Controllable synthesis, characterization, and growth mechanism of hollow $Zn_xCd_{1-x}S$ spheres generated by a one-step thermal evaporation method*

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Novel hollow $Zn_xCd_{1-x}S$ spheres that are uniform in size are synthesized through the one-step thermal evaporation of a mixture of Zn and CdS powder. From an X-ray diffraction (XRD) study, the hexagonal wurtzite phase of $Zn_xCd_{1-x}S$ is verified, and the Zn mole fraction (x) is determined to be 0.09. According to the experimental results, we propose a mechanism for the growth of $Zn_{0.09}Cd_{0.91}S$ hollow spheres. The results of the cathodoluminescence investigation indicate uniform Zn, Cd, and S distribution of alloyed $Zn_{0.09}Cd_{0.91}S$, instead of separate CdS, ZnS, or nanocrystals of a core-shell structure. To the best of our knowledge, the fabrication of $Zn_xCd_{1-x}S$ hollow spheres of this kind by one-step thermal evaporation has never been reported. This work would present a new method of growing and applying hollow spheres on Si substrates, and the discovery of the $Zn_{0.09}Cd_{0.91}S$ hollow spheres would make the investigation of $Zn_xCd_{1-x}S$ micro/nanostructures more interesting and intriguing.

Keywords: $Zn_xCd_{1-x}S$, hollow spheres, semiconductors, vapour deposition, growth mechanism

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1. Introduction

It was found that the unique physical and chemical properties of nanomaterials are size- as well as shape-dependent.[1] It is hence not surprising to find that the control of morphology is a crucial issue in nanotechnology. In the past decades, researchers have turned their attention to the controllable synthesis of nanomaterials in terms of architecture, size, morphology, and growth pattern of products.[2–8] As a unique micro/nanostructure, hollow spheres have attracted much attention because of their potential use in areas such as drug delivery, sensors, catalysis, photonic crystals, artificial cells, light fillers, and low-dielectric constant materials.[9–15]

As is well known, hollow spheres that are uniform in size can be prepared by a number of techniques, including hard or soft templates, chemical processes based on oriented attachment, Ostwald ripening, self-assembly, and chemically induced self-transformation.[16–26] For example, by using sulfonated polystyrene (SPS) microspheres as template, Ding *et al.*[25] synthesized micro-sized SnO_2@carbon hollow spheres. Liu *et al.*[26] fabricated nanostructured silica spheres by hydrolyzing tetraethylorthosilicate (TEOS) using cetyltrimethylammonium bromide (CTAB) as template. One can see that most of them are liquid-phase approaches, and reports on vapor-phase growth of hollow spheres are rare.

The properties of micro/nanostructures depend not only on their morphology but also on their chemical composition.[27] In the last decades, much effort has been devoted to the control of the bandgap of semiconductor materials via the tunable atomic ratio in solid solutions for applications in areas such as light-emitting diodes, solar cells, and biolabeling.[28–33] As a consequence, a great variety of alloyed materials such as $Zn_xCd_{1-x}Se$,[34] $Al_xGa_{1-x}N$,[35] $AgInS_2$–ZnS,[36] and $CuInS_2$–ZnS[37] have been fabricated. As a typical solid-solution semiconductor, $Zn_xCd_{1-x}S$ has been intensively investigated because of its potential applications in high-density optical recording using blue or even UV laser diodes.[38] Despite the fact that there are reports on the synthesis of $Zn_xCd_{1-x}S$ nanoparticles,[39,40] nanoribbons,[41] zigzag nanowires,[42] nanocombs,[43] and nanorods,[44] the synthesis of hollow $Zn_xCd_{1-x}S$ spheres using vapor-phase growth method has not been reported. We describe herein the synthesis of uniform $Zn_xCd_{1-x}S$ hollow spheres through a one-step low-pressure thermal evaporation method. It is worth pointing out that the approach is low-cost and the generation of product is highly reproducible. To the best of our knowledge, the fabrication of $Zn_xCd_{1-x}S$ hollow spheres using such an approach has never been reported before.

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2. Experiment

All the reagents were purchased from Nanjing Chemical Industrial Co. (analytical grade) and directly used without further purification. The approach adopted for the synthesis of $Zn_xCd_{1-x}S$ hollow spheres was similar to the low-pressure thermal decomposition process described previously.[45–47] In brief, a quartz tube (inner diameter: 50 mm; length: 800 mm) was installed in a tubular furnace. Then a ceramic boat loaded with 0.001-mol cadmium sulfide and 0.001-mol zinc powder was placed in the center of the tube. Acting as substrates, pieces of Si (100) with the exposed face coated with gold (thickness: 15 nm) were placed downstream. Prior to heating, the quartz tube was purged with Ar at a flow rate of 20 sccm (standard cubic centimeters per minute) for 1 h. Then by means of a mechanical pump, the pressure inside the quartz tube was maintained at ca. 10^{-3} Pa, and the temperature was raised to 650 °C in a span of 1 h. After 3 h at 650 °C, the furnace was turned off. With the introduction of a flow of Ar, the quartz tube was cooled down to room temperature (RT).

The materials formed on the Si (100) substrates were examined at RT for phase identification using an X-ray diffraction (XRD) measurement (CuKα radiation; Model D/Max-RA, Rigaku). The morphologies of samples were examined using a field emission scanning electron microscope (FESEM) (FEI Sirion 200, operated at an accelerating voltage of 5 kV), which is equipped with energy dispersive spectroscopy (EDS). The cathodoluminescence (CL) image of sample were collected over a high-resolution CL system at an accelerating voltage of 10 kV and a current of 2000 pA; the CL system was equipped with an ultrahigh vacuum scanning electron microscope and a Gemini electron gun (Omicron, Germany).

3. Results and discussion

The FESEM technique can provide information about the morphology of an entity without its original nature disturbed. One can see from Fig. 1(a) that the grains of the as-prepared material are spherical in morphology, which are uniform in size. They are harvested in large quantities and distributed evenly on the Si substrate. As arrowed in Fig. 1(b), the spheres are hollow, showing an average diameter of around 2 μm, which is further verified in Fig. 1(c). From the high-magnification FESEM image (Fig. 1(d)), one can see that the hollow sphere is porous and composed of nanoparticles. The EDS spectrum shows signals of Zn, Cd, S, Au, Si, and O (see the supporting information figure, Fig. SI). The Si and Au signals are attributed to the gold-coated Si substrate, where the Si signal is strong as a result of a monolayer of hollow spheres. The O signal suggested that there was oxidation of surface Zn and Cd during sample handling in air.

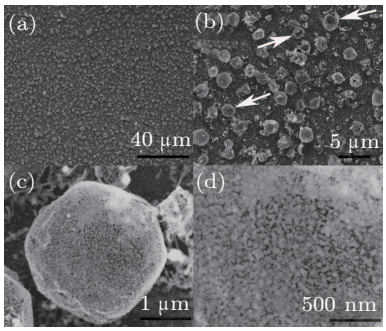


Fig. 1. FESEM images of $Zn_xCd_{1-x}S$ hollow spheres at different magnifications ((a)–(d)).

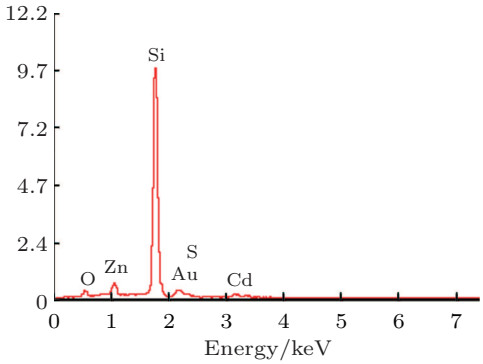


Fig. SI. (color online) EDS of $Zn_{0.09}Cd_{0.91}S$ hollow spheres.

In order to synthesize $Zn_xCd_{1-x}S$ hollow spheres in a controllable manner, we investigate the effects of the process parameters such as zinc powder, evaporation temperature, and evaporation time. From Fig. 2(a), with no zinc in the source, the product is CdS nanorods. One can spot a nanoparticle at the end of the CdS nanorod, a phenomenon typical of VLS growth.[48] As shown in Fig. 2(b), when the source is a mixture of cadmium sulfide and zinc powder at an evaporation temperature of 600 °C, small hollow spheres with an average size of 300 nm are generated. Compared with the hollow spheres prepared at 650 °C, the hollow spheres prepared at an evaporation temperature of 600 °C are small and distributed unevenly. At an evaporation temperature of 700 °C (Figs. 2(c) and 2(d)), evenly distributed flakes on Si wafer are gained. It is interesting to find that there are flakes that are gathered in the form of a sphere. It is apparent that under similar synthesis conditions, hollow spheres could not be fabricated in the absence of zinc powder, and 650 °C is the most appropriate evaporation temperature for the formation of $Zn_xCd_{1-x}S$ hollow spheres.

Figure 3 shows the typical XRD patterns of as-deposited products. Without zinc powder in source material, the XRD pattern of as-prepared nanorods (Fig. 3(a)) is identical to that of hexagonal wurtzite CdS, having $a = 0.4136$ nm and $c = 0.6713$ nm (JCPDS Card, No. 77-2306). At an evaporation time of 3 h or 8 h, the samples synthesized at an evaporation temperature of 650 °C display diffraction peaks that can be

indexed to the wurtzite phase of ternary alloyed $Zn_xCd_{1-x}S$ nanocrystals. For the $Zn_xCd_{1-x}S$ system, Zn mole fraction (x) can be obtained by the Vegard's law: $C_x = C_{CdS} + (C_{ZnS} - C_{CdS})x$ (where C_x, C_{CdS}, and C_{ZnS} are lattice constants along the c axes of $Zn_xCd_{1-x}S$, CdS, and ZnS crystals, respectively), in agreement with the experimental results of $Zn_xCd_{1-x}S$ solid solutions and thin films.[40,49–51] Here, the Zn mole fraction (x) is found to be 0.09. Compared with the hollow spheres harvested at an evaporation time of 3 h, the sample harvested at an evaporation time of 8 h shows sharp XRD peaks, indicating that the latter is of better crystallization. Based on the above results, we are sure that $Zn_{0.09}Cd_{0.91}S$ hollow spheres of uniform size and wurtzite phase are synthesized through the one-step thermal evaporation of a mixture of Zn and CdS powders at 650 °C.

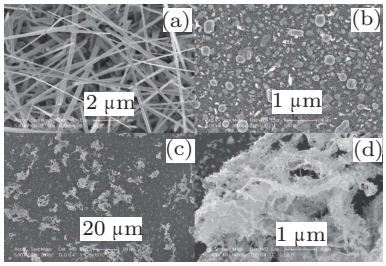


Fig. 2. FESEM image of sample obtained without zinc powder in source material (a); and FESEM images of samples harvested at different evaporation temperatures: 600 °C (b), 700 °C ((c) and (d)).

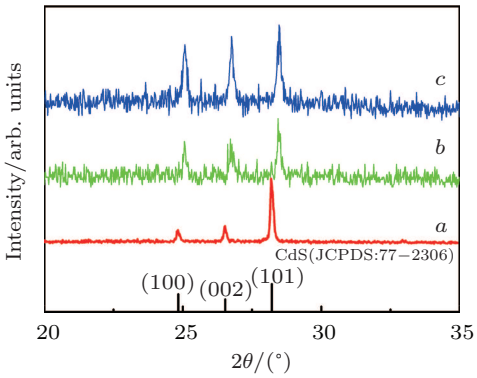


Fig. 3. (color online) XRD patterns of CdS nanorods (curve a), and $Zn_xCd_{1-x}S$ hollow spheres obtained at deposition time of 3 h (curve b) and 8 h (curve c).

In order to understand the growth mechanism of hollow $Zn_{0.09}Cd_{0.91}S$ spheres, we monitor the shape of intermediates with respect to time (by FESEM, Fig. 4). At a deposition time of 1 h (Figs. 4(a) and 4(b)), one can see a large number of grains (around 500 nm in size) with tilting fringe distributed evenly on the Si substrate. At a deposition time of 2 h (Figs. 4(c) and 4(d)), there are a large number of flakes with an average size of 3 μm distributed evenly on the Si substrate. They are composed of nanoparticles and are in curled form. It is hence deduced that the hollow $Zn_{0.09}Cd_{0.91}S$ spheres are evolved from this kind of flakes.

According to the above observations, we propose a mechanism for the growth of $Zn_xCd_{1-x}S$ hollow spheres, as shown schematically in Fig. 5. This is similar to ZnO microbowls grown on ITO glass substrate reported by Zhang *et al.*[52] As reported in previous studies,[53] CdS was decomposed to generate Cd vapor and S_2 gas, and Zn powder was in the form of Zn vapor at high temperature. The steps involved in the synthesis of $Zn_xCd_{1-x}S$ hollow spheres are as follows:

$$CdS(s) \rightarrow CdS(g), \tag{1}$$

$$2CdS(g) \rightarrow 2Cd(g) + S_2(g), \tag{2}$$

$$Zn(s) \rightarrow Zn(g), \tag{3}$$

$$2(1-x)Cd(g) + 2xZn(g) + S_2(g) \rightarrow 2Zn_xCd_{1-x}S(s). \tag{4}$$

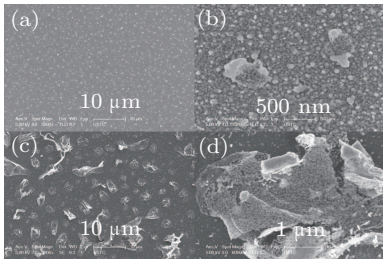


Fig. 4. FESEM images of samples obtained at deposition times of 1 h ((a) and (b)) and 2 h ((c) and (d)).

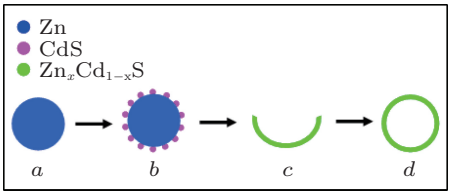


Fig. 5. (color online) Schematic illustration of the growth mechanism of $Zn_xCd_{1-x}S$ sphere obtained in our studies.

Because of the low melting point of Zn (419 °C), evaporated Zn vapor nucleates and further aggregates into Zn spheres on the Si substrate. It is possible that the Zn spheres are gradually covered by CdS. At higher temperatures, due to the escape of the enwrapped Zn through the CdS films, the fracturing of CdS spheres occurs, forming CdS grains with tilting fringe on Si substrate. Then, the tilting fringes develop into flakes of larger size. To reduce free energy, the flakes roll up to the formation of hollow spheres. In the course of generating the hollow spheres, Cd, Zn, and S_2 react to form $Zn_xCd_{1-x}S$. It is understood that due to the relatively fast sublimation of Zn at a lower temperature, the mole fraction of Zn in the prepared $Zn_xCd_{1-x}S$ hollow spheres is small (0.09).

The CL is a useful technique for characterizing the optical properties of nanostructures because of its high spatial resolution, and the structural information obtained by using secondary electron (SE) imaging. Generally, due to tunable

light sources of short wavelength and the high spatial resolution compared with those of the photoluminescence technique, the near-band-edge emission can be easily detected in the CL spectra. Shown in Fig. 6 are the SE and CL images of an individual hollow $Zn_xCd_{1-x}S$ sphere. From the SE image (Fig. 6(a)), one can give a morphological description similar to that of the FESEM study. Figure 6(b) shows the corresponding CL image that exhibits the uniform distribution of signals. The results indicate uniform Zn, Cd, and S distribution of the alloyed $Zn_xCd_{1-x}S$ nanostrcture, discarding the possibility of having separate CdS, ZnS, or core-shell-structured nanocrystals. Because of a number of the monolayers of $Zn_xCd_{1-x}S$ hollow spheres on Si substrate, the CL spectrum was difficult to collect and is not shown.

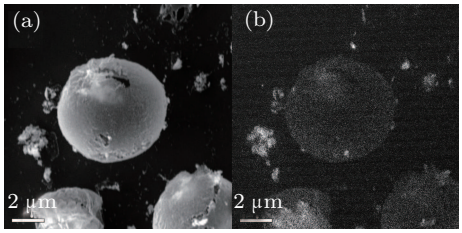


Fig. 6. SE image of an individual hollow $Zn_xCd_{1-x}S$ sphere (a), and the corresponding CL image (b).

4. Conclusions

By vapor-phase growth method, we synthesize novel $Zn_xCd_{1-x}S$ hollow spheres (hexagonal wurtzite phase; $x = 0.09$) that are uniform in size. The presence of Zn in the source material and the evaporation temperature are factors that determine the successful growth of the hollow spheres. The results of cathodoluminescence investigation indicate an even distribution of Zn, Cd, and S in the alloyed $Zn_{0.09}Cd_{0.91}S$ hollow spheres. It is envisaged that $Zn_xCd_{1-x}S$ hollow spheres of this kind can be utilized in the industry of nanodevices that are based on Si wafers. Meanwhile, the addition of hollow spheres into the micro/nano-$Zn_xCd_{1-x}S$ family will enrich the study of $Zn_xCd_{1-x}S$ as a whole.

Supplementary Information: EDS of $Zn_{0.09}Cd_{0.91}S$ hollow spheres.

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