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# Particles Dispersion Measurements and Size Distribution of Colloidal Copper Sulfides-Chitosan stabilized Nanocrystellites developed via Chemical Route

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**ABSTRACT**
*Copper sulphide commonly known as covellite and chalcocite exist in various stoichiometries among the transition metal sulphides, which have attracted considerable attention in the past several years. Although synthesis and physical characterization of nanocrystelline metal sulphides come under intense scrutiny but has significant interest and that's why it is still the subject of many researches owing to their important physical and chemical properties. During the past decade the chemical composition of the solvent opening new research areas to the stabilization of different nanoparticles specifically metal chalcogenides. Various factors such as mild temperature conditions, p$^{H}$, Concentration and the ratio of reagent with stabilizing or the reducing agent and these specific conditions able to improve chemical diffusion and support to fabricate the metastable material. Looking to the importance and wide application of the copper sulphide Nanocrystellites in the industry, present problem has been sorted out to fabricate the micro particles of selected metal sulphide versus the control of the nucleation and crystal-growth and accordingly dispersion measurements were done. Nanoparticles are attracted intensive attention not only in relation to biomedical research in vitro applications, especially in the detection of bio molecules, but also wide applications in the industry across the globe at present because of their unique properties. This report outlines the method development and samples preparation specifically for transition metal chalcogenides copper sulphide and technique standardization via chemical route applied moderate conditions. A key problem during the experiment is the particles dispersion and size distribution obtained during the sample preparation which needs to be focussed on the various phenomena so that the nanoparticles may disperse into individual unstable particles.*
***Key words:*** *Nano and highly crystalline, chemical route, dispersion measurements, metastable particles, Light scattering, Concentrated suspension.*

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## INTRODUCTION

Literature reveals the term Nanomaterials which are used interchangeably by a variety of different names i.e. nanoparticles, nanaocrystals, and optical quantum dots play vital role and have become one of the fast growing field as Science and Technology. Transition metal chalcogenides including sulphides, selenides and telluride generally found in minerals and have attracted widely attentions in recent decades due to the interesting fascinating properties they possess as they have number of commercial application in many fields such as pigments, semiconductors, fluorescence devices and even superconductors [1-3].
Semiconductor nanaocrystals which is chemically grown quantum dots having controlled particles sizes less than 10 nm possess various above mentioned properties originating from the confinement effect. Recent successful integration of luminescent II-IV Nanocrystellites more attractive and open an avenue in research and development field [4-7]. To this context, highly crystalline particles with almost monodisperse size distribution and regular as well as controlled morphology are required to fulfil the implementation of the applications. In fact, many different methods of preparation have been adopted to fulfil the said crystals, here we report, and in accordance of the objective, a general synthesis of metal

sulphides i.e. copper sulphides Nanocrystellites via simple chemical route applied herein provides a promising sample preparative approach to such chalcogenides.
Keeping the view and an urgent need to develop various sample preparation procedures present problem has been undertaken for fabricating target particles having controlled morphology by using a suitable naturally derived protective polymer chitosan, act as a reducing agent specifically for covellite and chalcocite. Here we reports copper acetate (II) reaction with thiourea which is used as sulfur source and reducing agent with stabilizing agent against a blank sample preparation under controlled synthesis process having stoichiometric copper sulphides nanoparticles via colloidal chemical route with certain modification in the methods applied earlier [8-9].

## MATERIALS AND METHODS

Copper sulfides colloidal particles were synthesized with certain modifications in the prescribed method of Shen *et al* [9] and Boey *et al* [8] by taking three different concentrations of Copper: chitosan ratio i.e. 1:2, 1:10 and 1: 20. Aqueous solution of copper acetate and thiourea solution was made ($2.0 \times 10^5$ M) where as chitosan solution ($1.0 \times 10^4$ M) was made in 1.5 % aqueous acetic acid (v/v) and then 2 ml of this solution was poured into 5 ml and 5.5 ml copper acetate and thiourea solution having set pHhHH value as 10 with aqueous ammonia. The composition of precursors for the synthesis of copper sulfides colloidal particles is given in Table 1.
Final volume was made in the reactant flask equipped with reflux condenser with water bath having capacity of 50 ml at moderate temperature (100 – 110 $^{\circ}$C) and different reaction time (15 - 90 min). Similarly, 10 ml and 20 ml of chitosan solution were poured separately into the same volume of the reactant and the reagent in the second and third phase of the experiment. A control experiment without stabilizer as blank was run to compare the data and accordingly a set of experiment run with prolonged reaction time.
Characterization was done by FTIR, UV-VIS Spectrophotometer (Shimadzu FTIR Spectrophotometer) followed by Dynamic light scattering (DLS) measurements was performed for size analysis in the concentrated suspension by Delsa ™ Nano, Beckman Coulter, USA.

Table 1 Composition of precursors for the synthesis of copper sulfides colloidal particles

| $Cu^{2+}$ in 50 ml reflux volume | Ratio of $Cu^{2+}$:Chitosan | Copper Acetate ($2.0 \times 10^5$) | Thiourea ($2.0 \times 10^5$) | Chitosan ($1.0 \times 10^4$) |
|---|---|---|---|---|
| $2.0 \times 10^6$ | 1:2 | 5.0 | 5.5 | 2.0 |
| | 1:10 | 5.0 | 5.5 | 10.0 |
| | 1:20 | 5.0 | 5.5 | 20.0 |

## RESULTS AND DISCUSSION

FTIR spectroscopy was carried out for confirming the polymer stabilized copper sulfide composite as the spectra of the product showed two bands at about 2900 and 619, which were seen in the sample with the stabilizing agent (Fig.,1) and it might be due to the $Cu_2S$ presence in the product. On the contrary no band due to the CuS was appeared which attribute the nil existence of the particular compound in the sample suspension because of its IR inactive nature [7] (Fig. 1a-b).
Present study summarizes an effort to develop the suspension with almost monodisperse size distribution of the nanoparticles having regular as well as controlled morphology which was required to fulfill the implementation of the applications for preparing crystalline particles. Results revealed that the highest population of the particles was found near 7.1 nm and large population between 60nm and 400 nm when the particle sizing analysis was done using dynamic light scattering of concentrated suspension.
During the study period most of the particles in prepared samples were appeared with polydispersity index 0.5 and above however, some suspension was found with monodisperse particles having polydispersity index 0.160 to 0.221. The results also quantifies that there are 0.1 % particles of the size 7.1 nm and again the same percentage at 7.7 nm and 8.4 nm then till the sizes up to 59.6 nm there were no particles present in the range of intermediate size so here we report that the percent wise target size population was 97.7nm (10%), 171.9(50%), and 302.8(90%), which was considered as target size (Table 1 and Figure 2-3).

**Fig1a-1b: FTIR Spectrum of polymer stabilized copper sulphide and pure chitosan**

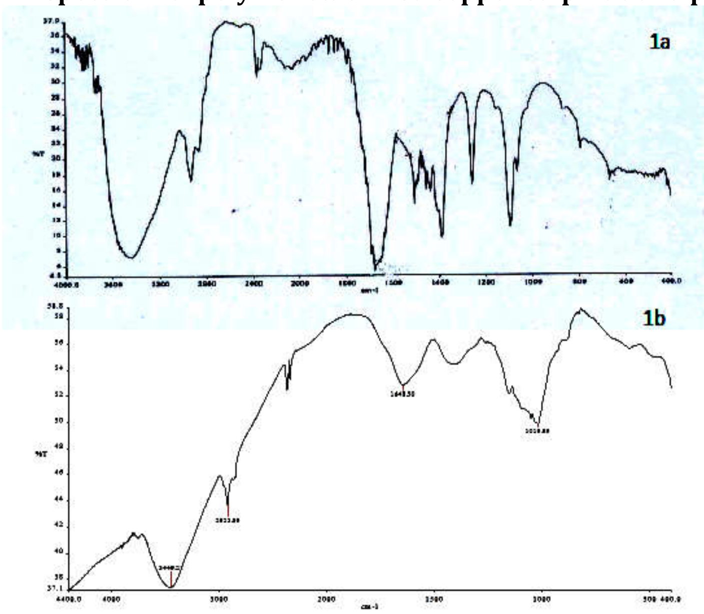



**Table 1: Size distribution of copper sulfides nanoparticles in concentrated suspension**

| Suspension-1 | | Suspension-2 | |
|---|---|---|---|
| Below 10 % (D10) | 19 nm | Below 10 % (D10) | 97.7 nm |
| Below 50 % (D50) | 75.8 nm | Below 50 % (D50) | 171.9 nm |
| Below 90 % (D90) | 374.9 nm | Below 90 % (D90) | 302.8 nm |
| Mean Diameter | 88.7 nm | Mean Diameter | 163.6 nm |

**Fig. 2: Size distribution of copper sulfide nanoparticles in concentrated suspension-1**

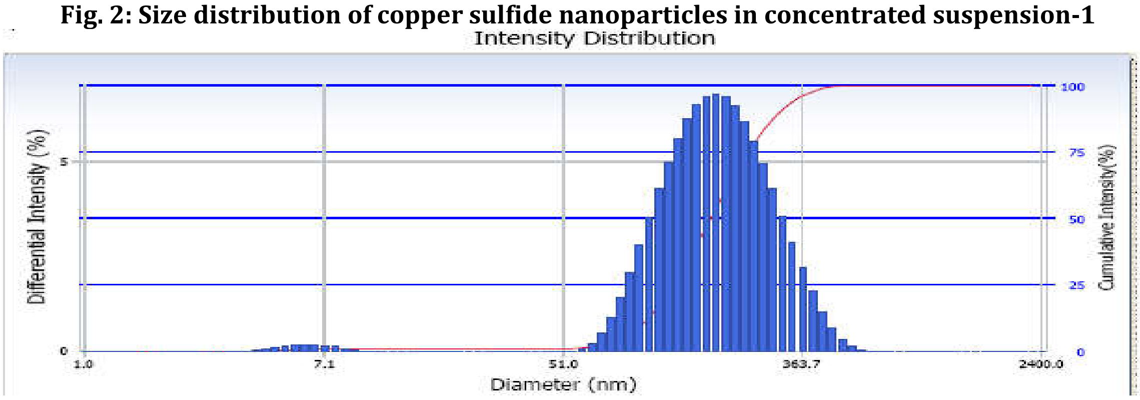
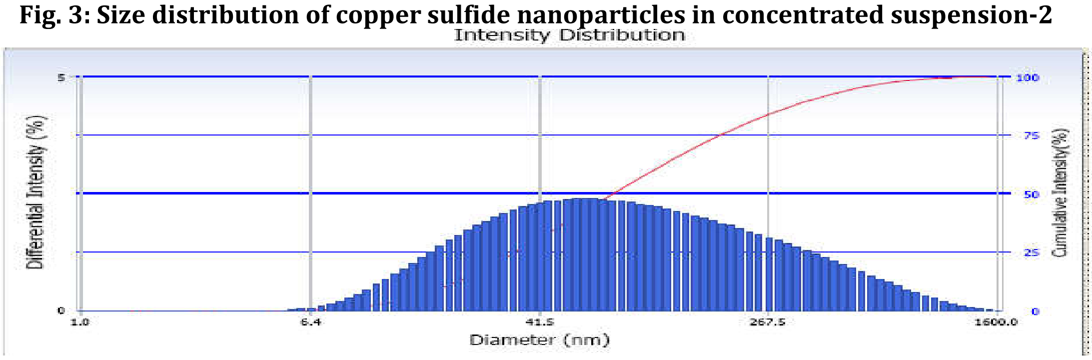



**Fig. 3: Size distribution of copper sulfide nanoparticles in concentrated suspension-2**




The sample was considered as an ideal sample by showing so narrow autocorrelation function where as the other sample which was prepared with prolonged reaction time showed particles mean diameter size 163.6 nm and the range was to be 6.4nm to 1600 nm which show big population having both wasted end. To conclude, it can be said that most of the nanoparticles of copper sulfides was found in the size range of 171.9 nm (Suspension1) and further efforts are needed for the formation of highly crystalline particles with almost monodisperse size distribution to fulfill the implementation of the applications of metal chalcogenides. Method development and its standardization were done, and the product obtained is green copper sulfide or covellite, CuS and $Cu_2S$ in an appropriate composition.

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