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Characterization of copper sulfide nanostructured spheres and nanotubes synthesized by microwave-assisted solvothermal method

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ABSTRACT

Copper sulfide nanostructured spheres and nanotubes were successfully synthesized, using a microwave-assisted solvothermal method, by the decomposition of $[Cu(CH_3CSNH_2)_2]Cl_2$ complexes, formed by the reaction of $CuCl_2·2H_2O$ and CH_3CSNH_2 in ethylene glycol at different pH values, and identified by CHNS/O and FTIR analyses. The decrease in bonding energy of N–H revealed the coordination of copper ions and thioacetamide molecules. It was specified that nitrogen atoms of thioacetamide molecules were used to form Cu–thioacetamide complexes. XRD, SEM, TEM and SAED analyses show that the products were hexagonal CuS spheres in an extremely low pH solution, and hexagonal CuS nanotubes at a pH 13. Their Raman spectra show sharp peaks at 473 cm^{-1}, identified as the S–S stretching mode of S_2 ions at the 4e sites.

1. Introduction

Copper sulfides are materials with different chemical formulae, ranging from copper rich (Cu_2S) to sulfur rich (CuS_2). They are widely used for different applications, such as p-type semiconductors, thermoelectric and photoelectric converters, high capacity cathode materials in lithium secondary batteries, solar radiation absorbers and nonlinear optical materials [1–4], depending on their stoichiometries and complex structures—including valence states of copper and sulfur atoms. Different shapes and sizes of the sulfides, such as nanocones [1], hollow spheres [3], nanoplates [4], nanobelts [1,5] and nanostructured flowers [6], were synthesized through various methods—including a facile precipitate-converting reaction [3], hydrothermal/solvothermal routes [1,4,6], and chemical method in combination with solvothermal route [5].

The microwave-assisted solvothermal synthesis has more advantage than the conventional solvothermal one, due to the rapid heating to a temperature of heat treatment, by increasing the kinetics of reaction by one to two orders of magnitude, leading to the formation of some novel phase with high crystallinity in the chemical system. This explanation shows the microwave-assisted solvothermal synthesis that is very rapid as compared to the conventional solvothermal reaction [7–9]. It is therefore for us to present the development of copper sulfide nanostructured spheres and nanotubes using the microwave-assisted solvothermal method.

2. Experiment

The 5 mmol each of $CuCl_2·2H_2O$ and CH_3CSNH_2 was dissolved in 40 ml ethylene glycol with different pH values, adjusted by KOH solution. The reactions proceeded in an acid digestion bomb (Parr Instrument Company) using 50% of 180 W microwave irradiation for 20 min. At the end of the process, the precipitates were washed with water and ethanol, and dried at 80 °C for 12 h.

The products were analyzed using an elemental analyzer (2400 Series II CHNS/O Analyzer Perkin Elmer) with cystine as a calibrating standard to mark the scale on the measuring equipment, Fourier transform infrared spectroscopy (FTIR, BRUKER TENSOR27) with KBr dilution, X-ray diffraction (XRD, SIEMENS D500) using Cu K_α line with the scanning 2θ angles ranging from 15 to 60°—a graphitic monochrom and a Ni filter, Raman spectroscopy (HORIBA JOBIN YVON T64000) using 50 mW and 514.5 nm wavelength Ar laser, scanning electron microscopy (SEM, JEOL JSM-6335F) operated at 15 kV and transmission electron microscopy (TEM, JEOL JEM-2010) at 200 kV.

3. Results and discussion

Thioacetamide is an organic sulfur compound with the formula of CH_3CSNH_2. It has lone pair electrons on nitrogen and sulfur atoms, and is able to donate lone pair electrons to form coordination compound with the vacant d-orbital of Cu cations. By adding thioacetamide and copper chloride in ethylene glycol solutions, light-green precipitates (Cu–thioacetamide complexes) were synthesized. The complexes were analyzed using CHNS/O analyzer and Fourier transform infrared (FTIR) spectroscopy. CHNS/O analyzer was used to characterize the qualitative carbon, hydrogen, nitrogen and sulfur using cystine as a calibrating standard. Table 1 compares weight percent of $[Cu(CH_3CSNH_2)_2]Cl_2$

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Table 1
Weight percent of C, H, N and S of [Cu(CH_3CSNH_2)$_2$]Cl_2 complexes, obtained from theory and CHNS/O analysis.

Complexes	Element	Weight percent of theory	Weight percent of CHNS/O analysis
[Cu(CH_3CSNH_2)$_2$]Cl_2	C	16.87	13.35
	H	3.51	3.14
	N	9.84	8.28
	S	22.53	22.33

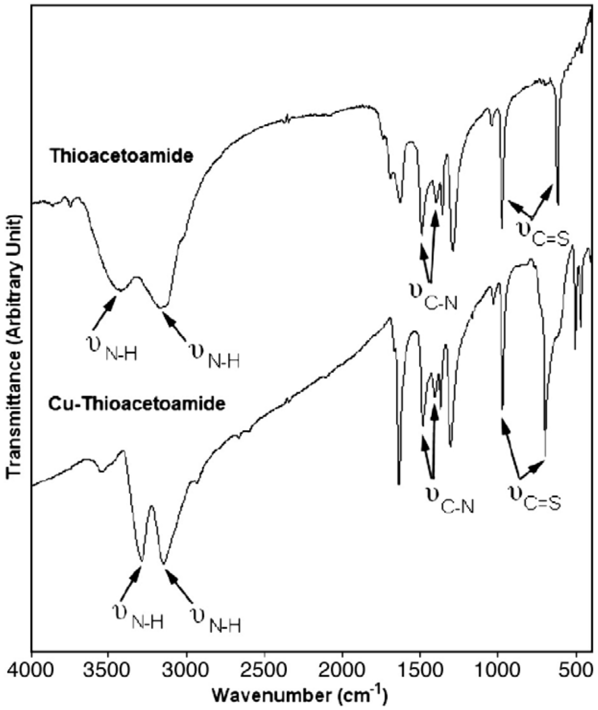

Fig. 1. FTIR spectra of thioacetamide and Cu–thioacetamide complexes.

complexes, obtained from the CHNS/O analysis and theoretical values. It was found that they are in good accordance.

FTIR spectra of thioacetamide and Cu–thioacetamide complexes are compared in Fig. 1. The N–H stretching vibrations shifted from 3392 and 3172 cm^{-1} of thioacetamide to 3293 and 3150 cm^{-1} of Cu–thioacetamide complexes. The C–N stretching vibrations of Cu–thioacetamide complexes were weaken and were a little shift relative to those of thioacetamide, but the C$=$S stretching vibrations have stayed the same and not changed. The decrease in bonding energy of N–H revealed the coordination of copper ions and thioacetamide molecules. It was specified that nitrogen atoms of thioacetamide molecules were used to form Cu–thioacetamide complexes [6]—caused by donating lone pair electrons on nitrogen atoms, to form coordination compound with the vacant d-orbital of Cu cations.

[Cu(CH_3CSNH_2)$_2$]Cl_2 complexes, obtained by copper (II) and thioacetamide (CH_3CSNH_2) coordination, were dissociated by microwave heating. Subsequently, CH_3CSNH_2 was hydrolyzed by H_2O to form H_2S, which further reacted with copper (II) ions to from copper sulfide crystalline [10,11].

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

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S \tag{2}$$

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \tag{3}$$

XRD patterns of the products are shown in Fig 2a. By comparing with the JCPDS No 78-0876 [12], the products were CuS phase with hexagonal structure. No impurities, such as CuO and others stoichiometric copper sulfide phases—Cu_2S, Cu_7S_8, etc., were detected in these products.

Atomic vibrations of CuS were studied using Raman spectroscopy. It is a fast method used to specify crystalline material qualities, including surface condition and homogeneity. Raman peaks of high-ordered crystals are very sharp, but those of low-ordered ones are rather broad. Hexagonal CuS crystalline has space group P6_3/mmc (D^4_{6h}), and a primitive unit cell contain twelve atoms, six of Cu and S each. Group theory analysis shows vibration modes of the zone-center optical phonons as $2A_{1g}+4B_{2g}+2E_{1g}+4E_{2g}+3A_{2u}+2B_{1u}+3E_{1u}+2E_{2u}$. Eight of $2A_{1g}+2E_{1g}+4E_{2g}$ modes are Raman active. Raman spectra (Fig. 2b) show sharp peaks of CuS at 473 cm^{-1}, identified as the S–S stretching mode of S_2 ions at the 4e sites [13]. Generally, vibration frequencies are controlled by atomic masses, force constant of lattice atoms, atomic bonds and others.

Figs. 3 and 4 show the morphologies of CuS products. In KOH-free solution (extremely low pH, Fig. 3a), SEM image shows a number of spheres with pores inside, each of which is composed of CuS nanoplates. When different pH values were adjusted (Fig. 3b–i), the products were composed of clusters of nano-sized particles at a pH 1, and gradually transformed into CuS nanotubes (pH 13) afterwards. No spherical

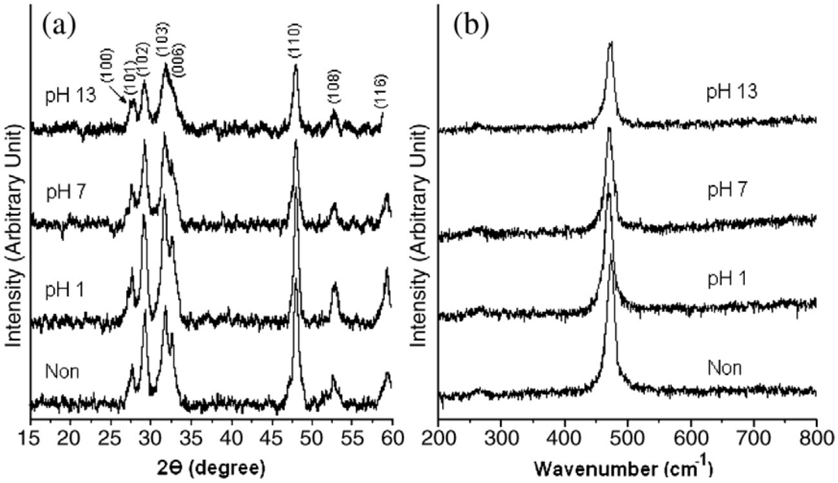

Fig. 2. (a) XRD patterns and (b) Raman spectra of CuS synthesized in different solutions, without and with pH adjusting by KOH solution.