



Synthesis of tube-like $\text{Cu}_{39}\text{S}_{28}$ micro-crystals via solvothermal route

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Solvothermal synthesis of copper sulphide ($\text{Cu}_{39}\text{S}_{28}$) microparticles by employing acetylacetone (Hacac) as the solvent is presented. Solvent acetylacetone is used for controlling the shape of the product. Morphological pattern and structure of the product were investigated by SEM and XRD, respectively. SEM images showed tube-like network structure of the product. The formation of $\text{Cu}_{39}\text{S}_{28}$ was confirmed by XRD analysis.

Keywords: Copper sulphide, solvothermal synthesis, acetylacetone, microstructure.

Introduction

Inorganic micro- and nanostructures with different morphologies are attracting increasing attention due to their unique properties. Both physical and chemical properties are significantly affected by the size, morphology, structure, composition and crystallinity of materials¹⁻⁴. Among the various metal chalcogenides, copper sulfides have attracted attention for their various applications in different fields, such as in solar cell devices^{5,6}, sensors^{7,8}, optical filters⁹, cathode materials in lithium batteries¹⁰⁻¹², peroxidase-like activity¹³, photocatalysis¹⁴⁻¹⁶, supercapacitors¹⁷, and thermoelectric materials¹⁸. Hence, many synthetic methodologies like hydrothermal/solvothermal technique, gas-solid reaction, microwave irradiation, thermolysis, CVD, electrodeposition, etc.^{7,19-27} have been adopted for the preparation of various $\text{Cu}_2\text{S}/\text{Cu}_x\text{S}$ micro/nanostructures.

The present paper describes a convenient solvothermal technique for the preparation of tube-shaped copper sulphide microparticles by applying Hacac solvent.

Experimental

In a Teflon-lined steel autoclave, $\text{Cu}(\text{NO}_3)_2$ (4 mM) and NH_2CSNH_2 (2 mM) were taken. 75% of this Teflon container was filled up with acetylacetone solvent. The autoclave was kept at 140°C for 12 h. The product was thoroughly cleaned with water and ethanol for number of times. After washing,

the product was dried at 60°C for 3 h in a vacuum.

The sample was identified by XRD, utilizing Seifert (3000 P) unit with monochromatic $\text{CuK}\alpha$ radiation (Ni filter). The morphological pattern and size of the sample were investigated by using SEM (Hitachi Model S-2300).

Results and discussion

The XRD pattern (Fig. 1) indicates that the diffraction peaks of the sample correspond to the $\text{Cu}_{39}\text{S}_{28}$ phase [JCPDS No. 36-0380]. In $\text{Cu}_{39}\text{S}_{28}$, the ratio of Cu:S is close to 1:1. The minute change of stoichiometry from Cu:S = 1:1

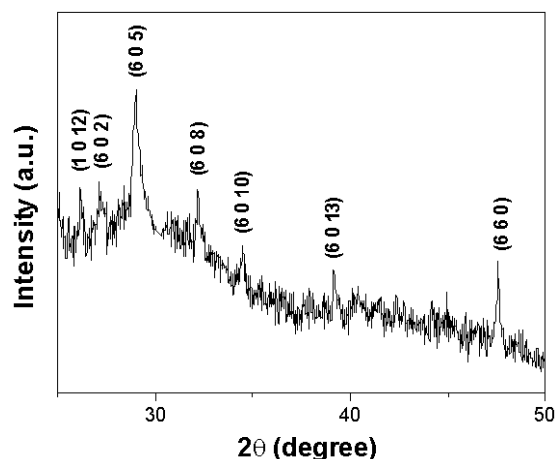


Fig. 1. XRD pattern of the sample synthesized from nitrate salt of copper using acetylacetone solvent.

can be explained by considering the conversion of a part of Cu^{2+} to Cu^+ ²⁸ under high temperature and pressure, present in the autoclave.

The morphology of the synthesized sample is studied by SEM measurements. SEM images reveal the tube-like morphology of copper sulphide. Tube-like network structures of the product with lower and higher magnifications are shown in Fig. 2a and 2b. The average diameter of the tube is estimated from SEM images and found to be 500 nm. Here solvent Hacac is utilized for controlling the shape of the product. In this reaction, at first, copper salt was solubilized in Hacac by forming $[\text{Cu}(\text{acac})_2]$ complex via chelation with the bidentate arms of acac. The complex molecule may form one-dimensional stacking of parallel molecules through a particular crystallographic axis^{29,30}. Previous literature revealed that a strong π - π and Cu - π interactions exist between the aforesaid stacked molecules³⁰, this may lead the orientation of the molecules in this particular direction. Under the

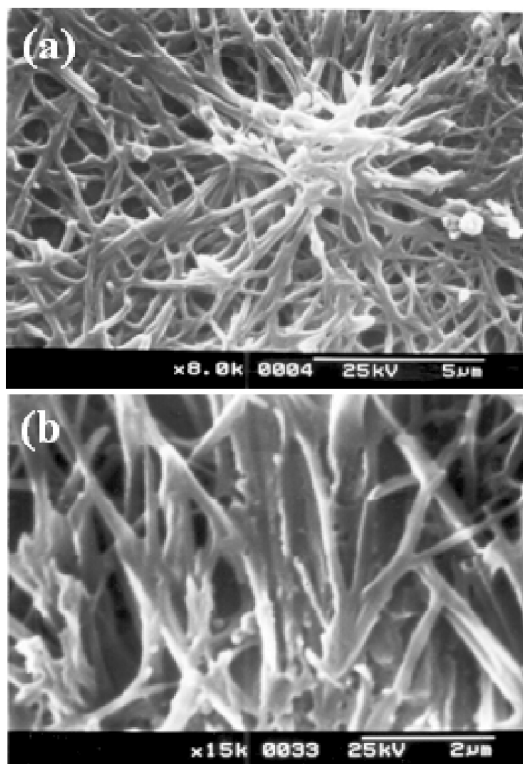


Fig. 2. SEM images of the sample (a) lower magnification and (b) higher magnification synthesized from nitrate salt of copper using acetylacetone solvent.

solvothermal condition, at high temperature and pressure, the above complex molecules tend to dissociate. An immediate reaction took place between the dissociated molecule with S^{2-} (coming from dissociated thiourea molecules at elevated temperature) which finally form copper sulphide microparticles; the organic Hacac solvent was gradually lost (b.p. of Hacac is 140°C at normal temperature and pressure)³¹.

A schematic diagram of synthesis of copper sulphide microcrystals is shown in Fig. 3.

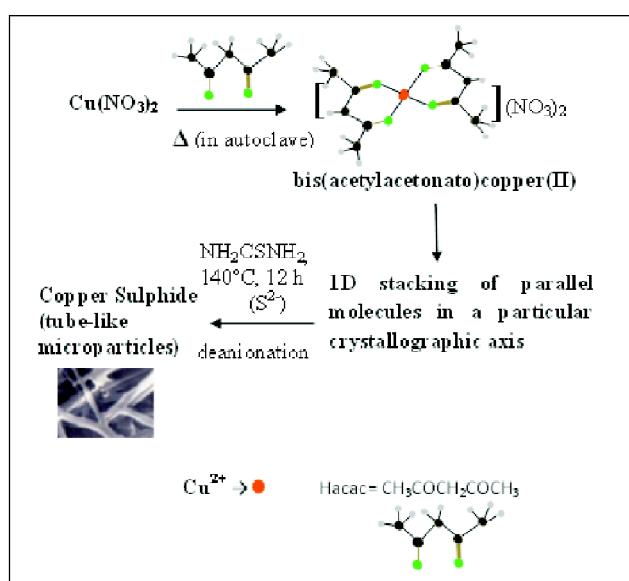


Fig. 3. Schematic diagram of the synthesis of copper sulphide microcrystal.

Conclusions

Tube-like copper sulphide submicron crystallites were prepared through solvothermal technique. A chelating agent, acetylacetone was used for controlling the morphology of the synthesized material. The formation of the nonstoichiometric $\text{Cu}_{39}\text{S}_{28}$ phase was revealed from XRD analysis.

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