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SYNTHESIS OF CuS WITH DIFFERENT MORPHOLOGIES BY REFLUXING METHOD: NANOPATICLES IN CLUSTERS AND NANOFLAKES IN SPONGE-LIKE CLUSTERS

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Clusters of CuS nanoparticles and sponge-like structures of CuS nanoflakes were synthesized by refluxing method at a temperature of 130 °C for 1.5-6 h using copper chloride ($CuCl_2 \cdot 4H_2O$) and thioacetamide (CH_3CSNH_2) as starting materials in deionized water to form $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes, specified by thermogravimetric, CHNS/O and Fourier transform inferred analyses. Phase and morphology were investigated by powder X-ray diffraction and scanning electron microscopy.

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1. Introduction

At present, nanostructured transition metal chalcogenide are very interesting materials because of the unusual physical and chemical properties including electrical conductivity, chemical sensing capability and ideal characteristics for solar energy conversion [1-4]. Copper sulfides have different formulae ranging from cooper rich (Cu_2S) to sulfur rich (CuS_2) to form a wide variety of mixed phases, of which at least five species are known to be stable at room temperature: covellite (CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.95}S$) and chalcocite (Cu_2S) [5]. They are widely used as p-type semiconductors, applications in the field of photothermal conversion, solar cell devices, super ionic materials, optical filters, gas sensors, materials in chemical sensors, thermoelectric cooling materials and lithium-ion batteries [1, 6-8]. Different shapes and sizes of copper sulfide such as nanoplates [1, 5, 6, 10, 11], spheres [7], hollow spheres [8], nanorods [9], tubes [12] and flowers [12] have been prepared via a number of methods including hydrothermal/solvothermal route [1, 7, 11], microwave assisted chemical bath deposition [5], microwave assisted hydrothermal/solvothermal process [9, 12] and sonochemical method [10, 13].

In this paper, we report the synthesis of copper sulfide nanoparticles and nanoflakes by direct decomposition of $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes and refluxing method. This method is simple, cost effective and a convenient route to synthesize a large amount of copper sulfide nanoparticles and nanoflakes.

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2. Experiment

CuS was synthesized from a stoichiometric copper chloride ($CuCl_2 \cdot 4H_2O$) and thioacetamide (CH_3CSNH_2, TAA) by refluxing method. In this research, 0.005 mol copper chloride was dissolved in 100 ml of deionized water and followed by stirring at room temperature. Then, thioacetoamide solution was added to Cu ionic solution, leading to the formation of light-green complexes. Then the complexes were transferred into a three-necked refluxing pot. The refluxing reactions were processed at 130 ^{o}C for 1.5 – 6 h. Finally green-black powders were synthesized, washed with distilled water and ethanol several times and dried in ambient air inside an electric oven at 80 ^{o}C for 24 h.

The products were analyzed by a Perkin Elmer TGA-7 thermogravimetric analyzer (TGA) with the heating rate of 20 ^{o}C.min^{-1} in nitrogen atmosphere. A 2400 Series II Perkin Elmer CHNS/O analyzer was recoded using cystine as standard. A Siemens D500 X-ray diffractometer (XRD) was carried out using Cu K_α radiation with the 2θ angle scanning from 20 to 60^{o} range, a graphitic monochromatized and a Ni filter. A Bruker Tensor 27 Fourier transform inferred (FTIR) spectrometer was recoded on the samples using KBr for dilution. A T64000 HORIBA Jobin Yvon Raman spectrometer was operated using 50 mW Ar green Laser with 514.5 nm wavelength. A JEOL JSM-6335F scanning electron microscope (SEM) equipped with an Oxfrod instruments INCA energy dispersive X-ray spectrometer (EDX) was operated at 35 kV.

3. Results and discussion

The light-green $[Cu(CH_3CSNH_2)_2]Cl_2$ complex was formed by mixing the solutions of $CuCl_2 \cdot 4H_2O$ and CH_3CSNH_2 at room temperature. TAA has lone pair electrons on nitrogen and sulfur atoms. Generally, the nitrogen ions were coordinated with the vacant d-orbital of copper ions to form complexes. By mixing the TAA and copper ionic solutions, the light-green complexes formed, investigated by CHNS/O, TGA and FTIR analyses.

In order to further study the thermal stability of $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes, the thermogravimetric analysis (TGA) was used to investigate the thermal stability at the temperature range of 50-600 ^{o}C in nitrogen atmosphere. The TGA analysis indicated two steps of distinct weight losses that could be observed at less than 170 ^{o}C and at 170-500 ^{o}C. When the temperature was lower than 170 ^{o}C, the step mainly corresponded to the desorption of water. On the other hand, the decomposition of the volatile components such as Cl_2, NH_3, H_2S and other organic compounds from TAA was detected at the temperature range of 170-500 ^{o}C. The total weight loss was 70 wt% from TGA analysis which was very close to the calculated value of 77 wt%. The quantities of C, H, N and S of the $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes were analyzed by CHNS/O analyzer. The atomic ratio of C : H : N : S of the complexes is 1.89 : 5.18 : 1 : 1.18 – in accordance with the CH_3CSNH_2 chemical formula of thioacetamide.

Bonding vibration of TAA and $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes were analyzed by FTIR as shown in Fig 1. These spectra were almost at the same but the N-H stretching vibrations of the complexes shifted to lower wavenumber, comparing to those of the TAA. They were at 3,392 and 3,172 cm^{-1} of TAA, and at 3,293 and 3,150 cm^{-1} of the complexes. The C-N stretching vibration of $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes became weakened and a little shift in wavenumber, as compared to the vibration of TAA. In this analysis, the C=S stretching vibration of both remained at the same [14-16]. The results confirmed the formation of the $Cu(CH_3CSNH_2)_2]Cl_2$ complexes due to the donation of lone pair electrons of nitrogen atoms of TAA to the vacant d-orbital of copper ions - in good accordance with the report of Gong et al in 2006 [16], who proposed the formation of $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes using FTIR analysis as compared to pure thioacetamide.

During refluxing, $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes were dissociated. TAA was hydrolyzed by water to generate H_2S. Further H_2S reacted with Cu^{2+} to synthesize green-black CuS powder. The reaction mechanism can be described as follows.

$$[Cu(CH_3CSNH_2)_2]Cl_2 \leftrightarrow Cu^{2+} + 2CH_3CSNH_2 + 2Cl^- \quad (1)$$

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COO^- + NH_4^+ + H_2S \quad (2)$$

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \quad (3)$$

When $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes were heated, they dissociated to form copper (II) ions and thioacetoamide. Then the thioacetoamide was hydrolyzed by H_2O to produce CH_3CONH_2 and H_2S. Finally, H_2S reacted with copper (II) ions to form crystalline copper sulfide [9, 12, 14].

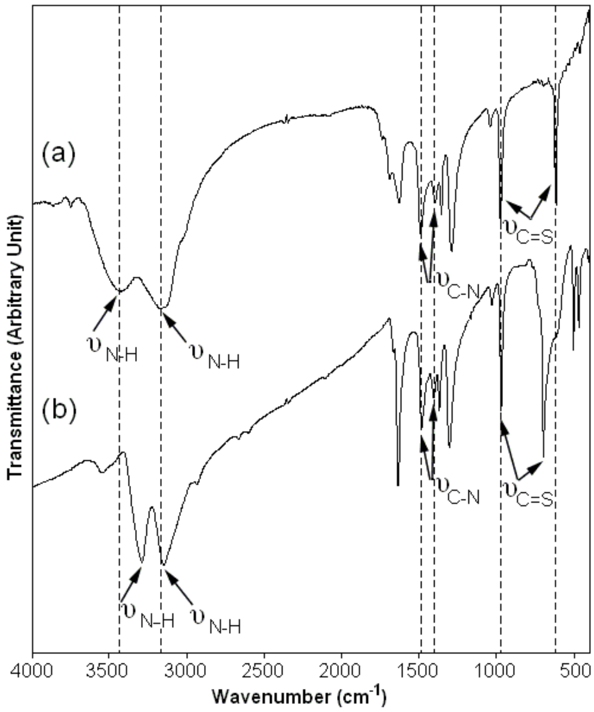

Fig. 1. FTIR spectra of (a) TAA and (b) $[Cu(CH_3CSNH_2)_2]Cl_2$ *complexes.*

XRD patterns of the products shown in Fig 2 were compared with the JCPDS file No. 78-0876 [17] and were specified as CuS hexagonal structure. The lattice parameters calculated from the plane spacing equation for hexagonal structure and Bragg's law for diffraction were a = 3.7852 Å and c = 16.3748 Å, very close to those of the JCPDS standard (a = 3.7960 Å and c = 16.3820 Å). No impurities such as CuO and other copper sulfide structures were detected in the experiment. The XRD peaks were rather broad, belonging to the nanoparticles.

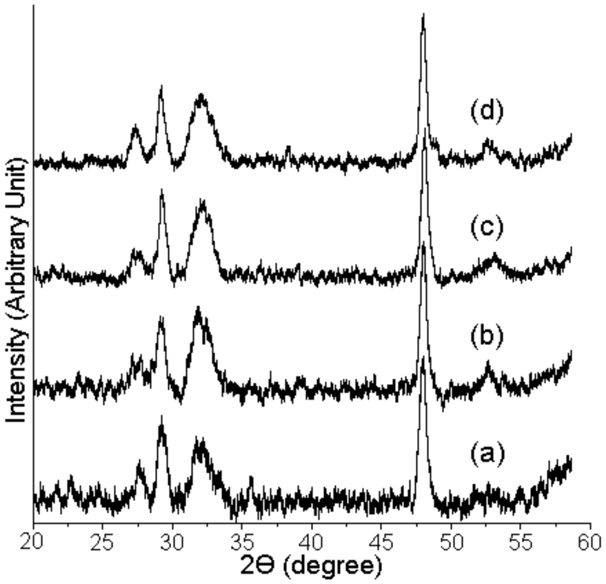

Fig. 2. XRD patterns of CuS synthesized by refluxing reactions at 130 °C for (a-d) 1.5, 2.0, 4.0 and 6 h, respectively.

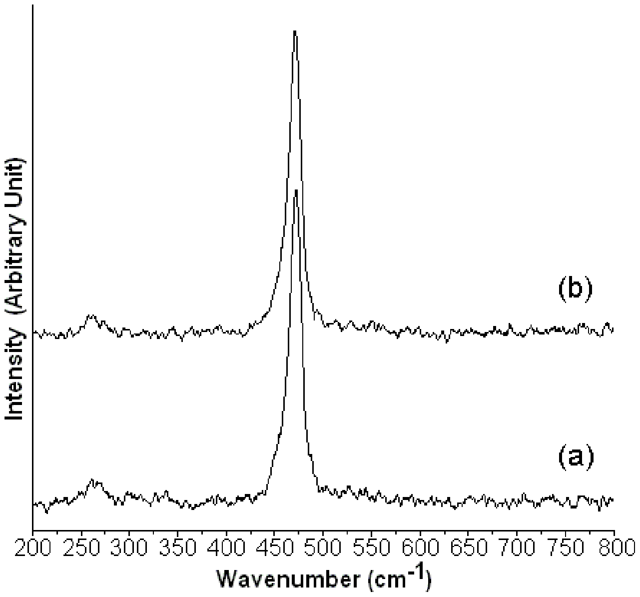

Fig. 3. Raman patterns of CuS synthesized by refluxing reactions at 130 °C for (a) 1.5 h and (b) 2.0 h.

Hexagonal CuS crystalline has P63/mmc (D^4_{6h}) space group and a primitive unit cell contains twelve atoms, six for copper and sulfur each. Group theoretical analysis shows the symmetries at the zone-center optical phonon modes as follows: $2A_{1g} + 4B_{1g} + 4E_{2g} + 3A_{2a} + 2B_{1u} + 3E_{1u} + 3E_{1a} + 2E_{2u}$, where eight modes of $2A_{1g} + 2E_{1g} + 4E_{2g}$ are active in Raman range [18]. Raman spectra (Fig. 3) show sharp peaks of CuS at 473 cm^{-1}, and can be assigned to be the S-S stretching mode of S_2 ions at the 4e sites [12-14]. Generally, vibration frequencies are controlled by atomic masses, force constant of lattice atoms, atomic bonds and others.

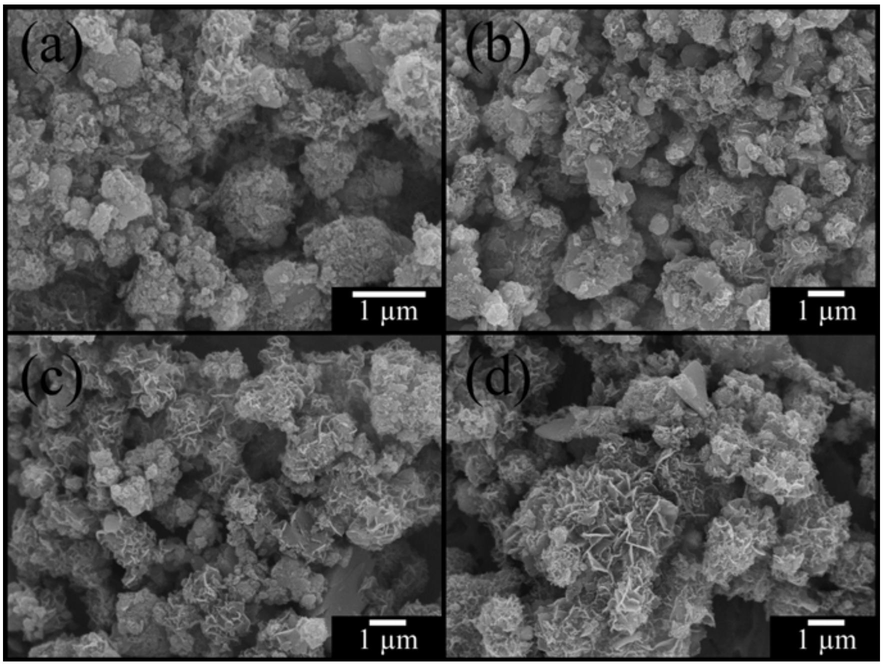

Fig. 4. SEM images of CuS synthesized by refluxing reactions at 130 °C for (a-d) 1.5, 2.0, 4.0 and 6 h, respectively.

Morphologies of the products were characterized by SEM as shown in Fig. 4. For 130 °C and 1.5 h refluxing, clusters of nanoparticles were detected. The products were evaluated as nanoflakes in clusters after refluxing for 4 h. But for 6 h refluxing, sponge-like structures of nanoflakes were achieved due to the crystal growth of some preferred structures or planes related to the surface energy of the planes [19]. EDX spectrum of CuS presented the Cu peak at 8.04 keV corresponding to the $K_{\alpha1,2}$ line, and the S peak at 2.31 keV corresponding to the $K_{\alpha1,2}$ line. The quantitative EDX analysis showed that the Cu : S atomic ratio was 48 : 52, closed to the 1 : 1 by atomic ratio of CuS.

4. Conclusions

CuS sponge-like structures of nanoflakes and clusters of nanoparticles were synthesized by the refluxing reaction of $CuCl_2 \cdot 4H_2O$ and CH_3CSNH_2 at different lengths of the reaction time, characterized by XRD and SEM. The effect of reaction time can play the role in the product morphologies. FTIR, TGA and CHNS/O analyses showed the formation, thermal stability and atomic ratio of the $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes.

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