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ZnS micro-spheres and flowers: Chemically controlled synthesis and template use in fabricating MS(shell)/ZnS(core) and MS (M = Pb, Cu) hollow microspheres

Yunhui Shi, Jun Chen *, Panwen Shen

Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, PR China

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Abstract

ZnS micro-spheres and flowers with the cubic structure were chemically synthesized through a simple one-step hydrothermal approach. The as-synthesized ZnS microspheres were further used as the templates to prepare MS(shell)/ZnS(core) composite spheres and MS (M = Pb, Cu) hollow spheres via ion-exchange method with the treatment of dilute HCl. The present method can be extended to the synthesis of other metal sulfides with shell–core or hollow structures. The as-synthesized ZnS, MS(shell)/ZnS(core), and MS microstructures show promising absorptions in UV and visible regions, indicating that the as-prepared microspheres are promising in the development of photoelectric devices.

Keywords: Hydrothermal synthesis; Hollow microsphere; Metal sulfides; Optical properties; Composite

1. Introduction

Transition metal sulfides like ZnS, PbS and CuS with excellent electrical and optical properties have a wide range of applications such as in the fields of flat-panel display, luminescent devices, infrared windows, light emitting diodes (LED), solar cells, ion-selective sensors, mode-locking in lasers, secondary batteries, and catalysis [1–4]. However, to bring their new types of applications and enhance the performance of currently existing photoelectric devices, research on modulating their existing optical properties is necessary.

The morphology of inorganic solid materials is an important factor to their properties and it is thus that the preparation of inorganic compounds with special morphologies has attracted a great deal of interest [5–7]. Up to now, various physical and chemical methods have been employed to prepare ZnS with the morphologies of porous nanoparticles [8,9], hollow nanospheres [10], and one-dimensional nanostructures [11,12]. However, to the best of our knowledge, there is no report on the synthesis of cubic ZnS with well-dispersed spherical or flower-like microstructures through simple one-pot hydrothermal approach. On the other hand, a variety of methods have been developed to generate hollow-structured semiconductor materials due to their improved physical and chemical properties over the corresponding counterparts [13,14]. For example, PbS hollow microspheres were synthesized in a PMMA-CS_2-ethanol aqueous system by a surfactant-assisted sonochemical route or γ-irradiation [15,16]. CuS hollow microspheres were prepared via solvothermal in ethylene glycol (EG) solvent or using thioglycolic acid (TGA) as the stability agent [17,18]. It can be seen that such methods usually require strict conditions or somewhat complicate manipulation, meaning that the shape-controlled synthesis of hollow-structured semiconductors needs to be further studied.

Inspired by a promising study on the formation of Ag_2Se nanocrystals through a cation-exchange reaction between Ag^+ and CdSe nanocrystals at room temperature [19], we here describe a novel route for the synthesis of PbS/ZnS (or CuS/ZnS) shell–core microspheres and hollow PbS (or CuS) spheres via a simple ion-exchange process. The basic idea behind this route is to take the advantage of the transfer between Zn^{2+} and other cations according to the different solubility of metal sulfides in aqueous solution. This simple and convenient method does not need any complicated apparatus and can be extended to the

* Corresponding author. Tel.: +86 22 2350 6808; fax: +86 22 2350 2604.
E-mail address: chenabc@nankai.edu.cn (J. Chen).

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preparation of other composite spheres and hollow spheres of metal sulfides. In addition, both the shell–core and hollow structured spheres possess broad UV–vis absorption that is quite different from the bulk counterparts, indicating their potential applications as window and absorber materials in optically improved solar cells.

2. Experimental

All reagents such as zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$) and sodium thiocyanate (NaSCN) were purchased from Tianjin Chemical Factory (China) with analytical grade, which were used without further purification.

The synthesis of ZnS microspheres and microflowers were carried out through a hydrothermal route and the probable chemical reactions involved in our present hydrothermal synthesis can be summarized as follows:

$$2ZnSO_4 + 2NaSCN + 4H_2O \rightarrow 2ZnS\,(\text{microspheres}) + (NH_4)_2SO_4 + Na_2SO_4 + 2CO_2\uparrow \quad (1)$$

$$Zn(CH_3COO)_2 + NaSCN + 2H_2O \rightarrow ZnS\,(\text{microflowers}) + CH_3COONH_4 + CH_3COONa + CO_2\uparrow \quad (2)$$

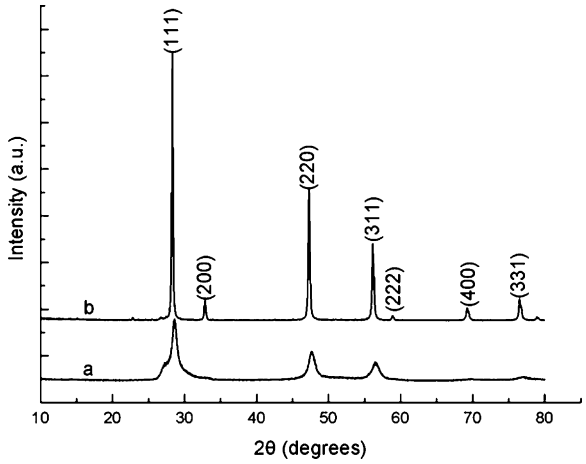

Fig. 1. XRD patterns of ZnS (a) microflowers and (b) microspheres.

In a typical experimental procedure, for the synthesis of ZnS microspheres, 0.3 mmol $ZnSO_4{\cdot}7H_2O$ and 0.6 mmol NaSCN were added into a Telfon-lined autoclave (25 ml), which was filled with 12 ml distilled water. After sealing, the autoclave was maintained at 180 °C for 18 h and then cooled to room tempera-

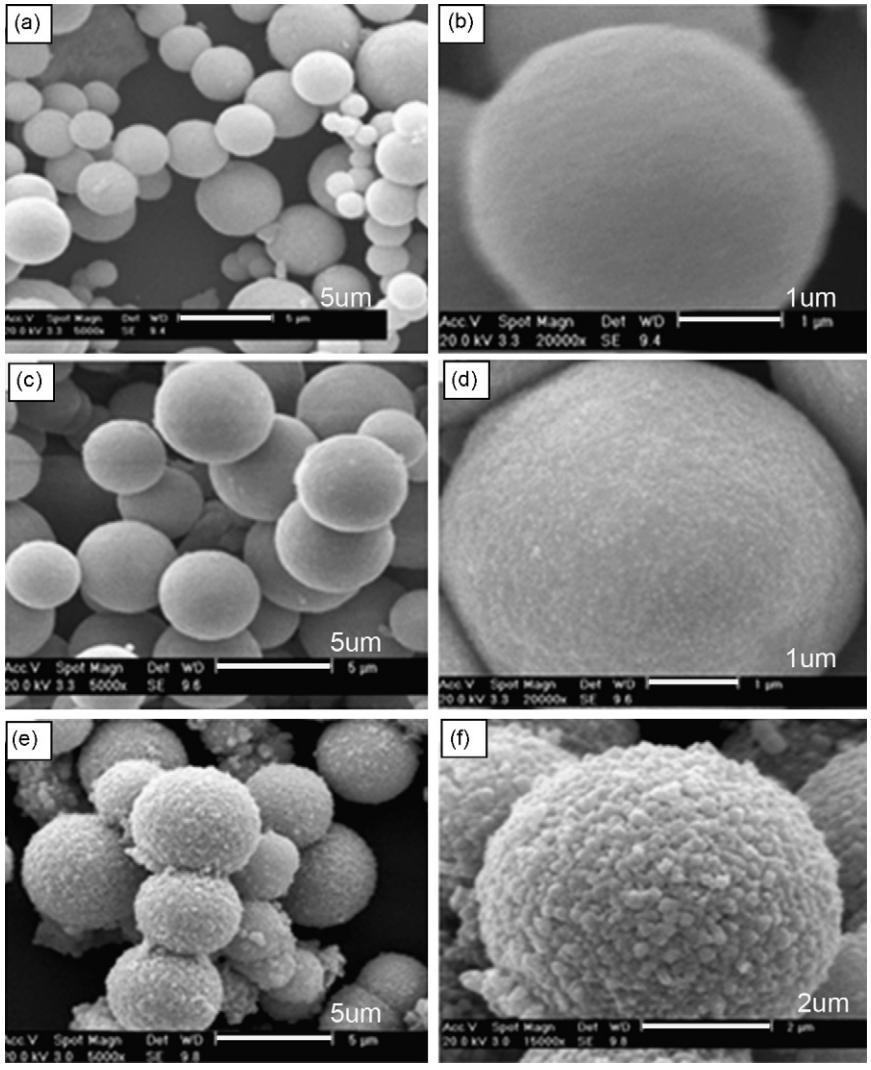

Fig. 2. SEM images of ZnS microspheres obtained after different hydrothermal time: (a and b) 6 h, (c and d) 12 h, (e and f) 18 h.