimental

Materials and Physical Measurements

All chemical reagents in this experiment were of analytical grade and used as received without further purification. A multiwave ultrasonic generator (Sonicator 3000; Band line, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 80 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The electronic spectrum of the sample was taken on Perkin-Elmer LS-55 luminescence spectrometer.

Preparation of $[Cu(en)_2]SO_4$

0.01 mol of $CuSO_4$ was dissolved in 20 ml of distilled water. 0.02 mol of ethylenediamine 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. Na_2SO_3 (0.15 mmol) and HCl (0.1 ml) were then added to the solution. 0.15 mmol

Table 1 Reaction conditions for preparation of Cu_2S nanoparticles from $[Cu(en)_2]SO_4$, TSC (sulfur source) and Na_2SO_3 (reducing agent)

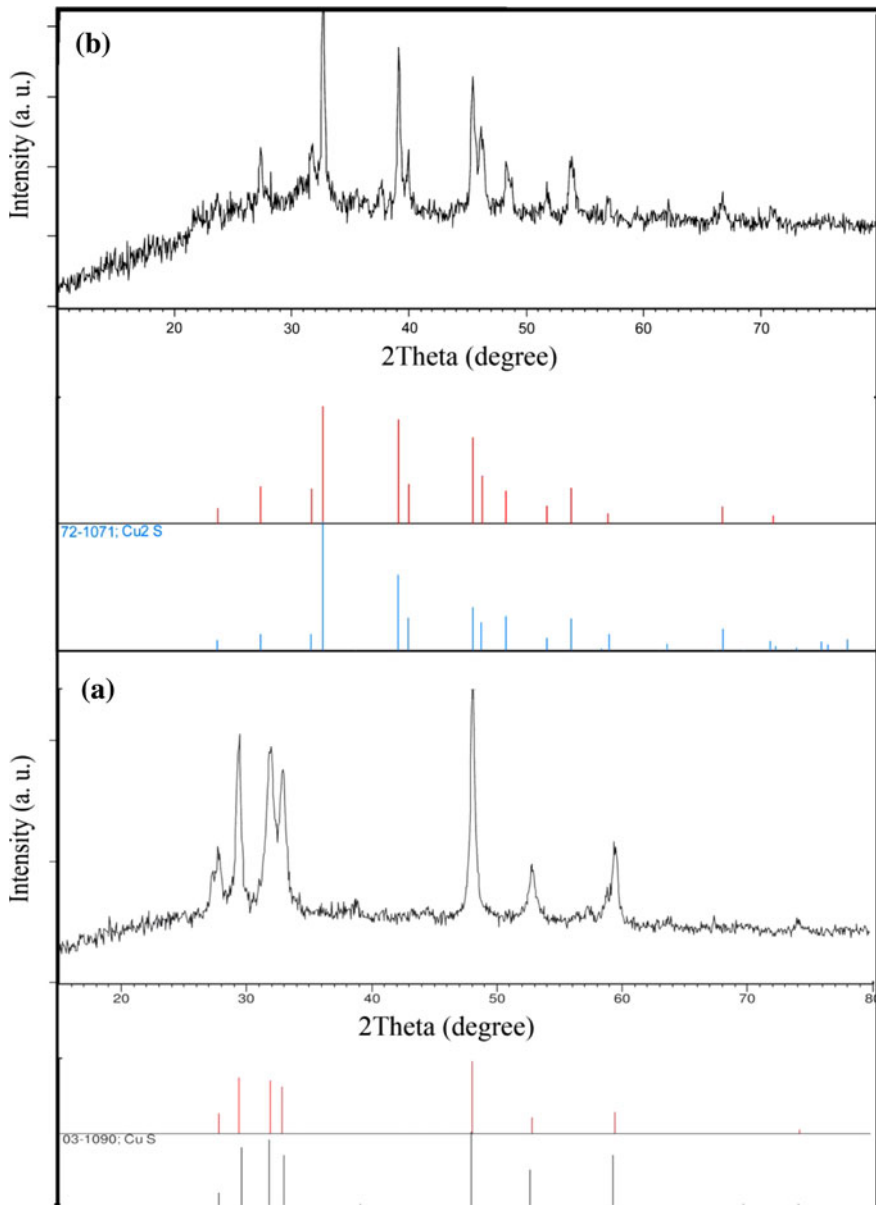| Sample no.	Time (min)	Power (W)	Product
1	30	55	CuS
2	30	55	Cu_2S
3	15	55	Cu_2S
4	45	55	Cu_2S
5	60	55	Cu_2S
6	30	35	Cu_2S
7	30	75	Cu_2S

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

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.
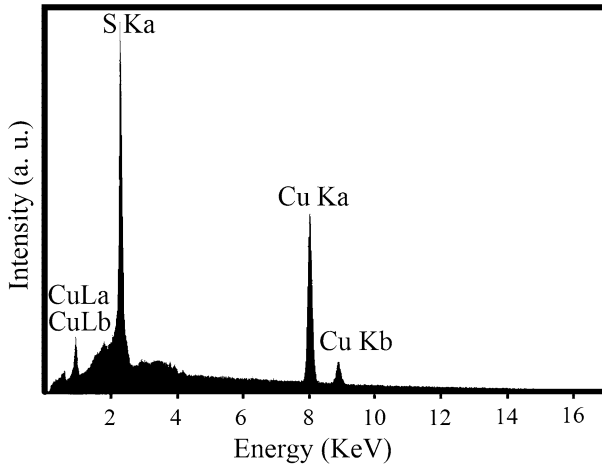
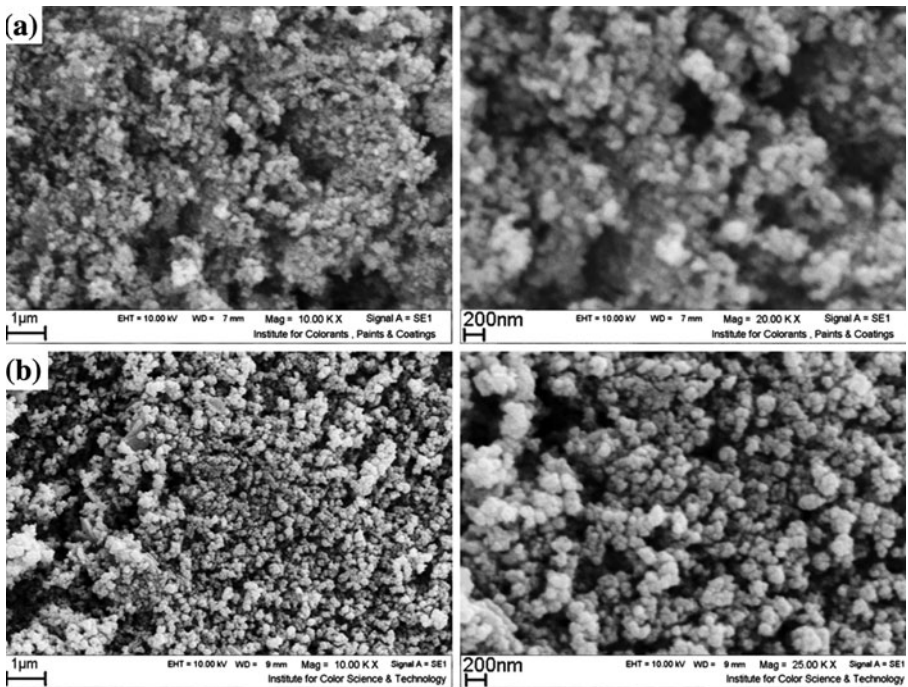**Fig. 2** EDX spectrum of the as synthesized Cu_2S nanoparticles

Fig. 3 SEM images of the products at 55 W and 30 min **a** sample no. 1 (CuS) and **b** sample no. 2 (Cu_2S)

Results and Discussion

The XRD results for samples no. 1 and 2 are presented in Fig. 1. By using $[Cu(en)_2]SO_4$ (without Na_2SO_3) pure CuS nanoparticles (JCPDS no. 03-1090)

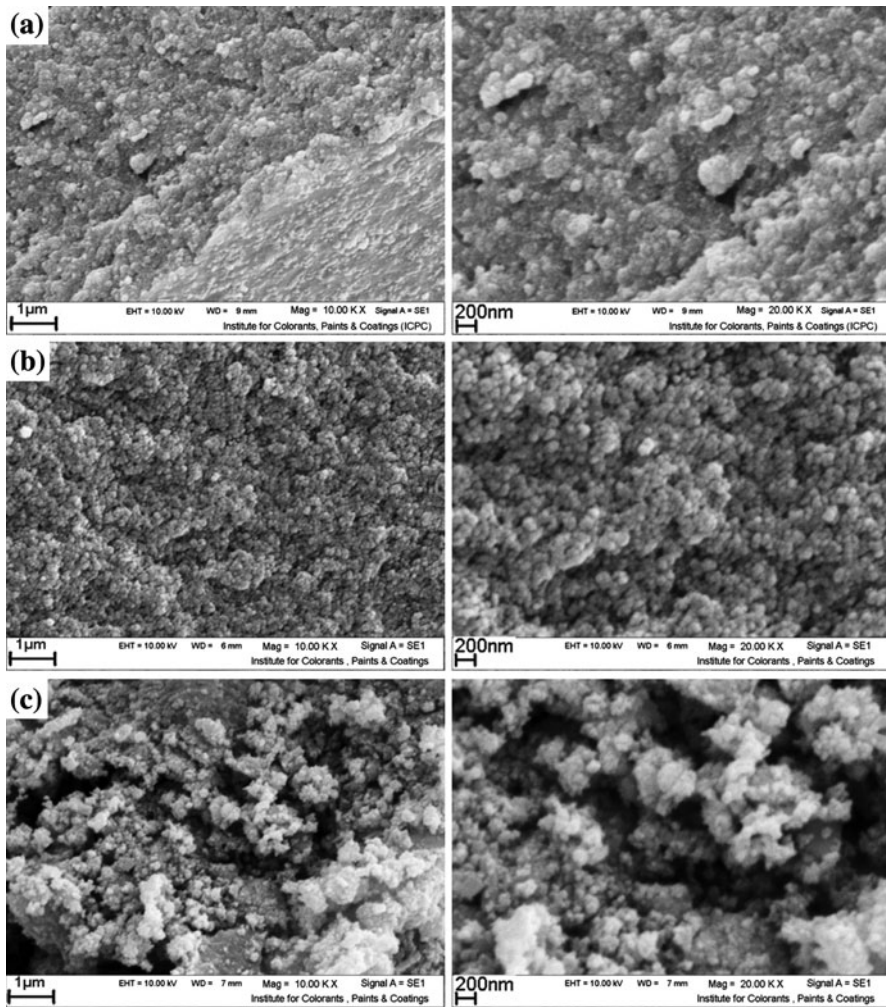**Fig. 4** SEM images of samples obtained at different times. Sample no. 3 (**a**), sample no. 4 (**b**), sample no. 5 (**c**)

obtained (Fig. 1a) while pure Cu$_2$S nanoparticles obtained when both [Cu(en)$_2$]SO$_4$ and Na$_2$SO$_3$ were used (Fig. 1b). All of the diffraction peaks in Fig. 1b can be indexed to the tetragonal structure of Cu$_2$S (space group P43212) which is very close to the values in the literature (JCPDS No. 72-1071 with lattice parameters a = b = 3.9962 Å, c = 11.2870 Å). 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 Debeys–Scherrer equation:

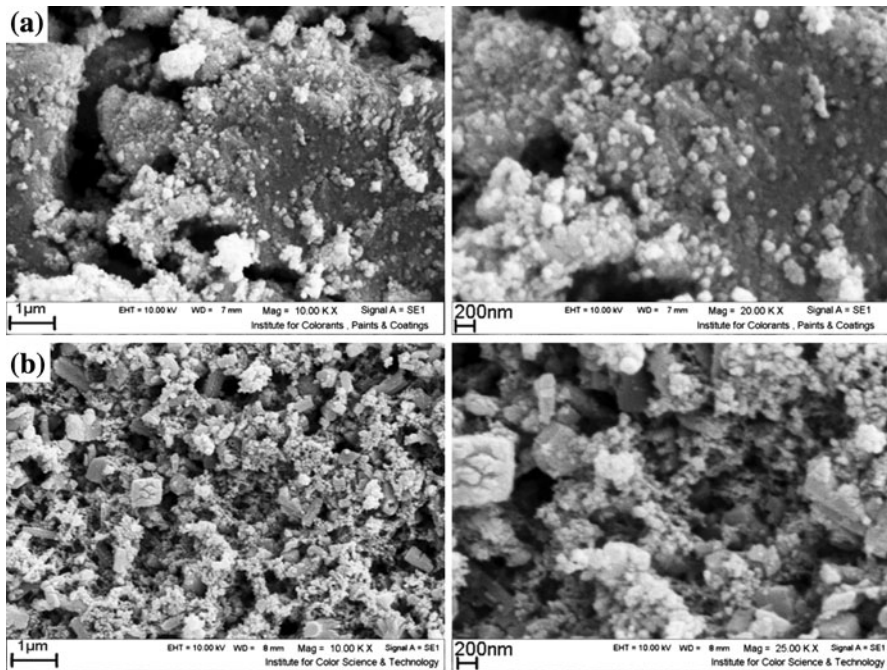$$Dc = \frac{k\lambda}{\beta \cos \theta},$$

Fig. 5 SEM images of samples obtained at different powers. Sample no. 6 (**a**), sample no. 7 (**b**)

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 [23–26]. The average crystallite diameter of the obtained products was about 25 nm.

The purity of the nanostructures was also confirmed by energy-dispersive X-ray analysis. The EDX spectrum of the Cu_2S crystals is shown in Fig. 2. The L_a, L_b, K_a and K_b lines of Cu and K_a 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 Cu_2S were successfully synthesized by the current synthetic route.

The morphology of the samples was revealed by scanning electron microscopy (SEM). Figure 3a shows SEM image of pure CuS nanoparticles obtained at 55 W for 30 min without Na_2SO_3 addition. Figure 3b shows SEM images of pure Cu_2S nanoparticles prepared in the presence Na_2SO_3 for 30 min at 55 W. For investigating the effect of sonication time on the morphology of the Cu_2S nanostructures, the reaction carried out in 15, 45, and 60 min. Figure 4a–c 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. 1 with the aging time of 30 min. Particles size decreased with increasing irradiation time. When the time is close to 60 min conglomerate effects are observed (Fig. 4c). At this condition, small nuclei obtained but when particles become small consumedly,
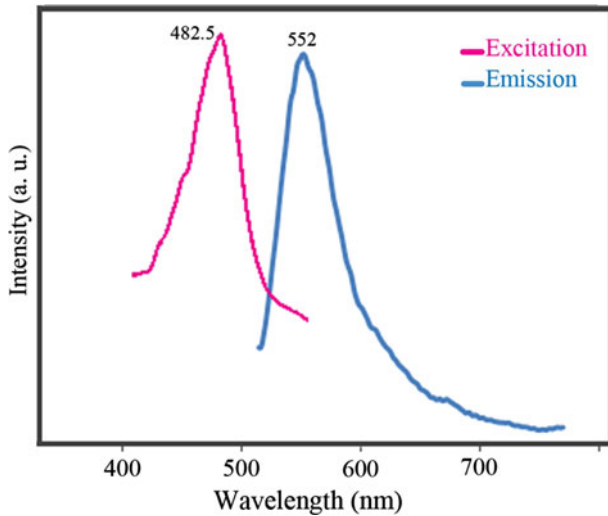
Fig. 6 PL spectrum of the as synthesized Cu₂S nanoparticles

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 which obtained between 30 and 45 min. Below this time, there is not enough energy to separate particles and upper this time due to large quantity of energy samples will fuse to each other. Figure 5 shows the SEM images of samples 6 and 7 that were obtained in different power 35 and 75 W, respectively. In the powers of fewer than 35 W microparticle are observed because they are not separated well and this power is not enough for them to be separated (Fig. 5a). With increasing power, the particles are smaller. When power reached to 75 W, agglomeration effects were observed (Fig. 5b). Particles produced at 55 W are uniform (Fig. 4b). Thus optimum power is 55 W for current experiment.

Figure 6 displays the photoluminescence behavior of as-prepared Cu₂S nano-structure dispersed in an ethanol solution. It show 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 Cu₂S which is 1.2 eV [6–8] the absorption spectrum of as-prepared samples exhibits a blue-shift (2.24 eV, 552 nm).

Conclusions

In summary, Cu₂S nanoparticles (without formation of other phases such as CuS and Cu₁.₈S) were successfully prepared using Na₂SO₃ as a weak reducing agent. This method is novel, simple and can be easily controlled. It was found that the CuS nanoparticles were formed by non-Na₂SO₃-assisted method. According to this mechanism, the Na₂SO₃ acted as a soft reducing agent leading to formation of the Cu₂S 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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