NAP-2013

Preparation of Stochiometric Cu2S Nanoparticles by Ultrasonic Method

M. Mousavi-Kamazani, M. Salavati-Niasari*

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317–51167, I. R. Iran

This study reports on the synthesis of Cu_2S nanoparticles via an ultrasonic method by employing Na_2SO_3 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 Cu_2S nanoparticle is about 25 nm. The calculated band gap of Cu_2S nanosparticle (2.24 eV) shows obvious blue shift

1. INTRODUCTION

Copper sulfides have attracted interest due to their special property and potential application [1, 2]. Among these materials Cu_2S (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 Cu_2S 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 Cu_2S nanostructures without other phases and impurities including CuS, $Cu_{1.8}S$, Cu_7S_4, and $Cu_{31}S_1$, so employing a facile and suite procedure for synthesis of pure Cu_2S nanostructures are important subject and received considerable attention. 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.

2. SYNTHESIS AND CHARACTERIZATION

2.1 The Method of Sample Manufacturing and Analysis

$[Cu(en)_2]SO_4$, was synthesized according to this procedure: 0.01 mol of $CuSO_4$ was dissolved in 20 ml of distilled water. 0.02 mol of ethylendiamin 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 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_2S
3	15	55	Cu_2S
4	60	55	Cu_2S
5	30	35	Cu_2S
6	30	75	Cu_2S

3. 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) obtained (Fig. 1a) while pure Cu_2S nanoparticles obtained when both $[Cu(en)_2]SO_4$ and Na_2SO_3 were used (Fig. 1b). All of the diffraction peaks in Fig. 1b can be indexed to the tetragonal structure of Cu_2S (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:

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

---

* salavati@kashanu.ac.ir

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.
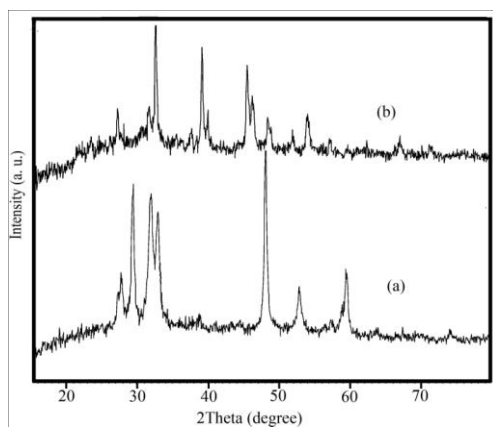
Fig. 1– XRD pattern of as synthesized sample (a) sample no. 1 (CuS) and (b) sample no. 2 (Cu_2S)

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.
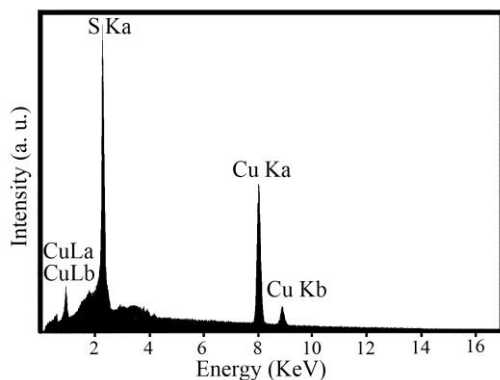

Fig. 2 – EDX spectrum of the as synthesized Cu_2S nanoparticles

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 Na_2SO_3 addition. Fig. 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 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.
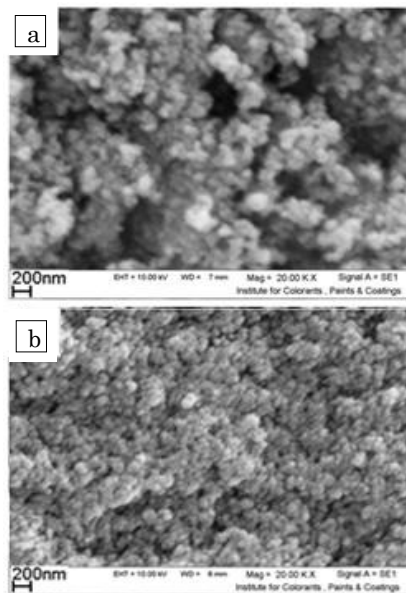
Fig. 3 – SEM images of the products at 55 W and 30 min (a) sample no. 1 (CuS) and (b) sample no. 2 (Cu_2S)

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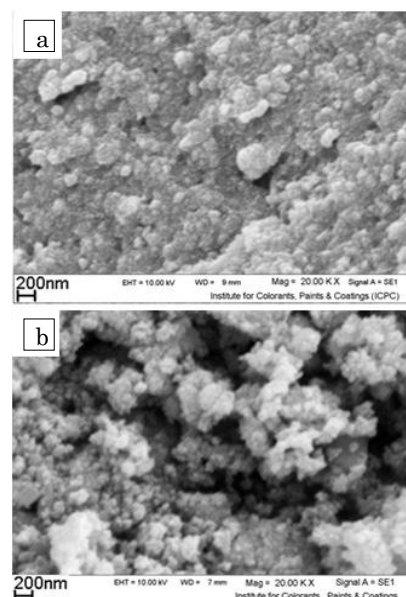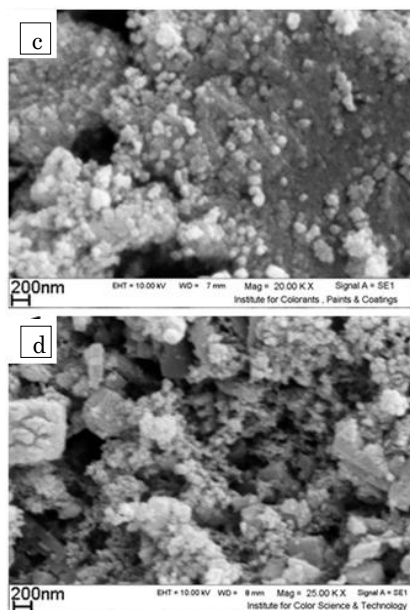
Fig. 4 – SEM images of samples 3 (a), 4 (b), 5 (c), 6 (d)

Fig. 5 displays the photoluminescence behavior of as-prepared Cu₂S nanostructure 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 [4] the absorption spectrum of as-prepared samples exhibits a blue-shift (2.24 eV, 552 nm).

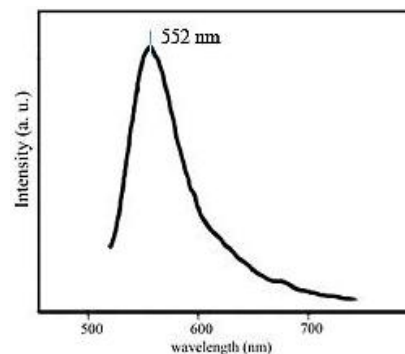**Fig. 5** – PL spectrum of the as synthesized Cu₂S nanoparticles

4. CONCLUSIONS

In summary, Cu₂S nanoparticles were successfully prepared using Na₂SO₃ as a weak reducing agent. 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.

ACKNOWLEDGEMENTS

REFERENCES

1. S. Wang, S. Yang, *Chem. Mater.* **13**, 4794 (2001).
2. X.H. Liao, N.Y. Chen, S. Xu, S.B. Yang, J.J. Zhu, *J. Cryst. Growth.* **252**, 593 (2003).
3. M. Peng, L.L. Ma, Y.G. Zhang, M. Tan, J.B. Wang, Y. Yu, *Mater. Res. Bull.* **44**, 1834 (2009).
4. M. Savelli, T.J. Bougnot, *Appl. Phys.* **31**, 213 (1979).
5. N. Pop, C. Nascu, V. Ionescu, E. Indrea, I. Bratu, *Thin Solid Films* **307**, 240 (1997).
6. Z. Nana, X.Y. Wangb, Z. Zhaoc, *J.Cryst. Growth* **295**, 92 (2006).
7. S. Gorai, D. Ganguli, S. Chaudhuri, *Mater. Chem. Phys.* **88**, 383 (2004).
8. S. Lv, H. Suo, X. Zhao, C. Wang, T. Zhou, S. Jing, Y. Xu, C. Zhao, *J.Alloy. Compd.* **479**, L43 (2009).
9. J.F. Zhu, Y.J. Zhu, M.G. Ma, L.X. Yang, L. Gao, *J. Phys. Chem. C.* **111**, 3920 (2007).
10. R. Jenkins, R.L. Snyder, *Chemical Analysis: Introduction to X-ray Powder Diffractometry* (New York: John Wiley & Sons, Inc, 90: 1996).