

不同温度下选择性合成硫氰酸亚铜与硫化亚铜微晶

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Selective Synthesis of CuSCN and Cu₂S Crystallites at Different Reaction Temperatures

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Abstract: Hexagonal CuSCN and cubic Cu₂S micro-scale crystallites have been selectively fabricated using CuCl₂·2H₂O and KSCN as the starting materials at 30 °C and 220 °C, respectively. The results reveal that the reaction temperature plays a key role in obtaining pure phase of CuSCN and Cu₂S crystallites. Nearly monodispersed Cu₂S nanocrystals were prepared by introducing surfactant into reaction system. The possible reaction mechanism is also discussed.

Key words: chalcogenides; selective synthesis; micro-crystallite

Sulfides of copper are in general of particular interest because of their ability to form products in a wide variety of compositions ranging from Cu₂S at the copper rich side to CuS₂ at the copper deficient side, including CuS, Cu₇S₄, Cu₉S₈, Cu₂S and so forth^[1,2]. They have been utilized as thermoelectric cooling material, optical filter, solar cell, and super-ionic material^[3,4]. Among these copper sulfides, Cu₂S (chalcocite) is an indirect semiconductor with a bulk band gap of 1.21 eV^[5], which has been extensively investigated, and widely used as a component of solar cells^[6]. Many works on the synthesis of Cu₂S with nano- to micro-scale architectures have been reported. For example, polycrystalline Cu₂S nanowires or nanotubes were

prepared via organic amine-assisted hydrothermal route^[7]. Single-crystal monoclinic Cu₂S nanowire arrays were also synthesized by flowing H₂S gas on copper substrate at room temperature^[8].

As a wide band gap and *p*-type semiconductor, CuSCN has two main phases of orthorhombic CuSCN (α -CuSCN) and hexagonal CuSCN (β -CuSCN). It is an excellent candidate material for dye-sensitized solid-state photovoltaic cells, solar cells, and catalyst for the synthesis of organic compounds^[9,10]. Several methods have been reported to synthesize CuSCN with different morphologies. Zhu et al. prepared porous α -CuSCN spheres by the reaction of CuO, NH₂OH and KSCN in the presence of gelatin at 10 °C^[10].

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In contrast to traditional solid-state synthesis routes, solution-phase approach has currently proven to be a promising method for fabrication, shaping, sizing and orientation of various inorganic materials in aqueous solution, which offers the advantages of enhanced purity, lower reaction temperature, higher film growth rate, as well as the possibility of acceleration of diffusion, adsorption, reaction rate and crystallization, especially under hydrothermal or solvothermal conditions^[11,12]. Many efforts have been currently focused on the fabrication of nanomaterials through solution-phase approach.

Herein, we present a solution-phase approach to selectively fabricate hexagonal CuSCN and cubic Cu₂S micro-scale crystallites using CuCl₂·2H₂O and KSCN as the starting materials at 30 °C and 220 °C, respectively. It is found that the reaction temperature plays a key role in obtaining pure CuSCN and Cu₂S crystallites. By introducing surfactant into the reaction system, we also prepared nearly monodispersed Cu₂S nanocrystals.

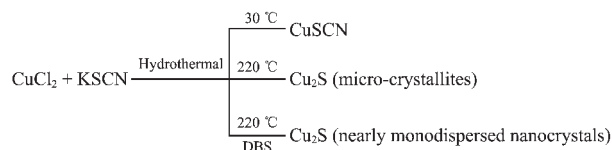
1 Experimental

All chemicals were analytical reagents purchased from Shanghai Chemical Reagents Company and used without further purification.

Synthesis of hexagonal CuSCN micro-scale crystallites: CuCl₂·2H₂O (2 mmol) and KSCN (4 mmol) were dissolved in 20 mL distilled water under stirring, respectively. Then they were mixed and maintained in a 50 mL Teflon-lined autoclave at 30 °C for 12 h. After completion of the reaction, the product was filtered, washed with distilled water and absolute ethanol for several times. After being dried at room temperature for 4 h, a white powder was collected for characterization.

Synthesis of cubic micro-scale and nanoscale Cu₂S crystallites: The procedure for the preparation of Cu₂S crystallites was similar to that of CuSCN except that the reaction temperature was 220 °C instead of 30 °C. In the case of preparation of nearly monodispersed Cu₂S nanocrystals, surfactant sodium dodecyl benzyl sulfate (DBS) was introduced into the system, and the other conditions were kept unchanged.

The whole experimental procedures can be summarized in the following scheme.



X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku D/max-rB X-ray diffractometer with Cu K α radiation ($\lambda=0.154\ 187\ \text{nm}$). Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

2 Results and discussion

Fig.1 is the typical XRD patterns of the sample obtained at 30 °C (a), and 220 °C (b) for 12 h. All the diffraction peaks in Fig.1(a) can be indexed as hexagonal CuSCN with the cell parameters of $a=0.385\ 0\ \text{nm}$, and $c=3.291\ \text{nm}$, which are in agreement with the reported values (JCPDS Card No.73-1855, $a=0.385\ 6\ \text{nm}$, and $c=3.290\ \text{nm}$). When increasing the reaction temperature to 220 °C, and keeping other conditions unchanged, the resulting XRD pattern is shown in Fig.1 (b). All the diffraction peaks in Fig.1(b) can be indexed as cubic Cu₂S with the cell parameter of $a=0.560\ 5\ \text{nm}$, consisting with the reported values (JCPDS Card No.65-2980, $a=0.560\ 0\ \text{nm}$).

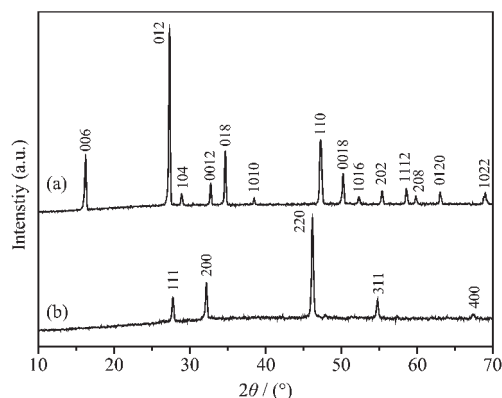


Fig.1 XRD patterns of the samples prepared at 30 °C (a) and 220 °C (b)

In our experiments, the reaction temperature plays an important role in producing phase-pure Cu₂S. XRD patterns of the products obtained at different temperatures are given in Fig.2,3. Fig.2(a) is the XRD

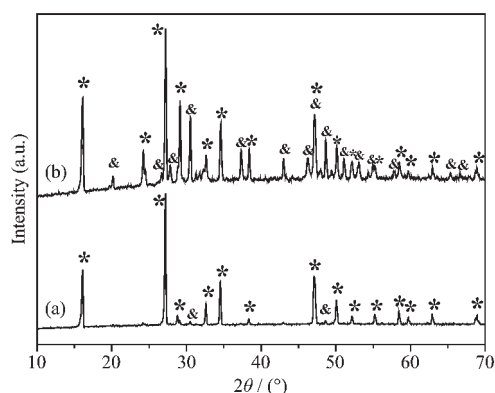


Fig.2 XRD patterns of the sample obtained at 80 °C (a) and 120 °C (b)

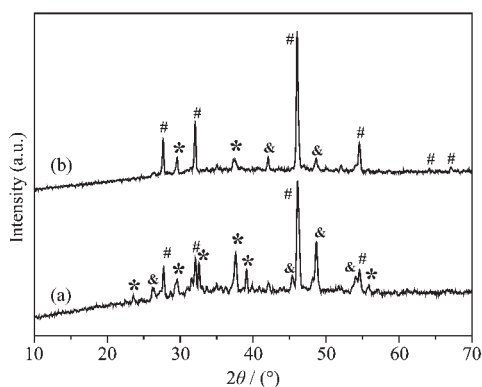


Fig.3 XRD patterns of the sample produced at 160 °C (a) and 180 °C (b) for 12 h

pattern of the sample obtained at 80 °C for 12 h, revealing that the as-prepared sample is mainly hexagonal CuSCN (JCPDS Card No.73-1855), and minor orthorhombic CuSCN (JCPDS Card No.70-0082) also exists. When increasing the reaction temperature to 120 °C, the corresponding XRD pattern in Fig.2(b) indicates that almost equal amount of hexagonal

CuSCN and orthorhombic CuSCN are simultaneous produced.

If the reaction temperature was further increased to 160 °C, the resulting XRD pattern in Fig.3(a) shows that cubic Cu₂S appears in addition to hexagonal CuSCN and orthorhombic CuSCN. As we can see from Fig.3 (b), cubic Cu₂S becomes dominant, with minor phase of hexagonal CuSCN, and orthorhombic CuSCN in the product when the reaction temperature is 180 °C.

Fig.4(a) is the representative TEM image of CuSCN obtained at 30 °C. It is found that CuSCN product is micro-scale crystallites with trig-angle shape. TEM image of the Cu₂S prepared at 220 °C without surfactant shown in Fig.4(b) shows that the sample was consisted of poly-dispersed ellipse spheres with an average diameter of 0.8~1.2 μm. If surfactant DBS was introduced, the Cu₂S obtained was nearly monodispersed nanoparticles with an average diameter of 30~100 nm (Fig.4(c)).

Because of the presence of a certain amount of DBS in the mixture, these DBS molecules would strongly and rapidly adsorb on the surfaces of the nascent nanoparticles, which would lead to the limited aggregation of Cu₂S clusters and the formation of stable colloids in a early stage of the reaction. During the heating process at 220 °C, the small amount of Cu₂S dissolved in the solution precipitated out as nanocrystallites. These nanopartilces were uniform in diameter due to the protective effect of DBS. So the surfactant molecules may function as controller kinetically by interacting with Cu₂S crystal faces of

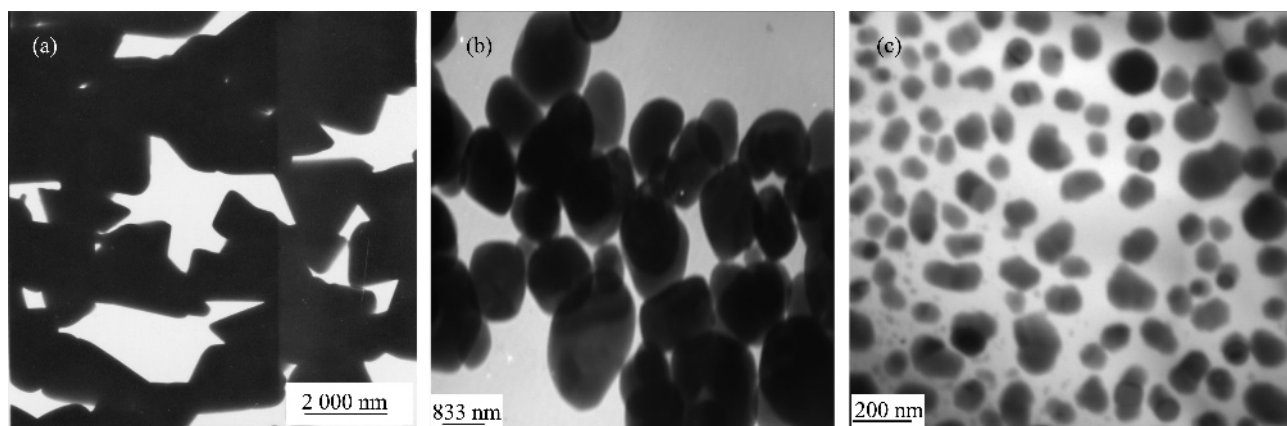
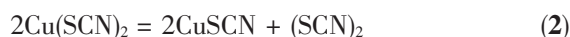
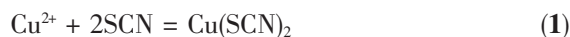


Fig.4 (a) TEM image of CuSCN obtained at 30 °C, (b) TEM image of Cu₂S prepared at 220 °C, (c) TEM image of Cu₂S produced at 220 °C with surfactant DBS

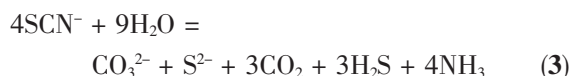
high energies through adsorption and desorption. The larger the lateral growth is restricted, the smaller diameter of the obtained crystallites. Of course, our understanding of the surfactant role is limited, further studies are still needed.

It is known that SCN^- anion is a good linker ligand, and has been extensively investigated in coordination chemistry and supramolecular chemistry^[13,14]. Recently, KSCN has been utilized as both the complex reagent and sulfur source to prepare SnS nanocrystals^[15] and CuInS_2 microspheres^[16] under solvothermal conditions. In the present study, KSCN was utilized to selectively prepare CuSCN and Cu_2S micro-scale crystallites at 30 °C and 220 °C, respectively.

If their respective solution of CuCl_2 and KSCN were mixed at 30 °C, some unstable precipitate ($\text{Cu}(\text{SCN})_2$) occurred. It would further transform into the stable phase of CuSCN^[17]. The involved reactions might be formulated as:



If the temperature is further increased, SCN^- will react with H_2O to produce H_2S . Meanwhile, as a reducing reagent, SCN^- can reduce Cu^{2+} to Cu^+ during the reaction process^[16]. The freshly formed Cu^+ further reacts with H_2S or S^{2-} to produce Cu_2S crystallites. The whole process might be formulated as follows:



On the other hand, $K_{\text{sp}}(\text{Cu}_2\text{S})$ is much more smaller than that of $K_{\text{sp}}(\text{CuSCN})$ ($K_{\text{sp}}(\text{Cu}_2\text{S})=2.0 \times 10^{-48}$, $K_{\text{sp}}(\text{CuSCN})=4.8 \times 10^{-15}$)^[18]. It is apparent that there is a strong tendency for freshly formed CuSCN to transform into more stable Cu_2S with the elongation of

time at a certain temperature.

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