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Controlled synthesis and optical properties of doughnut-aggregated hollow sphere-like CuS

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Abstract

Three-dimensional (3D) doughnuts-like copper sulfide (CuS) particles were successfully synthesized by a facile microwave hydrothermal method employing polyvinylpyrrolidone (PVP) as the surfactant. The products were characterized by X-ray diffraction, field-emission scanning electron microscopy and UV–vis diffuse reflectance spectra. Results show that the products are selectively fabricated by varying the S/Cu molar ratio from 3 to 7, exhibiting a morphology change from uniform aggregated spheres to single doughnuts-like structures. Comparison of the UV–vis absorption spectra of these particles reveals that an obvious red-shift of ~70 nm is found from the single doughnuts to the assembled doughnuts. Moreover, these spectra were calculated to show the bandgap of the as-prepared CuS particles varies from 1.46 eV to 1.64 eV with the morphology change from the single doughnuts-like to the aggregated spheres-like structures, respectively, indicating that the optical properties of the product may be strongly related to the state of their morphologies.

Keywords: Copper sulfide; Doughnut-like hollow spheres; Microwave hydrothermal method; Semiconductors

1. Introduction

In recent years, there has been increasing interest in the controlled synthesis of inorganic nano/microstructures with hollow interiors because of their widespread potential applications in the photonic crystals, catalysis, artificial cells, drug delivery and the protection of light sensitive components [1]. The general approach for preparation of hollow structures has involved the use of various removable or sacrificial templates, including hard ones such as monodisperse silica [2] or polymer latex spheres [3] as well as soft ones. However, hollow structures prepared from hard templating routes usually suffer from disadvantages related to high cost and tedious synthetic procedures. It is highly desirable to develop one-pot synthesis of hollow inorganic materials without hard templates.

As one of the most important semiconductors, copper sulfide (CuS) is a promising material with potential applications in many fields, such as photothermal conversion [4], electrodes [5], and solar cell devices [6]. The controlled synthesis and self-organization of CuS with special morphologies and sizes have attracted considerable attention in the recent decades due to their outstanding properties and potential applications in numerous fields. Considerable efforts have been devoted to the synthesis of various CuS morphologies such as nanorods [7], nanowires [8], nanoplates [9,10], nanoflakes [11] and tubular structures assembled by nanoflake-built microspheres [12]. Besides, the preparation CuS particles with hollow sphere-like strucutures is also under investigation [3,13,14] to show potential technological applications in optical [3] and sensoring [14] properties. However, long reaction times [3,14] and difficulties in controlling uniform shaped structures [15] still exist to expect further investigation on both synthesize approach improvment and precise morphology control of CuS particles.

In this work, a facile and economical microwave hydrothermal method is employed to prepare 3D CuS hollow microspheres aggregated by doughnut-like structures firstly.

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Besides, the aggregation of doughnuts can be controlled. The uniform aggregated doughnuts-like spheres and single doughnuts can be selectively fabricated by varying the S/Cu molar ratios from 3 to 7. And the bandgap of CuS particles changes with different aggregation of doughnuts. We propose that this finding might prove useful to control bandgap of semiconductors by varying the aggregations of building-blocks.

2. Experimental

In a typical synthesis process, $Cu(NO_3)_2 \cdot 3H_2O$ (0.726 g, 3 mmol), thiourea (0.684 g, 9 mmol), and PVP K30 (average molecular weight: 40000 g/mol) (0.4 g, 3.6 mmol, calculated in terms of the repeating unit C_6H_9NO FW=111) were dissolved in deionized water (50 mL) and stirred vigorously. The mixture was sealed in a 100 mL Teflon-lined autoclave. This autoclave was then put into an MDS-8 microwave hydrothermal system (Shanghai Sineo Microwave Chemistry Technology Co. Ltd., China). The operating power was set to 500 W with working frequency of ~2450 MHz. The system was set to the temperature-controlled mode to maintain at 150 °C for 20 min. Afterward, the as-prepared black precipitates were isolated by centrifugation and washed with deionized water and absolute ethanol for several times. Finally, the black precipitates were dried at 50 °C in a drying cabinet for 1 h. To investigate the effects of different S/Cu molar ratios on the phase composition and morphology of the products, the content of S^{2-} were controlled from 9 mmol to 21 mmol (S/Cu molar ratio from 3 to 7, respectively) with the content of Cu^{2+} kept unchanged.

The phase composition of the samples was characterized via X-ray diffraction (XRD) on a D/MAX-2200PC X-ray diffractometer with CuKα radiation (λ=0.15406 nm) at a scanning rate of 8° min^{-1} (Rigaku, Japan). To observe the product morphology and microstructures, field-emission scanning electron microscopic (FESEM) images were taken on a JSM-6700F field-emission scanning electron microscope. UV–vis diffuse reflectance spectra were recorded on a Lambda 950 spectrophotometer.

3. Results and discussion

3.1. Synthesis of doughnut-aggregated hollow spheres

Fig. 1A shows the typical FESEM images of products prepared at the S/Cu molar ratio of 3. The obtained particles showed a spherical morphology with an average diameter of ~2 μm. An interesting feature shown in Fig. 1B is that each sphere is assembled by many doughnuts-like structures with diameter of ~500 nm. These doughnuts have a concave surface, which appears to be formed by circles of different layers grown from inside out. Besides, several holes found on the surface of the sphere indicates that the sphere is hollow. This novel hollow sphere structure may find potential applications as containers to hold nanoparticles as well as controlling the release of drugs, cosmetics or chemical reagents.

3.2. Effect of S/Cu molar ratio

To investigate the effects of different S/Cu molar ratios on the phase composition and morphology of the products, a series of comparative experiments were carried out. Fig. 2A presents the XRD patterns of as-prepared samples at Cu/S molar ratio from 3 to 7. All of the peaks could be indexed to the standard hexagonal CuS which is consistent with the standard diffraction data (JCPDS Card No.06-0464, $a=b=3.792$ Å, $c=16.344$ Å). No other characteristic peaks are observed, indicating that the products obtained were pure covellite CuS.

Fig. 2B–G shows FESEM images of the as-prepared CuS obtained with different S/Cu molar ratios. When the S/Cu molar ratio increases to 4 (Fig. 2B), the doughnuts appear to be thicker and few dispersed single doughnuts were found. Besides, many broken sphere-like structures seen in Fig. 2B and C reveals not only the hollow structure of the spheres, but also the driven force of the aggregation of these doughnuts, which is believed to be the requirement of minimum surface energy. Fig. 2D shows the image of the products obtained at the S/Cu molar ratio of 6. Both of dispersed and aggregated doughnuts-like structures were found with bigger

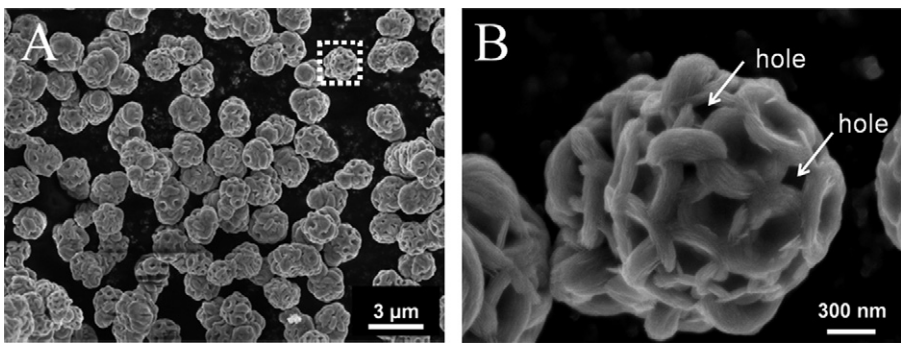

Fig. 1. FESEM of the as-prepared doughnut-aggregated sphere-like CuS: (A)with low-magnification; (B)with high magnification.

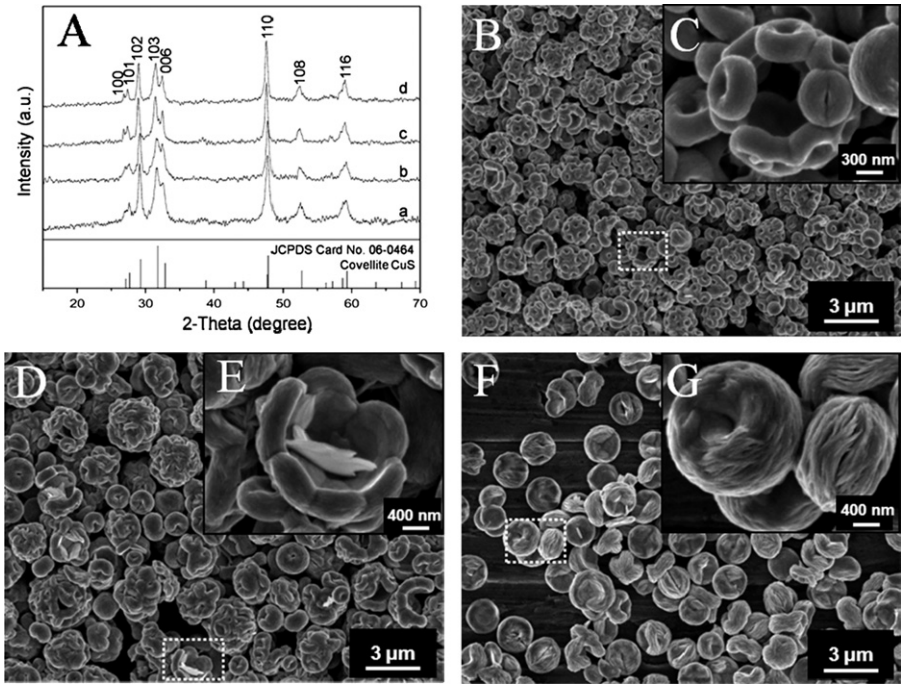

Fig. 2. XRD patterns and FESEM images of CuS particles prepared at different S/Cu molar ratios. (A)XRD patterns: (a) 3; (b) 4; (c) 6; (d) 7. (B∼G) FESEM images: (B,C) 4; (D,E) 6; (F,G) 7.

sizes of ∼1 μm, showing a mixed-morphology of single doughnuts and loose aggregated-spheres together (Fig. 2E). As the S/Cu molar ratio increases to 7, monodisperse doughnuts are obtained with the biggest average diameter of ∼2 μm and thickness of ∼1.3 μm (Fig. 2F). As shown in Fig. 2G, detailed observation of the side view indicates that this doughnut consists of many densely packed nanosheets with a thickness of ∼20 nm. By Combining the FE-SEM results together, it is exhibited that lower S/Cu molar ratio leads to doughnuts-aggregated hollow sphere-like structures. As the content of Tu increases, single doughnuts form with higher diameter and thickness to show a monodisperse dounghnut morphology of the product.

Based on the FESEM results above, it can be deduced that the S/Cu molar ratios have significant influences on the morphologies of the products, which may result from the Thiourea (Tu) contents to significantly affect the reactions under hydrothermal condition. Tu in the reaction acts not only as the sulfur source, but also as a ligand during the reaction to cooperate with free copper ions to form Tu–copper precursor in the solutions [16]. Thus, increasing the Tu content leads to the decrease of free copper ions in solution. This may lower the supersaturation of precursor solution during the product precipitation process to reduce the nucleation rate of CuS particles. Consequently, as the Tu–copper precursor slowly release the copper ions in the solution [16], the solution tend to crystallize the CuS particles (doughnuts) rather than nucleate new unit to obtain further grown CuS doughnuts with bigger sizes [17]. The stereohindrance effect generated with increased size of doughnuts may result in the loosening of the aggregated-spheres and the final formation of single doughnuts. In addition, the different aggregation of doughnuts may have some relationship with the Tu–copper complexes with different molar ratios of S/Cu molar ratio in the liquid phase [18,19]. Different Tu–copper complexes have different molecular structures to affect the nucleation of CuS particles, resulting in the different aggregation of doughnuts. However, the mechanism for the formation of CuS with different assembled structures obtained via a microwave hydrothermal method still needs further investigation.

3.3. Effect of PVP concentration

In order to understand the effect of PVP on the morphology of microparticles, the concentration of PVP was changed from 0.06 M to 0 M while keeping the other reaction conditions the same as in the typical synthesis. As shown in Fig. 3, doughnut-shaped particles are found when the PVP concentration is decreased from 0.06 to 0.04, and finally to 0.02 M. The average particle diameters are found increasing from ∼1.1 μm to ∼1.4 μm, and to ∼2.4 μm. Moreover, the average particle thickness can be seen increasing from ∼0.4 μm to ∼0.8 μm, and ∼1.2 μm. While the experiments were carried out without PVP, no doughnuts but flower-spheres assembled by disordered sheet-like structure could be found from the as-obtained product morphology (Fig. 3D). Thus, it is suggested that the sheet-like structure is directed by the addition of PVP to form the doughnut morphology.

To explain the role of the PVP during the preparation, it may act as a directing agent to lead the growth of

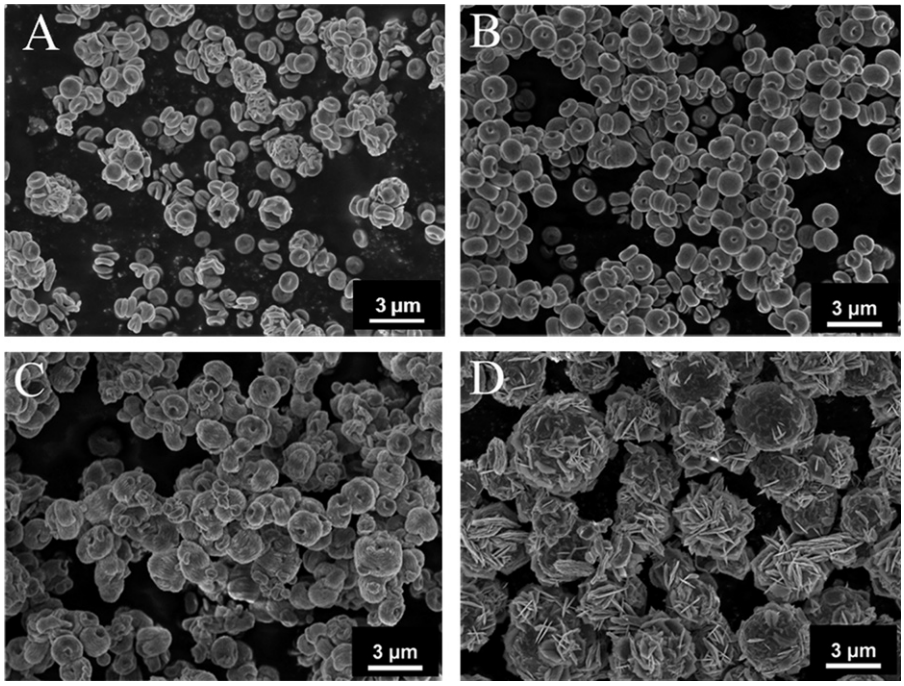

Fig. 3. FESEM images of CuS particles prepared at different PVP concentration: (A) 0.06 M; (B) 0.04 M; (C) 0.02 M; (D) 0 M.

doughnut structure. It is presumed that PVP molecules may be attached on the surfaces of the sheet-like particles by their C=O, and –OH groups to create nucleation sites with higher surface energy [20,21]. The crystallization may prefer to start from these nucleation sites to form a new layer of sheet-like structure that is parallel to the original sheets [22], which could be confirmed by the disordered product morphology that are obtained without PVP. Consequently, as the ordered sheet-like structure grows thicker, the outer surfaces are relatively easy to attract more PVP. This may finally lead to the preferred crystallization on the outer surfaces and higher resolution rate in the inner region to form a doughnut-like structure [23,24].

3.4. Optical properties of the as-obtained CuS with different structures

The typical optical properties of CuS aggregated hollow microspheres and doughnuts were characterized by UV–vis diffuse reflectance spectra (Fig. 4(a)). Both hollow spheres and doughnuts have a strong and broad absorption in the visible range from 400 to 800 nm to show great potential applications in the fields of photocatalytic and solar cells. By comparing with the absorption peak of single doughnut-like CuS crystallites, the aggregated CuS spheres exhibit a distinct redshift, which may result from the internal stress generated in the process of aggregation and assembly [25–27] . As a direct band-gap semiconductor [15], the relationship between the adsorption coefficient (α) near the absorption edge and the optical band gap (E_g) obeys the following formula $(\alpha hv)^2 = A(hv - E_g)$ [12], where hv is the incident photon energy, and A is a constant. Thus, as illustrated in Fig. 4(b), the band gap for CuS hollow aggregated spheres is 1.46 eV, while the band gap for CuS with single doughnut morphology is 1.64 eV. The phenomenon illustrates that the band gap of CuS sphere assembled structure is strongly related to the morphology of the aggregation of doughnuts.

4. Summary

In summary, we have successfully synthesized aggregated hollow sphere-like CuS particles by a facile microwave hydrothermal method with the assistance of PVP. The results show that the S/Cu molar ratio is found to greatly affect the product morphology without changing its phase. By varying the S/Cu molar ratios from 3 to 7, the obtained CuS particles could be selectively fabricated to show aggregated spheres and single doughnuts-like structures. And doughnuts with controllable size and thickness can be obtained through varying the concentration of PVP, confirming that PVP plays an important role in the formation of microparticles with different shapes and sizes. The UV–vis diffuse reflectance spectra of these two morphologies exhibit an obvious difference on their absorption peak positions, where the aggregated spheres exhibit a distinct redshift to the monodisperse dounghnuts-like structures. Corresponding calculation results exhibit the optical bandgap of 1.46 eV and 1.64 eV to aggregated spheres and monodisperse dounghnuts-like CuS particles. This result indicates the obtained CuS particles optical performance is easily controlled by changing the S/Cu molar ratio under microwave-irritated hydrothermal

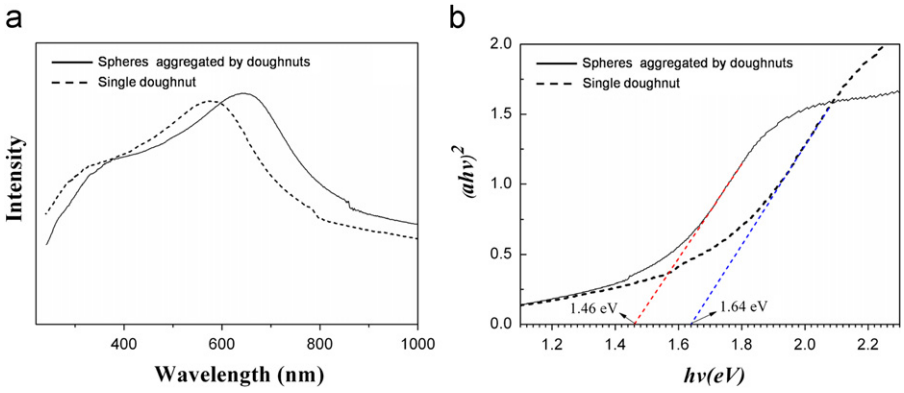

Fig. 4. (a) UV–vis diffuse reflectance spectra of CuS with different morphologies; (b) the relationship between $(\alpha hv)^2$ and hv.

conditions, which is considered to be a facile approach to prepare other sulfide materials that involve well-defined shapes and precisely controlled morphologies.

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