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# Formation of CuS with flower-like, hollow spherical, and tubular structures using the solvothermal-microwave process

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**Abstract**

$CuCl_2 \cdot 2H_2O$ and $CH_3CSNH_2$ were dissolved in ethylene glycol, and followed by the addition of NaOH to form solutions with different pH values. Reactions proceeded in surfactant-free solutions contained in an acid digestion bomb using a microwave irradiation at different conditions. Pure CuS (hcp) with flower-like, hollow spherical, and tubular structures were detected, and had the same vibration wavenumber at 474 $cm^{-1}$. They displayed two emission peaks at 411, and 432 nm. The formation of CuS with different morphologies was proposed according to the analytical results.


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*Keywords:* Surfactant-free solutions; Solvothermal-microwave process; CuS; Flower-like structure; Hollow spheres; Tubular structure

## 1. Introduction

CuS with flower-like, hollow spherical, and tubular structures in nanometer and micrometer sizes is a very attractive material due to its specific structures and novel properties. It has a wide variety of applications, such as solar cells, superionic materials, and optical filters [1]. CuS was produced by different methods, such as spray pyrolysis [2], solvothermal process [3], sonochemistry [4], and microwave synthesis [5]. Surfactants, templates, and other additives were used to control the morphologies in most processes. For solution in a digestion bomb, microwave heating is a very attractive method due to focusing a large amount of energy into the chemicals under high pressure. The purpose of this research is to produce CuS with flower-like, hollow spherical, and tubular structures in surfactant-free solutions with different pH values using the solvothermal-microwave process in an acid digestion bomb.

## 2. Experiment

The 5 mmol each of $CuCl_2 \cdot 2H_2O$ and $CH_3CSNH_2$ was dissolved in 40 mL ethylene glycol. The pH was adjusted using NaOH. The solutions were stirred at ambient temperature. The reactions proceeded in an acid digestion bomb using 180 W cyclic microwave irradiation for 24 and 72 cycles (1200 and 3600 s). Each cycle was 50 s long. It was on for $x$ s and off for $50 - x$ s. The irradiation percents for every cycle were $2x = 20\%$, 30%, 50%, and 60%. An increase in the irradiation percent of each cycle had an influence on the system by raising its temperature. The number of cycles is the time that the reaction proceeded in both the on and off states. At the conclusion of the test, the products were washed with water and ethanol, dried at 80 °C for 12 h, and intensively analyzed.

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## 3. Results and discussion

To determine the phase of the products, their XRD spectra (Fig. 1) were compared with that of the JCPDS software (reference code: 78-0876) [6], and specified as CuS (hcp). No other characteristic peaks of impurities were detected although they were produced using different conditions. The degrees of crystallinity were increased with the increase in the irradiation percents of each cycle, and numbers of the heating cycles (Fig. 1a), identified by the narrower and higher peaks. When more energy was supplied to the system, atoms violently vibrated and aligned in a periodic array in the lattice. Different pH values (Fig. 1b) did not play a significant role in the diffraction peaks, and degree of crystallinity.

To produce CuS in an acid digestion bomb, $CuCl_2 \cdot 2H_2O$ and $CH_3CSNH_2$ were mixed in ethylene glycol and stirred at ambient temperature. The existence of precipitates (copper–thioacetamide complex) which were subsequently decomposed by the microwave irradiation [7], is shown

$$CuCl_2 + 2CH_3CSNH_2 \xrightarrow{\text{Ethylene glycol}} [Cu(CH_3CSNH_2)_2]^{2+} + 2Cl^-$$

$$[Cu(CH_3CSNH_2)_2]^{2+} \xrightarrow{\text{microwaveirradiation}} CuS(\text{black})$$

To show that copper–thioacetamide complex was definitely produced, FTIR spectra (Fig. 2) of $CH_3CSNH_2$ and the precipitates (copper–thioacetamide complex, $[Cu(CH_3CSNH_2)_2]Cl_2$) were analyzed. For $CH_3CSNH_2$, C=S stretching vibrations were detected at 735 and 984 $cm^{-1}$, and N–H stretching vibrations at 3178 and 3443 $cm^{-1}$. Corresponding vibrations of the complex were at 710 and 978 $cm^{-1}$ for C=S stretching, and 3153 and 3305 $cm^{-1}$ for N–H stretching. The two C=S peaks of $CH_3CSNH_2$ became weakened. The 710 $cm^{-1}$ C=S vibration tended to split into two peaks. Both C=S and N–H peaks shifted to the lower wavenumbers due to the reduc-

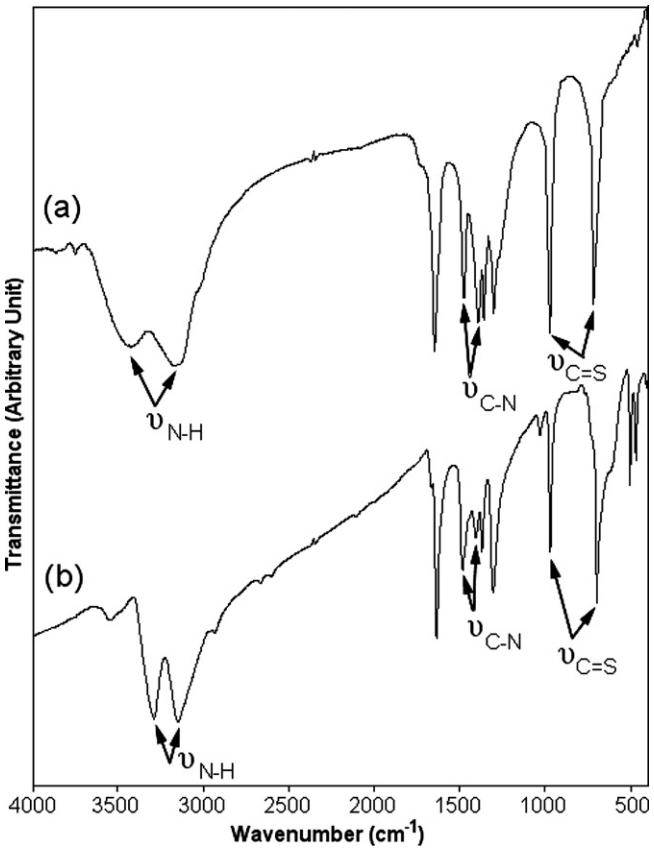


Fig. 2. FTIR spectra of (a) $CH_3CSNH_2$ and (b) $[Cu(CH_3CSNH_2)_2]Cl_2$.

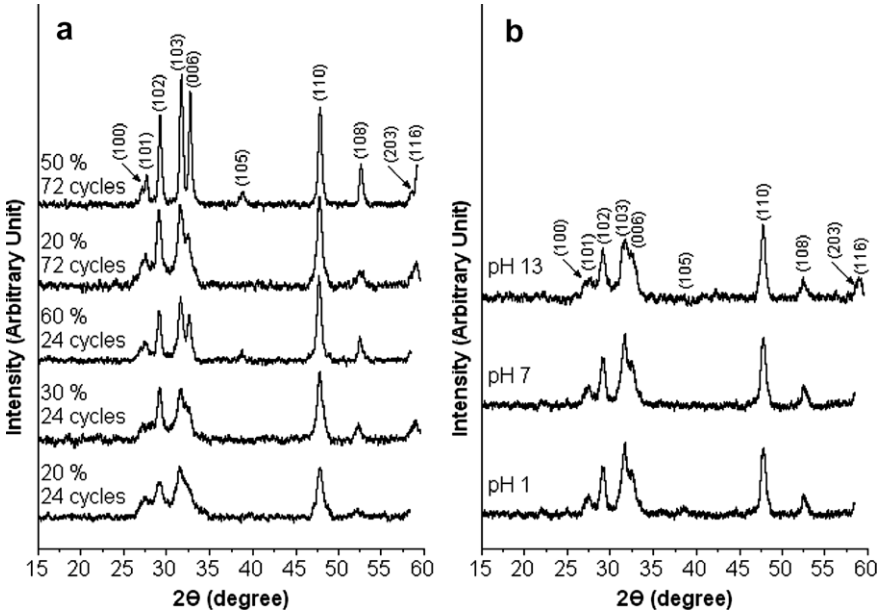


Fig. 1. XRD spectra of the products produced using (a) an extremely low pH value at different irradiation percents of each cycle and numbers of heating cycles, and (b) different pH values at 50% irradiation for 24 cycles.