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Preparation of γ-MnS hollow spheres consisting of cones by a hydrothermal method

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ABSTRACT

γ-MnS hollow spheres consisting of cones were successfully prepared by a dodecanethiol-assisted hydrothermal process at 180 °C for 24 h, employing manganese acetate tetrahydrate and L-cysteine as precursors. The diameter of the γ-MnS hollow spheres is 3–6 μm. The synthesized product was characterized by XRD, FESEM, UV–vis spectrometer, and fluorescence spectrophotometer. The formation mechanism of the γ-MnS hollow spheres consisting of cones is discussed. The optical properties were also investigated.

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1. Introduction

Manganese sulfide (MnS) is one of the most important VIIB–VIA magnetic p-type semiconductors with a wide gap (Eg $(T=0)\approx 3.7$ eV) [1]. It holds many intriguing potential applications, such as in solar cells as a window/buffer material, short-wavelength optoelectronic materials, solar selective coatings, processing of information for the electronic devices, and optical mass memories and storage [2–4]. MnS has three different polymorphs: the green stable rock salt structure (α-MnS), the pink metastable zinc blende structure (β-MnS), and the wurtzite structure (γ-MnS) [5]. Till now, various shapes of MnS nano- and microcrystals have been achieved by a hydrothermal, solvothermal, thermolysis, and spray-produced process [6–13]. Especially, the rod-like morphologies and unique "methane-like" four-branched rod clusters were found in meta-stable γ-MnS [14]. MnS microspheres with a novel hierarchical structure were prepared through a simple solution method [15]. Generally, the synthesis of metastable phase γ-MnS is still a challenging and intriguing task [6].

Recently, our group has focused on fabricating semiconductor nanostructures by various methods [16–18]. In this report, pure γ-MnS hollow spheres consisting of cones were successfully prepared by a dodecanethiol-assisted hydrothermal process, which is obviously different from the γ-MnS hollow spheres consisting of γ-MnS nanoparticles or γ-MnS rods with hierarchical architectures prepared by other groups [12,13]. The optical properties of MnS hollow spheres consisting of cones were investigated, and the formation mechanism of the MnS hollow spheres consisting of cones was also discussed.

2. Experimental section

All the chemicals were of analytical grade and purchased from Shanghai Chemical Reagent Co. In a typical procedure, equivalent molar amounts (1.4 mmol) of manganese acetate tetrahydrate, L-cysteine, and 0.5 g dodecanethiol were dissolved in 20, 20, and 30 mL distilled water under an ultrasonic treatment of 20 min, respectively. Manganese acetate tetrahydrate solution was added to dodecanethiol and given a 2-min ultrasonic treatment. Then the resulting solution was mixed with L-cysteine solution. The final mixed solution was sealed into an 80 mL Teflon-lined stainless steel autoclave, and heated at 180 °C for 24 h in an

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electric oven. The autoclave was cooled to room temperature naturally when the reaction time was gotten to the required time. The product was collected by centrifugation at 8000 rpm for 10 min and washed with distilled water and absolute ethanol several times to remove the excess reactants and byproducts. Finally, the product was dried in an oven at 60 °C for 6 h.

Scanning electron microscopy (SEM) images were obtained on a FEI Sirion 200 field emission scanning electron microscope (FESEM). The X-ray diffraction (XRD) pattern of the products was recorded by a PANalytical B.V. (Philips) χ' Pert PRO XRD with Cu Kα radiation at a scanning rate of 0.02° s^{-1} in a 2θ range of 20–80°. The UV–vis absorption spectrum was recorded on a SHIMADZU UV-2550 UV–vis spectrometer. The photoluminescence spectrum was measured on a JASCO FP6500 fluorescence spectrophotometer.

3. Results and discussion

A typical XRD pattern of as-synthesized MnS hollow spheres at 180 °C for 24 h is shown in Fig. 1a. All the diffraction peaks can be indexed to the pure hexagonal structured γ-MnS with lattice constants $a = 3.9790$ Å, $b = 3.9790$ Å, $c = 6.4466$ Å, which is in good agreement with the standard data from JCPDS card 40-1289 ($a = 3.9792$ Å, $b = 3.9792$ Å, $c = 6.4469$ Å). No impurity phase can be detected. The strong and sharp diffraction peaks indicate that the as-obtained product is well-crystalline. Figs. 1b–e show that the SEM images of the MnS hollow spheres consist of cones obtained at 180 °C for 24 h; the concentrations of manganese acetate tetrahydrate and L-cysteine are both 0.02 mol/L, the dosage of dodecanethiol is 0.5 g in 70 mL solution. The low- and high-magnification SEM images are shown in Fig. 1b and c, clearly showing that the as-synthesized products are sphere-like crystals with the diameter of 3–6 μm. The inset in Fig. 1b is the SEM image of an open sphere, which shows that the product is a hollow sphere. This kind of MnS hollow sphere consists of cones (Fig. 1d and e), which has not been reported previously. The length of the cone is about 2 μm and the diameter of the bottom of the cone is about 500 nm.

Figs. 2a and b show that the irregular MnS aggregations consisting of rods with the diameter of about 500 nm were obtained without dodecanethiol under the same other conditions. The result indicates that dodecanethiol plays an important role in the formation of MnS hollow sphere consisting of cones. Also the dosage of dodecanethiol affects the formation of MnS hollow spheres consisting of cone. When the dosage of dodecanethiol is increased to 0.7 g, Fig. 2c indicates that the major product is the broken MnS hollow spheres. It is well-known that dodecanethiol is flammable. The forming gases of dodecanethiol are easy to spurt out under the high temperature and pressure of the hydrothermal process when the dosage of dodecanethiol is increased. When the dosage of dodecanethiol is decreased to 0.3 g, the MnS hollow spheres were also obtained (Figs. 2d and e).

L-cysteine also plays a key role in the formation of MnS hollow spheres consisting of cones. When L-cysteine is replaced by mercaptoethanol under the same other conditions, Figs. 2f and g show that larger sheet-like γ-MnS microcrystals can be obtained. There are several functional groups in the L-cysteine molecule, such as $-NH_2$, $-COOH$, and $-SH$, which have a strong tendency to coordinate with inorganic cations. Some metal sulfide nanostructures have been prepared in the presence of cysteine, where cysteine can act not only as a complexing agent but also as a sulfur source and structure-directing molecule [6,19–21]. It is rationally speculated that L-cysteine can coordinate with Mn^{2+} in our system.

To study the following growth mechanism for MnS hollow sphere consisting of cones, the time-dependent experiments were carried out at 2, 3.5, and 12 h under the same other conditions. Figs. 3a and b indicate that the MnS hollow spheres consisting of particles were obtained. The diameter of the MnS hollow spheres

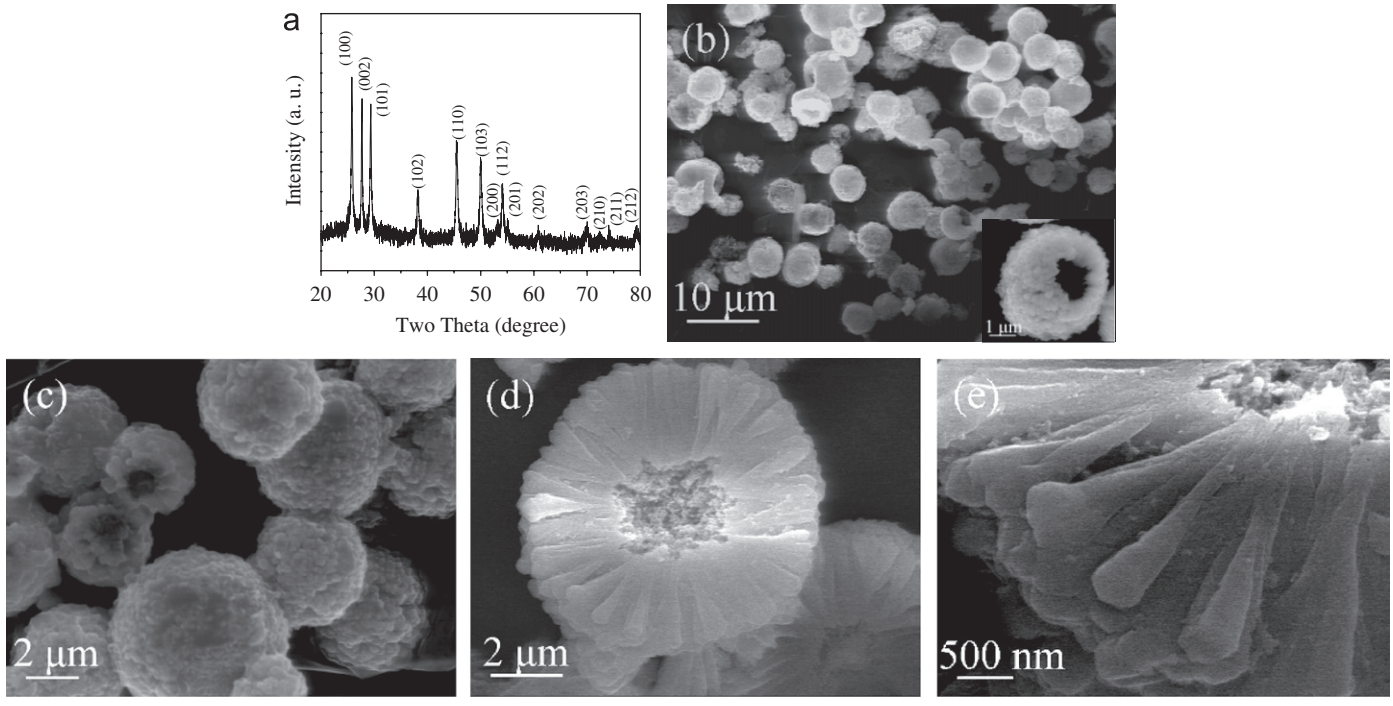

Fig. 1. XRD pattern and SEM images of the as-prepared MnS hollow spheres consisting of cones at 180 °C for 24 h; the concentrations of manganese acetate tetrahydrate and L-cysteine are both 0.02 mol/L; the dosage of dodecanethiol is 0.5 g in 70 mL solution. (a) XRD pattern; (b) low-magnification SEM image; the inset is the SEM image of an open hollow sphere; (c) high-magnification SEM image; (d) SEM image of a half MnS hollow sphere; (e) high-magnification SEM image of the selected area of a half MnS hollow sphere in (d).

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