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THERMAL BEHAVIOR AND DECOMPOSITION OF COPPER SULFIDE NANOMATERIAL SYNTHESIZED BY AQUEOUS SOL METHOD

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Very simple and economical route was adopted to synthesize copper sulfide (CuS) nanomaterial using microwave irradiation with various precursors. This method depends upon the internal thermal heating of solution. Copper sulfate pantahydrate ($CuSO_4$-$5H_2O$) was used as copper ion contributor while sodium thiosulfate pantahydrate ($Na_2S_2O_3$-$5H_2O$) and thiourea (H_2NCSNH_2) were used as sulfur ion sources. **X**-Ray diffraction (XRD) revealed the hexagonal phase with crystallite size in the range of 30 nm to 50 nm of the product material. The Scanning electron microscopy (SEM) confirmed the spherical morphology. Thermal behavior was observed using Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analyzer (TGA). Thermal analysis showed different phase transitions like CuS to $Cu_{1.8}S$, Cu_2S, $CuSO_4$, $CuO{\cdot}CuSO_4$, CuO and Cu_2O at various temperatures in the presence of oxygen while formation of $CuSO_4$ and $CuO{\cdot}CuSO_4$ was absent under nitrogen environment. It is observed that the morphology of CuS nanomaterials played an important role in the stoichiometry of the thermal phase transitions.

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1. Introduction

Microwave heating is produced due to direct interaction of microwave irradiation with reacting materials [1-2]. Heat is produced within the material, rather than other typical heating approaches in which heat is generated outside then transfer to the material. Microwave internal heat process helps to reduce the time of reaction, low energy expenditures and make possible to synthesize new materials [3]. This heating technique is more efficient, very simple and much faster as compared to conventional heating methods. Therefore, microwave synthesis technique has been extensively used in numerous fields as radiopharmaceuticals, in preparation of inorganic complex compounds, metal sulfides and oxide, several organic reactions and plasma chemistry [4].

Recently, transition metal sulfides have claimed substantial response of researchers because of their exciting morphology, electrical, optical and thermal properties [5–7]. From the discovery of photovoltaic behavior of CuS as donor material and its deposition with CdS resulted high rate efficiency. Therefore, CuS is a potential candidate that could be used in the areas of solar energy conversion, gas sensors, IR detectors, electrochemical cells, and catalytic properties [8-15]. A lot of work has been

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reported on formation of various morphologies (strip type, rod-like, needle, wires, tubular and spheres) of copper sulfide [16]. Researchers provided a significant path to CuS regarding their interesting thermal oxidation processes [17-20]. It is well-known fact that the thermal decomposition of CuS is influenced by synthesis conditions. By using these synthesis conditions, different copper sulfides ($Cu_{1.8}S$, Cu_2S), copper oxysulfates ($CuO{\cdot}CuSO_4$) copper sulfates (Cu_2SO_4, $CuSO_4$) copper oxides (Cu_2O and CuO), were obtained by setting different experimental conditions like microwave irradiation power, temperature, time and atmosphere [21–25].

In this study, a straight forward synthetic route to fabricate nanocrystalline copper sulfide was adopted. The thermal phase transition was tested in different environment (air and nitrogen). Stoichiometry involved in decomposition was also studied.

2.Experimental work

2.1 Materials

Copper sulphate pentahydrate ($CuSO_4$-$5H_2O$), sodium thiosulfate pantahydrate ($Na_2S_2O_3$-$5H_2O$) and thioureas (H_2NCSNH_2) were all supplied by Unichem Laboratories Ltd. All these chemicals were analytical pure, and used as received without further purification.

2.2 Fabrication of CuS

CuS nanocrystalline materials were fabricated using $CuSO_4$-$5H_2O$ and H_2NCSNH_2. These materials were dissolved individually in distilled water to obtain Cu^{+2} and S^{-2} solutions. These solutions were prepared using same molarities and mixed drop wise keeping 1:2 ratio under constant stirring at room temperature. The stirred solution was irradiated for 30 minutes using the microwave (2.45 GHz) with 1:5 switching intervals. After irradiation, resulting precipitate (sample a) was filtered and washed with ethanol, then dried at room temperature. Similarly, thiourea was replaced with $Na_2S_2O_3$-$5H_2O$ and mixed drop wise in the solution of $CuSO_4$-$5H_2O$ under constant stirring. The resulting solution was irradiated for 15 minutes (sample b) and 30 minutes for (sample c) as shown in Table 1.

Table 1: Reaction Parameters

Samples	Copper Contributor	Sulfur Contributor	Time	Switching Intervals
a	$CuSO_4$-$5H_2O$	H_2NCSNH_2	30	1:5
b	$CuSO_4$-$5H_2O$	$Na_2S_2O_3$-$5H_2O$	15	1:5
c	$CuSO_4$-$5H_2O$	$Na_2S_2O_3$-$5H_2O$	30	1:5

2.3 Characterization

Crystalline structure of CuS nanomaterial was recorded using X-Ray diffractometer model PANalytical X'Pert PRO XRD Company Ltd., Holland with CuKα characteristic radiation (λ = 0.15418 nm) operated at 40 kV and 40 mA. The step size of $0.05^\circ\ s^{-1}$ was applied to record the pattern in the 2θ range of 20–70°. To study the morphology of the materials, particle size and shape were carried out by scanning electron microscope (SEM, JOEL JSM-6480). Differential scanning calorimetric (DSC) and Thermogravimetric analysis (TGA) measurement of samples were examined using TGA, SDT Q600 (TA Instrument) in control environment to observe the weight variation, phase modifications, thermal oxidation and reduction in CuS nanomaterial.

3. Results and Discussion

The XRD patterns recorded for samples synthesized with various precursors are shown in figure 1. It revealed that products have high crystallinity and mostly all peaks of CuS nanoparticles matches perfectly, as referenced to JCPDS card number 00-001-1281. The pattern showed the presence of hexagonal phase CuS with lattice constants a = 3.8020 A°, b = 3.8020 A° and c = 16.4300 A° respectively. The XRD curve of CuS exhibits some of the characteristics peaks of $CuSO_4$ (indicated with * in Fig. 1a) caused by the oxidation of CuS nanoparticles, which are very reactive and sensitive for their large surface to volume ratio. The crystallite size was evaluated using Sherrer’s formula and found to be in the range of 30 to 50 nm.

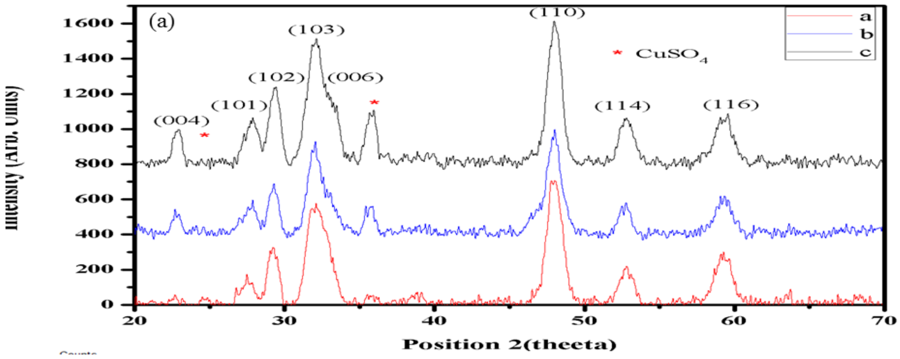

Fig. 1: XRD Pattern of CuS nanoparticles (a) and reference pattern (b)

In Fig. 2 (a-f), the SEM images of the final product of CuS nanocrystalline materials are displayed. Fig. 2a represents the aggregative progression of CuS nanoparticle (sample a) to spherical shape and this shape is visible in Fig 2b, where some non-interactive particles are also present. The size of spheres was estimated from SEM, in the range of 500 nm to 1 µm.

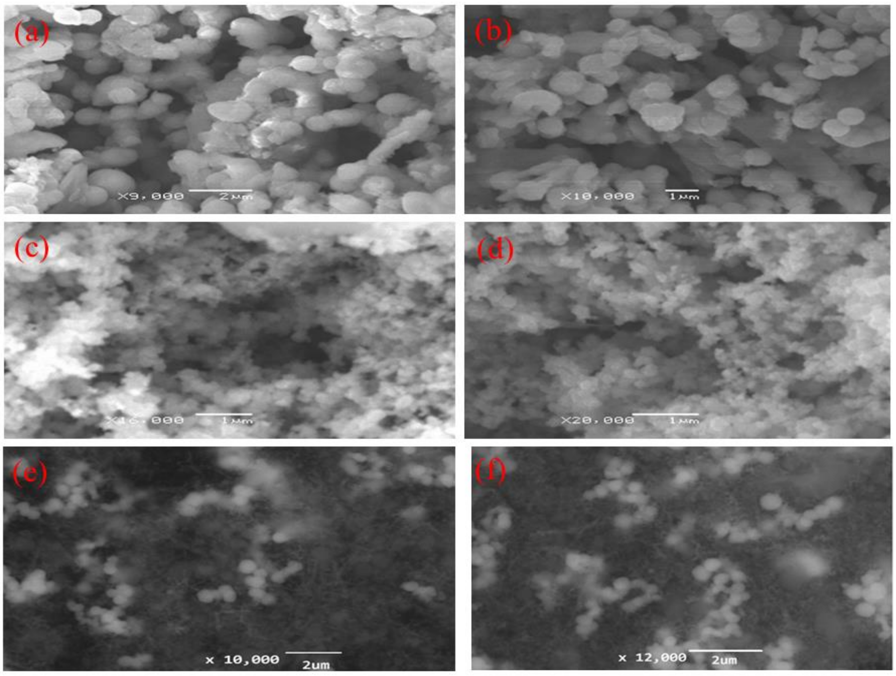

Fig. 2: SEM images of CuS nanomaterial prepared with different precursor Fig. (a,b) of sample a, (c,d) sample b and (e,f) sample c.

The image of sample "b" depicts that rate of aggregation process depends upon microwave irradiation (power and time) as shown in Fig. 2 (c-d). This sample (b) was synthesized using microwave irradiation (2.45 GHz, 800 W) with switching intervals 1:5 (160 W) for 15 min by a microwave oven. In this sample, the irradiation time was short relative to samples (a and c) therefore, aggregation process was probably slow to assemble nanoparticles into particular shape. In sample "c" aggregation of nanoparticle was improved by escalating time of microwave irradiation with switching intervals 1:5 (160 W) to get definite morphology as shown in Fig. 2 (e-f). Size of sphere was around 400-600 nm by deeply observing these images.

Mostly, natural and synthesized Copper Sulfide shows fascinating thermal behavior/ oxidation with several stages

During thermal process, other sulfides ($Cu_{1.8}S$ and/or Cu_2S), oxides (Cu_2O and/or CuO), and sulfate (Cu_2SO_4, $CuSO_4$, $CuO \cdot CuSO_4$) were formed. Above 900^{0}C, CuO was yielded due to decomposition of sulfates [26–30].

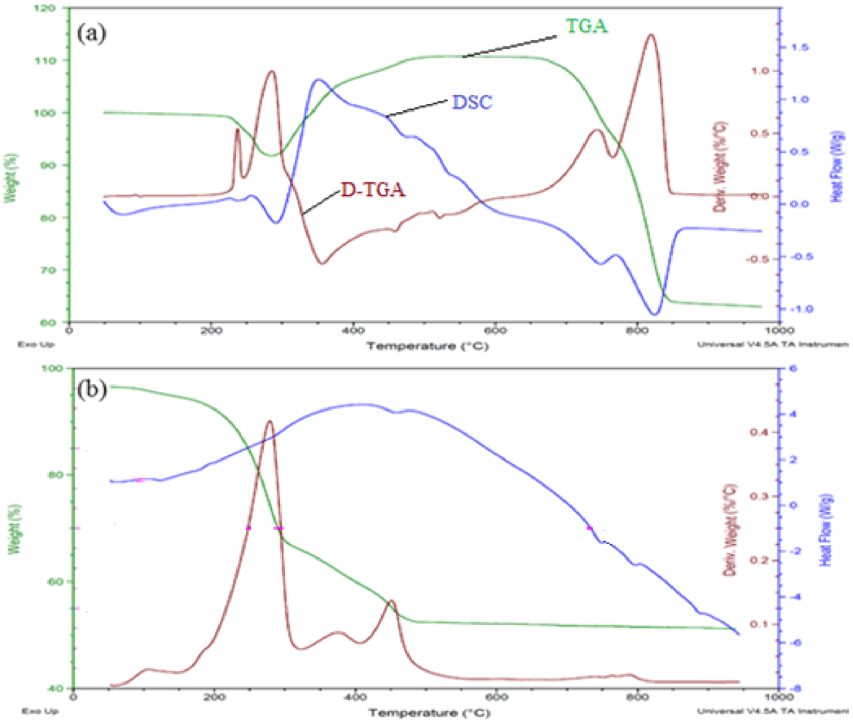

Fig. 3 : DSC/TGA of CuS nanoparticles (sample a) in air (a) and N_2 (b).

To study the change of phases during crystallization, simultaneously (DSC/TGA) analysis was performed in an air environment as shown in fig. 3. The sample (a) was treated from room temperature to 975 ^oC with ramp rate of 10 ^oC / min. From figure 3a, TGA curve indicates that the initial weight loss start in the temperature range 230 - 320 ^oC , while corresponding DTGA curve merge up and DSC curve shows an exothermic and then endothermic reaction, are due to removal of sulfur contents and dehydration of water content respectively. The reactions are as

$$1.8\,CuS \longrightarrow Cu_{1.8}S + 0.8\,S$$
$$CuS \cdot H_2O \longrightarrow CuS + H_2O$$

Around 320 ^oC, a large exothermal peak can be seen in DSC curve as well as a mass increment of about 20 % was observed around 625 ^oC, which indicates oxidation of copper sulfides to form copper sulfate and oxisalfate as confirmed by TGA and DTGA peaks. The reaction can be written as

$$2CuS + 2O_2 \longrightarrow 2CuSO_4$$
$$2\ CuS + O_2 \longrightarrow Cu_2S + SO_2$$
$$2Cu_2S + 5O_2 \longrightarrow 2CuO{\cdot}CuSO_4$$
$$4\ CuS + 8O_2 \longrightarrow 2\ CuO\text{-}CuSO_4 + 3SO_2$$

Similarly, in the temperature range of 630-840 ^{o}C, a downward trend of TGA curve represents a heavy weight loss (45 %) associated with endothermic DSC peak, resulting in conversion of copper sulfate and oxisalfate to copper oxides (CuO, Cu_2O), as.

$$20\ Cu_{1.8}S + 47O_2 \longrightarrow 18\ CuO{\cdot}CuSO_4 + 2\ SO_2$$
$$2\ CuO{\cdot}CuSO_4 \longrightarrow 4\ CuO + 2\ SO_2 + O_2$$

To confirm the phase changes in sample 'a', DSC/TGA was performed under continuous supply of nitrogen at 100 ml/min maintaining ramp rate of 10 ^{o}C / min. The oxidation process and formation of SO_2 and sulfates were limited during the whole scan. It can be seen from figure 3b that weight loss (32 %) occurs below 320 ^{o}C is due to the removal of water content and at 500 ^{o}C, CuS was converted into $Cu_{1.8}S$ and Cu_2S with 15 % mass loss in the sample. No mass increment of exothermic oxidation was observed confirming the unavailability of oxygen as can be seen from the following reaction.

$$CuS{\cdot}H_2O \longrightarrow CuS + H_2O$$
$$1.8\ CuS \longrightarrow Cu_{1.8}S + 0.8\ S$$

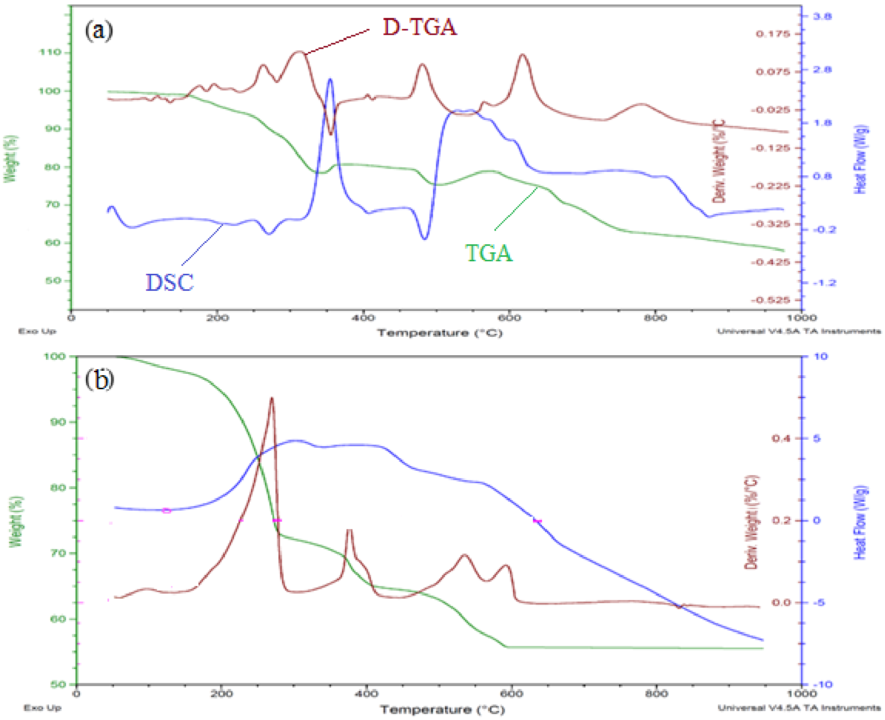

Fig. 4 : DSC/TGA of CuS nanoparticles sample b in air (a) and N_2 (b).

Thermal analysis of sample 'b' was performed with previously set condition in the air as well as in nitrogen atmosphere which is shown in Fig. 4(a)-(b) respectively. The decomposition proceeds in the following steps. TGA curve depicts that the first mass loss upto 300 ^{o}C is due to the removal of water content and corresponding endothermic peak emerged at 275 ^{o}C. Further, a small mass increment is observed at 370 ^{o}C with a sharp exothermic peak, which point out the formation of copper sulfate and/or

oxysulfate. The endothermic mass loss at about 500 ^{o}C represents that partial decomposition of $CuSO_4$ is present in the sample as identified in the XRD graph (Fig 1a). Moreover, mass escalation around 575 ^{o}C corresponds to the formation and decomposition of copper sulfate and oxysulfate to form CuO.
When sample "b" was treated under nitrogen environment with same conditions as discussed above, TGA curve depicts a mass loss (27 %) from 50-270 ^{o}C because of water content in sample and other weight losses occur at 400 ^{o}C and 600 ^{o}C are associated with formation of low content copper sulfides ($C_{1.8}uS$ and CuS) and decomposition of $CuSO_4$ contents existing in the sample respectively as.

$$CuSO_4 \xrightarrow{\hspace{3cm}} CuO + SO_2 + 0.5\, O_2$$

4. Conclusions

CuS nanomaterial has successfully synthesized using different precursor materials under microwave irradiation for various times. The XRD pattern revealed that sharp and intense peaks representing the crystallinity in CuS. The resulted CuS nanomaterial has spherical morphology with average particle size of 600 nm. Copper sulfide thermal oxidation behavior is an astounding and multi-step process. Allied phase changes are very much dependent on synthesis method adopted. During heating progression in air atmosphere, CuS releases the SO_2 and produce Cu_2S and $Cu_{1.8}S$ at 200-300 ^{o}C. This lead to an exothermic conversion of copper sulfate and oxysulfate at relatively higher temperature 400 to 600 ^{o}C, subsequently endothermic decomposition of copper sulfate and oxysulfate occur to form CuO. There is no mass increment observed in nitrogen environment due to unavailability of O_2 required for the thermal oxidation process.

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