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Solvothermal synthesis of copper sulfide semiconductor micro/nanostructures

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ABSTRACT

Covellite copper sulfide (CuS) micro/nanometer crystals in the shape of hierarchical doughnut-shaped, superstructured spheric-shaped and flowerlike architectures congregated from those nanoplates with the thickness of 20–100 nm have been prepared by a solvothermal method. The as-obtained CuS products were characterized by means of scanning electron microscopy (SEM), X-ray diffractometry (XRD) and energy-dispersive X-ray spectroscopy (EDS). A systematic investigation has been carried out to understand the factors influencing the evolution of CuS particle morphology which found to be predominant by solvent, surfactant, sulfur resource and copper salt. The possible formation mechanism for the nanostructure formation was also discussed. These CuS products show potential applications in solar cell, photothermal conversion and chemical sensor.

1. Introduction

The controlled synthesis of nanomaterials has attracted much attention, not only as a result of their fundamental shape- and size-dependent properties and important technological applications, but also for their self-assembling potential for use in devices [1–9]. Furthermore, the precise control of their chemical composition, crystal structure, size shape and surface chemistry allows one to observe the unique properties of nanocrystals, and to tune their chemical and physical properties as desired [10–17]. Copper sulfide (Cu_xS, $x = 1–2$) is well-known to form a wide variety of nonstoichiometric and mixed phases, of which at least five are known to be stable at room temperature: covellite (CuS) in the 'sulfur-rich region'; and anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.95}S$), and chalcocite (Cu_2S) in the 'copper-rich region'. Cu_xS compounds with different stoichiometries have a wide range of well-established and prospective applications in solar cell, photothermal conversion and chemical sensor [1,2].

Recently, we have successfully demonstrated that Cu_2S and CuS micro/nanoparticles can be used as the precursor or template for fabricating porous and hollow CuO capsules [1]. However, detailed formation mechanisms of Cu_2S and CuS products have not yet been investigated. Herein, we give a systematic research on the solvothermal synthesis of a variety of micro/nanostructured CuS and Cu_2S, which include monodisperse doughnut-shaped, spheric and flowerlike CuS microparticles consisting of nanoplates and Cu_2S submicrospheres with a uniform diameter.

2. Experimental

Copper sulfide micro/nanostructured products were prepared via a solvothermal technique in a Teflon-lined stainless steel autoclave. In a typical synthesis of hierarchical doughnut-shaped particles, 2 mmol $Cu(NO_3)_2{\cdot}5H_2O$ was dissolved in 25 ml dimethylsulfoxide (DMSO) to form a clear solution, then 0.4 g poly (vinyl pyrrolidone) (PVP) and 4 mmol thiourea were added to this solution under vigorous stirring. Afterwards, this solution was transferred into a 30 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 110–160 °C for 15–30 h. After the solution was cooled down to room temperature, the obtained black solid products were collected by centrifuging the mixture, which were then washed with absolute ethanol several times and dried at 60–80 °C for 6 h for further characterizations. For hierarchical spheric and flowerlike microparticles consisting of CuS nanoplates, N, N-dimethylformamide (DMF) and sulfur powder were used as the solvent and sulfur resource, respectively.

The as-prepared samples were characterized by X-ray diffractometry (XRD) on a Rigaku-Dmax 2400 diffractometer equipped with a graphite monochromatized Cu Kα radiation flux at a scanning rate of $0.02^\circ\ s^{-1}$ in the 2θ range of 5–80°. Scanning electron microscopy (SEM) images were taken with a JEOL-5600LV scanning electron microscope, using an accelerating voltage of 20 kV. Energy-dispersive X-ray spectroscopy (EDS) microanalysis of the samples was performed during SEM measurements.

3. Results and discussion

Fig. 1a shows the typical XRD pattern of the as-synthesized CuS doughnut-shaped particles. All peaks in Fig. 1a match well with the

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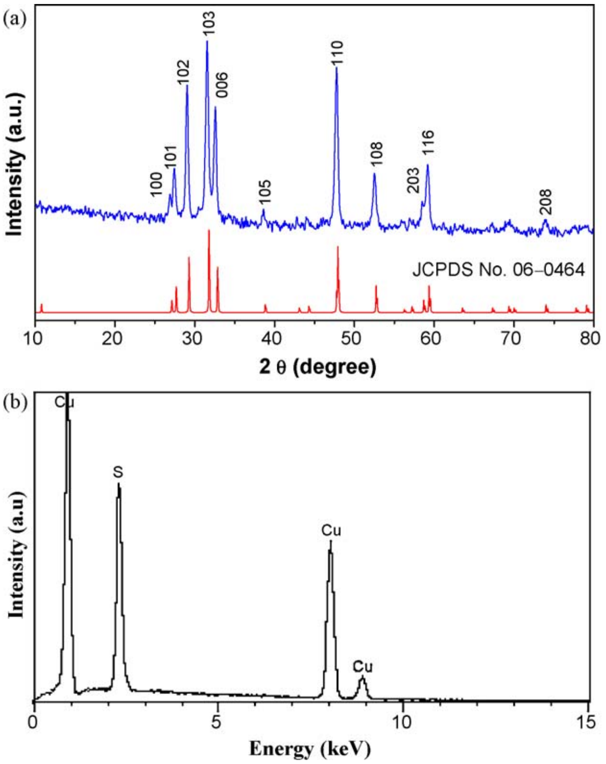

Fig. 1. XRD pattern (a) and EDS pattern (b) of the as-synthesized CuS doughnut-shaped particles.

hexagonal CuS structure (JCPDS No. 06-0464) with cell parameters $a = 3.792$ Å and $c = 16.34$ Å. No other impurities, such as $Cu_{1.8}S$, Cu_7S_4, $Cu_{1.96}S$ and Cu_2S were detected, indicating a high purity of the final products. EDS analysis was also performed for these CuS particles, as shown in Fig. 1b. Only copper and sulfur elements were detected, and their atomic ratio is about 1:1, which is in agreement with the stoichiometric ratio of CuS.

The morphology and size of these products were further examined by SEM. Fig. 2a shows that the products consist of relatively uniform doughnut-shaped microparticles with an average size of 1.5 μm. These hierarchical structures are composed of densely packed layers of nanoplates. The 3D hierarchical structure is so sufficiently stable that they could not be broken into discrete nanoplates even after a long-time ultrasonication. The formation of hierarchical doughnut-shaped CuS has been confirmed by high-magnification image, as shown in Fig. 2b. It is interesting that there is a concave on each surface of microparticles. Moreover, the close examination of the rims of particles reveals a layer-by-layer growth style (Fig. 2c).

To understand the formation process of such a multilayer structure, the time-dependent shape evolution process was followed by a careful examination of the intermediate. Fig. 3 shows SEM images of CuS obtained after different reaction stages. It can be revealed that monodisperse CuS flat and round nanoplates formed after reacting for 4 h because of its intrinsic crystallographic structure [14,18,19]. The size of CuS nanoplates is calculated from Fig. 3b to be about 500 nm in diameter and 50 nm in thickness. Besides these nanoplates, there are small quantities of distorted nanoplates in the sample. As the reaction time was increased to 10 h, many flat nanoplates tend to form distorted plates, which also piled

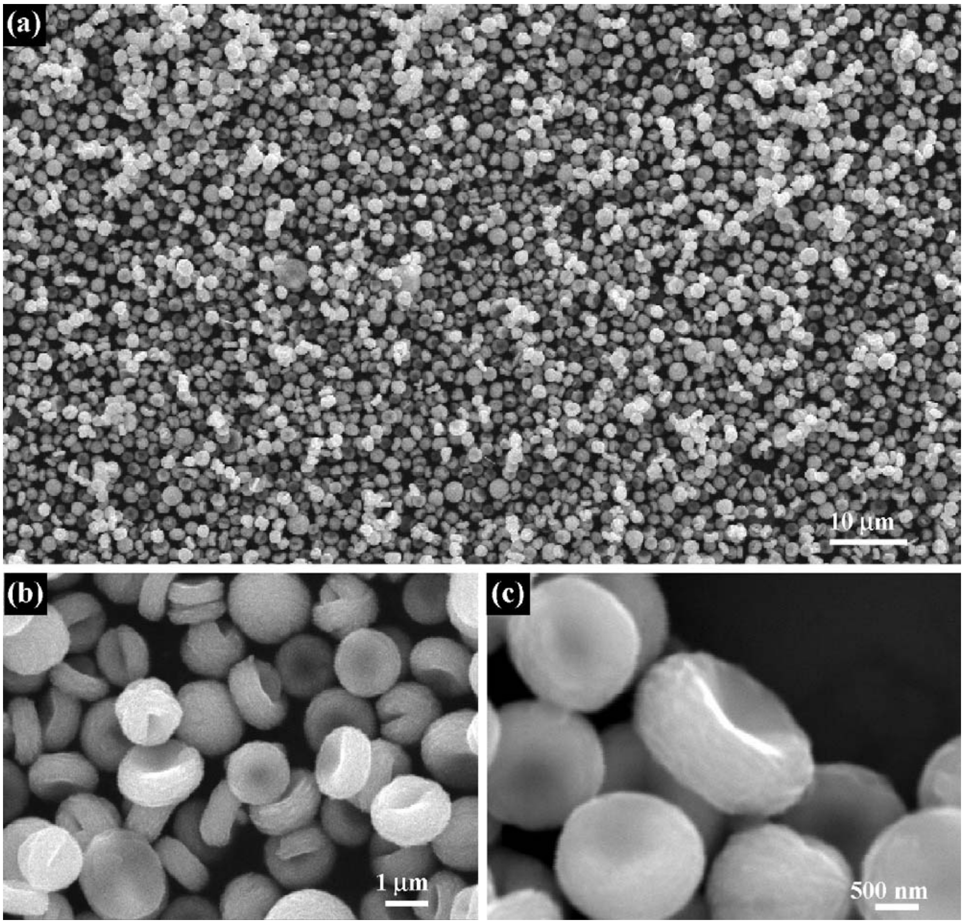

Fig. 2. SEM images of CuS doughnut-shaped microparticles synthesized at 120 °C for 24 h: (a) low-magnification image. (b and c) Local magnified images in (a).

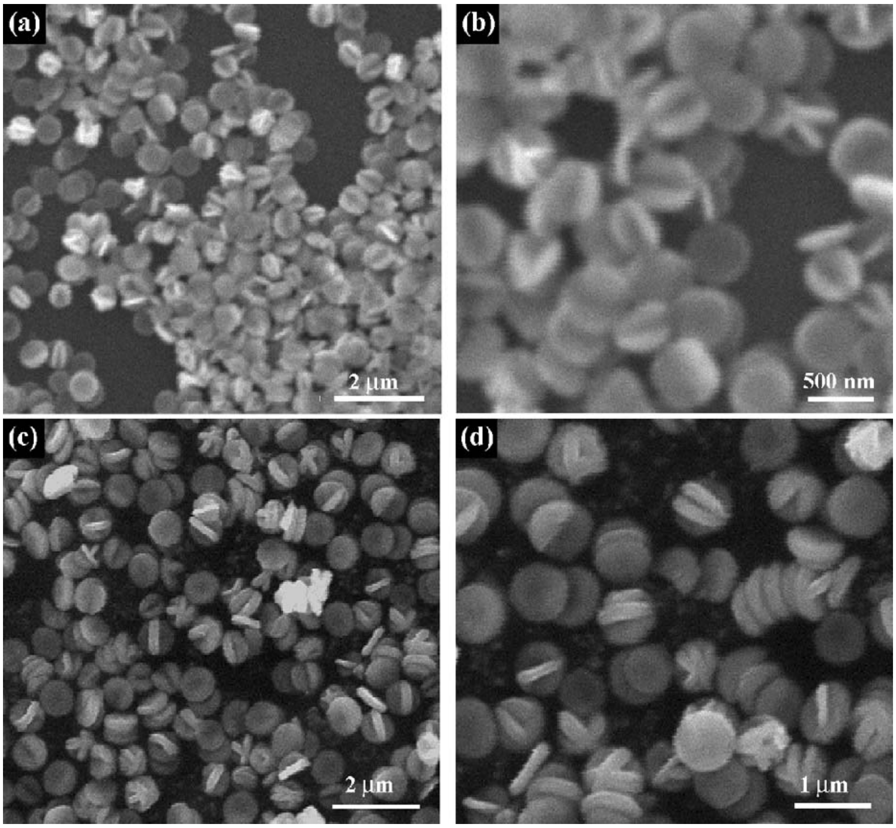

Fig. 3. SEM images of CuS products obtained after different reaction stages: (a and b) 4 h, round nanoplates; (c and d) 10 h, distorted round nanoplates self-assembled layer-by-layer.

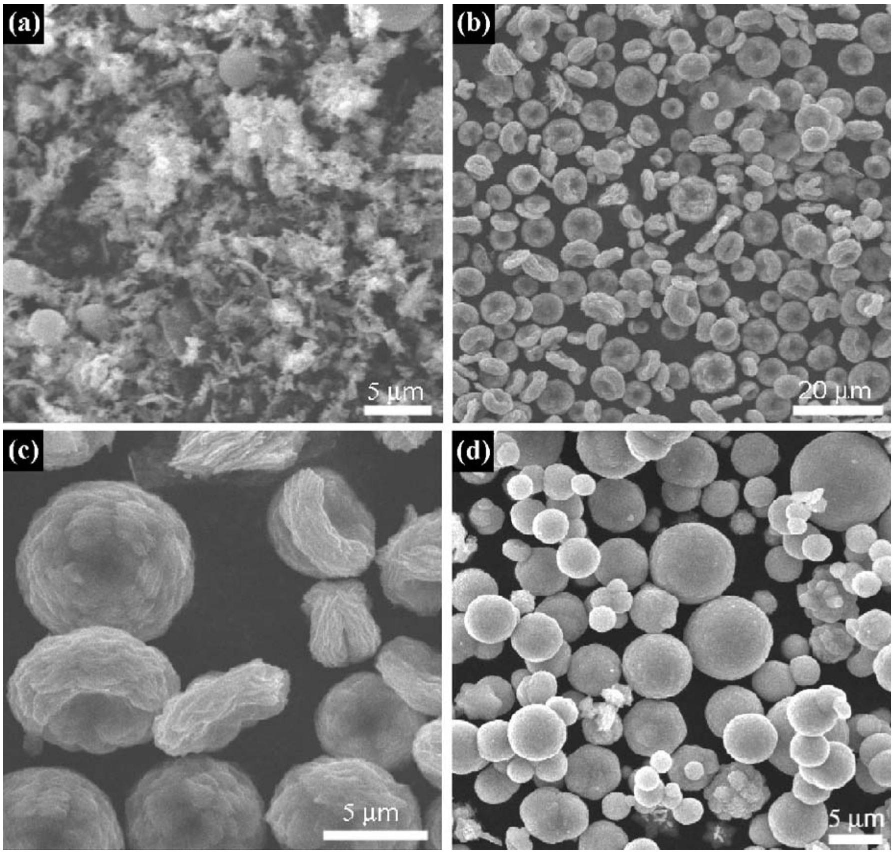

Fig. 4. SEM images of CuS products obtained under different conditions: (a) using $CuCl_2 \cdot 2H_2O$ as Cu^{2+} source, (b and c) using $Cu(CH_3COO)_2 \cdot H_2O$ as Cu^{2+} source, (d) without PVP while keep other reaction conditions constant.

up to form multilayer structure in a layer-by-layer manner (Fig. 3c and d). Finally, the hierarchical doughnut-shaped CuS were obtained when the reaction time was increased to 24 h (Fig. 2). In the current reaction process, as the action temperature is low (120 °C), DMSO does not decompose and release CH_3SH, and the thiourea is the only sulfur source. When no thiourea was added, no CuS products were obtained. According to current results, the formation mechanism of the 3D structure can be proposed. First, many round nanoplates form at the first initial stage. Then, at aging long time, instead of piling up to form a column, the round plates tend to wrinkle up and form notched template for further development. Finally, the following crystal growth is confined within the concave portion on both sides of the template, thus developing a well-defined doughnut-shaped 3D architecture.

It is noteworthy that the existence of PVP apparently has a significant effect on the formation of the current morphology. When no PVP was added, we only got polydisperse microspheres (Fig. 4d). In this system, the selective interaction of these particles with PVP may promote the formation of such a structure. Furthermore, the use of other Cu^{2+} sources with different anions such as $Cu(CH_3COO)_2{\cdot}H_2O$ and $CuCl_2{\cdot}2H_2O$ did not lead to particles with the similarly morphology (Fig. 4a–c). The solvent also plays a great role in the formation of the doughnut-shaped structure. When DMF was used as the solvent instead of DMSO, monodisperse Cu_2S submicrospheres with a diameter of about 900 nm were obtained (Fig. 5a). The related XRD pattern (Fig. 5b) reveals that pure Cu_2S crystals with the cubic structure (JCPDS No. 84-1770) were prepared. Since no strong reducing agents were added in our staring solution, it is thought that DMF solvent has been working as a weak reducing agent in the synthesis (the formic acid HCOOH is a reducing agent generated from the hydrolysis of DMF).

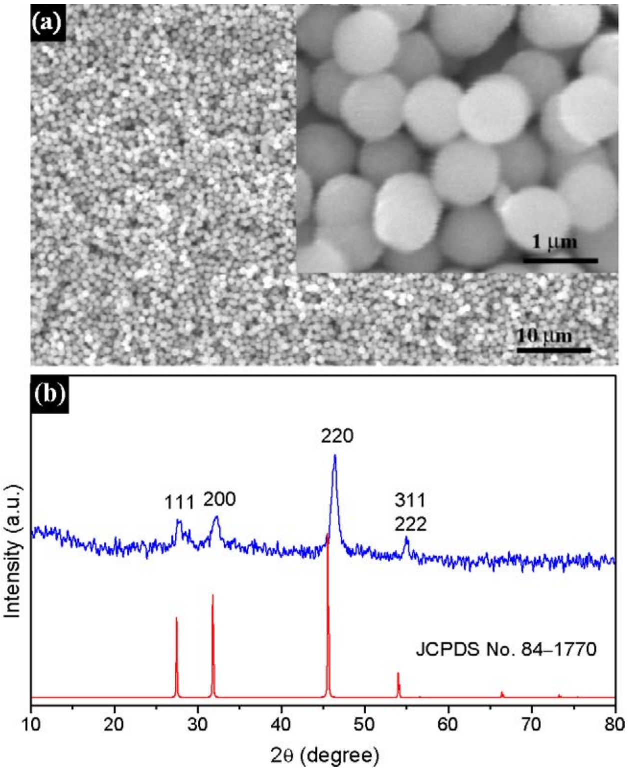

Fig. 5. SEM images and XRD pattern of Cu_2S submicrospheres with DMF as the reaction solvent: (a) SEM images show that these Cu_2S products are monodisperse, with the uniform size of 900 nm, the inset of (a) is the high-magnification SEM image of Cu_2S submicrospheres, (b) XRD pattern of submicrospheres shows that these monodisperse products are pure Cu_2S crystals with the cubic structure.

Furthermore, with DMF as the reaction solvent, different morphologies of CuS crystals have been successfully achieved. For example, hierarchical structured CuS microspheres were obtained when inorganic sulfur powder was used as the sulfur resource. SEM images in Fig. 6a clearly show that all the particles are in a form of hierarchical microspheres with the diameter distribution of about 3–5 μm. High-magnification SEM image (Fig. 6b) reveals that the microspheres are constructed from the assembly of nanoplates. The close examination of these image shows that the

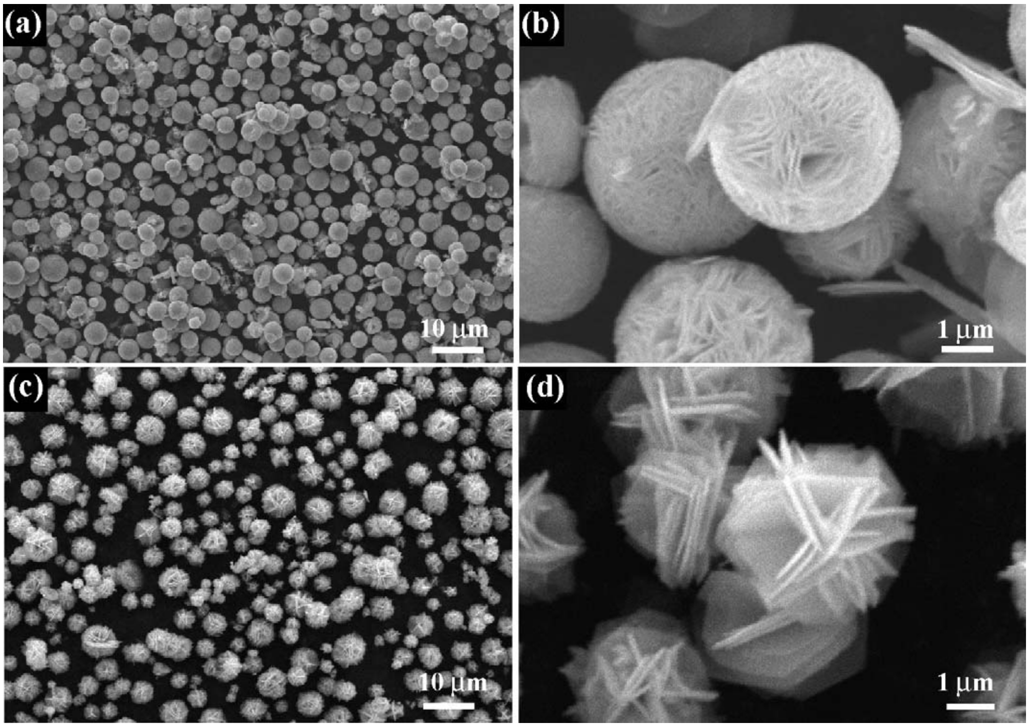

Fig. 6. SEM images of superstructured spheric (a and b) and flowerlike (c and d) architectures congregated from CuS nanoplates. These products were prepared with DMF as the solvent and sulfur powder as the sulfur source, respectively.

thickness of constituent nanoplates is 20–50 nm. These superstructured microspheres are relatively uniform in size and these CuS nanoplates adhere firmly to each other. However, when the surfactant PVP was absent during the reaction process, only polydisperse flowerlike CuS particles were obtained (Fig. 6c and d), which firmly confirms that these CuS nanoplates adhere together through the function of surfactant PVP.

4. Conclusions

We have successfully demonstrated that a viable and effective solvothermal route is established to prepare pure covellite CuS micro/nanocrystals at relatively low temperature. Three main uniform morphologies of doughnut-shaped, superstructured spheric and flowerlike architectures have been achieved, all of which are composed of CuS nanoplates. Furthermore, monodisperse chalcocite Cu_2S submicrospheres in the diameter of about 900 nm have also been fabricated when sulfur powder was used as the sulfur resource. The crystal growth and morphology evolution process have been systematically investigated by means of XRD, EDS and SEM. The tunable nanostructured copper sulfide products are ideal candidates for studying nanoarchitecture-dependent performance for applications in different fields.

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