Synthesis of Cu$_2$S nanostructures using microwave method

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In this work a surfactant free microwave method for preparation of Cu$_2$S nanostructure is reported. Cu$_2$S nanostructures (without formation of other phases such as CuS and Cu$_{1.8}$S) were prepared using Na$_2$SO$_3$ as a weak reducing agent. The effect of different parameters such as time and power of irradiation on the morphology and particle size of the samples have been investigated. The nanostructures were characterized by X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), photoluminescence (PL) and ultraviolet-visible (UV-vis) spectroscopy.

Keywords: Nanostructure; Semiconductors; Cu$_2$S.

1. INTRODUCTION

Cu$_2$S (chalocite) is a p-type semiconductor with a bulk band gap of 1.21 eV which can be used in catalyst, biosensors and optoelectronic devices [1-5]. Hence, many studies have focused on finding a simple method for synthesis of Cu$_2$S nanostructures such as nanoparticles [6], nanowires [7], nanoplate [8], dendrites [9] and hollow microspheres [10]. The main purpose is synthesis of pure Cu$_2$S nanostructures without other phases such as CuS, Cu$_{1.8}$S, Cu$_7$S$_4$ and Cu$_{31}$S$_{11}$ [11]. By employing microwave irradiation CuS nanostructure is mainly obtained [12]. It seems that, in the microwave synthesis of Cu$_2$S, the polyol solvent is not sufficient for reduction of Cu$^+$ to Cu$^+$. We have been interested in the synthesis of sulfide nanostructures for a few years so in this paper we report a simple method for preparation of Cu$_2$S nanostructures by employing Na$_2$SO$_3$ as a weak reducing agent [13-16]. Nanostructures were synthesized from reaction between copper (II) salicylate (Cu(Hsal)$_2$) and thiosemicarbazide. The influence of different parameters such as type of copper source, power and time of irradiation were also studied.
2. EXPERIMENTAL
2.1 Materials and physical measurements

All the chemical reagents were of analytical grade and were used without further purification. X-ray diffraction (XRD) patterns were recorded by a Philips-X’pertpro, X-ray diffractometer using Ni-filtered Cu Kα radiation. Fourier transform infrared (FT-IR) spectrum was recorded by a Nicolet Magna-550 spectrometer in KBr pellets. The electronic spectrum of the sample was taken on Perkin-Elmer LS-55 luminescence spectrometer. Scanning electron microscopy (SEM) images were obtained on LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Pt to make the sample surface conductor and prevent charge accumulation. The UV-vis spectrum of the sample was taken on a JASCO UV–visible (Model V-670) scanning spectrometer.

2.2 Preparation of copper (II) salicylate (Cu(Hsal)2)

0.01 mol of Cu(NO3)2 3H2O was dissolved in 20ml of distilled water. 0.02 mol of sodium salicylate was dissolved in 20 ml of distilled water and was then added to the solution slowly. The mixture was stirred and heated (80 °C) for 5h. The white obtained precipitate was centrifuged, washed with ethanol and distilled water and dried at 50 °C.

2.3 Preparation of copper sulfide nanocrystals

Copper precursor (0.3 mmol) was dissolved in 40ml of propylene glycol. Na2SO3 (0.15mmol) and HCl (0.1 ml) were then dissolved in the solution. 0.15mmol thiosemicarbazide was then added to the solution. Afterward, the solution was exposed by microwave irradiation with different powers and times. The microwave oven followed a working cycle of 30s on and 70s off (30% power). The black obtained precipitates were centrifuged, washed with ethanol and distilled water and dried at 50°C at vacuum oven for 10h. The summarized parameters of different conditions are listed in Table 1.

Table 1 The summarized parameters of different reactions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Copper source</th>
<th>Na2SO3</th>
<th>Power</th>
<th>Time</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig 2</td>
<td>CuSO4</td>
<td>-</td>
<td>750</td>
<td>5</td>
<td>Impure Cu2S CuS</td>
</tr>
<tr>
<td>Fig 3a</td>
<td>Cu(Hsal)2</td>
<td>-</td>
<td>750</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Fig 3b</td>
<td>Cu(Hsal)2</td>
<td>√</td>
<td>750</td>
<td>2</td>
<td>Cu2S</td>
</tr>
<tr>
<td>Fig 3c</td>
<td>Cu(Hsal)2</td>
<td>√</td>
<td>750</td>
<td>3.5</td>
<td>Cu2S</td>
</tr>
<tr>
<td>Fig 3d</td>
<td>Cu(Hsal)2</td>
<td>√</td>
<td>750</td>
<td>5</td>
<td>Cu2S</td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

XRD patterns of as-obtained samples at 750W in 5 min are shown in Fig. 1. Impure Cu2S was obtained using CuSO4 precursor (Fig 1b). CuS nanostructure was obtained by use of Cu(HS)2 (Fig 1a), while pure Cu2S (JCPDS no. 02–1284) was obtained when both Cu(HS)2 and Na2SO3 were used (Fig 1c). Fig. 2 shows SEM images of impure Cu2S powders obtained with CuSO4 at two different magnifications. Fig. 3a shows SEM image of pure CuS nanoparticles obtained with Cu(HS)2 without Na2SO3 and images of pure Cu2S obtained with Na2SO3 at 750W in different times 2, 3.5, 5, 6.5 and 8 min are shown in Fig 3b-3f respectively. When the reaction time was lasted, from 5 to 8, nanoparticles with bigger diameter were obtained that is consistent with Oswald ripening.

**Figure 1** XRD patterns of the as-synthesized products (a) CuS (without Na2SO3) (b) impure Cu2S (with CuSO4) and (c) pure Cu2S (with Na2SO3).
**Figure 2** SEM images of impure Cu2S achieved with CuSO4 at 750W in 5min.
Dependence of morphology and particle size of the products with irradiation power was also investigated. SEM images of products at different intensities at 300, 600 and 900W are shown in Fig 4a-4c respectively. As shown in Fig. 4c, when the power increases from 600 to 900 non-uniform particles with average diameter of 100–300 nm were obtained. Results show in higher powers growth stage overcome to nucleation stage and bigger particles will be achieved. The influence of various factors on the morphology of the products is schematically shown in Fig 5.
Figure 4 SEM images of the obtained Cu$_2$S at (a) 300W (b) 600W (c) 900W.
**Figure 5** The effect of different parameters on the morphology of the products.

Fig. 6 shows TEM image of Cu2S nanostructures obtained with Cu(HSal)2 for 5 min at 750W (Fig 3d). The purity of the nanostructures was also confirmed by energy-dispersive X-ray analysis. EDX analysis of CuS nanoparticles and Cu2S nanostructures are illustrated in Fig 7a and 7b respectively. The L\textsubscript{a}, K\textsubscript{a} and K\textsubscript{b} lines of Cu and K\textsubscript{a} of S are obviously observed.
Figure 6 TEM image of Cu2S nanostructure obtained at 750W in 5 min.

Figure 7 EDX analysis of (a) CuS nanoparticles and (b) Cu2S nanostructures.
The UV–vis absorption spectrum of the as-synthesized Cu2S nanocrystals was recorded as shown in Fig. 8. Compared with bulk Cu2S, which has an absorption onset at about 1020 nm [1, 2], the absorption edge of obtained Cu2S nanostructures exhibit a blue-shift, which is attributed to the quantum confinement of charge carriers in the nanoparticles [16]. Photoluminescence measurement of Cu2S was carried out at room temperature with excitation wavelength 398 nm which are laid out in Fig. 9. The PL spectrum was consisted of a strong peak at 461 nm that can be ascribed to a high-level transition in Cu2S semiconductor crystallites. It has been reported that this kind of band edge luminescence arises from the recombination of excitons and/or shallowly trapped electron–hole pairs [16]. Fig. 10 shows FT-IR spectrum of the Cu2S nanostructure at 750 W in 5 min. Absorption at 3441 cm⁻¹ is attributed to the O-H bond and absorptions at 1624 cm⁻¹ and 1231 cm⁻¹ are also related to C=O and C-O bonds respectively. These peaks proved the presence of a low amount of salicylate (precursor) on the surface of Cu2S nanostructure.

Figure 8 UV–vis absorption spectrum of Cu2S nanostructure.
Figure 9 Room temperature photoluminescence spectrum of Cu$_2$S.

Figure 10 FT-IR spectrum of Cu$_2$S nanostructure.
4. CONCLUSIONS

Cu$_2$S nanostructures were synthesized via microwave method employing Na$_2$SO$_3$ as a weak reducing agent. This method is rapid, simple and can be easily controlled. It was found that the CuS nanoparticles were formed by non-Na$_2$SO$_3$-assisted. According to this echanism, the Na$_2$SO$_3$ acted as a soft reducing agent leading to formation of the Cu$_2$S nanocrystals. Influence of different parameters such as time and power on the morphology of the products was also investigated. Results show Na$_2$SO$_3$ and salicylate are key factors for formation of the Cu$_2$S phase.

References
