Fabrication and Characterization of ZnS Hollow Nanostructures in Micelle System

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ZnS hollow vessels, short tubes and hollow spheres have been fabricated in large scale by a simple micelle method. Power X-ray diffraction (XRD) pattern indicates that the as-obtained product is hexagonal ZnS. Large blue shift in UV–vis spectrum suggests that the hollow nanostructures have quantum confinement effect.

As an important member of the wide-gap semiconductors, ZnS has been extensively investigated.[1] It is among the oldest and probably the most important materials used as phosphorhost.[2] By doping ZnS with different metals,[3] a variety of luminescent properties excited by UV, X-rays, or cathode rays have been observed. Moreover, ZnS has potential application in novel photonic crystal devices operating in the region from visible to near-IR.[4] It is also used as a kind of photocatalyst, which has unique catalytic functions compared to those of TiO_2.[5] In the past decade, enormous studies on the synthesis of nanometer ZnS crystals have been reported, such as ZnS quantum dots,[6] ZnS nanoporous nanoparticles,[7] ZnS hollow spheres,[8] ZnS nanorods,[9] ZnS nanowires,[10] and ZnS lamellar mesostructured nanofibers.[11] But ZnS hollow vessels, a kind of specific morphology, have not been reported to the best of our knowledge. Herein we report a simple procedure to fabricate ZnS hollow nanovessels, nanotubes, and hollow nanospheres controlled in a CS_2–surfactant–ethylenediamine micelle system via interface reaction route. Transmission electron microscopy (TEM), X-ray powder diffraction (XRD), UV–vis spectroscopy, and fluorescence spectroscopy were used to investigate the morphology and properties of the as-obtained product, and a reasonable mechanism has also been speculated.

In a typical process of fabricating ZnS hollow nanostructures, a CS_2–sodium dodecyl benzene sulfonate (SDBS)–ethylenediamine micelle system was prepared at 25 °C. Then aqueous $Zn(OAc)_2$ solution was added into it, and the mixture was heated to a certain temperature and kept at the same temperature for 30 min (detailed experiment process is in Supporting Information S1). To understand the growth mechanism of the product, experiment was performed at a different reaction temperature while other conditions were not changed.

The structure and morphology of samples were investigated by TEM. Figure 1a is a typical panorama TEM image of hollow vessels obtained at 50 °C, which shows the product is primarily composed of hollow and winding vessel-like nanostructures, the yield can be up to 90 percent. The external diameter is 80–100 nm and the length is up to micrometer scale and the thickness of the wall is 10–20 nm. The hollow structure is further confirmed by TEM images with higher magnification in Figure 2b, the strong contrast difference in all of the vessels with dark edge and bright center can be clearly seen. Experiments also showed that the reproducibility was very good.

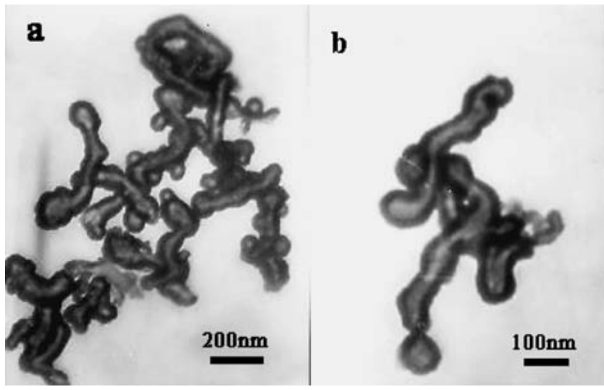

Figure 1. TEM images of ZnS hollow vessels obtained at 50 °C, a) panorama image; b) image with larger magnification.

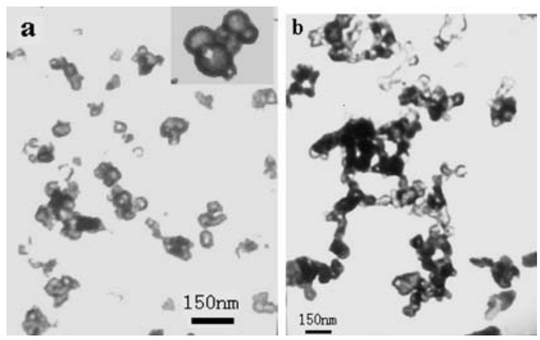

Figure 2. TEM images of a) ZnS hollow spheres obtained at 40 °C; b) the product obtained at 50 °C after 10 min reaction time.

Some short straight tubes coexisting with vessels are found (TEM pattern is shown in S2a). The end of these tubes is closed, the diameter and length are 80–100 nm and 400–500 nm, respectively. Some slightly bent tubes with a length of the order of micrometer are also observed and the typical TEM image is presented in S2b.

By keeping other conditions unvaried but a lower reaction temperature, i.e., 40 °C, the product is mainly composed of hollow spheres as shown in Figure 2a and the inset in it is an enlarged image of the hollow spheres. It also can be found that some hollow spheres have the tendency to be transformed into hollow vessels. The external diameter of the hollow spheres is 30–50 nm and the thickness of the shell is about 8–10 nm.

The XRD patterns shown in Figure 3a are for ZnS hollow vessels and spheres, which are consistent with the reported pattern in the literature.[7] The diffraction patterns of the two samples are very similar and are in good agreement with hexagonal

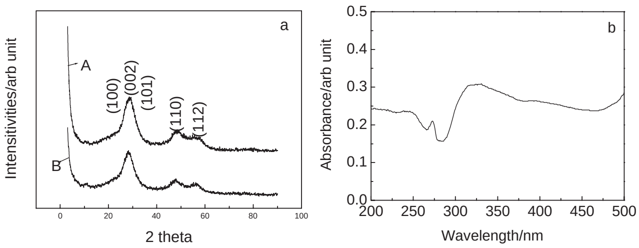

Figure 3. a) The XRD patterns of the ZnS hollow nanostructures: A) hollow vessels; B) hollow spheres. b) Room-temperature UV–vis absorption spectrum of the hollow vessels.

ZnS (space group: $p63lm(186)$) with lattice constants $a = 3.777$ and $b = 6.188$ Å (JCPDS No. 80-0007). Estimated by Scherrer's equation, the crystallite size in these nanostructues is about 10 nm, which is consistent with the result of TEM and indicates that these hollow nanostructures are composed of nanoparticles with a size of 10 nm or so and they are polycrystalline.

It is known that there exists reaction between CS_2 and ethylenediamine as follows:

$$H_2NCH_2CH_2NH_2 + CS_2 \rightarrow H_2NCH_2CH_2NHCSSH, \quad (1)$$

$$n(H_2NCH_2CH_2NHCSSH) \rightarrow [HNCH_2CH_2NHCS]_n + nH_2S. \quad (2)$$

When Zn^{2+} ions were introduced into the solution, they would be chelated by ethylenediamine and be carried by ethylenediamine from the water phase to the oil–water interface, where they reacted with H_2S released in situ and became mineralized around the oil droplets.

When the reaction temperature was at 40 °C, which was below the boiling point of CS_2 (46.3 °C), only mineralization took place and the shape of product was determined by the shape of micelles, so only hollow spheres were formed. Whereas the temperature was increased up to 50 °C, evaporated CS_2 gas flows made the micelles to distort even crack to form several clefts at the same time of mineralization. Under the magnetic stirring, part-mineralized broken micelles would contact with each other and connect into a whole body, so hollow vessels including some tubes were produced. To verify the proposed mechanism, we took out a part of sample from the system after 10 min of the reaction duration at 50 °C, the result is shown in Figure 2b, broken hollow spheres can be clearly seen and lots of which connect each other.

The surfactant played an important role in the formation of the hollow nanostrucrures of smaller size. Huang and co-workers have prepared CdS submicrometer hollow spheres with similar system but without surfactant, only hollow spheres were obtained and the diameter was 150–250 nm.[12]

The effect of surfactant concentration and species on the morphology of product was tentatively investigated by adding different amounts of SDBS or other surfactant into the system without other conditions changed, the detailed results can be obtained in S3.

The UV–vis spectrum of ZnS hollow nanostructures as-prepared is shown in Figure 3b, compared with the bulk ZnS (344 nm),[11] the absorption peaks for the hollow vessels are markedly blue-shifted. Additionally, according to the UV–vis spectrum, the optical band gap energy of the ZnS hollow vessels could be estimated to be about 3.97 eV, which is larger than that of bulk ZnS (3.7 eV, 300 K). These suggest that the hollow nanostructures have obvious quantum confinement effect, which is consistent with the result of XRD. Fluorescence spectrum of the samples ($\lambda_{ex} = 325$ nm) is shown in S4. Further studies on the photoproperties of ZnS hollow nanovessels and nanospheres are needed.

As it is well known that the properties and applications of nanomaterials are largely dependent on their size, shape, and texture. Additionally, hollow structure represents an important class of materials that are potentially useful for a wide range of applications, such as carriers for the controlled release of medicine, protecting membranes, bioactive substances, basic materials of artificial cells, highly effective catalysts, fuel cells, confined reactors, etc.[13] We believe that this kind of novel ZnS hollow vessels fabricated by us will present more new properties and applications especially in the aspect of photocatalysis.

In summary, ZnS hollow nanovessels, nanotubes, and nanospheres have been prepared via a simple micelle route with a high production rate. The UV–vis absorption spectrum shows that they exhibit interesting optical properties and, therefore, are expected that they have potential application in photocatalysis and optical as well as electronic devices.

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References

1 E. Monroy, F. Omnes, and F. Calle, *Semicond. Sci. Technol.*, **18**, R33 (2003).
2 R. Chen and D. J. Lockwood, *J. Electrochem. Soc.*, **149**, 69 (2002).
3 a) R. N. Bhargava, D. Gallagher, X. Hong, and D. Nurmikko, *Phys. Rev. Lett.*, **72**, 416 (1994). b) G. A. Marking, C. S. Warren, and J. B. Payne, U. S. Patent, 217 B2, 6610 (2003). c) S. Lee, D. Song, D. Kim, J. Lee, S. Kim, I. Y. Park, and Y. D. Choi, *Mater. Lett.*, **58**, 342 (2004). d) A. K. Alshawa and H. J. Lozykowski, *J. Electrochem. Soc.*, **141**, 1070 (1994).
4 W. Park, J. S. King, C. W. Neff, C. Liddell, and C. J. Summers, *Phys. Status Solidi B*, **229**, 949 (2002).
5 a) I. Salcm, *Catal. Rev.—Sci. Eng.*, **45**, 205 (2003). b) A. L. Linsebigler, G. Lu, and J. T. Yates, *Chem. Rev.*, **95**, 735 (1995).
6 Y. Zhao, Y. Zhang, H. Zhu, G. C. Hadjipanayis, and J. Xiao, *J. Am. Chem. Soc.*, **126**, 6874 (2004).
7 J. Hu, L. Ren, Y. Guo, H. Liang, A. Cao, L. Wan, and C. Bai, *Angew. Chem., Int. Ed.*, **44**, 1269 (2005).
8 Y. Xie, J. Huang, B. Li, Y. Liu, and Y. Qian, *Adv. Mater.*, **12**, 1523 (2000).
9 J. Xu and Y. Li, *J. Colloid Interface Sci.*, **259**, 275 (2003).
10 a) Q. Wu, N. Zheng, Y. Ding, and Y. Li, *Inorg. Chem. Commun.*, **5**, 671 (2002). b) R. Lv, C. Cao, and H. Zhu, *Mater. Res. Bull.*, **39**, 1517 (2004).
11 J. Li, Y. Xu, D. Wu, and Y. Sun, *Chem. Lett.*, **33**, 718 (2004).
12 J. Huang, Y. Xie, B. Li, Y. Liu, Y. Qian, and S. Zhang, *Adv. Mater.*, **12**, 808 (2000).
13 a) Z. Zhong, Y. Yin, and G. Byron, *Adv. Mater.*, **12**, 206 (2000). b) Y. Yin, Y. Lu, and B. Gates, *Chem. Mater.*, **13**, 1146 (2001).

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