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Self-assembly of CuS nanoparticles to solid, hollow, spherical and tubular structures in a simple aqueous-phase reaction

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ABSTRACT We report fabrication of CuS particles with solid, hollow, spherical and tubular structures in a simple aqueous system under microwave irradiation, employing $CuSO_4$ and $Na_2S_2O_3$ as the starting materials without assistance of any surfactant or template. Energy-dispersive X-ray analysis and an X-ray powder diffraction pattern proved that the product is hexagonal CuS phase. The morphologies of the product were observed by scanning electron microscopy and transmission electron microscopy. Some factors affecting the morphologies of the product are discussed.

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1 Introduction

In the past decade, considerable interest has been focused on the study of the precise control over the size and shape of nanoparticles, owing to their distinguished chemical, catalytic, optical and electronic properties, which depended on the size of the nanoparticles, in bulk solids and device components [1, 2]. In particular, the development of the self-assembly technique offers opportunities to exploit the unique optical and electronic properties of nanoparticles and possibilities to probe new, potentially collective phenomena [3]. Usually, the assembly of nanoparticles is realized via electrostatic interaction, intermolecular force, hydrogen bonds and so on. So, to fabricate nanostructural materials successfully via the self-assembly route, a well-designed reaction is required to produce nanoparticles with a narrow size distribution and a high degree of shape control and to assemble the nanoparticles produced into a desirable nanostructure simultaneously [4]. Diverse complex and ordered structures, such as ordered clusters [5], spheres [6] and superlattices [7, 8], have been constructed from nanoparticles as building blocks by the self-assembly route. However, compared with the preparation of discrete nanoparticles, the assembly of nanoparticles into well-defined superstructures is still a challenge in material science.

Copper sulfides are a particularly interesting class of metal sulfides due to their ability to form various stoichiometric products including covellite (CuS), anilite (Cu_7S_4), digenite (Cu_9S_5), djurleite ($Cu_{1.95}S$) and chalcocite (Cu_2S) [9], and extensive applications in areas such as semiconductors and solar energy conversion [10]. As useful minerals, the mineralogical and technological properties of copper sulfides have been studied extensively [11]. Many methods have been developed for the preparation of copper sulfides, including solid-state reaction [12], spray pyrolysis deposition [13], the sonochemical route [14], solvothermal synthesis [15] and the molecular precursor route [16–18]. Recently, Wang and Yang reported a surfactant-assisted route to fabricate crystalline copper sulfide nanowire arrays from rough oxidized copper surfaces under hydrogen sulfide atmosphere [19]. Lu et al. described the synthesis and assembly of copper sulfide nanoparticles to nanowires, nanotubes and nanovesicles by an organic amine-assisted hydrothermal process [3].

Herein, we designed a simple system for the preparation of CuS particles and the assembly to solid, hollow, spherical and tubular structures in a one-pot reaction, employing a microwave irradiation technique [20–22]. The system contained only water, $CuSO_4$ and $Na_2S_2O_3$, without the assistance of any surfactant or template. All reactions were completed within 30 min. Experiments showed that the shape of the CuS particles was related to the starting $CuSO_4/Na_2S_2O_3$ molar ratio.

2 Experimental

2.1 *Preparation of the product*

In a typical experiment, all reagents are analytically pure and used without further purification. 0.005 mol $Na_2S_2O_3$ and 0.0025 mol $CuSO_4$ were separately dissolved in distilled water. Then, $Na_2S_2O_3$ solution was added to $CuSO_4$ solution dropwise under stirring. Finally, the above system was heated in a microwave oven (2.45 MHz, 650 W) with the power of 20% for 30 min. The black precipitates were collected, washed with distilled water and absolute ethanol several times and dried in air at 50 °C for characterization use.

2.2 *Characterization of the product*

An X-ray powder diffraction (XRD) pattern was recorded on a Japan Rigaku D/max γ_A X-ray diffractometer equipped with graphite monochromatized Cu K_α radiation

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($\lambda = 0.154178$ nm), using a scanning rate of 0.02 degree/s in 2θ ranges from 20° to 65°. Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were obtained on a JEOL JEM-200CX transmission electron microscope, employing an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) analysis were carried out on a scanning electron microscope (Hitachi X650/EDAX, PV9100).

3 Results and discussion

Fig. 1 shows the XRD pattern of the product prepared from the above system. All diffraction peaks can be indexed as the hexagonal CuS by comparison with data from JCPDS file no. 6-464. No characteristic peaks of other impurities were observed. The further evidence for the formation of CuS came from EDX analysis, which is given in Fig. 2. Only Cu and S peaks are found and, according to the calculation of peak areas, the molar ratio of Cu/S is $\sim 49:51$, which is very close to the $1:1$ of CuS.

The morphologies of the as-prepared product were investigated by TEM (Fig. 3). Some tubes and aggregated particles are observed. In Fig. 3a, besides some aggregated particles, a thick tube with 1000 nm in outer diameter and 800 nm in inner diameter and a thin tube with 350 nm in outer diameter and 250 nm in inner diameter can be clearly seen. The lengths of the tubes were some tens of microns and were composed of small particles. Figure 3b depicts another TEM image, which was magnified 20 000 times; some particles can be clearly seen on this tube. Figure 3c shows the selected-area electron diffraction pattern of the tubes. The concentric rings imply the polycrystalline structure of the tubes, which confirmed the result of the TEM observation.

The SEM image further proves the formation of tubular products. Figure 4 shows the SEM image of the as-prepared product in this simple system. Some small spherical particles and tubes with open ends can be found.

It was found that the morphologies of the product were related to the $CuSO_4/Na_2S_2O_3$ molar ratio of the starting materials. Preparing four solutions with $CuSO_4/Na_2S_2O_3$ molar ratios of $1:1$, $1:2$, $1:3$ and $1:4$ and keeping the remaining experimental conditions constant, three different morphologies were obtained, including solid spherical particles, tubes (with a small amount of solid spherical particles) and spherical hollow structures (Fig. 5). Only solid spherical particles were prepared when the starting $CuSO_4/Na_2S_2O_3$ molar ratio of $1:1$ was employed (Fig. 5a) while, when

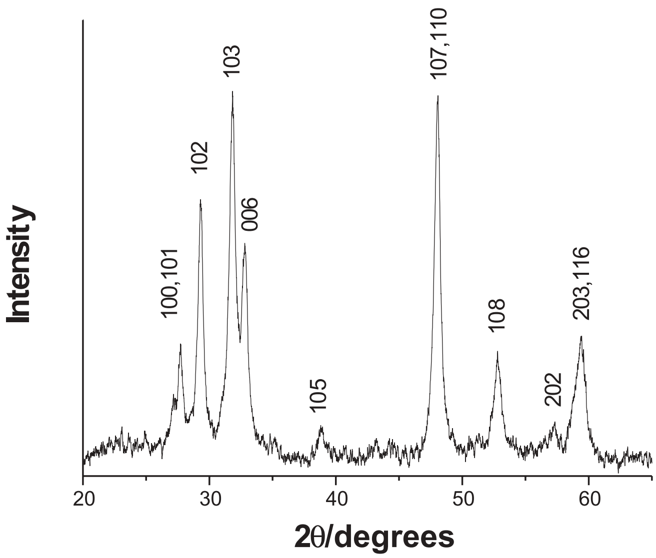


FIGURE 1 XRD pattern of the product prepared from the system of the starting $CuSO_4/Na_2S_2O_3$ molar ratio of $1:2$

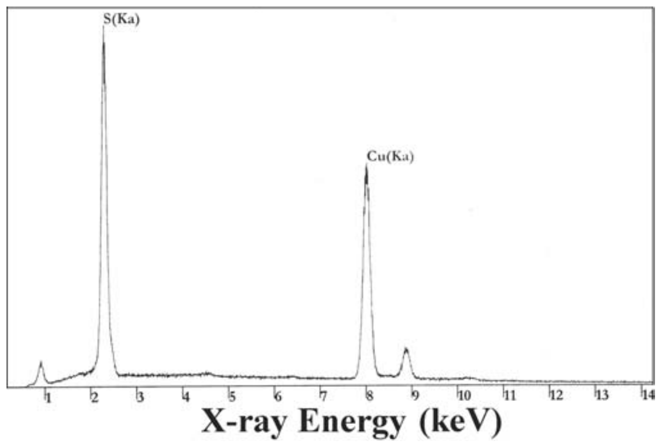


FIGURE 2 EDX analysis of the as-prepared product shown in Fig. 1

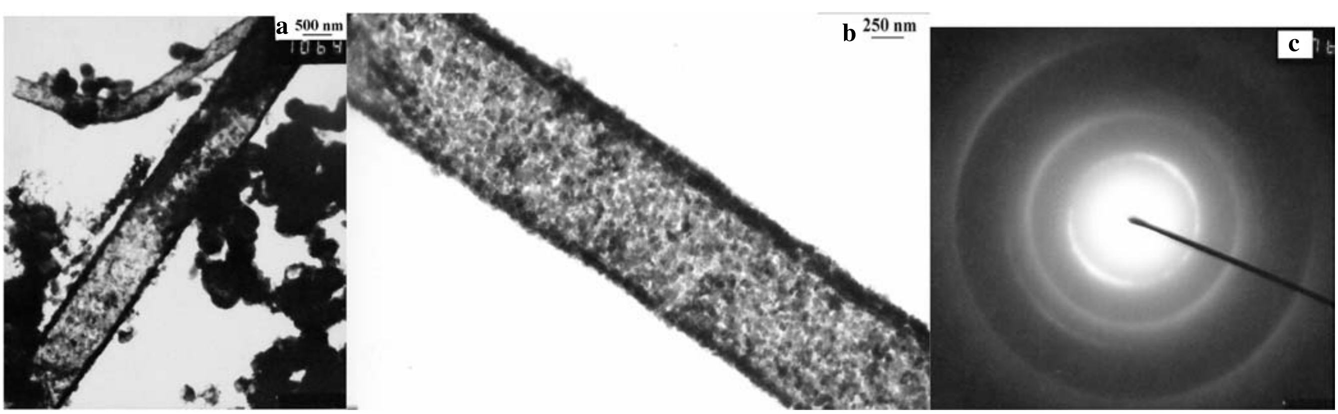


FIGURE 3 TEM images of the as-prepared product from the system of the starting $CuSO_4/Na_2S_2O_3$ molar ratio of $1:2$. **a** Tubes and aggregated particles, **b** an individual tube composed of many small particles and **c** SAED pattern of **b**

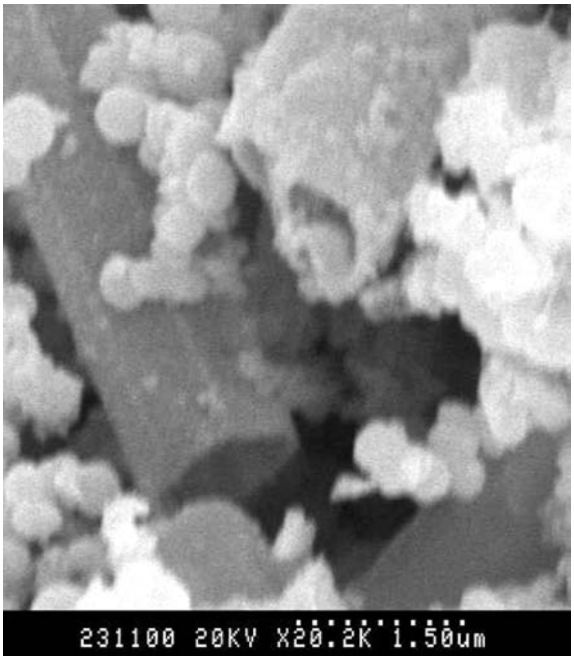


FIGURE 4 SEM image of the as-prepared product from the system of the starting $CuSO_4/Na_2S_2O_3$ molar ratio of 1 : 2

the $CuSO_4/Na_2S_2O_3$ molar ratio was 1 : 2, a great deal of tubes embedded in solid spherical particles could be observed (Fig. 5b). Further increasing the $CuSO_4/Na_2S_2O_3$ molar ratio to 1 : 3 and 1 : 4, solid spherical particles and tubes disappeared but, instead, a great deal of spherical hollow structures were found (Fig. 5c and d).

In this work, the system contains only three components: copper ion source, sulfur ion source and water; so, without doubt, the formation and self-assembly of CuS nanoparticles is related to the interaction between copper and sulfur ion sources. It is well known that a $S_2O_3^{2-}$ ion can hydrolyze to release a S^{2-} anion, which reacts with Cu^{2+} to produce CuS. At the same time, due to the coordination of $S_2O_3^{2-}$ ions to Cu(II) in CuS nanoparticles, excess $S_2O_3^{2-}$ ions can circumfuse a CuS nanoparticle to form a passive layer. It is obvious that the concentration of the $S_2O_3^{2-}$ ion is an important factor to affect the structure and density of the passive layer surrounding the CuS nanoparticles and, therefore, it may change the self-assembly mode of the CuS nanoparticles. As a result, the shape of the product is changed. For example, when the molar ratio of $CuSO_4/Na_2S_2O_3$ is up to 1 : 1, all $S_2O_3^{2-}$ ions are exhausted in the reaction and no $S_2O_3^{2-}$ ions coordinate to the CuS nanoparticles, which results in the formation of solid spheres. On increasing the molar ratio to 1:2, one time of $S_2O_3^{2-}$ remains. Due to the strong affinity between Cu and S, the excess $S_2O_3^{2-}$ ions bind to the CuS nanoparticles, but are not too dense. When the as-produced CuS nanoparticles aggregate, to some extent spatial hindrance makes the assembly curve along the radial direction, which is favorable to the formation of tubular structures. Further raising the molar ratio to 1 : 3 or 1 : 4, two or three times the amount of $S_2O_3^{2-}$ remains. The dense $S_2O_3^{2-}$ ions bind on the surface of the CuS nanoparticles. Serious spatial hindrance forces the assembly to curve along all directions, which results in the formation of the hollow spherical structures. The above possible processes are illuminated in Fig. 6.

Furthermore, keeping the power of the microwave irradiation and the starting $CuSO_4/Na_2S_2O_3$ molar ratio of 1 : 2 constant, the irradiation time was reduced to 20 min, and a number of tubular particles could still be fabricated (Fig. 7). Tubular CuS particles decreased sharply if the irradiation time

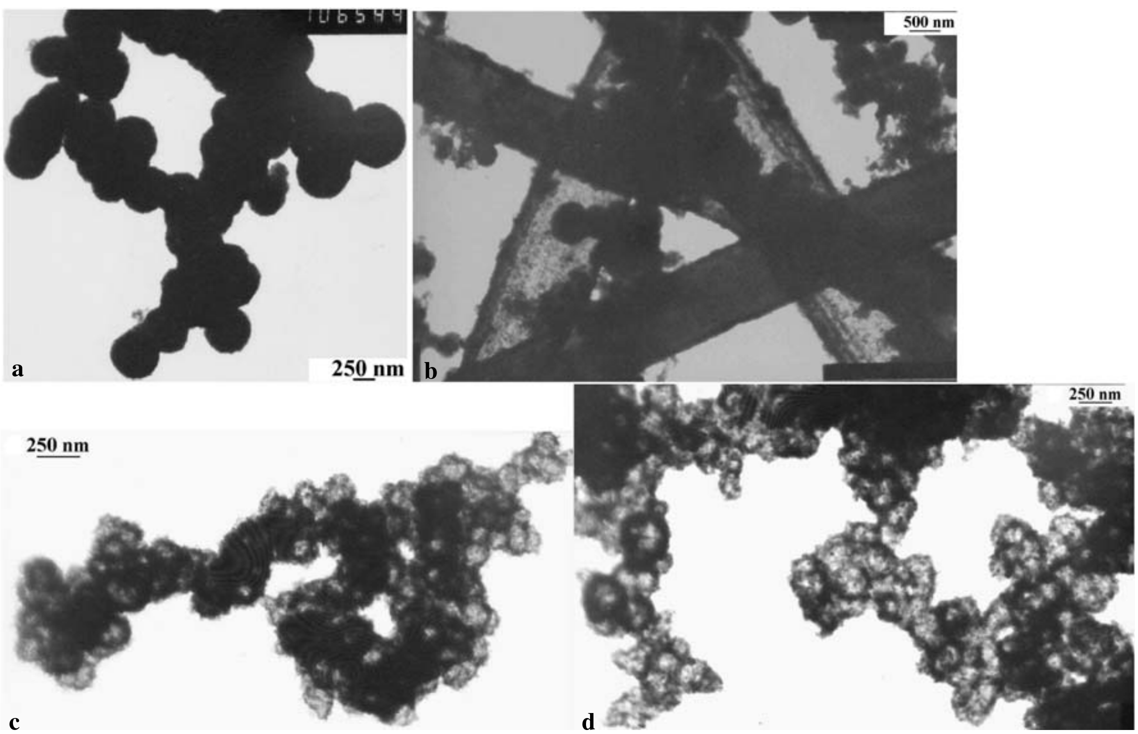
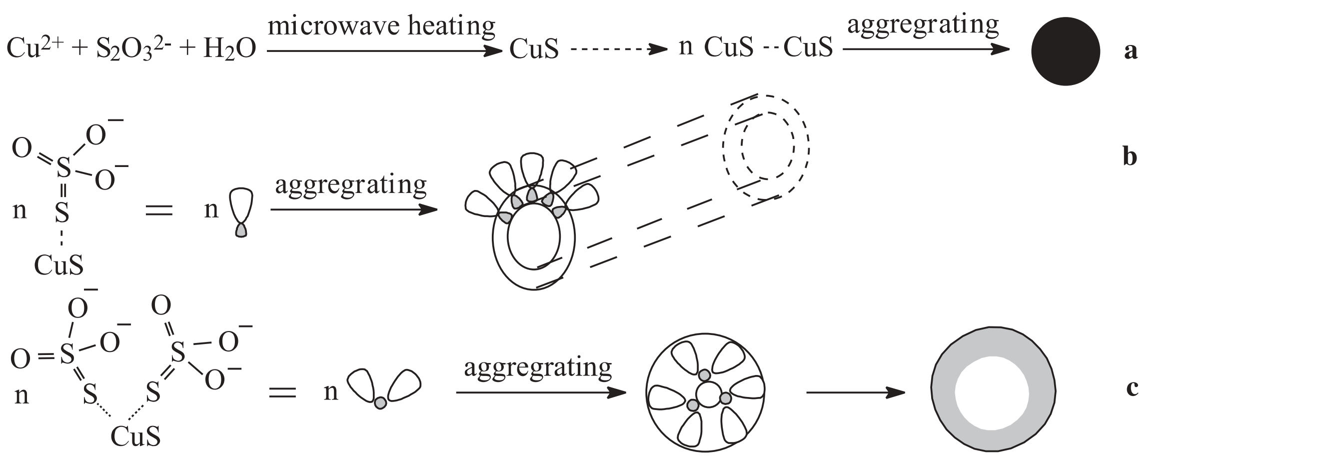


FIGURE 5 TEM images of the products obtained from various starting $CuSO_4/Na_2S_2O_3$ molar ratios: **a** 1 : 1, **b** 1 : 2, **c** 1 : 3 and **d** 1 : 4



CuS --CuS stands for the aggregation of CuS particles.

FIGURE 6 The possible formation mechanism of CuS nanoparticles with solid, hollow, spherical and tubular structures. The $CuSO_4/Na_2S_2O_3$ molar ratios: (a) 1 : 1, (b) 1 : 2 and (c) 1 : 3 (the formation process with the molar ratio of 1 : 4 is similar to that of 1 : 3)

is shortened to 10 min. Also, experiments showed that the tubes and solid spherical particles always coexisted in the final product.

In general, higher power makes the system keep a boiling state, which does not assist the formation of tubular structures. This conclusion was confirmed by our experiment. Keeping the starting $CuSO_4/Na_2S_2O_3$ molar ratio of 1:2 and the reaction time of 30 min constant, the power of the microwave oven was increased to 40%; only solid spherical particles were obtained (Fig. 8a). It is obvious that the larger the microwave

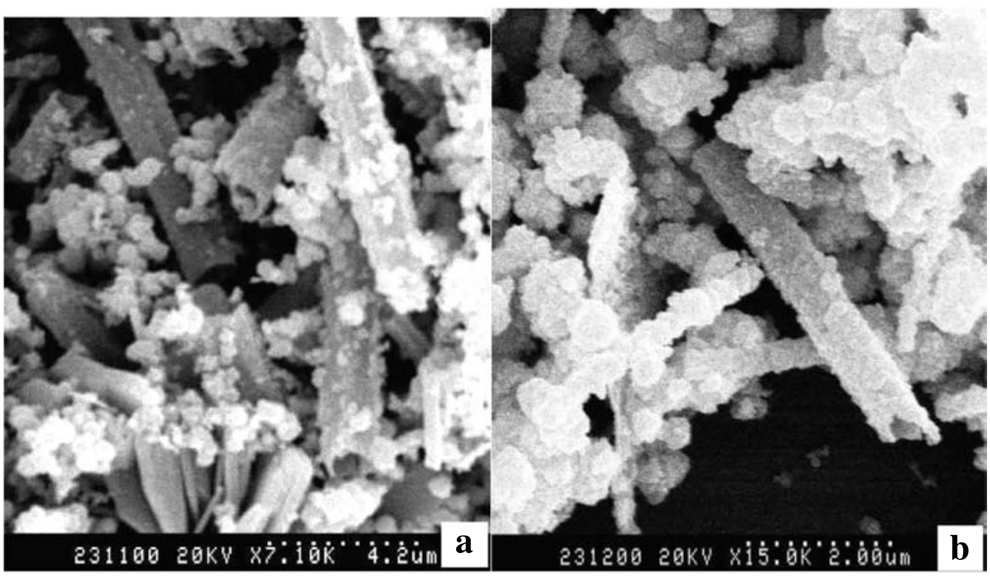


FIGURE 7 SEM images of the product prepared from the system of the starting $CuSO_4/Na_2S_2O_3$ molar ratio of 1 : 2. Irradiation time: **a** 20 min and **b** 10 min

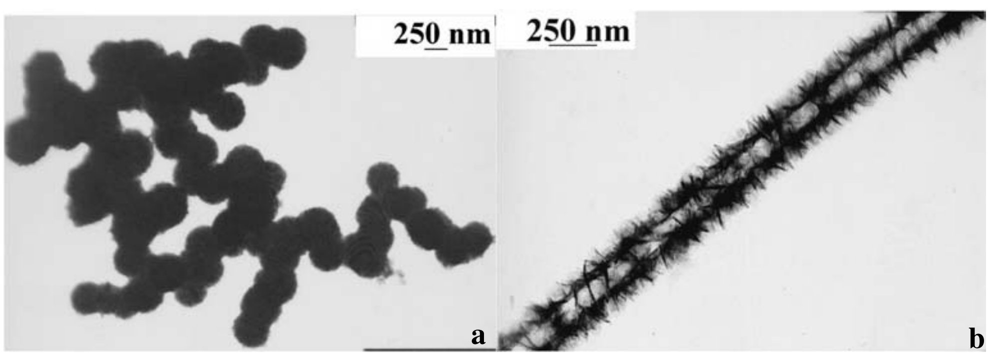


FIGURE 8 TEM images of the products: **a** aggregated particles prepared in the system of the $CuSO_4/Na_2S_2O_3$ molar ratio of 1:2 under the power of 40% and **b** a single tube composed of whiskers from the system of the $CuCl_2/Na_2S_2O_3$ molar ratio of 1 : 2 under the power of 20%

power, the faster the formation rate of CuS nanoparticles and the violent reaction condition is unfavorable to the formation of the passive layer of $S_2O_3^{2-}$ on CuS nanoparticles, because most of the $S_2O_3^{2-}$ ions are decomposed, which is favorable to the formation of the solid spheres. In addition, the formation of the tubular structures was also related to the anion. When $CuCl_2$ was used as copper source instead of $CuSO_4$, the tubes composed of a whisker-like structure were obtained (Fig. 8b). Since the remaining experimental conditions were not changed, the above result indicated that the counter-ion played an important role in the formation process of tubular structures.

4 Conclusions

CuS particles with solid, hollow, spherical and tubular structures have been prepared in a simple aqueous system, employing $CuSO_4$ and $Na_2S_2O_3$ as copper and sulfur ion sources, respectively, under microwave irradiation. Experimental results showed that a great deal of tubes with solid spherical particles were obtained when the starting $CuSO_4/Na_2S_2O_3$ molar ratio of 1 : 2 was used; and that only spherical hollow/solid structures were produced when increasing/decreasing the starting molar ratio. The irradiation time and power of the microwave oven and the counter-ion of the copper source also affected the formation of tubular products. The above results can be reproduced easily and the shape of the product can be controlled via varying the starting molar ratio of $CuSO_4/Na_2S_2O_3$. However, the free control of the size of the product needs still studying.

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