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Full Length Research Paper

An investigation on a mild hydrothermal route to CuS nano and submicro structures

K. Zare[1], M. Darouie[1], F. Mollaamin[2] and M. Monajjemi[1]*

[1]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.
[2]Department of Chemistry, Qom Branch, Islamic Azad Unviversity, Qom, Iran.

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In this contribution, CuS nanostructures of various morphologies have been synthesized by manipulating time and choosing different copper sources via a mild hydrothermal method. The products were characterized by XRD, SEM, EDX and TEM analysis methods. Studies showed that after a definite time depending on the chosen copper source, the obtained pure CuS nanocrystals show a tendency towards self assembly and creating plate, rode, and wire like nano and submicro structures.

Key words: Nanoparticles, nanostructure, hydrothermal, CTAB.

INTRODUCTION

Recently, nanostructured materials have attracted great attention in the fields of experimental and theoretical chemistry sciences (Monajjemi et al., 2009, 2008). Due to extensive dependence of the properties and application of nano structured semiconductors on their crystal phase, size, composition and shape, synthesizing of highly tuned nanocrystals has been a challenging issue (Sun and Xia, 2002). Recently, copper sulfides have gained extensive attention on account of their various stoichiometrics. Unique optical, electronic, chemical characteristics of CuS (Erokhina and Erokhin, 2003; Janata et al., 1994; Raevskaya and Stroyuk, 2004) have caused it to be applied in many fields such as catalysts (Raevskaya and Stroyuk, 2004), solar cells, optical filters (Monajjemi et al., 2008; Sakamoto et al., 2003), enhanced conductive coatings on polymers (Monajjemi et al., 2008) and so on. Synthesis of green copper sulfide (covellite) is of interest because it shows electrical conductivity like metals (Monajjemi et al., 2011). With regard to synthesize pure and uniform CuS nanocrystals, many methods have been proposed including sonication (Wang et al., 2002), template assisted growth (Mao et al., 2004; Monajjemi et al., 2009; Wang and Yang, 2000), beam irradiation (Zhou et al., 2008), solid state reactions, solvothermal (Lu et al., 2002; Zou et al., 2007), and hydrothermal processes (Zhang et al., 2004; Tang et al., 2004; Jiang, 2005). CuS nanostructures have been prepared in a variety of architectures such as flakes and disks (Zhang and Gao, 2003), nanowhisker (Puspitasari et al., 2007), hollow spheres (Zhu et al., 2005), nanorods (Ou et al., 2005), trepange like and flower like (Tang et al., 2004), and urchin- like (Zhu et al., 2004) structures. Here in, we describe a mild hydrothermal method for the synthesis of spherical, quadrate, nano and submicrorod CuS structures. Effects of the copper source and reaction time on the morphology, size and yield of CuS nanostructures have been investigated.

*Corresponding author. E-mail: m_monajjemi@yahoo.com.

MATERIALS AND METHODS

The reactants used in this study were $Cu(CH_3COO)_2.H_2O$ and $Cu(NO_3)_2.3H_2O$, thiourea, cetyltrimethylamoniume bromide. All the chemical materials were of analytical grade and purchased from Merck™ Company.

Preparation of CuS nanoparticles without applying surfactant

In a typical procedure, 3 mmol of thiourea solution in 35 ml of deionized distilled water was added slowly to a solution of 1.5 mmol of copper salt in 35 ml of deionized distilled water at 80°C. The colour of the mixture changed from blue to green and then dark green. This solution was transferred into a 100 ml stainless steel

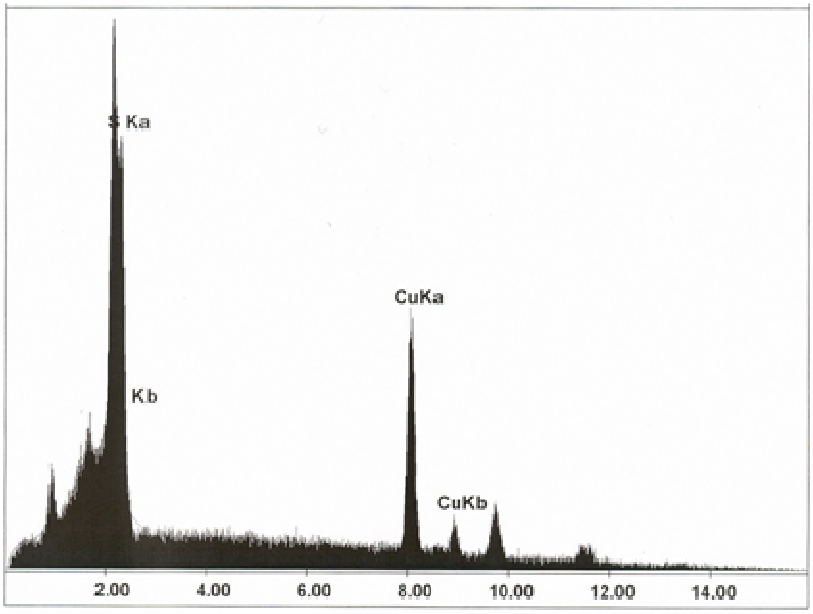

Figure 1. EDX pattern of the product obtained by $Cu(ac)_2.H_2O$, Tu and CTAB.

autoclave, sealed and kept at 80°C for 24 h. Subsequently, the system cooled to the room temperature, centrifuged and washed with deionized distilled water and ethanol several times. The obtained black precipitate was dried under vacuum at 60°C for 12 h.

Preparation of CuS nanoparticles using CTAB surfactant

While stirring, a solution of 1.5 mmol of copper salt in 20 ml deionized distilled water was added to a solution of 2.1 mmol of CTAB in 30 ml of deionized distilled water at low speed. The mixture was refluxed at 80°C for 1 h. Under vigorous stirring, 3 mol of thiourea in 20 ml deionized distilled water was added to the mixture. The blue mixture turned into green and then dark green. The obtained green sols were transferred into a 100 ml stainless steel autoclave, sealed and kept at 80°C for 24 h. Then, the system was cooled down to the room temperature and 25 ml of ethanol was added into the obtained solution. The product was centrifuged and washed with deionized distilled water several times and dried under vacuum at 60°C for 12 h.

The crystal phase and particle sizes of the synthesized products were studied by X-ray powder diffraction method, using Siemens D5000 diffractometer (Cu Kα radiation, λ = 1.54056Å) in 2θ ranges from 5 to 70°. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were taken on a Philips XL30 scanning electron microscope. Transmission electron microscopy (TEM) images were taken on a Philips CM120 microscope.

RESULTS AND DISCUSSION

Two different copper sources of $Cu(ac)_2.H_2O$ and $Cu(NO_3)_2.3H_2O$ are used to synthesize CuS nanoparticles in the presence and absence of CTAB surfactant.

Figure 1 shows the EDX pattern of the product obtained by the reaction of copper acetate monohydrate and thiourea after 24 h. The patterns correspond to Cu and S and the extra peaks are attributed to Au which the nanoparticles were coated with. The EDX patterns are approximately similar for all the products. No impurity is found and Cu:S ratio approximately equals to 1.

XRD patterns of the prepared CuS samples are given in Figure 2. All the reflections are attributed to pure hexagonal phase CuS covellite. The entire diffraction patterns match with the data reported in the literature (JCPDS card no. 06-0464). The patterns illustrate that the whole products are well crystalline and pure which conforms to EDX results.

Yields of the products after 12 h were about 62 and 65% when $Cu(CH_3COO)_2.H_2O$ and $Cu(NO_3)_2.3H_2O$ were used as copper sources, respectively. After 24 h, the yields became 84% in the case of $Cu(ac)_2.H_2O$ and 90% when $Cu(NO_3)_2.3H_2O$ was used. It can be concluded that a longer reaction time can increase the product yield and declines the unreacted copper sources.

TEM images of the products obtained using $Cu(ac)_2.H_2O$ after 12 and 24 h are shown in Figures 3 a and b, respectively. As it is clear, after 12 h, the morphology of the product is spherical while after 24 h, particles have a quadrate plate like morphology. However, the crystal sizes of the products calculated using scherrer's equation [Dutta and Dolui, 2008] shows that the size of the particles are about 9 nm and there is no size enhancement during a longer reaction time. It can be deduced that when the reaction time gets longer than 12 h the particles have a tendency towards setting beside each other in order to create polycrystalline quadrate

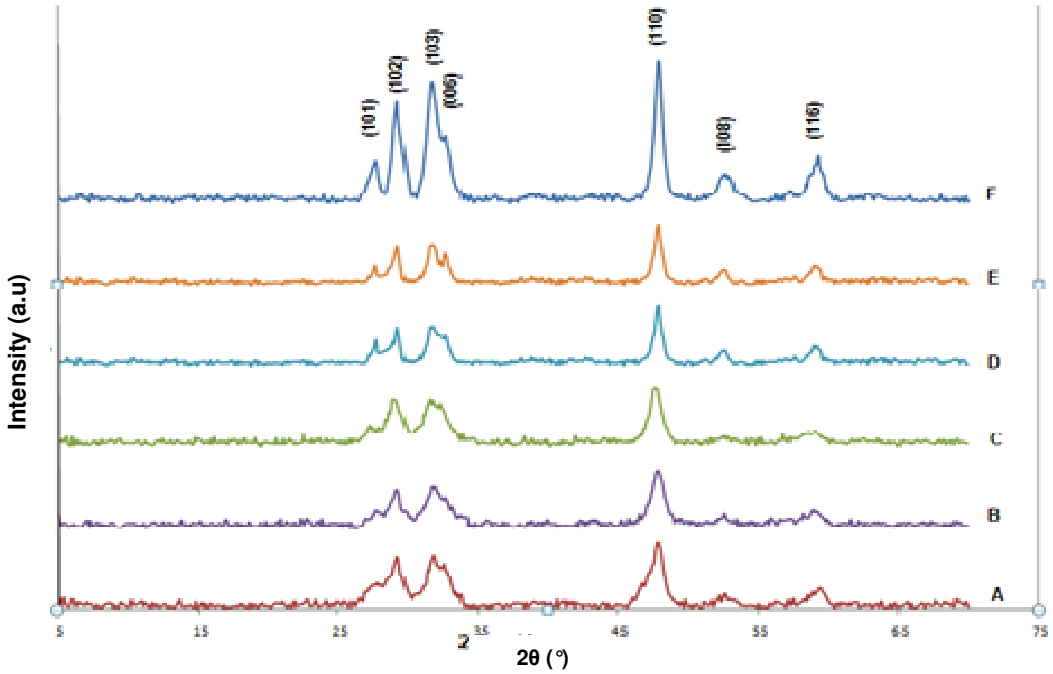

Figure 2. XRD patterns of the products prepared with; (A) $Cu(ac)_2.H_2O$ and Tu after 12 h, (B) $Cu(ac)_2.H_2O$ and Tu after 24 h (C) $Cu(ac)_2.H_2O$, Tu and CTAB after 24 h (D) $Cu(NO_3)_2.3H_2O$ and Tu after 12 h (E) $Cu(NO_3)_2.3H_2O$ and Tu after 24 h (F) $Cu(NO_3)_2$. $3H_2O$, Tu and CTAB after 24 h.

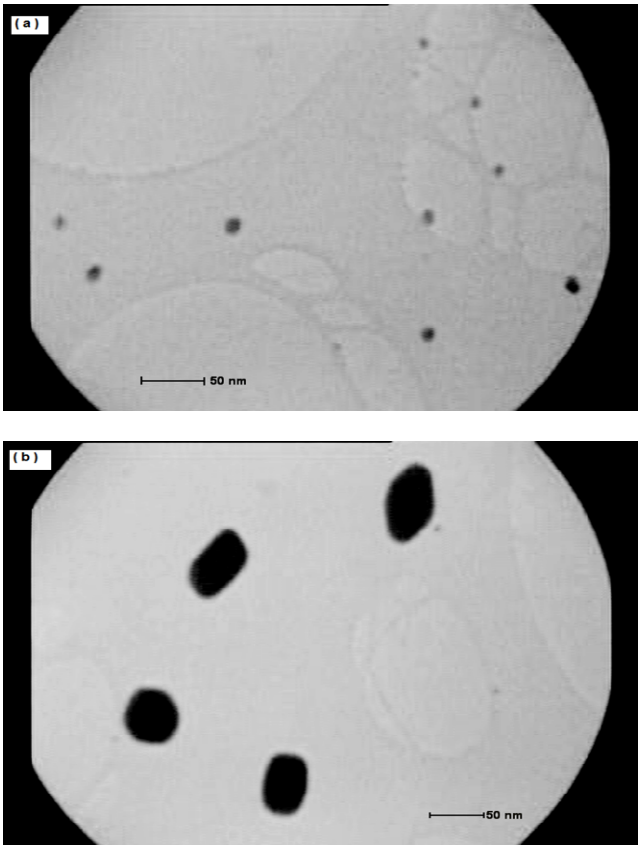

Figure 3. TEM images of the products prepared with $Cu(ac)_2.H_2O$ and Tu after (a) 12 h and (b) 24 h.

plates.

Figures 4a to d show the TEM images of the products synthesized with applying $Cu(NO_3)_2.3H_2O$ and Tu at 12, 16 and 18 h after the beginning of the reaction, respectively. As it is shown in Figure 4a, after 12 h the particles have an elliptical shape. The particles have a mean size of about 15 nm calculated by Scherrer's equation. However, Figure 4b and c show that after 16 h the CuS nanocrystals were self assembled in one dimension and arranged in a rode shape structures. The diameters of the obtained nanorods are between 30 to 70 nm. Figure 4d is taken after 18 h from the beginning of the reaction. At this stage, the obtained product has a mean diameter of 85 nm. This image reveals that the nanorods got branched and curved over time and created a nano wire like morphology over time. The SEM images of the product obtained after 24 h are shown in Figure 5a and b. As it is shown, the more one dimensional assembly of CuS nanoparticles caused the formation of submicro wires. Figure 5a reveals that the obtained wires are curved and along with some spherical particles. The mean diameter of the CuS submicro wires is about 600 to 800 nm. Figure 5b shows that some of the submicro wires are branched.

Figure 6a and b are SEM images of the products prepared in the presence of CTAB surfactant. In the case of the product shown in Figure 6a the copper source was $Cu(ac)_2$. H_2O and the $Cu(NO_3)_2.3$ H_2O was used to prepare sample shown in the Figure 6b. The images reveal that after the initial nucleation CTAB restrains the

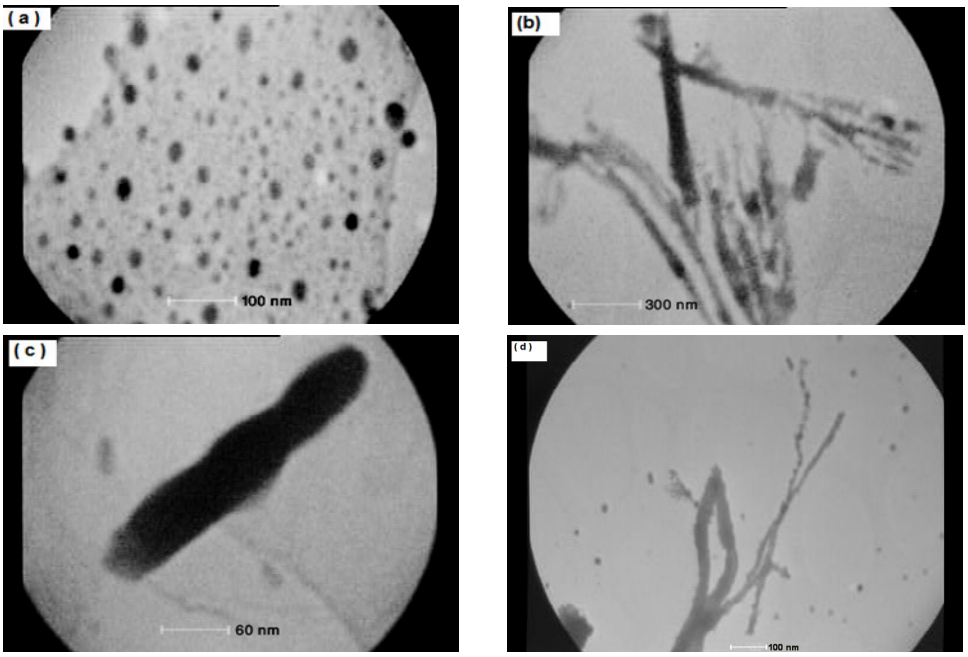

Figure 4. TEM images of the products prepared with $Cu(NO_3)_2.3H_2O$ and Tu after (a)12 h (b) 14 h (c) 16 h and (d) 18 h.

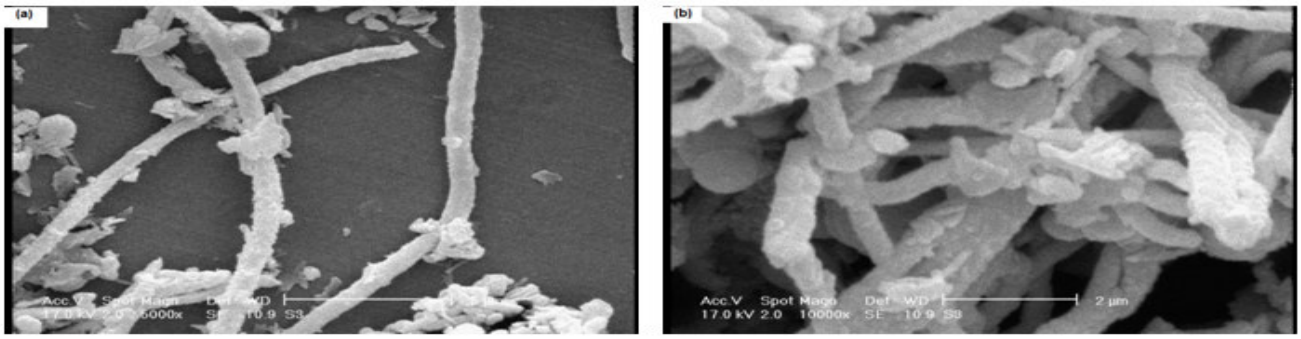

Figure 5. SEM images of the products prepared with (a) $Cu(NO_3)_2.3H_2O$ and (b) Tu, respectively after 24 h.

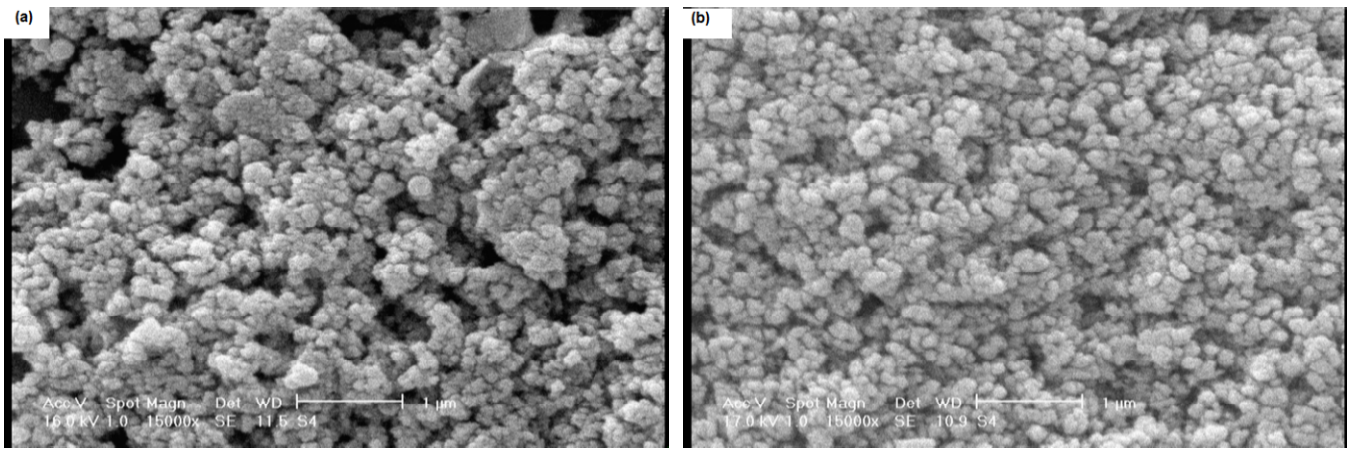

Figure 6. SEM images of the products prepared in the presence of CTAB, Tu, 24 h and; (a) $Cu(ac)_2.H_2O$, and (b) $Cu(NO_3)_2.3\ H_2O$.

nanoparticles from aggregating and hinders the formation of plate or rode like morphologies while in the absence of CTAB both the aforementioned structures are seen. The mean crystal size of the products obtained by the use of $Cu(ac)_2$. H_2O and $Cu(NO_3)_2.3H_2O$ in the presence of CTAB were about 7 and 12 nm, respectively.

These data were calculated by Scherrer's equation. It can be seen that by employing CTAB the particle sizes have been reduced which are due to steric hindrance effect of the CTAB.

Conclusion

In summary, CuS nanocrystals have been synthesised by the use of $Cu(ac)_2.H_2O$ and $Cu(NO_3)_2.3H_2O$ as copper sources and thiourea in the absence and presence of CTAB surfactant. The reactions were carried out in various reaction times via a hydrothermal method. It was found out that variation of copper source and reaction time affect the morphologies, size and yields of the products, that is, spherical and elliptical CuS nanoparticles were obtained after 12 h by the application of $Cu(NO_3)_2.3H_2O$ and $Cu(ac)_2.H_2O$, respectively. While CuS quadrate particles were achieved using $Cu(ac)_2$. H_2O after 24 h, and CuS nanorods and submicro wires were synthesised using $Cu(NO_3)_2.3H_2O$ after 16 and 24 h from the onset of the reactions, respectively, Investigations also showed that a longer reaction time increases the yield and the use of CTAB surfactant prevents the particles from forming rode or plate like structures and decreases the particle size due to steric hindrance after initial nucleation.

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