

## MICROWAVE HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF COPPER SULFIDE WITH DIFFERENT MORPHOLOGIES

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CuS products with different morphologies (flower-like, nanoparticles and nanoplates) have been synthesized by microwave-hydrothermal method using different sources of copper ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , CuBr and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sulfur ( $\text{CH}_3\text{CSNH}_2$  and  $\text{NH}_2\text{CSNH}_2$ ). The as-synthesized CuS products were analyzed by XRD, SAED and Raman spectroscopy. XRD patterns of the products can be indexed to hexagonal CuS phase as compared to JCPDS database no. 78-0876. Raman spectra show a sharp peak of CuS at  $470 \text{ cm}^{-1}$ , assigned to the S-S stretching mode of  $\text{S}_2$  ions at 4e sites. In addition, their morphologies were investigated by SEM and TEM. They were found that the products shaped like microflowers, nanoparticles and nanoplates controlled by the starting materials.

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### 1. Introduction

Copper sulfide (CuS) as an important p-type semiconductor has gained much attention because of its unique optical and electrical properties, including other physical and chemical properties [1-3]. Copper sulfides exist in a wide variety of compositions, ranging from copper-rich chalcocite ( $\text{Cu}_2\text{S}$ ) to copper-deficient villamaninite ( $\text{CuS}_2$ ) with other intermediate compounds: covellite (CuS), djurleite ( $\text{Cu}_{1.95}\text{S}$ ) and anilite ( $\text{Cu}_{1.75}\text{S}$ ) [4, 5]. Copper sulfide has potential applications for solar cells, optical filters, super-ionic materials, thin films and composited materials, including high capacity cathode material in lithium secondary batteries, nanometer-scale switches, catalyst supporters and nonlinear optical material [1, 2, 6].

The hydrothermal method is the most common synthesis technology, because of its ease of operation with less expensive equipment. However, the conventional hydrothermal method has some disadvantages, such as long synthesis time and high energy consumption. The microwave hydrothermal method, as a modification of the conventional hydrothermal, prompts much rapid reaction due to the interaction of microwave with molecular reactants. In addition, it offers further advantages, such as energy saving, simplicity and low cost; therefore, it has the potential of being used in large-scale commercial productions [7]. Thus, this paper presents the synthesis of copper sulfide with nanosized and microsized particles by a microwave-hydrothermal method.

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## 2. Experiment

Each 5 mmol of different sources of copper ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{CuBr}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sulfur ( $\text{CH}_3\text{CSNH}_2$  and  $\text{NH}_2\text{CSNH}_2$ ) was dissolved in 40 ml deionized water. To synthesize copper sulfide, the reactions proceeded in acid digestion bombs (Parr microwave digestion bomb No. 4782) by 180 W cyclic microwave radiation for 24-72 cycles (20-60 min). For each cycle of 50 s with the reaction proceeded in both the on and off states, the process was on for x s and off for 50-x s. The irradiation percentages for every cycle were  $2x = 20\%$ ,  $30\%$ ,  $40\%$ ,  $50\%$  and  $60\%$ . An increase in the irradiation percent of each cycle had an influence on the system by raising its temperature. At the conclusion of the test, the products were washed with water and ethanol, dried at  $80^\circ\text{C}$  for 12 h and intensively analyzed.

The products were analyzed by X-ray diffraction (XRD, SIEMENS D500) and using  $\text{Cu K}_\alpha$  radiation with the scanning angle range  $2\theta$  from  $15$  to  $60^\circ$ , a graphitic monochrome and a Ni filter. Raman spectrophotometer (T64000 HORIBA JOBIN YVON) was operated using 50 mW Ar green Laser with 514.5 nm wavelength. A scanning electron microscope (SEM, JEOL JSM-6335F) and a transmission electron microscope (TEM, JEOL JEM-2010) as well as selected area electron diffraction (SAED) were operated at 15 kV and 200 kV, respectively.

## 3. Results and discussion

The effect of microwave irradiation power and reaction time by the processing of  $\text{CuCl}_2$  and thioacetamide as copper and sulfur sources at 20 % of 180 W for 20-60 min and 20-60 % of 180 W for 20 min was investigated. XRD patterns of the products as shown in Fig. 1 can be indexed to hexagonal  $\text{CuS}$  structure as compared to the JCPDS database no. 78-0876 [8]. No impurities such as  $\text{CuO}$  and other copper sulfide phases were detected. Upon increasing of the microwave power and reaction time, the XRD intensities of the products were also increased, showing that the crystalline degree of the products was increased as well. The 60 % of 180 W and 20 min processing (highest crystalline degree) was selected for studying the effect of different starting sources. XRD patterns of the products with different copper and sulfur starting sources are shown in Fig. 2. They can be identified to hexagonal  $\text{CuS}$  structure, according to the JCPDS database no. 78-0876 [8], except for the use of  $\text{CuBr}$  and thiourea as copper and sulfur sources - the mix phases of  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  were synthesized.

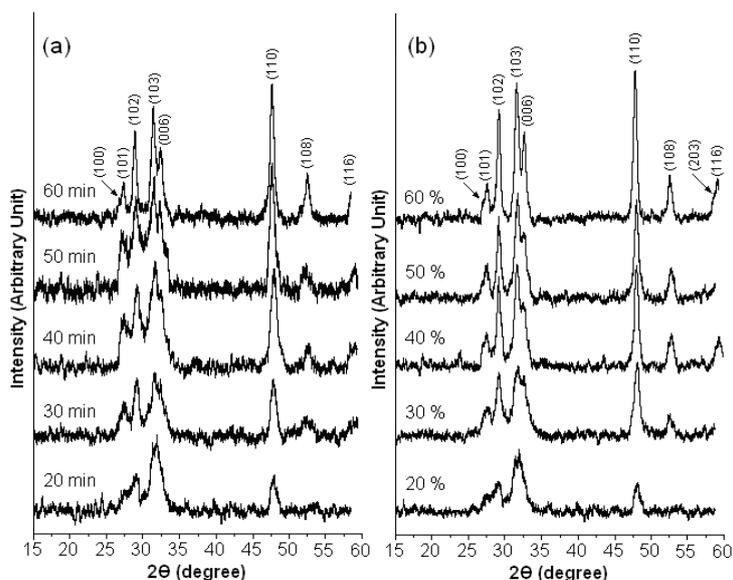


Fig. 1 XRD patterns of  $\text{CuS}$  synthesized using  $\text{CuCl}_2$  and  $\text{CH}_3\text{CSNH}_2$  as starting materials by microwave-hydrothermal method at (a) 20 % W for 20-60 min and (b) 20-60 % W for 20 min.

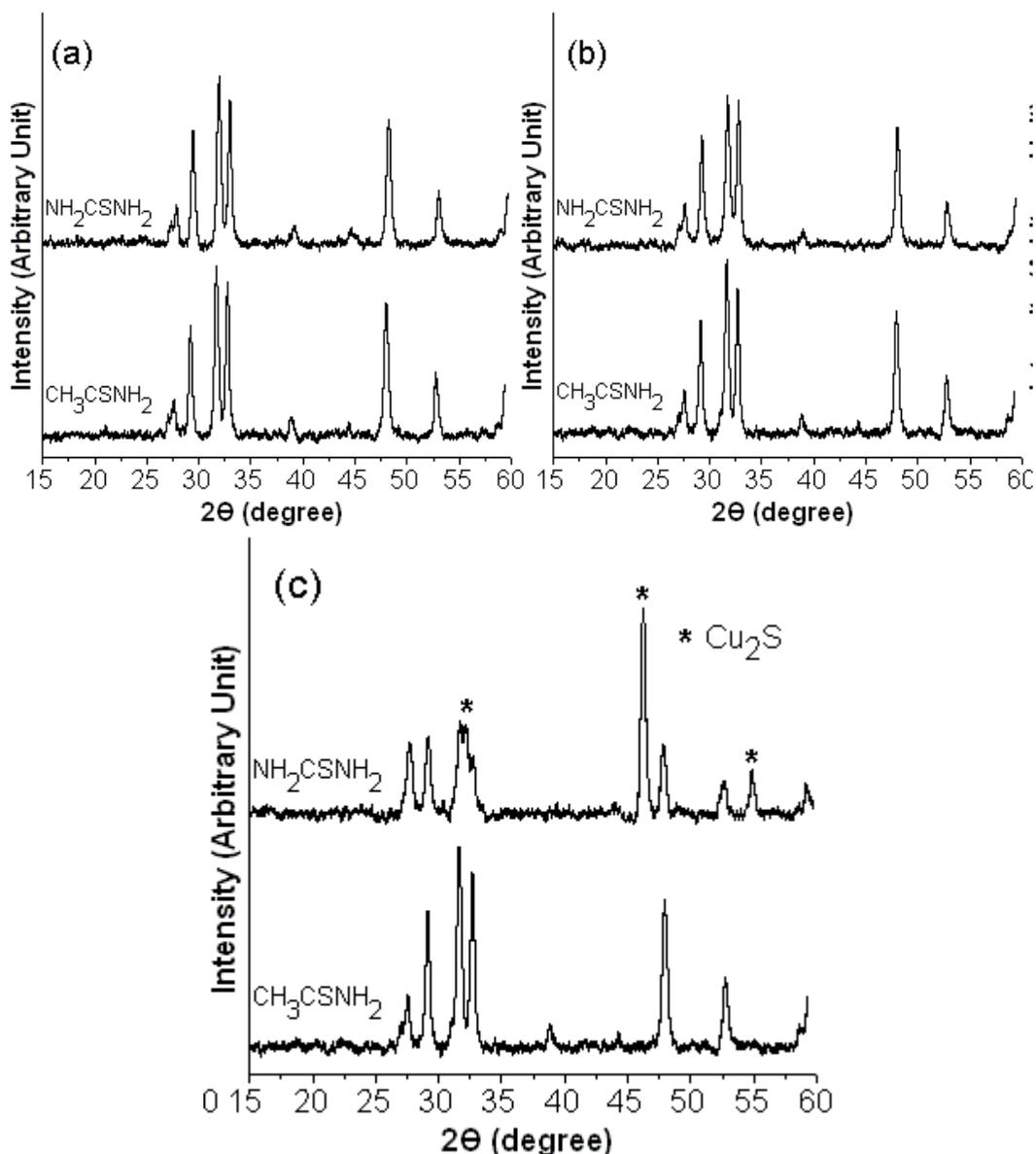


Fig. 2 XRD patterns of CuS synthesized using (a)  $\text{CuCl}_2$ , (b)  $\text{Cu}(\text{CH}_3\text{COO})_2$  and (c)  $\text{CuBr}$  as copper sources by microwave-hydrothermal method at 60 % W for 20 min.

Hexagonal CuS crystal has space group of  $\text{P6}_3/\text{mmc}$  ( $\text{D}_{6h}^4$ ) and a primitive unit cell contain twelve atoms of  $6(\text{CuS})$ . Group theoretical analysis shows the symmetries of the zone-center optical phonon modes as follows:  $2\text{A}_{1g} + 4\text{B}_{2g} + 2\text{E}_{1g} + 3\text{A}_{2u} + 2\text{B}_{1u} + 3\text{E}_{1u} + 4\text{E}_{2g} + 2\text{E}_{2u}$ , where eight modes of  $2\text{A}_{1g} + 2\text{E}_{1g} + 4\text{E}_{2g}$  are active in Raman range. Raman spectra (Fig. 3) show a sharp peak of CuS at  $470\text{ cm}^{-1}$  which can be assigned to the S-S stretching mode of  $\text{S}_2$  ions at 4e sites [9-11].

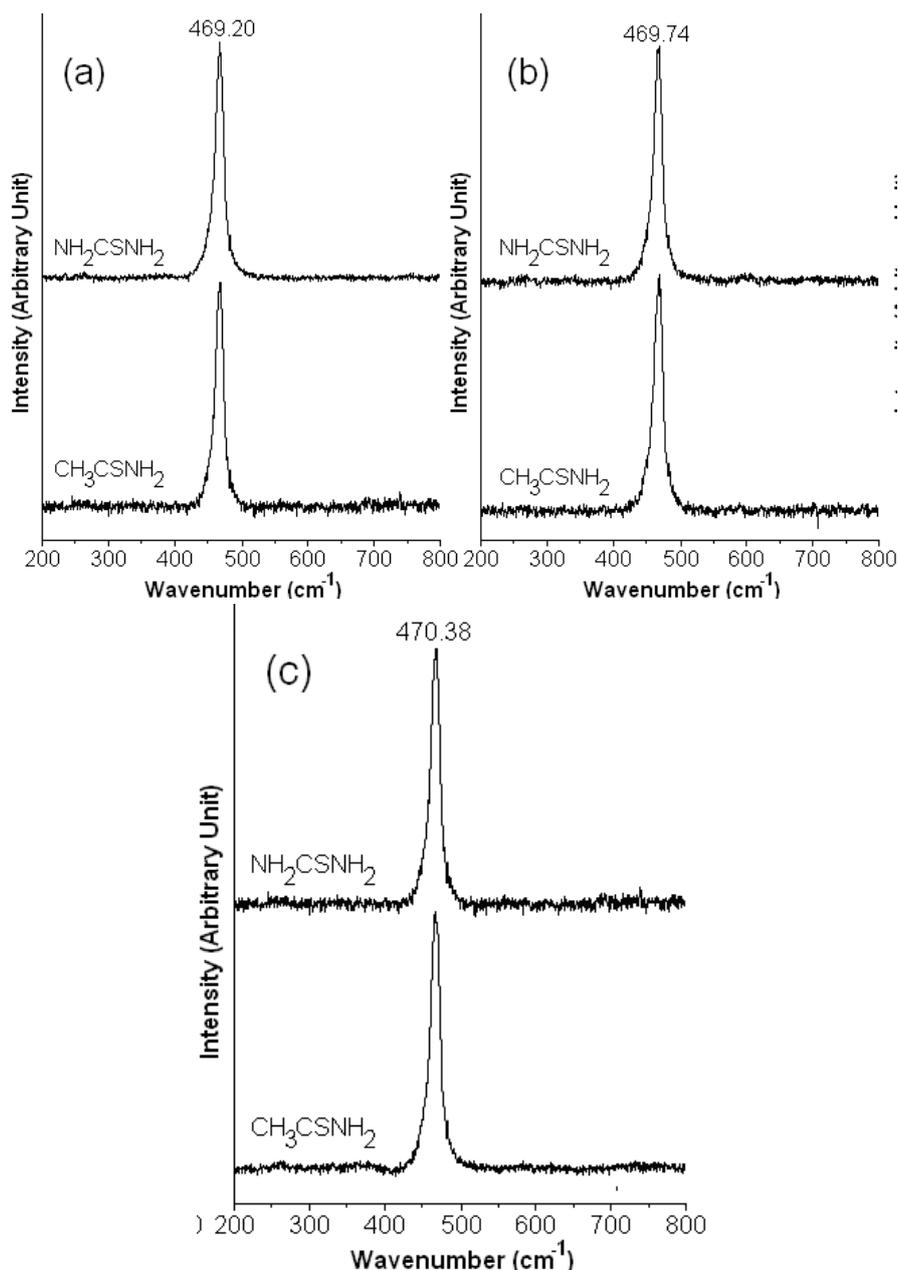
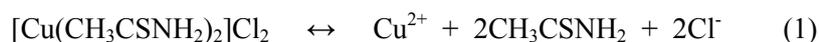
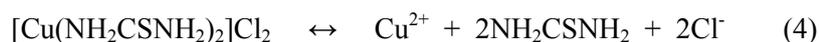


Fig. 3 Raman spectra of CuS using (a)  $\text{CuCl}_2$ , (b)  $\text{Cu}(\text{CH}_3\text{COO})_2$  and (c)  $\text{CuBr}$  as copper sources synthesized by microwave-hydrothermal method at 60 % W for 20 min.

During microwave hydrothermal processing,  $[\text{Cu}(\text{CH}_3\text{CSNH}_2)_2]\text{Cl}_2$  complexes were dissociated and thioacetamide hydrolyzed and generated  $\text{H}_2\text{S}$  to react with  $\text{Cu}^{2+}$  ions, by turning the precipitates into green-black CuS powder [9, 10, 12]. The reactions could be described below.



The reaction of  $[\text{Cu}(\text{NH}_2\text{CSNH}_2)_2]\text{Cl}_2$  complexes under microwave hydrothermal processing is as follows [7, 13, 14].



When  $[\text{Cu}(\text{CH}_3\text{CSNH}_2)_2]\text{Cl}_2$  /  $[\text{Cu}(\text{NH}_2\text{CSNH}_2)_2]\text{Cl}_2$  was heated by a microwave radiation, it dissociated to synthesize copper (II) ions and thioacetamide / thourea. Then  $\text{H}_2\text{NCSCCH}_3$  /  $\text{H}_2\text{NCSNH}_2$  was hydrolyzed by  $\text{H}_2\text{O}$  to form  $\text{CH}_3\text{CONH}_2$  /  $\text{H}_2\text{NCONH}_2$  and  $\text{H}_2\text{S}$ . Finally,  $\text{H}_2\text{S}$  reacted with copper (II) ions to form copper sulfide precipitates [7, 9, 10, 12-14].

In case of using  $\text{CuBr}$  as a copper source, it has a possible path way to produce  $\text{CuS}$ .  $\text{Cu}^+$  in the solution was not stable. It underwent disproportionation in which  $\text{Cu}^+$  species was simultaneously reduced and oxidized to form two different products [11].



With the assistance of microwave radiation,  $\text{Cu}^0$  was further oxidized to  $\text{Cu}^{2+}$  by  $\text{H}_2\text{S}$ . Then,  $\text{Cu}^{2+}$  reacted with  $\text{S}^{2-}$  to synthesize  $\text{CuS}$ .

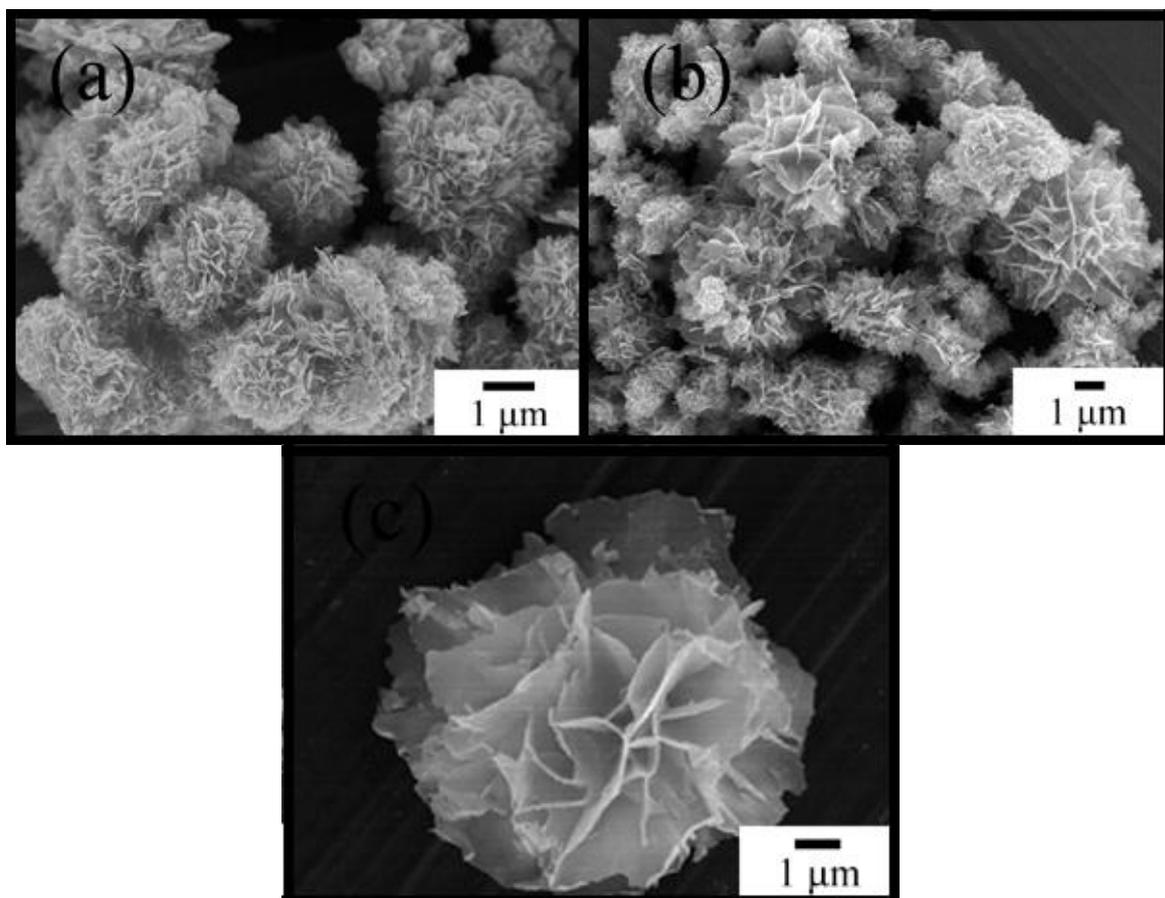
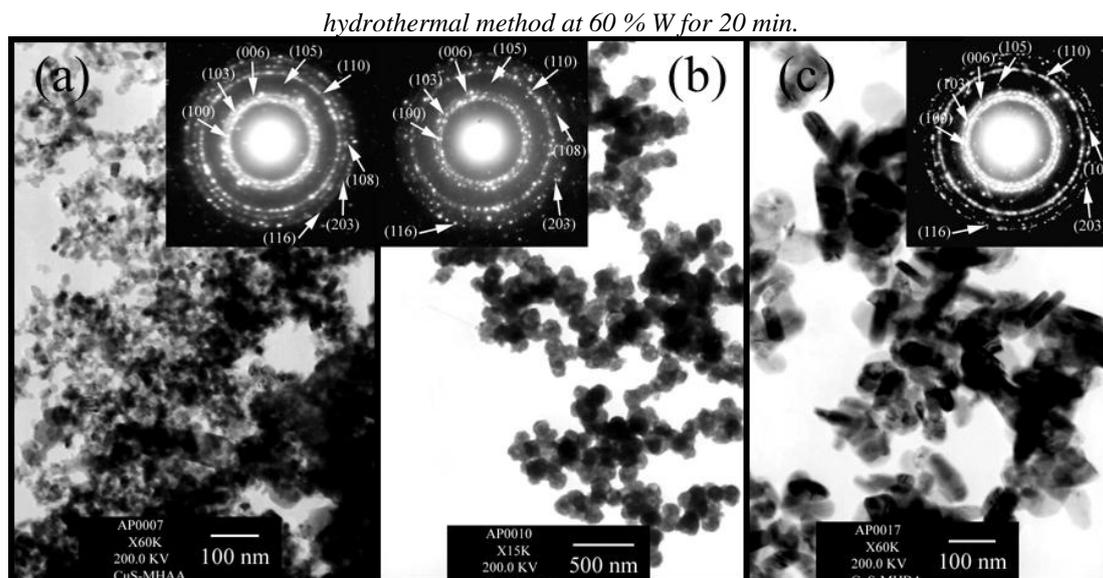


Fig. 4 SEM images of  $\text{CuS}$  synthesized using (a)  $\text{CuCl}_2$  and  $\text{CH}_3\text{CSNH}_2$ , (b)  $\text{CuCl}_2$  and  $\text{NH}_2\text{CSNH}_2$  and (c)  $\text{CuBr}$  and  $\text{CH}_3\text{CSNH}_2$  as copper and sulfur sources by microwave-



*Fig. 5 TEM images and SAED patterns of CuS synthesized using (a)  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{CH}_3\text{CSNH}_2$ , (b)  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{NH}_2\text{CSNH}_2$  and (c)  $\text{CuBr}$  and  $\text{NH}_2\text{CSNH}_2$  as copper and sulfur sources by microwave-hydrothermal method at 60 % W for 20 min.*

Morphologies of the products synthesized using different copper and sulfur sources were characterized by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). At constant 60 % of 180 W for 20 min with the same copper source ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and different sulfur sources ( $\text{CH}_3\text{CSNH}_2$ ,  $\text{NH}_2\text{CSNH}_2$ ) and  $\text{CuBr}$  and  $\text{CH}_3\text{CSNH}_2$ , the products (Fig. 4) were assemblies of nanoflakes (microsized flowers). To show more detail, ultrasonic vibration was done for the synthetic products in a beaker containing ethanol. A liquid was dropped on a copper grid and dried in ambient atmosphere for TEM analysis. TEM images and SAED patterns (Fig. 5) of the selected products were characterized. They were composed of round nanoparticles with <20 nm in diameter for  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and thioacetamide as starting materials and nanoparticles around 50 nm for  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and thiourea as starting materials. When  $\text{CuBr}$  and thiourea were used as starting materials, the  $\text{CuS}$  nanoplates would be synthesized. The SAED patterns show eight concentric rings corresponding to diffraction planes of the crystalline  $\text{CuS}$ . The interpretation from SAED and XRD patterns are in good accordance. The diffraction planes of the products are (100), (103), (006), (105), (110), (108), (203) and (116). The rings are diffuse and hollow showing that the products were composed of very fine nanoparticles. Different product morphologies were influenced by sulfur sources, which have different structure formulas. They were influenced by different oxidation states of copper as well. Nucleation and growth of the particles can play roles in the morphologies. The crystal growth of some preferred structure or planes relates to the surface energy of the planes in the specified condition.

#### 4. Conclusions

This research has been success in the synthesis of  $\text{CuS}$  with different morphologies (microflowers, nanoparticles and nanoplates) by microwave-hydrothermal method using different sources of copper ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{CuBr}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sulfur ( $\text{CH}_3\text{CSNH}_2$  and  $\text{NH}_2\text{CSNH}_2$ ). They were found that copper and sulfur sources are key parameters in controlling morphologies of finally  $\text{CuS}$  products.

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