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CHARACTERIZATION OF COPPER SULFIDE HEXANANOPLATES, AND NANOPARTICLES SYNTHESIZED BY A SONOCHEMICAL METHOD

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CuS hexanoplates and nanoparticles were prepared by sonochemical method in ethylene glycol as a solvent for 5 h. The products were characterized by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), and energy dispersive X-ray (EDX) analysis. X-ray diffraction patterns detected only pure hexagonal CuS phase. Raman spectra show peaks at 473 cm^{-1}, corresponding to the lattice vibration mode of S-S. Their morphologies were investigated by transmission electron microcopy, and the stoichiometric formula was also quantified.

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1. Introduction

Currently, nanostructured materials have been found to exhibit anomalous properties, which are totally different from their bulk. The physical and chemical properties are influenced by particle sizes, caused by quantum confinement effects. Nanostructure transition metal chalcogenides, such as CdS, ZnS, HgS and PbS, show very unusual physical and chemical properties, comparing to their bulks [1-4]. CuS is one of the most important semiconductors which has a direct band gap of 2.5 eV for bulk hexagonal wurtzite structure [5]. Copper sulfides have different stoichiometry, ranging from copper rich (Cu_2S) to sulfur rich (CuS_2), which have wide application use as p-type semiconductors, solar cells, and optical filters [5-9]. Different shapes and sizes of transition metal chalcogenides have been prepared by both the chemical and physical routes, including hydrothermal/solvothermal method [4,6,7], microwave irradiation [2,3], and chemical vapor deposition method [10]. In addition, solution method can be used to produce such the nanostructured oxides without using metal catalysts or templates with better crystal quality, preferably at lower growth temperature. It was found to be convenient and economical process.

Sonochemical process is very attractive for preparing nanostructured materials. The process can lead to more uniform particle-size distributions, smaller sizes, slightly higher surface area, and better thermal stability. The phase purity was achieved more easily than by the conventional one. When ultrasonic radiation is supplied to chemical solutions, molecules vibrate in accordance with the radiation frequency and heat develops inside. The effects of ultrasound

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radiation on chemical reactions are due to the very high temperatures and pressures that develop during the sonochemical cavity collapse by acoustic cavitation. There are two regions of sonochemical activity, the inside of the collapsing bubble and the interface between the bubble and the liquid [1,11].

The purpose of the present research is to prepare CuS hexananoplates and naoparticles in ethylene glycol by the sonochemical method. This process is very simple, attractive, novel and convenient route to obtain a large amount of product quantity.

2. Experiment

CuS was prepared by using stoichiometric copper acetate hydrate ($Cu(CH_3COO)_2{\cdot}H_2O$), sulfur powder (S) and sodium hydroxide (NaOH) with mole ratio of 1:4:6, and encoded as sample 1. Firstly, 0.005 mol copper acetate hydrate was dissolved in 30 ml ethylene glycol and stirred at room temperature. Then sulfur powder and sodium hydroxide were added to the copper acetate solution. The mixture was sonicated in an ultrasonic baht (35 kHz) for 5 h. Finally, green-black precipitates were achieved, washed with distilled water and absolute ethanol several times, and dried in air at 80 ^{o}C for 24 h. This product was compared with another product which prepared using copper acetate hydrate and sodium sulfide nanohydrate ($Na_2S{\cdot}9H_2O$) as starting materials at mole ratio of 1:1 in ethylene glycol by sonochemical process for 5 h at room temperature, and encoded as sample 2.

The products were analyzed by an X-ray diffractometer (XRD, Siemens D500) using Cu K_α radiation with a scanning 2Θ angle ranging from 10 to 60^{o} with a graphitic monochrom Ni filter, Raman analyzer (HORIBA JOBIN YVON T64000) using 50 mW Ar laser with 514.5 nm wavelength, transmission electron microscope (TEM, JOEL JEM-2010) operated at 200 kV, and energy dispersive X-ray (EDX) analyzer (JEOL, JSM-6335F) operated at 15.0 kV.

3. Results and discussion

Fig. 1 shows XRD patterns of the samples 1 and 2 prepared by sonochemical process for 5 h. Comparing to the JCPDS file no. 78-0876 (a = b = 3.7960 Å and c = 16.3820 Å) [12], they were the hexagonal CuS structure. No impurities such as CuO and other nonstoichiometric copper sulfides were detected. The XRD peaks were quite broad, indicating these samples were composed of nanocrystalline particles.

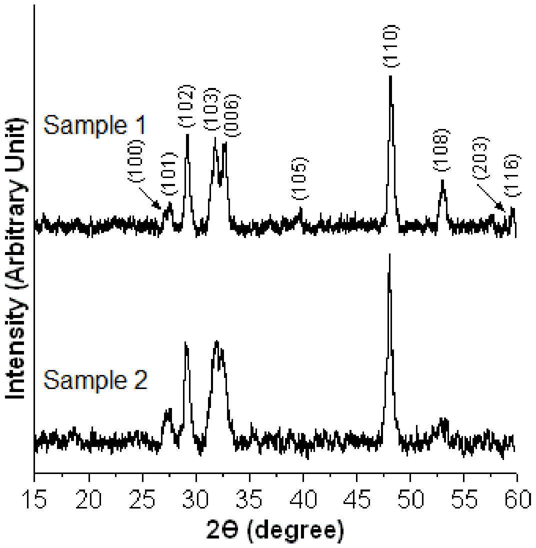

Fig. 1 XRD patterns of the samples 1 and 2, synthesized by sonochemical process for 5 h.

Raman analysis of a semiconductor is quite fast to quantify crystalline quality, including surface condition and homogeneity. Crystalline products present sharp Raman peaks. But for amorphous or polycrystalline materials, their Raman peaks are rather broad. Hexagonal CuS crystalline has space group P63/mmc and a primitive unit cell contain twelve atoms, six for Cu and S each. Raman spectra (Fig. 2) show a sharp peak of CuS at 473 cm^{-1}, assigned to the S-S stretching mode of S_2 ions at 4e sites [14-16].

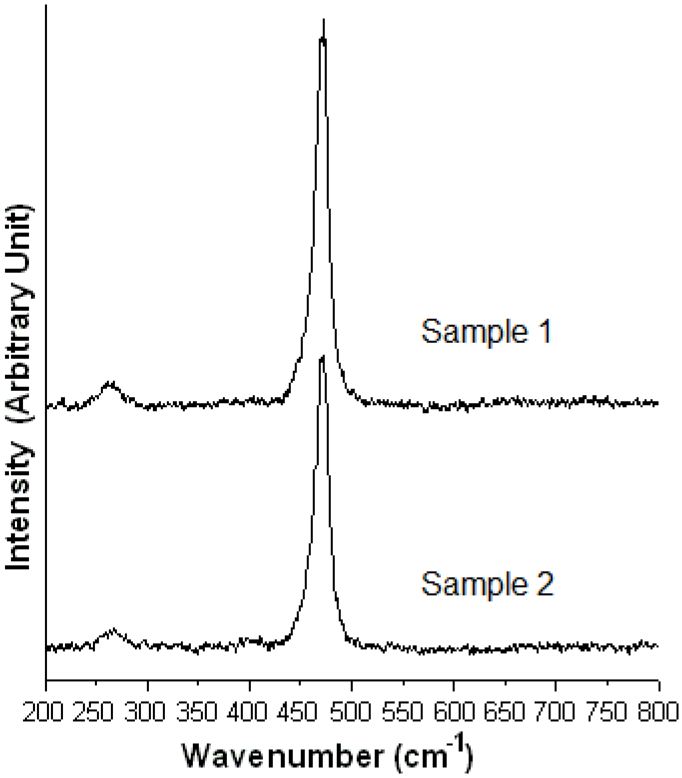

Fig. 2 Raman spectra of the samples 1 and 2, synthesized by sonochemical process for 5 h.

Morphologies of the samples were analyzed by transmission electron microscope as shown in Fig. 3. They were hexananoplates for sample 1 with 100 nm wide and 20 nm thickness, and nanoparticles for sample 2 with 10-30 nm particle sizes. Their selected area electron diffraction (SAED) patterns are randomly bright spots showing that the products were composed of good crystalline with different orientations. The rings were interpreted and specified as the (100), (103), (006), (105), (110), (108), (203) and (116) planes, in accordance with those of the corresponding XRD spectra.

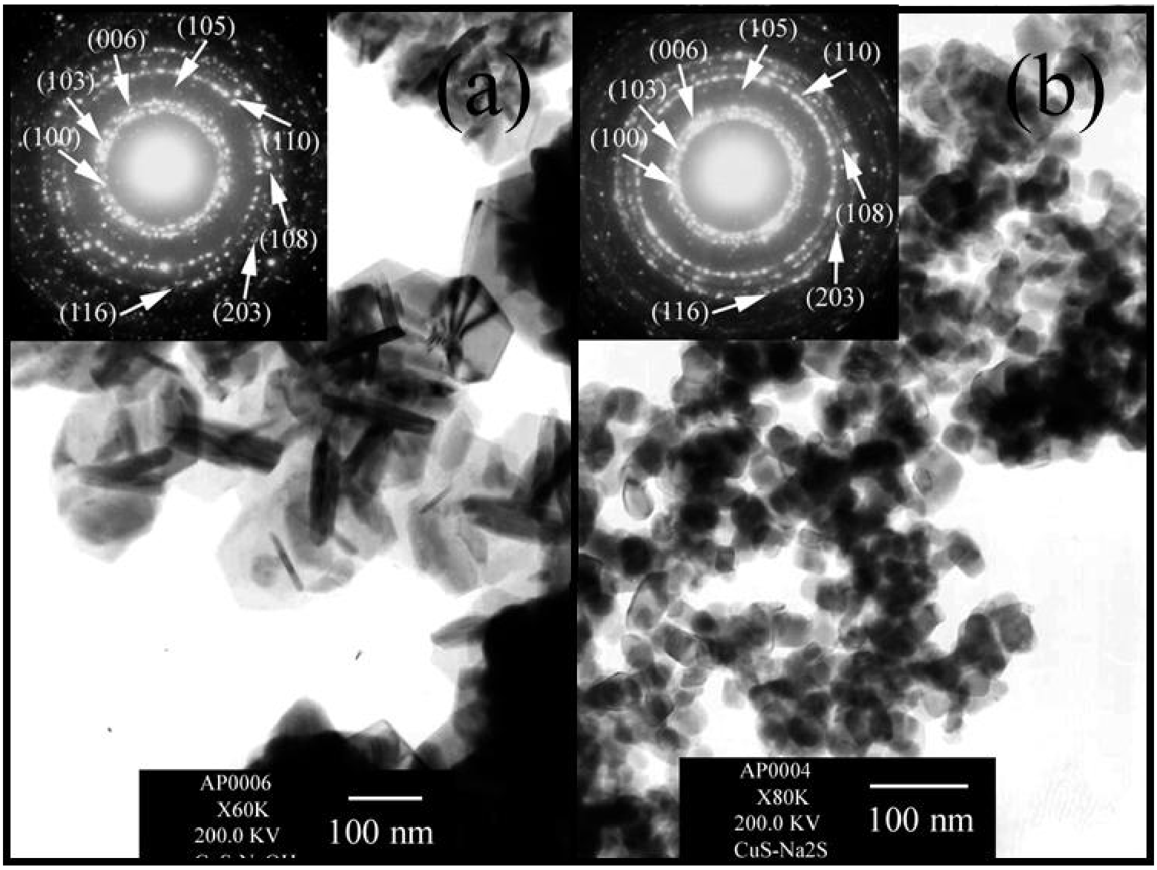

Fig. 3 TEM images and SAED patterns of CuS, (a) sample 1 and (b) sample 2, synthesized by sonochmical process for 5 h.

The chemical reactions are able to describe as follows:

$$4S + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O \tag{1}$$

$$Na_2S + Cu^{2+} \rightarrow CuS + 2Na^+ \tag{2}$$

In the first reaction, sulfur powder reacted with sodium hydroxide to generate S^{2-}. Subsequently, S^{2-} reacted with Cu^{2+} to form CuS (sample 1). When Na_2S was used, it reacted directly with Cu^{2+} to form CuS (sample 2) under the sonochemical process [3]. Copper sulfide nucleated and grew to form CuS hexananoplates (sample 1) in the solution containing NaOH, and nanoparticles (sample 2) in the NaOH-free solution.

EDX spectra of the CuS presented the Cu peak at 8.04 keV (1.54 Å) corresponded with the $K_{\alpha1,2}$ line, and S peak at 2.31 keV (5.37 Å) identified as $K_{\alpha1,2}$ line. The quantitative analysis of Cu:S atomic ratio was 48:52, very close to 1:1, and in accordance with its chemical formula.

4. Conclusions

A facile method for the synthesis of CuS hexananoplates and nanoparticles by sonochemical method was reported. In the present report, the starting materials played the important roles in controlling their morphologies. X-ray diffraction patterns show only pure hexagonal CuS phase. Raman spectra show the highest peak at 473 cm^{-1}, corresponding to the lattice vibration mode of S-S. This sonochemical method was very fast, and did not require high temperature processing. Thus it has more advantage over other methods.

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