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Morphology Controlled Synthesis of Copper Sulphide Microparticles by using Various Copper Precursors

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Abstract: **The present study revealed the effect of different copper salts on the morphological patterns of copper sulphide crystals. Different copper precursors such as copper chloride, copper nitrate, copper sulphate and copper acetate have been used for this purpose. Various morphologies of copper sulphide microparticles like different types of dendritic flowers, hexagonal, triangular, and spherical particles have been synthesized successfully. The product molecules were identified by using XRD and the morphological patterns of the crystals were observed by SEM.**

Index Terms: **Copper sulphide, Crystal morphology, Precursor effect, Solvothermal synthesis, X-ray diffraction pattern**

I. Introduction

Research work on particle size and shape tailored synthesis of semiconducting metal chalcogenides has drawn much attention for the past few years due to their interesting properties and important applications in various fields. Among other chalcogenides, copper sulphide, a good prospective optoelectronic material, has been widely used for various applications like electro conductive coatings (Yamamoto et al., 1992), solar cell (Neville, 1995), electrodes (Minghui et al., 2010), catalysis (Li et al., 2011), low temperature gas sensor applications (Sagade & Sharma, 2008), selective radiation filters, photodetectors (Nair & Nair, 1991), nanoscale switches (Sakamoto et al., 2003), superionic materials (Balapanov et al., 1986), efficient photo catalyst (Peng et al., 2009), biosensors (Lee et al., 2007) etc. As the tuning of properties of copper sulphide can be done by varying the shape, size and stoichiometric composition of the molecule (Lee et al., 2007; Zhao et al., 2009), an array of techniques (Gorai et al., 2004 & 2005 ab; Liu et al., 2005; Du et al., 2006; Lee et al., 2007; Peng et al., 2009; Zhao et al., 2009; Mousavi-Kamazani et al., 2012; Li et al., 2016; Wei et al., 2016; Rahmani et al., 2017) have been utilized to synthesize copper sulphides having controllable nano/microstructures. In our previous paper (Gorai et al., 2005ab) we reported the formation of dendritic flower like structure of copper sulphide crystals by employing $Cu(NO_3)_2$ as Cu-precursor and ethylenediamine (en) as solvent through solvothermal technique. In the present work, for the development of copper sulphide crystals with varying morphologies, a combination of various copper salts (as the source of copper) with thiourea in presence of ethylenediamine solvent under solvothermal condition were used. This is done for gathering an idea about the role of different copper precursors in controlling the shape of copper suphide [Cu_xS ($x \leq 2$)] in presence of ethylenediamine solvent. The experimental results indicate the formation of different morphological patterns as a function of the selection of copper precursors. The findings of the present paper may be applicable for the shape tailoring of nanoparticles also under suitable conditions. It was observed from the previous literature (Galdikas et al., 2000) that thick films of Cu_xS can be used for the detection of CH_3COCH_3 (acetone), C_2H_5OH (ethanol), and ammonia (NH_3) gas at room temperature. Another study revealed that the gas sensing ability can be varied with the variation of stochiometry and morphological patterns of Cu_xS materials (Setkus et al., 2001). Therefore, copper sulphides having different microstructures synthesized by the present method may be applied to detect CH_3COCH_3, C_2H_5OH and NH_3 gas.

II. Experimental

Copper sulphide synthesis was done by choosing four different Cu(II) precursors namely, $Cu(NO_3)_2$, $Cu(CH_3COO)_2$, $CuCl_2$ and $CuSO_4$. A mixture of 4 mM of one type of copper salt

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along with 2 mM of NH_2CSNH_2 (thiourea) was taken into a Teflon-lined steel autoclave and four different sets of reactions were performed by taking the four said copper precursors. In each case 75% volume of the autoclave (70 ml) was filled up with ethylenediamine and was kept into an oven at 130°C for 12h. Finally, at room temperature the black product was collected. It was washed many times with water and ethanol, respectively. In a vacuum at 60°C, the washed product was dried for 3h. The obtained powder samples were named Sample I, II, III and IV, respectively.

The synthesized samples were identified by XRD (Seifert, 3000P) using monochromatic CuKα radiation (Ni filter). The morphological patterns and particle size of the samples were estimated from SEM (Hitachi, S-2300).

III. RESULTS AND DISCUSSION

Figure 1(a-d) represents the XRD spectra of the products obtained from nitrate, acetate, chloride, and sulphate salt of copper respectively. The diffraction peaks of the samples synthesized from nitrate, acetate and chloride salt of copper show the formation of monoclinic Cu_2S [JCPDS No. 33- 0490], whereas the sample obtained from sulphate salt of copper corresponds to Cu_7S_4 [JCPDS No. 33-0489].

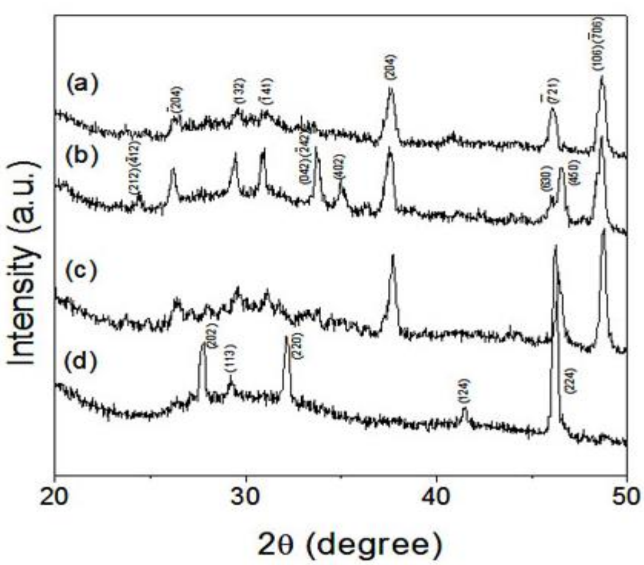

Fig. 1. XRD spectra of the products obtained from (a) nitrate, (b) acetate, (c) chloride, and (d) sulphate salt of copper.

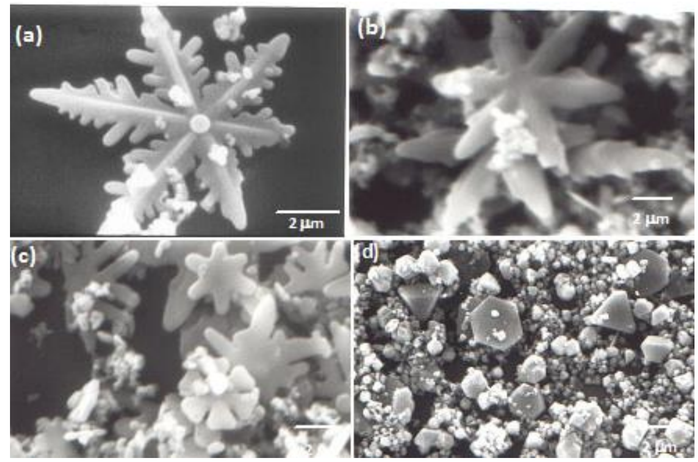

Fig. 2. SEM images of the samples obtained from (a) nitrate, (b) acetate, (c) chloride, and (d) sulphate salt of copper.

Figure 2(a-d) represents the SEM images of samples I, II, III and IV respectively. The figures (a-c) show that samples prepared from nitrate, acetate, chloride salt of copper have six petals flower-like morphology, but the patterns of flower-like shape and size changes with the changing of copper salts. In case of using sulphate salt of copper various shaped crystals like hexagonal, triangular, and spherical are observed (figure 2d).

In our previous paper (Gorai et al., 2005a) a probable mechanistic pathway for the development of a flower like pattern was reported. It was observed that ethylenediamine played an important role to control the morphological pattern and chemical composition of copper sulphide crystals at a constant temperature (130°C) (Gorai et al., 2005a). In the present reaction condition, different copper salts were dissolved in ethylenediamine solvent by forming copper ethylenediamine complex. This complex ion may form self-assembly (by linking via hydrogen bond) under the solvothermal treatment which assists to grow oriented molecules (Li et al., 1999). In the autoclave, at high temperature and pressure activated ethylenediamine reduced the Cu^{2+} ion to Cu^{+} ion (Su, 1999; Li et al., 2000). An intermediate having a chain form of metastable molecular-building blocks (Gorai et al., 2005b) was developed by the reaction of thiourea molecules with the aforesaid complex ions (Eq. 3). The stability constant ($\log_{10}\beta_2$) values for $[Cu(en)_2]^{2+}$ (20.0) and $[Cu(en)_2]^{+}$ (10.8) reveal that when Cu^{2+} is reduced to Cu^{+}, the stability of $[Cu(en)_2]^{+}$ is decreased. Therefore, with the increase of reaction temperature, deamination from the aforesaid complex species took place (Su, 1999) and finally at our optimum reaction condition thiourea molecule dissociated and copper sulphide was formed.

The probable reaction mechanism of the formation of Cu_xS ($x \leq 2$) in presence of ethylenediamine are given below:

$$Cu^{2+} + n\,en \rightarrow [Cu(en)_n]^{2+} \qquad Eq. (1)$$

$$[Cu(en)_n]^{2+} \xrightarrow[(in\ autoclave)]{under\ high\ temp.\ \&\ Pressure} [Cu(en)_n]^{+} \quad Eq.(2)$$

$$[Cu(en)_n]^{+} + xNH_2CSNH_2 \rightarrow [(Cu(en)_n]^{+}.xNH_2CSNH_2 \quad Eq.(3)$$

$$[Cu(en)_n]^{+}.xNH_2CSNH_2 \xrightarrow[decomposition\ of\ thiourea]{130℃,\ 12h,\ deamination} Cu_xS \ Eq.(4)$$

Figure 3 depicts the formation of copper sulphides with different morphologies on changing the anions (used in the different copper precursors). The rate of formation of the copper ethylenediamine complex and the deamination rate from the complex species (under heat treatment) depend on the counter anion present in the copper precursor (Prabhumirashi & Khoje, 2002). These steps follow different mechanistic pathways depending on the counter anion present with the complex species (Prabhumirashi & Khoje, 2002), leading to the growth of the product molecule (nuclei). The growth rate differences and preferential adsorption of anions onto the crystal planes of the product molecule dictate the morphology of the final products.

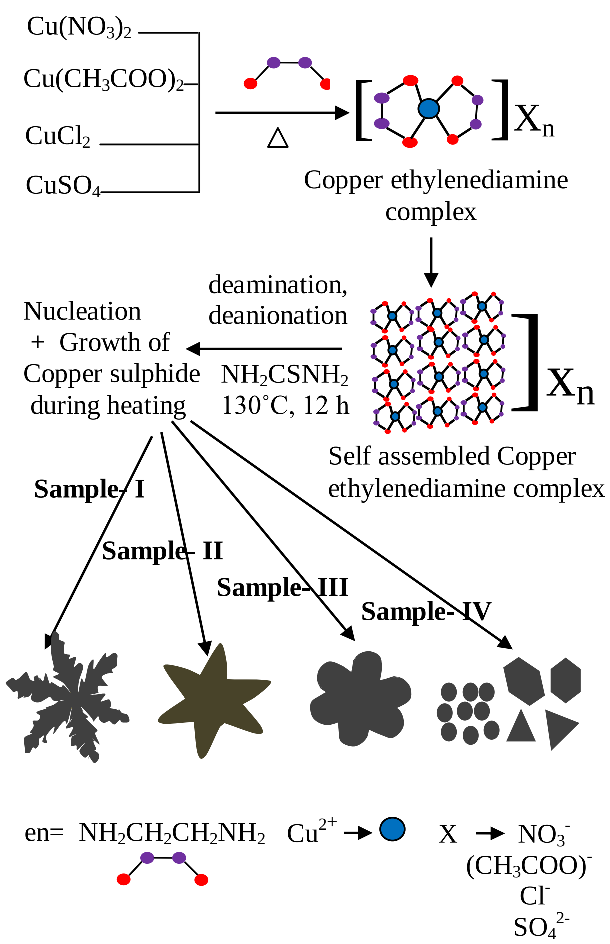

Fig. 3. Schematic diagram of the formation of different self-assembled Cu_xS microstructures obtained by using different copper salts.

A previous study (Prabhumirashi & Khoje, 2002) on thermal decomposition of copper(II)ethylenediamine complex revealed that the deamination step in ethylenediamine complexes of copper nitrate, acetate and chloride followed nearly phase boundary reactions, cylindrical symmetry (R_2) mechanism whereas, for ethylenediamine complex of copper sulphate, random nucleation F_1 mechanism was followed. This may lead to a similar type of growth (in the present case, dendritic flower-like) when copper nitrate, acetate and chloride salts were used and a different type for using copper sulphate precursor. The variations in the patterns and size of flower-like dendrites in samples I, II and III may be explained by considering that the adsorption of a specific anion on some crystallographic planes results in the variation of solid-liquid interfacial energy which would change critical nucleus size for particular anionic system (Celikkaya & Akinc, 1990; Singh et al., 2013). On the other side, the anions adsorb onto a particular crystal face of copper sulphide may hinder the growth in that particular plane and accelerate the growth in other planes, leading to copper sulphide particles with different morphologies.

CONCLUSION

Different Cu(II) salts and thiourea were treated at 130°C for 12 h in presence of ethylenediamine solvent under solvothermal condition. The precursors have played a significant role in altering the morphological pattern of the copper sulphide. Powder prepared from nitrate, acetate, chloride salt of copper have six petal flowers like morphology, but the patterns of flower like shape and size changes with the changing of copper salts. A mixture of various morphological patterns like hexagonal, triangular and spherical are observed when copper sulphate is used as precursor material.

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