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ScienceDirect
Materials Letters 62 (2008) 2567–2570
materials letters
www.elsevier.com/locate/matlet

Single-crystal snowflake of Cu_7S_4: Low temperature, large scale synthesis and growth mechanism

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Received 13 November 2007; accepted 20 December 2007
Available online 28 December 2007

Abstract

Non-stoichiometric copper sulfides (Cu_7S_4), with uniform hexapetalous snowflake-like morphology in high yield have been synthesized successfully by a simple and facile one-step solvothermal route with a low temperature (150 °C). Copper chloride and thiourea were chosen as the reactants in an ethylenediamine solution. The role of ethylenediamine as a structure-directing coordination molecular template responsible for the morphologies of the copper sulfides and its role as a reducing agent for the non-stoichiometric have been discussed. In addition, temporal growth of the dendrites can be readily followed in this preparation via time-resolved microscopic analysis. The formation mechanism based on the experiments has been proposed.

Keywords: Crystal growth; Nanomaterial; P-type semiconductors; Diffusion-limited process

1. Introduction

Low dimensional systems with specific size and morphology offer fundamental scientific opportunities for studying the influence of shape and size with respect to physical and chemical properties. As p-type semiconductors [1,2], copper sulfides are good prospective optoelectronic material [3,4], which are often used as components of solar cells [5,6], candidates of high temperature thermistors [7], superionic materials [8] and in many chemical sensing applications [9,10]. Because of its unique optical and electrical properties, copper sulfide is also widely used as thin films [1,11], and composite materials [5,12]. Various methods such as solid-state metathesis reaction, self-propagating high temperature synthesis, CVD, and Microwave assisted Elemental-Direct-Reaction route have been developed to prepare copper sulfide system [13,14]. Recently, nanocrystalline copper sulfides were prepared by a hydrothermal process. Using reductant, Cu_7S_4 was also prepared from Cu_9S_8 in a relative low temperature chemical process [15]. However, for methods mentioned above, templates, reductants, or a high temperature treatment were required. Up to now, few studies have reported on one-step synthesis route of Cu_7S_4 crystal.

Herein, we report a simple route to grow six-fold symmetric Cu_7S_4 crystal with snowflake-like morphology via a mild one-step solvothermal process at a relatively low temperature. Surfactants or a further reduction step was not needed in our synthesis route. With the heat treatment time increasing, the obtained products exhibit a dendrite crystal growth process.

2. Experimental section

All the reagents used in the following experiments are analytical grade without further purification (purchased from Shanghai chemical Industrial Co.). Ethylenediamine (EN) was used as solvent and complexing reagent. Thiourea was adopted as the sulfur source, and copper chloride as the copper source. In a typical synthesis process: 0.618 g copper chloride was put into 50 ml ethylenediamine under continuous stirring. When the solution color changed from transparent to dark blue, 0.182 g thiourea was added into the above solution. After 10 min stirring, these solutions were transferred into Teflon lined stainless steel autoclaves, which were sealed and maintained at 150 °C for 12 h. Different reaction time experiments of 2 h, 4 h, and 8 h

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0167-577X/$ - see front matter
doi:10.1016/j.matlet.2007.12.050

were carried out, while the other conditions were kept unchanged. After the reaction has completed, the resulted gray precipitate was centrifugalized, washed several times with deionized water and ethonal, and finally dried at 60 °C for 4 h in air.

The morphologies of the synthesized samples were characterized by field emission scanning electron microscopy (FE-SEM, FEI, Sirion 200). The composition of the product was detected by energy dispersive X-ray spectroscopy (EDX) attached to the FE-SEM. X-ray photoelectron spectrum (XPS) was used to further confirm the formation of the product. The crystal structure of the sample was examined by X-ray diffraction (XRD, Philips PW-1710 X'Pert diffractometer with Cu Kα radiation $\lambda = 1.5406$ Å).

3. Results and discussion

Well-defined snowflake-like Cu_7S_4 crystals (12 h for heat treatment time) are shown in Fig. 1(a). The image demonstrates that the six-fold symmetric hierarchical nanostructures are in large quantity and uniform shape. From the high magnification image of Fig. 1(b), Cu_7S_4 has a unique flat snowflake-like structure with six symmetrical dendritic trunks extending radially from the center. Each trunk has two sides of branches growing outwards at about 60° to the trunk and in the same plane. The length of trunk and branches ranges about 2 μm and 0.2 μm.

Fig. 2(a) shows the XRD patterns of the synthesized samples (12 h for heat treatment time). All the reflections in the pattern can be indexed from those of a standard sample of Cu_7S_4 [JC-PDS card no: 23-0958], indicating the pure Cu_7S_4 has been obtained. EDX-spectrum of copper sulfides was shown in Fig. 2(b). The peak at 2.31 keV is from sulfide, and the peaks at 0.95, 8.04, and 8.09 keV are due to copper, respectively. The corresponding EDX result shown in Fig. 2(b) also reveals that the products are only composed of Cu and S elements with an atomic ratio of Cu to S about 7:4. The composition inferred from the EDX pattern is consistent with the XRD result.

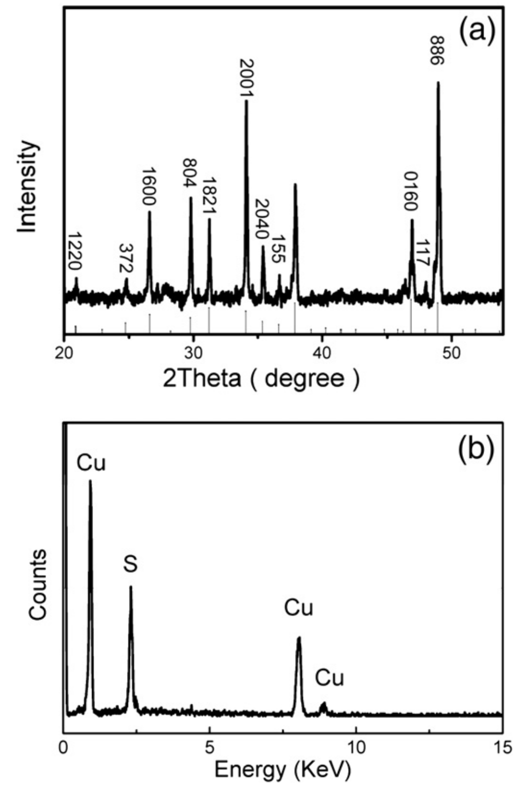

Fig. 2. XRD pattern of the as synthesized copper sulfides (12 h). The bars indicate the peak positions and relative strengths given in JC-PDS 23-0958 (a) and the corresponding EDX results (b).

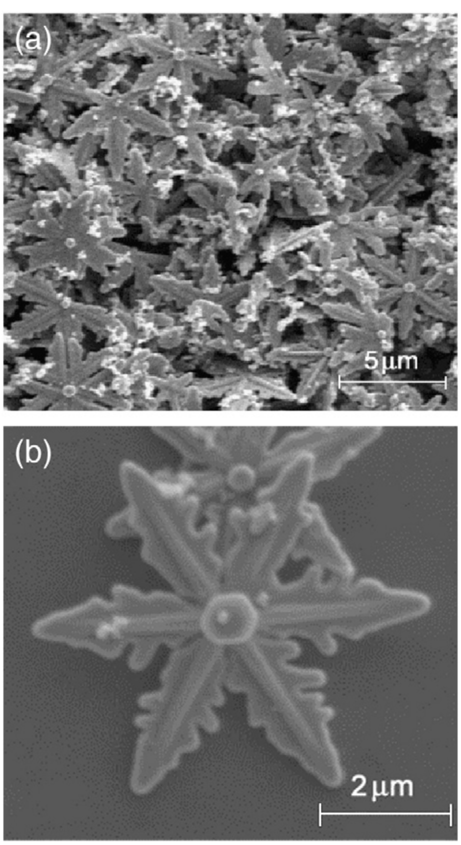

Fig. 1. The image of the as synthesized copper sulfide (12 h) crystals (a) and the high magnification FE-SEM image of the products (b).

X-ray photoelectron spectrum (XPS) can further confirm the formation of the product. As shown in Fig. 3(a), the binding energy values are 932.75 eV for $Cu_2P_{3/2}$ and 952.25 for $Cu_2P_{1/2}$; Fig. 3(b) shows that S2p is 161.85 eV. These binding energies are in well-agreement with that of reported literature of Cu_7S_4 and are different from that of Cu_2S and CuS [16]. Fig. 3(c) shows that the kinetic energy of auger peak recorded from our sample is 917.2 eV, which is different from that of Cu_2S (917.6 eV) and other copper sulfides. Quantification of peaks gives a similar result with the EDX result of the sample. Pure Cu_7S_4 has been obtained.

To investigate the growth process of the snowflake-like Cu_7S_4, a series of experiments were carried out. The samples obtained in the solution process for 2, 4, 8 and 12 h (final product) were studied by FE-SEM. Three obvious evolution stages could be observed and are shown in Fig. 4. The whole process can be expressed as follows. In the initial stage (Fig. 4(a)), a hexangular tabular form appears. When the treatment time prolonged to 4 h, small ribs grow radicalized in one direction between adjacent tabular edges as shown in Fig. 4(b). After heat treatment for 8 h, the main products are in a six-branched shape (seen in Fig. 4(c)), according to which, each small rib grows up to about 200 nm. Provided a treatment time of 12 h, the products are mainly well-defined snowflake-like crystals as Fig. 1(b) shows. Consequently, a typically dendrite morphology forms; each rib grows to be a main rib

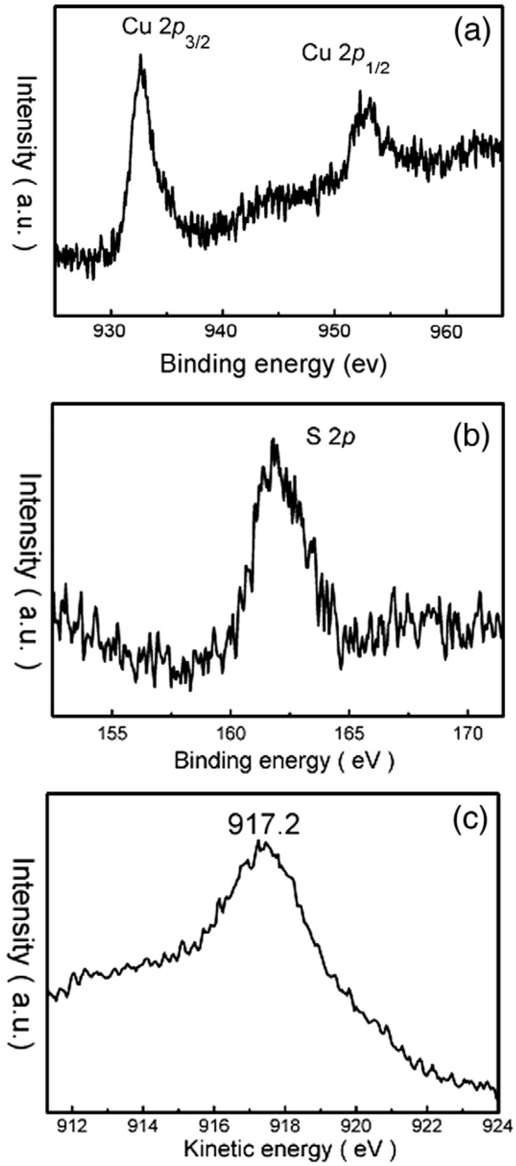

Fig. 3. X-ray photoelectron pattern of the samples (12 h). (a), (b) and (c) refer to Cu2p, S2p and the auger peak of Cu_7S_4, respectively.

with side ribs at both sides. On the basis of observed morphologies in different stages, it is obvious that the growth of snowflake-like Cu_7S_4 is initiated from the center of the crystal and extends outwards to form the trunks and later the branches, which suggest that the dendritic structures are grown through a diffusion-limited process from the crystal center [17,18] rather than through an oriented attachment of nanoparticles [19] and a rotation-induced coalescence mechanism [20]. Unfortunately it was still not clear how the nanoflowers with few petals evolved at the initial stage of the ripening process and further study of this issue is under way. On the other hand, the formation of 2D dendritic structures in an anisotropic manner in this case also indicates a possible templating effect of the EN.

The growth of dendritic Cu_7S_4 is similar to that of solvothermal synthesis of CdS nanorods in EN [21]. In our experiment, EN plays an important role. Firstly, $CuCl_2{\cdot}2H_2O$ dissolved in EN might form a complex, and the high temperature and pressure increases the reducing atmosphere and transforms the Cu^{2+} to Cu^{+} [22] in the autoclave. The complex with bi-ligands can be linked by hydrogen bond to form a self-assembly. Moreover, the S^{2-} from the decomposition of thiourea (>120 °C) may have combined with the self-organized $[Cu\ (EN)_n]^+$ to form Cu_7S_4 nucleus, which assists the oriented growth to form a hexangular tabular form at the early stage as shown in Fig. 4(a). As the temperature rises up to 150 °C, thiourea decomposes completely with the heating time being elongated. As a result, a high concentration of S^{2-} appears and causes a non-equilibrium condition for a fast crystallization rate. Thereby, a typically dendrites crystal growth process can be observed from Fig. 4(a) to Fig. 4(b), (c), and Fig. 1(b) in sequence. Pure Cu_7S_4 was obtained under a high temperature and an auto-generated vapor pressure [23].

In summary, uniform hexapetalous snowflake-like Cu_7S_4 nanostructures were synthesized via a simple one-step solvothermal process

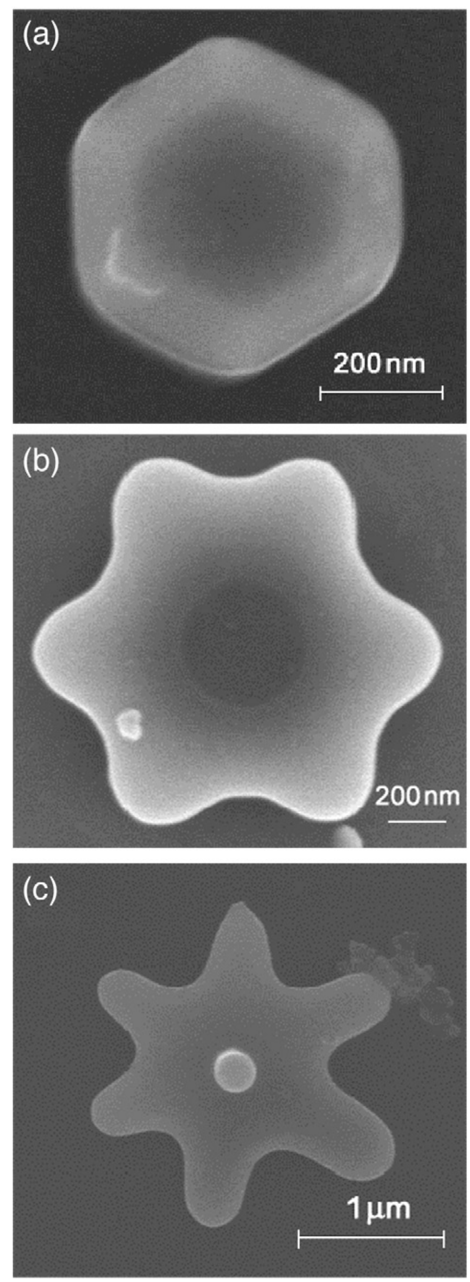

Fig. 4. FE-SEM images of typical copper sulfide crystal synthesized at different heat treatment time. (a) Hexagonal tabular form (2 h); (b) quasi gear-like hexangular tabular form (4 h); (c) gear-like tabular form with six-fold symmetric branches (8 h).

at a relatively low temperature. A typical dendrite crystal growth and morphology evolution progress were elucidated by the FE-SEM observations. The mechanism based on the experiments was proposed.

Acknowledgments

This work is supported by the Major Research Plan of the National Natural Science Foundation of China (grant 90406008 and 10604055) and the National Major Project of Fundamental Research (grant no. 2005CB623603).

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