

One-step Hydrothermal Method to Synthesize Self-encapsulated ZnS Micron Core-shell Spheres on a Large Scale

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(Received May 31, 2005; CL-050702)

Uniform self-encapsulated ZnS micron core-shell spheres have been synthesized on a large scale using metallic zinc powder and NaHSO_3 as starting reagents in distilled water at 200°C for 50 h. The as-prepared samples are characterized with XRD, FE-SEM, TEM, and PL. A possible formation mechanism is briefly discussed.

Recently, many research efforts have been focused on the area of wide band gap semiconductor materials because of their potential applications in short wavelength optical devices.¹ ZnS, an important semiconductor compound of II-VI group, with a wide band gap energy of 3.7 eV at 300 K, shows various luminescence properties such as photoluminescence,² electroluminescence,³ mechanoluminescence,⁴ and thermal luminescence.⁵ Therefore, ZnS is a traditional phosphor widely used in flat-panel display, electroluminescent devices, infrared windows, sensors, lasers,⁶ and as an LED when doped.⁷ Generally, the spherical morphology compared with other shapes has the low-light scattering at the surfaces due to the high-packing densities.⁸ However, sulfide phosphors degrade and hinder electron emission owing to dispersing into the vacuum and contaminating the field emitter if ZnS with spherical shape is exposed to the outside directly. So some compounds such as large band-gap semiconductor materials, polymers, or insulators⁹ have been used to cover their surface with a shell, forming core-shell structures, to enhance the stability. However, to the best of our knowledge, reports about ZnS with self-coated core-shell structures are limited.¹⁰ In this paper, ZnS with self-encapsulated core-shell structures is synthesized through the self-aggregation process using a one-step hydrothermal route. Such novel structure is also achieved via a solution-based catalytic route^{11,12} or in situ source-template interface reaction route.¹⁰ However, our whole process needs no catalyst or toxic precursors and template.

In a typical process, 20 mmol of NaHSO_3 is dissolved in 40 mL of distilled water in a 50-mL Teflon-lined stainless steel autoclave, and then 5 mmol of Zn powder is added into the autoclave without stirring. The autoclave is sealed and maintained at 200°C for 50 h. Following, the autoclave is allowed to cool to room temperature. The solid precipitate is filtered off, washed several times with carbon disulfide, distilled water and absolute ethanol, and then dried in vacuum at 60°C for 4 h.

The phase purity of the as-prepared products is determined by X-ray diffraction (XRD) using a Philips X'pert diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541874$ nm). Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM) are applied to investigate the morphology. The measurements are carried out with an X-650 scanning electron microanalyzer and a field emission scanning electron microanalyzer (JEOL-6700F), respectively. Transmission electron

microscopy (TEM) is operated on a Hitachi 800 microscopy. The room temperature photoluminescence (PL) spectrum is performed on a Jobin Yvon-Labram spectrometer with a He-Cd laser.

A typical XRD pattern of the products is shown in Figure 1, in which all of the reflections can be readily indexed to cubic zincblende crystal structure (JCPDS 80-0020). The diffraction peaks correspond to the (111), (200), (220), and (311) planes of the cubic crystalline ZnS. No impurities such as ZnO, Zn(OH)₂ could be detected in this product.

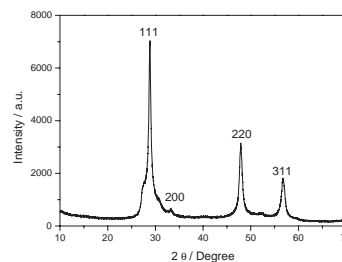


Figure 1. XRD pattern of as-prepared ZnS.

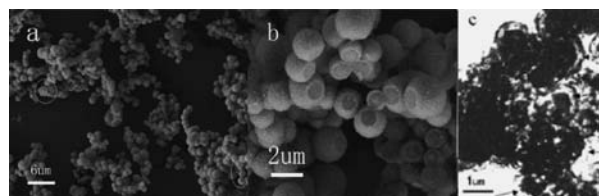


Figure 2. (a) Low-magnification FE-SEM, (b) high-magnification FE-SEM, and (c) TEM images of the as-prepared ZnS. The white rings shown in Figure 2a show open self-encapsulated core-shell spheres. Arrows in Figure 2c point to some characteristic self-encapsulated core-shell spheres.

The morphology and microstructure of the as-prepared samples are investigated with FE-SEM and TEM. From FE-SEM image (Figure 2a), it is obvious that more than 90% of the as-prepared ZnS is spherical with diameters ranging from 1.5 to $3.0\ \mu\text{m}$. Figure 2b and the white rings shown in Figure 2a exhibit the “opened” structure. The obvious contrast of brightness and darkness in edge and center of the spheres, indicating different packing densities, shows the nature of core-shell structures. Close observation (Figure 2b and the white rings shown in Figure 2a) shows that surfaces of these spheres are constructed by many nanoparticles with diameters ranging from 50–150 nm and that the cores also consist of nanoparticles but tightly aggregated. From TEM image (Figure 2c) of the products, the observation results also confirm the self-encapsulated core-shell nature of the spheres. Interestingly, there is gap about 100–

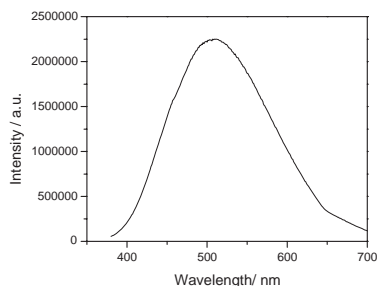


Figure 3. Photoluminescence spectrum of the as-prepared ZnS.

400 nm (indicated with arrows in Figure 2c) between core and shell being found. This phenomenon is similar to the former reported.¹⁰ The core is about 0.5–1.5 μm in diameter, and the shell thickness ranges from 50 to 200 nm. In addition, it could be shown that the core-shell spheres are sensitive to beam irradiation during TEM examination. This may be related to their thin and porous walls. A similar phenomenon can be also found in former reports concerning hollow spheres.¹³

The room-temperature PL spectrum of the as-prepared ZnS, shown in Figure 3, is obtained with an excitation wavelength of 325 nm. The green emission at about 508 nm, which is similar to that of nanoparticles at 511 nm,¹⁴ may be attributed to a self-activated center presumably formed between a zinc vacancy and a shallow donor associated with a sulfur vacancy.^{14,15} The broadened peak is due to the small dimension of the nanoparticles in the spherical walls.

The chemical reaction in the process to obtain self-encapsulated ZnS core-shell spheres can be formulated as follows:



The metallic zinc powder is used as zinc source, so high temperature (200 °C) is proper to make zinc powder react completely.

To investigate the growth process of self-encapsulated ZnS core-shell spheres, series of experiments are carried out. The products and their morphologies are influenced greatly by the reaction time. After heating for 24 h, there is a lot of metallic zinc unreacted (aggregated into thin zinc foil). The initial products, separated carefully from unreacted metallic zinc, mainly consist of irregular colloids particles (Figure 4a), which connect each other. After reacting for 40 h, only a little unreacted zinc is left, and many spheres with diameter of 1–2 μm can be observed (Figure 4b).

On the basis of the results of our experiments, it is possible to interpret the formation of the self-encapsulated ZnS core-shell spheres as follows: (1) Small ZnS amorphous colloids are initially formed under the synthetic condition. And the initially formed colloids tend to aggregate, so they assemble together but loosely with a spherical appearance. (2) As the reaction proceeds, the re-

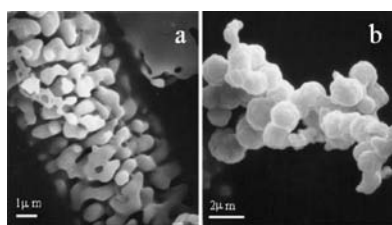


Figure 4. SEM images of the products obtained after heating for (a) 24 h and (b) 40 h.

action rate slows down with the decrease of the reactants concentration. As a result, the reaction system is inclined to provide a thermodynamically stable environment. The newly formed ZnS colloids tend to nucleate and grow larger to be nanoparticles, and the nanoparticles have better crystallization than the above-mentioned sphere-like colloids. Therefore, newly formed uniform ZnS nanoparticles are grown on the surface of each agglomerate. (3) The loosely adhered colloids in the spheres with many amorphous components have a tendency to be gradually crystallized, so the spheres tend to shrink. Since the surface has been fixed by well-crystallized nanoparticles, the shrinkage is apt to separate the sphere into two parts; finally the core and shell are formed. The whole process is similar to recent work reported by Xia et al. on the catalytic growth of Pt nanowires¹¹ and Xie et al. on the catalytic growth of α -MnO₂ nanorods.¹²

In summary, the novel self-encapsulated ZnS micron core-shell spheres have been successfully obtained through a one-step hydrothermal method under mild and easily controlled conditions. The self-encapsulated ZnS micron core-shell spheres achieved may be of interest for potential applications. And this method may be used for preparing other materials with self-encapsulated core-shell morphology.

Financial support from the national Science Foundations of China is gratefully acknowledged.

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