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ORIGINAL ARTICLE

The novel and economical way to synthesize CuS nanomaterial of different morphologies by aqueous medium employing microwaves irradiation

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Abstract CuS nano/submicro materials with different morphologies were synthesized with spherical, tubular, leaf-like and strip type structures in a simple aqueous system under microwave irradiation and sunlight and employing Cu $(CH_3COO)_2$, $CuSO_4{\cdot}5H_2O$, $CuCl_2$, and as copper source and H_2NCSNH_2, $Na_2S_2O_3{\cdot}5H_2O$ and CH_3CSNH_2 as sulfur sources. The starting materials were used without assistance of any surfactant or template. An X-ray powder diffraction pattern confirms that the product was CuS with hexagonal phase. Scanning electron microscopy was used to observe the morphologies of the product. Different Phase transitions in CuS with respect to temperature are studied by DSC/TGA. The dependence of morphologies of product on different experimental conditions was also discussed.

Keywords CuS · Nanomaterial · Self assembly · Morphology · Thermal oxidation · Scanning electron microscopy · X-ray diffraction

Introduction

Since the past few years, researchers are showing inclusive concentration on the study of the appropriate control over the size and shape of Nanomaterials. Nanomaterials show illustrious and exceptional chemical, optical, catalytic, magnetic, and electronic properties depending on the size of the nanoparticles (Shipway et al. 2000; Wong et al. 2002). Self-assembly technique offers chances to utilize the distinctive optical and electronic properties of nanoparticles and promise to investigate new prospectively collective trends (Lu et al. 2002). The assembly of nanoparticles is understood through intermolecular force, electrostatic interaction, and hydrogen bonding, etc. Thus, to synthesize nanomaterials effectively by the means of self-assembly, an elegant reaction is mandatory to fabricate nanoparticles with a fine size distribution and a high extent of shape control, and to accumulate the formed nanoparticles into a desired nanostructure concurrently (Brust and Kiely 2002), such as ordered clusters (Brousseau et al. 1999), spherical shape (Boal et al. 2000), and tubular shape (Wu et al. 2006; Ni et al. 2004). On the other hand, compared with the synthesis of distinct nanoparticles, the well-defined superstructures of nanoparticles by self-assembly is a challenge in material science. Copper monosulfide (CuS) is renowned as one of the vital transition metal semiconductors (Cui et al. 2004) It can also be used as p-type semiconductors (Sakamoto et al. 2003). CuS covellite stacked CuS4–CuS3–CuS4 layers which are held together by covalent S–S bonds (Nair and Nair 1989) thus introducing notable properties in it. As a useful mineral, have outstanding potential optoelectronic material. It is a potential candidate for solar cell application, IR detectors, sensors, electrochemistry cells, and catalysts (Yang et al. 1997; Ahmadi et al. 1996; Lindroos et al. 2000; Erokhina et al. 2003; Podder et al. 2005; Setkus et al. 2001; Blachnik and Muller 2000; Rodriguez et al. 2000; Huang et al. 2001), There are many ways adopted to the synthesize CuS, such as solid-state reaction (Wang et al. 2006), hydrothermal

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synthesis (Tezuka et al. 2007; Jiang et al. 2005) sonochemical treatment (Xu et al. 2006), and photochemical deposition method (Yang et al. 1997). In this current research, micro- and nano-sized CuS material with different morphologies such as assemblies of nanoparticles into solid spheres, leaf-like and strip-type structures were successfully synthesized from different copper and sulfur sources in aqueous medium by exposure of microwave irradiation and under sunlight. No templates and catalysts were used in the method, which is very simple and novel.

Experimental work

Materials

All reagents used in this experiment were of analytical grade purity, purchased from the commercial market, and were used without further purification. For all the reactions, the copper acetate mono hydrated Cu $(CH_3COO)_2{\cdot}H_2O$, copper chloride $CuCl_2$ and copper sulfate pantahydrate $CuSO_4{\cdot}5H_2O$ were used as Cu sources, and thiourea (Tu) H_2NCSNH_2, thioacetamide CH_3CSNH_2 and sodium thiosulfate pantahydrate $Na_2S_2O_3{\cdot}5H_2O$ were used as sulfur sources, respectively.

Sample 1

In this sample H_2NCSNH_2 as sulfur source provides the sulfur ion for the reaction and similarly Cu $(CH_3COO)_2{\cdot}H_2O$ as copper sources provides the copper ion for the reaction. Solutions were prepared for copper and sulfur sources for required molarities in 1:2 ratios. Then, solution of copper source was added to solution of sulfur source dropwise under tough stirring condition. The mixed solution was then treated under microwave irradiation (2.45 GHz) at 160 W for 25 min, black ppt were formed, which were collected and washed with distil water and ethanol many times.

Sample 2 and 3

In 2nd and 3rd samples $CuCl_2$ and $Na_2S_2O_3{\cdot}5H_2O$ were used as copper and sulfur sources; aqueous solution with 2:3 molar ratio were prepared for copper and sulfur sources, respectively; dropwise addition under stirring condition was done as in sample 1 and then mixed green solution was treated in two different environments, employing microwave irradiation (180 W, 30 min) and under sunlight (max day temp $\sim$38°C); products were collected in the form of black ppt and then washed again and again with distilled water and ethanol.

Sample 4

We dissolved 7 mmol $CuSO_4{\cdot}5H_2O$ and 21 mmol CH_3CSNH_2 in 100 mL water separately and then added sulfur source solution into cooper source solution dropwise slowly under stirring condition; light green solution formed, which is treated under microwave irradiation by a domestic microwave oven at 180 W power for 30 min; black ppt formed, which were collected for washing with distilled water and ethanol many time (Table 1).

Powder X-ray diffraction (XRD) data were recorded and collected on the XRD model MPD X'PERT PRO of PANalytical Company Ltd., Holland, using Cu $K\alpha$ *as characteristic* radiation ($\lambda = 0.15418$ nm) with θ–θ configuration. The measurements were made in 2θ ranging from 20° to 70°. Study was mainly done by the software X'Pert HighScore of the same company. Scanning electron microscopy (SEM) images were taken using a scanning electron microscope (JOEL JSM-6480). **a** Differential Scanning Calorimeter (DSC) and thermal thermogravimetric analysis (TGA) were performed by SDT Q600 of TA Instrument in control environment for thermal Oxidation, weight loss, and Phase changes in Copper Sulfide.

Characterization of the product

Figure 1 give the XRD patterns for the synthesized products. Samples were well crystallized. All diffraction peaks can be indexed as the hexagonal CuS by comparison with data from JCPDS file no. 00-001-1281 with lattice constants $a = 3.8020$ Å, $b = 3.8020$ Å and $c = 16.4300$ Å; no other characteristic peaks of any other impurity were observed.

The morphologies of the as-prepared CuS nanotubes were investigated by SEM. In Fig. 2a, tubes and some aggregated particles were observed with an average thickness, or diameter of tubes is 150 nm. The length of the tubes is some microns. Fig. 2a, b illustrates other SEM images, which were magnified by 30,000 and 40,000 times. In these images copper sulfide nanotubes were more prominent and can be seen easily.

The morphologies of the as-synthesis nanospheres were investigated by SEM (Fig. 3). Many spheres and cumulated

Table 1 Reaction parameters for different morphologies

CuS morphology	Cu:S	Environment	Power (W)	Time
Tubular	1:2	Microwave irradiation	160	30 min
Leaf-like	2:3	Microwave irradiation	180	25 min
Strip type	2:3	Sunlight	~	6 h
Spheres	1:3	Microwave irradiation	180	30 min

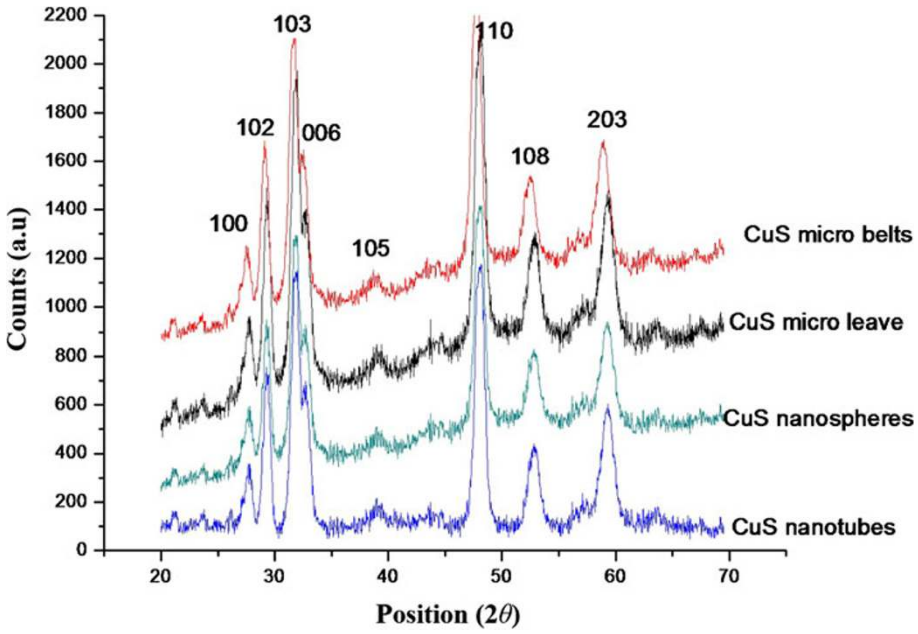

Fig. 1 XRD pattern of CuS nanomaterial

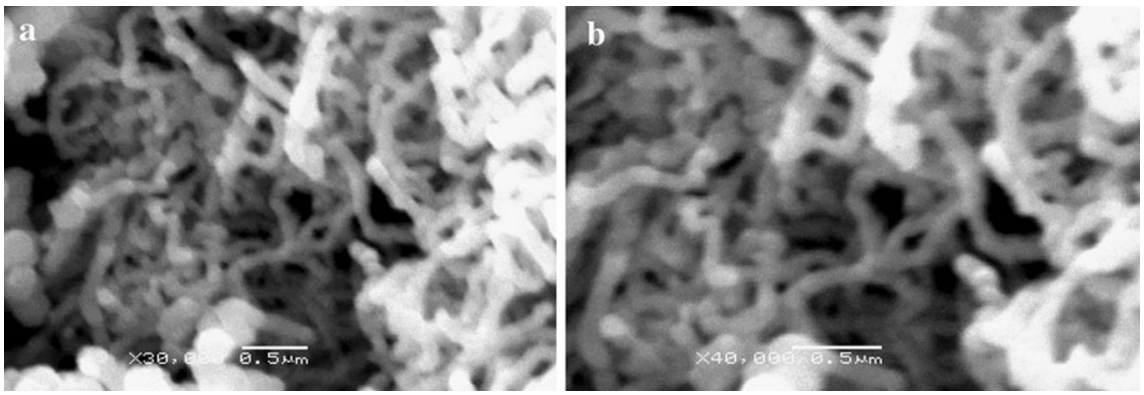

Fig. 2 **a**, **b** SEM image of the product with tubular morphology prepared from the system of the starting Cu $(CH_3COO)_2/H_2NCSNH_2$ molar ratio of 1:2

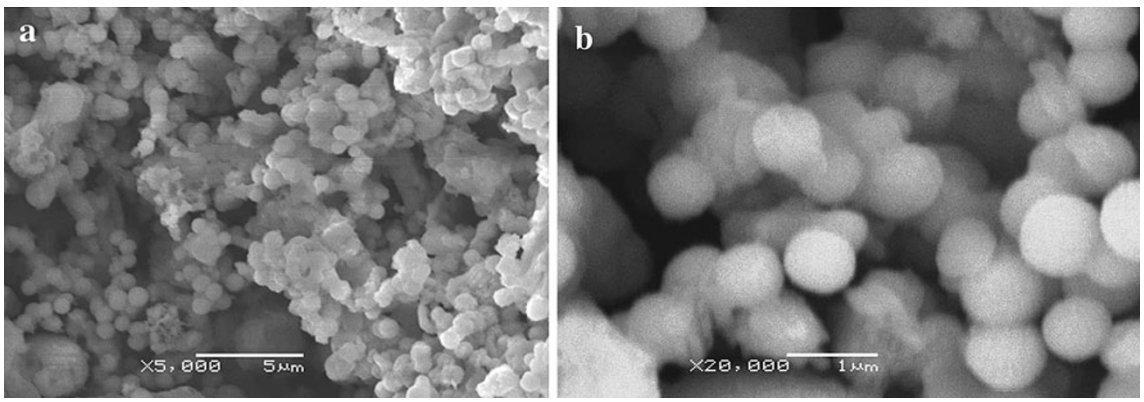

Fig. 3 **a**, **b** SEM images of the product with sphere morphology prepared from the system of the starting $CuSO_4/CH_3CSNH_2$ molar ratio of 1:3

particles are observed. In Fig. 3a, besides some aggregated particles, mostly spheres have radius in the range of 400–600 nm. Figure 3b shows another SEM image, which was magnified 20,000 times; a few particles can be visibly seen on the spheres. Figure 3a, b shows that the size distribution is not very wide.

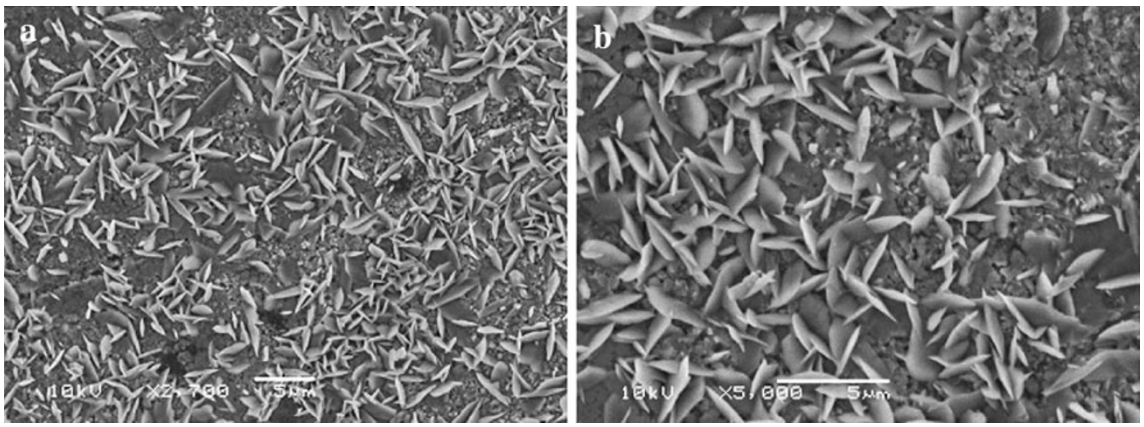

Fig. 4 SEM images of the product with leave-like morphology prepared from the system of the starting $CuCl_2/Na_2S_2O_3$ molar ratio of 2:3

For sample 2, the leaf-like morphology was observed in SEM images, as shown in Fig. 4a, b. These leaves have very sharp edges; the average length of these leaves is 2.5 μm, but at the edges are very thin as compared with length, which is nearly of 200 nm; here we can also see aggregated nano particle around the leaves.

The third sample prepared under sunlight has solid strip-type morphology which is clearly observed in Fig. 5. These strips have length and width of few microns; this sample was treated under sunlight which possesses a range of radiation of different frequency; that is why they have a random type of shape.

It was established that the morphologies of the product were associated with the molar ratio of copper and sulfur sources, the starting materials. Three solutions were prepared with different copper and sulfur sources having molar ratios of 1:3 and 2:3, using different environment. In our experiment, the system contains only three components: water, copper and sulfur ion sources. The arrangement and self-assembly of CuS nanoparticles are associated with the interaction between copper and sulfur ion sources, in sample 1, During the synthesis, Cu $(CH_3COO)_2$ reacts with H_2NCSNH_2 in water in numerous steps and copper complex ($[Cu(H_2NCSNH_2)]^{2+}$) was produced. Then, the complex was decomposed to CuS by microwave irradiation (Chen et al. 2003). H_2NCSNH_2 and H_2O react to produce H_2S. Afterward, microwave irradiation decomposed H_2S (Huang et al. 2004). S^{2-} produced and further reacted with Cu^{2+} to produce CuS; in sample 4, CH_3CSNH_2 reacts with copper source in similar fashion as H_2NCSNH_2:

$$Cu^{+2} + (NH_2)_2CS \rightarrow Cu\left[(NH_2)_2CS\right]^{+2}$$

$$(NH_2)_2CS + H_2O \rightarrow 2NH_3 + CO_2 + H_2S$$

$$Cu\left[(NH_2)_2CS\right]^{+2} + H_2S \rightarrow CuS(\text{nanoparticles}) + (NH_2)_2CS + 2H^{+1}$$

$$n\ CuS\ (\text{nanoparticles}) \rightarrow [CuS]_n(\text{nano material})$$

For sample 2 and 3, $CuCl_2$ and $Na_2S_2O_3$ are used as copper and sulfur sources.

It is well known that a $S_2O_3^{-2}$ ion can hydrolyze to form H_2S, which reacts with Cu^{+2} to produce CuS.

$$S_2O_3^{-2} + H_2O \rightarrow SO_4^{-2} + H_2S$$

$$Cu^{+2} + H_2S \rightarrow CuS\ (\text{nanoparticles}) + 2H^{+1}$$

$$n\ CuS\ (\text{nanoparticles}) \rightarrow [CuS]_n(\text{nano material})$$

Availability of Sulfur and copper ions play very important role in the formation of different morphologies; when we kept the ratio as 2:3, S^{2-} coordinated with Cu^{2+} to form CuS nanoparticles, S^{2-} ions are more then Cu^{2+}; they could not aggregate with CuS in max dimension, so two-dimensional structure was obtained. When we use 1:3 ratio, S^{2-} ions had many more ways to aggregate with Cu^{2+} and that is why spherical morphology was formed.

From the above discussion it may be concluded that, with change in nature of irradiation and molar ratio, reaction kinetics are strongly affected and morphology of the product may be changed.

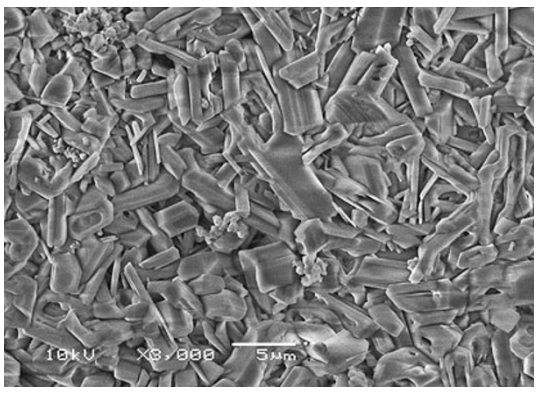

Fig. 5 SEM image of the product with strip-type morphology prepared from the system of the starting $CuCl_2/Na_2S_2O_3$ molar ratio of 2:3

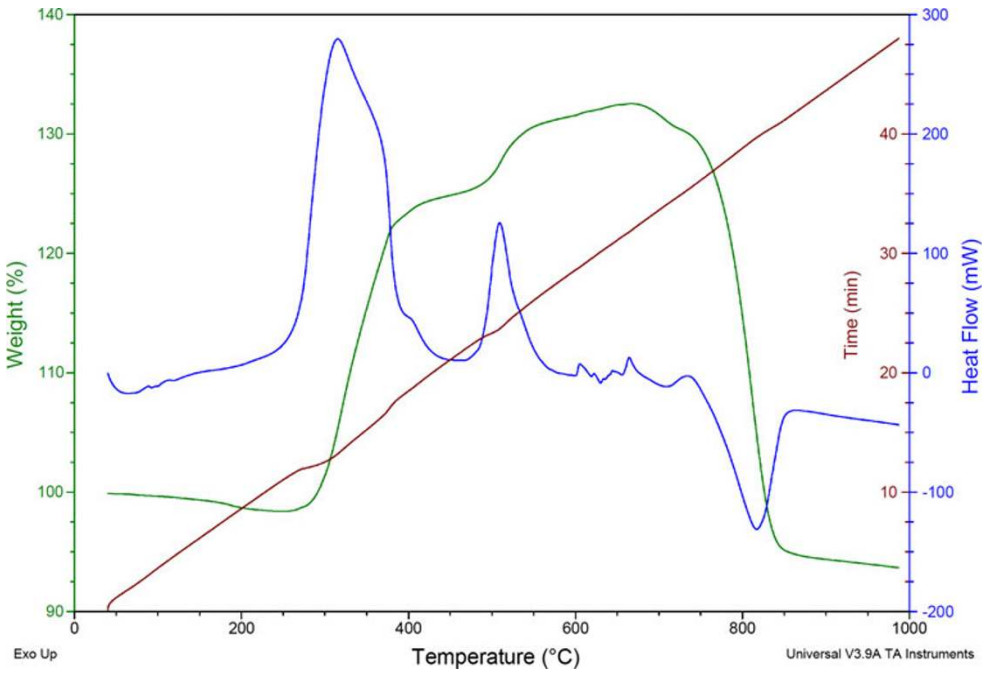

Fig. 6 DSC/TGA of copper sulfides (CuS)

Thermal behavior of CuS

Differential Scanning Calorimeter (DSC) and thermal thermogravimetric analyses (TGA) for CuS were done by SDT Q600 of TA Instrument in air; the thermal decomposition curves (DSC/TGA) of copper sulfides (CuS) are depicted in Fig. 5.

Mainly, the thermal decomposition of natural and synthesized CuS studies reveals the involvement of four steps (Chen et al. 2006; Kontny et al. 2000; Godoiková et al. 2006):

1. Formation of sulfides (Cu_2S) with lesser sulfur content linked with evolved SO_2.
2. Oxidation of the presented sulfides moreover to copper oxides (Cu_2O and CuO).
3. By reaction of copper oxide, oxygen and releasing SO_2, oxysulfates ($CuSO_4$, and $CuO{\cdot}CuSO_4$) are formed
4. Decomposition of oxysulfates gives CuO

CuS suffers a minute mass loss at 275°C, which is due to the partial conversion of CuS to Cu_2S. Conversion to Cu_2S is an exothermal reaction; corresponding exothermic peak appears out at 270°C in the DSC as clearly seen in Fig. 6. It was followed by a mass increment of 20% at 380°C, which is related to the oxidation of copper sulfides (CuS, Cu_2S) to $CuSO_4$ and again more 10% mass increment due to $CuO{\cdot}CuSO_4$ formation; then a huge mass loss took place after 700–830°C, which is said to have been caused by the conversion of $CuO{\cdot}CuSO_4$ and $CuSO_4$ to CuO; corresponding endothermic peak emerges at 820 (Table 2).

Table 2 Phase changes during DSC/TG

Conversion	Temperature (°C)	Mass variation (%)	Heat flow (mW)
CuS Cu_2S	275	−3	+20
CuS, Cu_2S $CuSO_4$	380	20	+250
CuS, Cu_2S $CuO{\cdot}CuSO_4$	500	10	+90
$CuO{\cdot}CuSO_4$, $CuSO_4$ CuO	780	−48	−135

Conclusion

CuS with Different Morphologies has been successfully prepared in a simple aqueous base system, using different copper and sulfur ion sources, treated under microwave irradiation and sunlight. Experimental results shows fine morphology (spherical, tubular leave-like, strip-type) of synthesized CuS. The time, nature of radiation (microwave or Sunlight), power of the microwave oven and the molar ratio of copper and sulfur sources effect the formation of products. Uniform structure was abstained by using microwave irradiation due to cyclic process. The decomposition of copper sulfide (CuS) is multifaceted in nature. The related solid state transformations and phase changes depend upon synthesizing route. Thermal decomposition of CuS gives Cu_2S at 275°C then converted to $CuSO_4$ at 380°C, and then $CuO{\cdot}CuSO_4$ formed at 500°C, $CuSO_4$ shows much stability and decomposed at 780°C into CuO.

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