

Facile Synthesis of Hollow ZnS Nanospheres in Block Copolymer Solutions

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Introduction

Hollow spheres with nanometer-to-micrometer dimensions having tailored structural, optical, and surface properties represent an important class of materials that are potentially useful for a wide range of applications such as delivery vehicle systems, photonic crystals, fillers, and catalysts.^{1–4} Recent efforts to prepare inorganic hollow spheres have been focused on inorganic precipitation processes using a variety of sacrificial templates including silica spheres,^{4,5} polystyrene latex spheres,^{2,6–8} resin spheres,⁹ vesicles,¹⁰ liquid droplets,^{3,11} and miniemulsion¹² or microemulsion¹³ droplets. In addition, micelles formed by block copolymers have been employed as templates for the fabrication of hollow spheres of various inorganic materials including MoO_3 ,¹⁴ CaCO_3 ,¹⁵ and Ag .¹⁶ In a recent work, block copolypeptides have been used to cooperatively assemble SiO_2 and Au nanoparticles into hollow spheres.¹⁷

Recently, many efforts have been devoted to the morphological control of chalcogenide semiconductor nanocrystals and their assemblies owing to their technological importance.^{11,18–20} For example, submicrometer-sized hollow ZnS spheres have been synthesized by using silica⁵ and polystyrene⁸ spheres as sacrificial templates, respectively. Hollow CdS, CuS, and NiS spheres were produced through an interface-mineralizing route in CS_2 solutions,^{11,21} whereas hollow Ag_2S spheres were produced under hydrothermal conditions.²² Generally, the sizes of the obtained hollow chalcogenide spheres are larger than

100 nm. Polydisperse hollow CdS nanospheres (20–100 nm) were yielded through mineralization of cubic lyotropic liquid crystals formed by a block copolymer.²³ However, it remains a challenge to develop simple methods for the fabrication of uniform hollow nanospheres of chalcogenide semiconductors. Herein, we report a one-pot, facile synthesis of hollow ZnS nanospheres (50–70 nm) in aqueous solutions of a triblock copolymer at room temperature.

Experimental Section

The Pluronic amphiphilic triblock copolymer P123, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}} = 5800$), was obtained from Aldrich. In a typical synthesis, 0.2 g of P123 was dissolved completely in 8 mL of water, and then 1 mL of 0.5 mol L^{-1} zinc acetate and 1 mL of 0.5 mol L^{-1} thioacetamide (TAA) were added to the solution, followed by 10 min of sonication in a normal ultrasonic bath (50 Hz). Then, the mixture was maintained under a static condition at 27 °C for 10 h, and the slow release of S^{2-} ions from TAA led to the formation of ZnS particles. The resulting solution was centrifuged for 5 min at 3000 rpm, and a white precipitate was obtained. After removal of the supernatant, the remaining solid was washed with ethanol and H_2O , successively. The final product was dried as a powder at 50 °C. In the experiment, the polymer concentration in the solution was varied from 5 to 40 g L^{-1} to investigate its effect on the formation of hollow ZnS spheres. The obtained products were characterized with conventional transmission electron microscopy (TEM, JEOL JEM-200CX, 160 kV), high-resolution TEM (HRTEM, Hitachi H-9000HAR, 300 kV), X-ray diffraction (XRD, Rigaku Dmax-2000, Cu $\text{K}\alpha$ radiation), UV–visible spectroscopy (Shimadzu UV-250), and thermogravimetric analysis (TGA, LCT-1).

Results and Discussion

Figure 1a presents a typical TEM image of hollow ZnS nanospheres obtained at a P123 concentration of 20 g L^{-1} , which shows that the hollow spheres are rather uniform with diameters ranging from 50 to 70 nm and a shell thickness of about 15 nm. The rough surface of the shell indicates that the shell could consist of primary nanoparticles. The related electron diffraction (ED) pattern shows principally five rings which correspond to the (111), (200), (220), (311), and (222) planes of zinc blende, the cubic ZnS phase, respectively. The fact that the rings are somewhat broadened also indicates the presence of ZnS nanocrystals. The HRTEM image obtained from the central part of a single hollow ZnS nanosphere (Figure 1b) shows well-resolved lattice fringes with d spacings corresponding to zinc blende, confirming that the shell of the hollow spheres consists of ZnS nanocrystals. The image also revealed that the primary ZnS nanocrystals have an average crystal size of ~ 4 nm.

The XRD pattern of the hollow ZnS nanospheres is shown in Figure 2a, which suggests that the product comprises ZnS crystals with the zinc blende structure. An average crystallite size of about 4 nm was estimated according to the line width analysis of the (111) diffraction peak based on the Scherrer formula, which is in good agreement with the HRTEM observation. Figure 2b presents the UV–vis absorption spectrum of the hollow ZnS nanospheres, which was recorded after the powder sample was dispersed in ethanol. It shows an absorption

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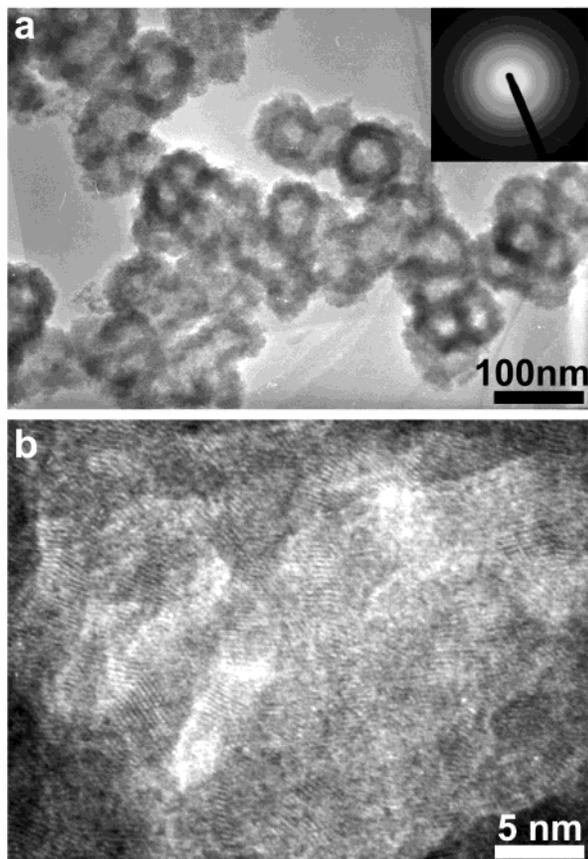


Figure 1. TEM (a) and HRTEM (b) micrographs of hollow ZnS nanospheres in the presence of P123. [P123] = 20 g L⁻¹. The inset shows the corresponding electron diffraction pattern.

peak at 305 nm, which is considerably blue-shifted from 340 nm for bulk zinc blende ZnS because of quantum size effects. The spectrum shows a long absorption tail due to scattering by the particles in the dispersion system, which is reminiscent of the absorption spectrum of thioglycerol-capped ZnS nanocrystallites (3.5 nm).²⁴ Basically, the position of the excitonic peak will not be influenced by the long tail in the spectrum. It has been documented that the optical absorption of the ZnS nanocrystals with a size of 3.5 nm exhibits an excitonic peak at 288 nm, and the presented variation of band gap versus the size of ZnS nanocrystallites indicates that an excitonic peak at 305 nm, corresponding to a band gap of 3.78 eV, would correspond to a ZnS crystallite size of about 4 nm.²⁴ This suggests that the size of the ZnS nanocrystals constituting the hollow nanospheres is about 4 nm, which is in good agreement with the results obtained from both TEM and XRD. Thermogravimetric analysis of the as-dried powder sample in air shows three weight loss steps in the TGA curve: 5.1 wt % loss corresponding to water desorption (up to 200 °C), 4.6 wt % loss corresponding to desorption and decomposition of occluded polymer (200–500 °C), and 8.5 wt % loss corresponding to oxidation of ZnS (500–650 °C). This result suggests that only a rather small amount of polymer was occluded in the hollow structures, indicating that the ZnS shell comprising primary particles was not completely solid and most of the copolymers were washed out through the small holes in the closed shell, leading to the formation of really hollow ZnS spheres. Hollow spheres fabricated by using soft templates in solutions usually consisted of a porous rather than solid

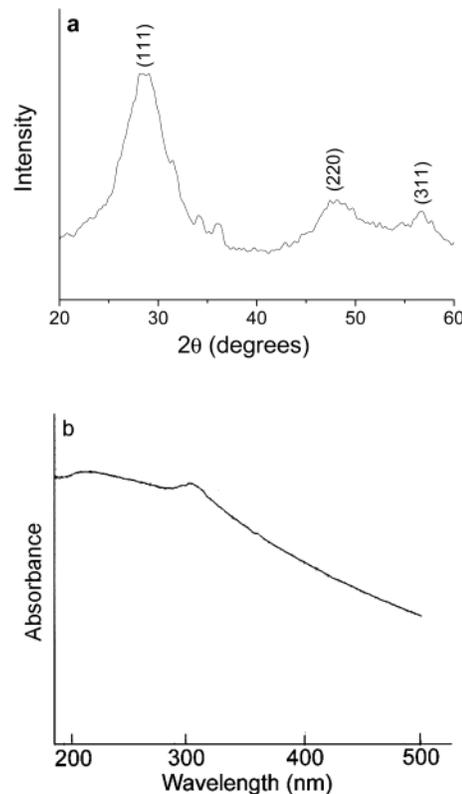


Figure 2. XRD pattern (a) and UV-vis absorption spectrum (b) of hollow ZnS nanospheres in the presence of P123. [P123] = 20 g L⁻¹.

shell that allowed for the transport of organic templates out of the shell upon washing.^{15,16}

ZnS particles have also been synthesized at varied polymer concentrations, and typical TEM micrographs of the obtained products are shown in Figure 3. As shown in Figure 3a, the product obtained at a lower polymer concentration, namely, 5 g L⁻¹, is composed of solid spheres (100–200 nm), which consist of primary ZnS nanocrystals (~4 nm). As the polymer concentration is increased to 10 g L⁻¹, the product exhibits loose spheres (80–160 nm), which show many inner pores with sizes less than 10 nm (Figure 3b). Increasing the polymer concentration to 20 g L⁻¹ results in the formation of the hollow ZnS nanospheres shown in Figure 1. If the polymer concentration is further increased to 40 g L⁻¹, the product is a mixture of many hollow ZnS spheres (Figure 3c) and some large solid ZnS spheres (not shown). The hollow spheres thus obtained have 80–120 nm outside diameters, which are larger than the 50–70 nm outside diameters obtained at a lower polymer concentration of 20 g L⁻¹; however, the shell thickness is almost the same (~15 nm). The UV-vis spectrum of ZnS particles with morphologies such as loose spheres and solid spheres is very similar to that of the ZnS hollow nanospheres, suggesting that the optical properties of different ZnS structures were dictated by the properties of the primary 4 nm ZnS particles and essentially did not change upon their association into larger structures.

Amphiphilic triblock copolymers such as P123 can self-assemble into micelles when the polymer concentration exceeds the critical micelle concentration (cmc) in aqueous solution. The equilibrium of the triblock copolymer system will change upon addition of inorganic precursors, and a new competition among all species, including unimers, will be triggered until a new equilibrium is reached.²⁵ Our preliminary dynamic light scattering (DLS) experi-

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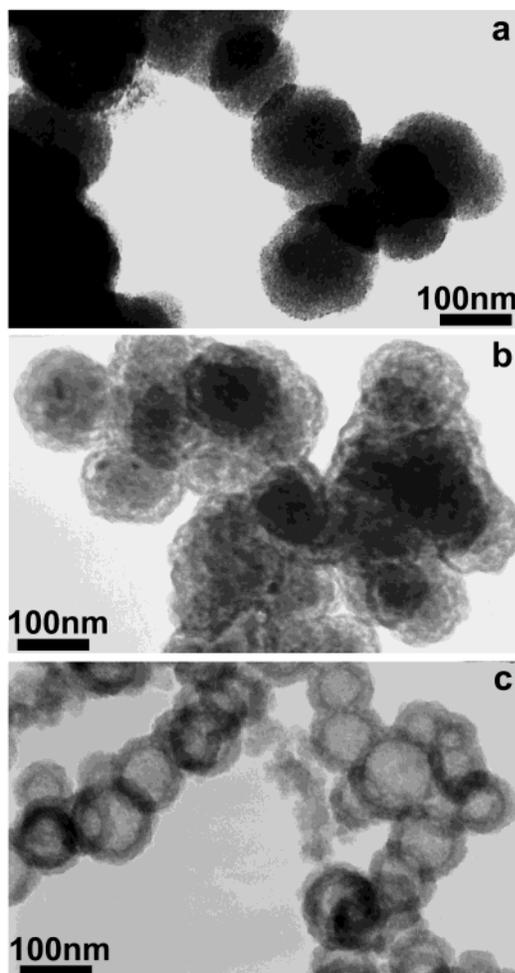


Figure 3. TEM micrographs of ZnS particles obtained in the presence of P123. [P123]: (a) 5, (b) 10, and (c) 40 g L⁻¹.

ment has shown that at 27 °C, the diameter of P123 micelles at a P123 concentration of 20 g L⁻¹ is 17.8 nm, which is consistent with the result reported previously.²⁶ When 0.05 mol L⁻¹ TAA was present in the polymer solution, the micelle size was measured to be 17.4 nm, nearly identical to that in the pure P123 solution. However, when 0.05 mol L⁻¹ zinc acetate was present in the polymer solution, the DLS experiment suggests there are some large aggregates (considerably larger than 200 nm) in

addition to the original polymer micelles (19.0 nm). It indicates that there is a strong complexation interaction between P123 and Zn²⁺ ions, which could lead to the formation of large P123 aggregates or clusters of P123 micelles in the solution.

In the current situation, hollow ZnS spheres with outer diameters of 50–70 nm and inner diameters of 20–40 nm were produced through the reaction between the Zn²⁺ ions and the S²⁻ ions released from TAA in the solution of P123. It appears that the hollow spheres were formed not by directly templating the original P123 micelles but by templating dynamic templates such as larger P123 aggregates formed during the precipitation process due to the interaction between the polymer and various inorganic species. It has been suggested that the development of inorganic hollow structures may perturb the initial organic templates in solutions, resulting in an adaptive construction.^{15,16} It was also expected that when P123 concentration was increased from 5 to 20 g L⁻¹, the probability for the formation of large P123 aggregates would increase, leading to the transition of the ZnS products from solid spheres through loose spheres to hollow spheres. However, if the P123 concentration was further increased to 40 g L⁻¹, the concentration of large P123 aggregates in the solution would be so high that in addition to the formation of larger hollow spheres, some primary ZnS particles tended to aggregate to form large solid spheres, resulting in a mixture of hollow ZnS spheres and solid ZnS spheres.

In summary, hollow ZnS nanospheres with diameters ranging from 50 to 70 nm and a shell thickness of about 15 nm have been synthesized by using thioacetamide as the sulfur source in aqueous solutions of the triblock copolymer P123 at room temperature. We expect that this convenient synthetic route to hollow ZnS nanospheres may be extended to the synthesis of other technologically important chalcogenide semiconductor hollow nanospheres.

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