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 CuSO₄ and Na₂S₂O₃ 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 depend 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 (Cu₇S₄), digenite (Cu₅S₅), djurleite (Cu₁₉S₅S) and chalcocite (Cu₂S)[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, CuSO₄ and Na₂S₂O₃, 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 CuSO₄/Na₂S₂O₃ 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 Na₂S₂O₃ and 0.0025 mol CuSO₄ were separately dissolved in distilled water. Then, Na₂S₂O₃ solution was added to CuSO₄ 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 γA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation
(\(\lambda = 0.154178\) nm), using a scanning rate of 0.02 degree/s in \(\theta\) 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\(_2\)S\(_2\)O\(_3\) molar ratio of the starting materials. Preparing four solutions with CuSO\(_4\)/Na\(_2\)S\(_2\)O\(_3\) 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\(_2\)S\(_2\)O\(_3\) molar ratio of 1 : 1 was employed (Fig. 5a) while, when