

Preparation and characterization of CuS Nanomaterials by solvothermal method

R.Suja, D.Geetha and P.Ramesh

Abstract – The preparation and characterization of pure semi conducting transition metal sulfide (CuS) Nano particles using copper nitrate trihydrate and thiourea via an inexpensive and simplistic route called solvothermal synthesis. The CuS nonmaterial was synthesized at 125 °C for three different calcination time viz., 10, 15 and 20 hrs. The synthesized products were characterized by UV-Vis, FT- IR, XRD and SEM/EDS. The analysis confirmed the copper sulfide nano particles are below 35 nm. The calcination time affecting the CuS size and stability of the particles have also been investigated.

Keywords: Nanomaterials, Copper sulfide, solvothermal and calcination time.

1 INTRODUCTION

Transition metal sulfides have been an innovative field of research due to number of interesting optical, catalytic and electronic [1],[2]and[3] properties and applications. One of the transition metal sulfides, copper sulfide (CuS) is an important P-type semiconductors with copper vacancies in the lattice have been studied [4] extensively for their application. Such as cathode materials in Lithium rechargeable batteries , solar cells, optical filters, sensors and super conductor at low temperature below 1.6K [5],[6],[7]and[8].

Various synthesis approaches have been developed to fabricate CuS nanostructures, including nanowires, nanobelts, nanorods, nanotubes, whiskers, nanocrystals and super structures by different methods like solvothermal and hydrothermal, template assisted growth, microwave irradiation [9],[10]and[11] and so on.

Compared with other preparation methods, solvothermal technique has been considered as a mild mean to synthesize nanostructure materials. Nanosphere like structures were obtained by controlling the reaction parameters (calcination time). The focus of this work is to describe the particle size and characterize the prepared nano copper sulfide (CuS) synthesized at a temperature 125°C at three different calcinations hours (10,15 and 20 hours.)

2 EXPERIMENTAL SECTIONS

2.1 Experimental Materials

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In a typical synthesis all reagents were analytically pure. Copper nitrate tri hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), Thiourea ($\text{Tu}, \text{SC}(\text{NH}_2)_2$) and ethanol were purchased and used as such without further purification.

2.2 Synthesis

1mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 40ml ethylene glycol. Then 2mmol ($\text{Tu}, \text{SC}(\text{NH}_2)_2$) was added the above mentioned solution under the continuous stirring over the period 45 min. The solution change into light green colour then the solution was transferred into Teflon-lined stainless steel Auto clave and maintained at 125°C for different calcination time 10hrs, 15hrs and 20hrs. The mixer was then allowed to cool at room temperature finally, the produced black precipitation was collected and washed with ethanol and deionized water several times to remove impurities and dried at 60°C for 4hrs.

2.2 Characterization

X-ray powder diffraction (XRD) of the products was carried out on **XPRT-PRO** diffractometer with $\text{Cu K}\alpha$ radiation $\lambda=0.15406$ nm, at a scanning rate of 0.0205^{-1} in the 2θ range from 10° to 80° . SEM/EDS analysis was carried out on a Scanning Electron Microscope (JEOL-JSM – 5610 LV with INCA EDS). UV-Vis absorption spectra were recorded on **UV-Visible spectrophotometer (SHIMADZU-UV 1800)**, employing the deionized water as the reference. Fourier Transformation Infrared (FTIR) spectrum was recorded by FTIR spectrometer (PERKIN ELMER – spectrum R X I).

3 RESULT AND DISCUSSION

3.1 XRD Analysis

Fig 1(a, b and c) shows the XRD patterns of the synthesized CuS under different reaction times 10 hrs, 15hrs and 20 hrs

at 125°C temperature. It can be seen that the final CuS product agrees well with the standard pattern in the JCPDS card No: 06-0464

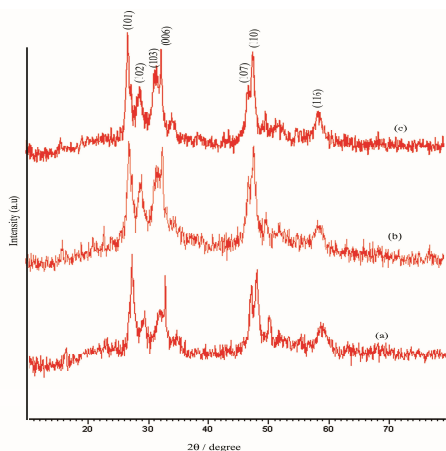


Fig.1 The XRD patterns of the CuS nano materials obtained at 125°C with reaction time (a) 10hrs, (b) 15 hrs and (c) 20hrs.

For estimating the diameter (D) of the nanoparticles of CuS, Scherrer formula have been used, $D = 0.9 \lambda / \beta \cos \theta$ where λ is wavelength, β is full width at half maximum (FWHM) and θ is angle of diffraction. The estimated size of CuS nanospheres was found to be in the range from 20-35 nm. The particular peak in the X-ray diffractogram is generated due to coherent scattering of X-rays from the particular lattice planes. The size of the domain scattering region (CSR) in a direction parallel to a diffraction plane is related with the inverse of FWHM (β) of the respective diffraction peak. An initially large domain contributing coherently to that respective XRD peak will produce a line only but finite resolution of the instrument itself and other factors will broadening in β has been taken into account in this study. Broadening of XRD lines is also associated with small particle size of the coherently diffracting crystallites or strains present within the sample or both [11].

3.2 UV - Visible Spectroscopy

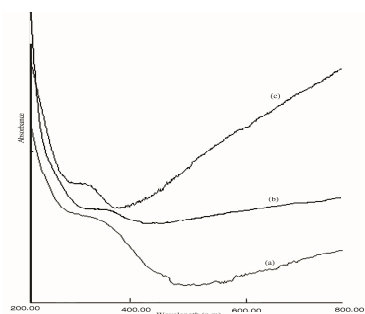


Fig. 2. UV- Visible absorption spectra of CuS nano materials at 125°C with reaction time (a) 10hrs, (b) 15 hrs and (c) 20 hrs.

The spectroscopic study on copper sulfide with different calcination times was reported in the fig 2 (a, b and c). It has been described that the overall structure of the spectrum was not affected by the size of the particles [12]. The UV-Vis spectra of CuS exhibited some difference at the maximum absorption wavelength. The λ_{max} of CuS nanospheres were 330 nm, 271 nm and 269 nm for 10 hrs, 15 hrs and 20 hrs (CuS samples) respectively in CuS nanobelts [13].

The absorption peak gradually decreases with the prolonged time. The UV-Vis absorption is much broader in the visible range. It indicated that the structure of CuS leads to the broadening of optical absorption, therefore CuS structure have great potential in the field of opto electronics.

3.3 FTIR Analysis

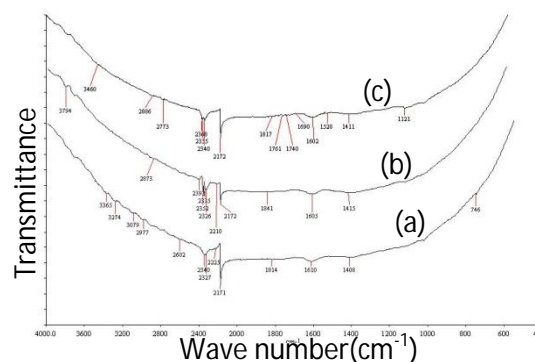


Fig. 3. FTIR spectra of CuS nano materials at 125°C with reaction time (a) 10hrs, (b) 15 hrs and (c) 20 hrs.

Copper sulfide nanoparticles formation were studied using FTIR at constant temperature 125°C and different calcinations time 10hrs, 15 hrs and 20hrs. Thiourea was gradually hydrolyzed to produce S^{2-} and react with Cu^{2+} ions of copper nitrate tri hydrate [14]. The FTIR spectrum of CuS powder fig 3(a, b and c) presented main absorption bands due to asymmetric C=O stretching of copper nitrate trihydrate at 1610 cm^{-1} . The strong peak 2171 cm^{-1} and 2172 cm^{-1} in the CuS spectra is possible from oxidation production. The CuS nanoparticles may be bound CuS and OH unit of ethylene glycol.

3.3 SEM/EDS Analysis

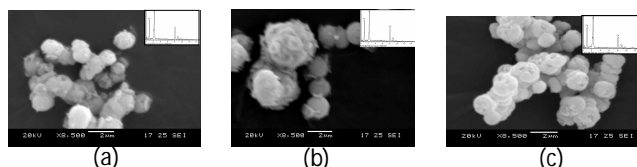


Fig. 4. SEM /EDS Photographs of CuS nano materials at 125°C with reaction time (a) 10 hrs, (b) 15 hrs and (c) 20 hrs.

To investigate the growth process of the nanosphere like morphology obtained by solvothermal route with the temperature value 125°C, time dependent experiments were carried out. Fig. 4 shows the morphologies of product synthesized under different reaction times. It can be seen that the product consists of a aggregate of fine nanospheres at this stage Fig.4 (a). The initially formed nanosphere have a low aspect ratio with time prolonged to 15 hrs, more number of nanospheres were found the aspect ratio tended to be higher as shown in Fig.4(b). Uniform nanosphere like morphology was formed when the precursor solution was experienced solvothermal treatment for 20 hrs as shown in Fig. 4(c). Therefore, the source of uniform nanosphere formation was revealed based on the analysis.

The factor (calcinations time) affecting the morphology of CuS can be described to the reaction time. As shown in Fig.4 (a), same is a mixture of nanoparticles. The average diameter of nanosphere is 35 nm, whereas at 15h and 20h exhibits clear nanospheres and the average diameter 27 nm and 24nm respectively show in Fig. 4(b) and 4(c). It reveals that different reaction time results in the formation of Uniform nanosphere morphology. A typical EDX pattern of as prepared CuS nanosphere, it demonstrates that the sample consists of Cu and S.

4 Conclusion

Copper sulfide nanosphere with a uniform surface morphology was successfully fabricated. The reaction times have a remarkable influence on the nucleation which leads to the formation of CuS nanospheres. X-ray diffraction analysis of pure CuS showed that the sample have crystalline structure. The estimated particle size of undoped CuS nanospheres by the XRD studies was found for 10 hrs 35 nm, for 15 hrs 27 nm and for 20 hrs 24 nm. For increasing the reaction time the particle size have been decreased. The FTIR study of this samples shows that the main band corresponding to the formation of CuS compound appears around 2171cm^{-1} which confirms of the sample.

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