# Synthesis and Characterization of Monodisperse ZnS Nanospheres

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The monodisperse ZnS nanospheres were synthesized by a solvothermal method. The nanospheres were characterized using XRD, TEM, UV–vis, and photoluminescence spectra. The results demonstrate that ZnS nanospheres are highly crystalline. The strong photoluminescence emission at 450 nm (blue) can be observed in the ZnS nanospheres.

Because of quantum confinement effects semiconductor nanoparticles have unique optical and electrical properties.[1–5] Zinc sulfide (ZnS), a band gap material with $E_g$ of 3.66 eV at room temperature, is a traditional phosphor widely used in flat-panel display, eletroluminescent devices, infrared windows, sensors, and lasers.[6–8] Doped ZnS with selected metal cations is a promising material for mechano-optic applications.[9] In general, the optimization of chemical composition, particle size distribution, and morphology is required for more efficient luminescence of phosphor materials. Among them, the monodisperse spherical morphology is an important factor for lower light scattering at the surfaces as well as higher packing densities. It is desired to prepare monodisperse nanospheres for foundational and application studies.

Up to now, many synthetic methods have been employed to prepare ZnS nanocrystals. ZnS nanobelts were fabricated via thermal evaporation.[10,11] ZnS nanowires were prepared by laser ablation–catalytic growth process.[12] ZnS nanorods can be obtained by surfactant-assisted soft chemistry method, microemulsion method, and solvothermal route.[13–15] The aggregation phenomenon of monodisperse ZnS nanospheres prepared by microwave irradiation still exists.[16] Monodisperse ZnS can be achieved by size-selective photocorrosion, but synthesis process is very complicated.[17] In order to achieve monodisperse nanospheres some templates have to be used.[18,19] Therefore, it remains a challenge to develop simple method for the fabrication of monodisperse ZnS nanospheres. The solvothermal process has recently been extensively applied to synthesis and design of materials with new structures and properties because the suitable solvents/stabilizing agents can prevent the particles from agglomeration.

In this work, a novel solvothermal route for the preparation of monodisperse ZnS nanospheres is reported. This solvothermal process has many advantages in comparison with other methods.[17–21] It does not require organometallic or toxic precursors and is carried out at the low temperature. By employing a suitable capping agent and the reaction conditions, the ZnS nanospheres with a monodispersity in shape and size can be obtained. The UV–vis absorption and photoluminescence (PL) properties of ZnS nanospheres are investigated, respectively.

Oleic acid was used as the capping agent to synthesize ZnS nanospheres because they can directly interact with the metal ions by complex formation to hinder nanocrystals agglomeration. The analytical grade regents were used as starting materials. In typical procedure, 2 mmol of $ZnCl_2$ was firstly added to a mixture containing 4-mL oleic acid and 3-mL triethylamine at room temperature. A solution of zinc–oleic complex was obtained by heating the above resulting mixture at 180 °C for 3 h. Then 6 mmol of elemental sulfur was dissolved in 3 mL of oleic acid as the sulfur source, and was put into the solution of zinc–oleic complex at room temperature. The reactants were sealed in a 20-mL Teflon-lined autoclave and placed in an air oven, which was heated at 180 °C for 60 h. After the reaction was completed, the autoclave was taken out of the oven and allowed to cool to room temperature. The particles were separated by precipitation with the addition of ethanol to the solution. Then the resulting particles were separated by centrifugation and dried at 60 °C. To investigate the effect of post-treatment on crystallinity and PL properties of nanospheres, a part of the samples was annealed in the quartz tube under argon atmosphere at 600 °C for 1 h.

Powder XRD patterns of the various ZnS nanospheres are shown in Figure 1. The broadening of peaks in the XRD pattern indicates the nanocrystalline nature of the samples. The patterns can be indexed as the cubic zincblende structure (from the weak peaks observed around the main peak at 28 degree, a little amount of wurtzite ZnS is also in the sample), which is very consistent with the values in the standard card (JCPDS No. 5-0566). The particle size estimated from XRD patterns using Debey–Scherrer formula is 10 nm, which show that post-treatment has no effect on crystallite size, but results in an increase in crystallinity of nanospheres.

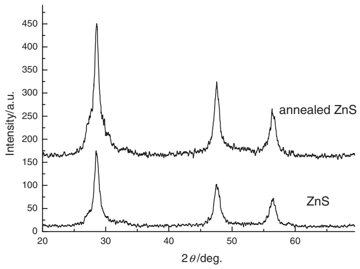

**Figure 1.** XRD patterns of ZnS nanospheres.

Figure 2 shows the TEM images of the ZnS nanospheres. From Figure 2a, it is observed that all the nanospheres are monodisperse. The uniformity of nanosphere size with an average diameter of 100 nm is demonstrated. From higher magnification TEM image (see Figure 2b), it can be seen that each nanosphere consists of many ultrafine particles.

The selected area electron diffraction (SAED) pattern in Figure 2c indicates that nanospheres are highly crystalline and it is typical for the cubic ZnS phase. The three diffraction rings correspond to the (111), (220), and (311) reflections, which are fully according with the XRD results. The HRTEM image demonstrates well-resolved diffraction fringes of the particles lattices

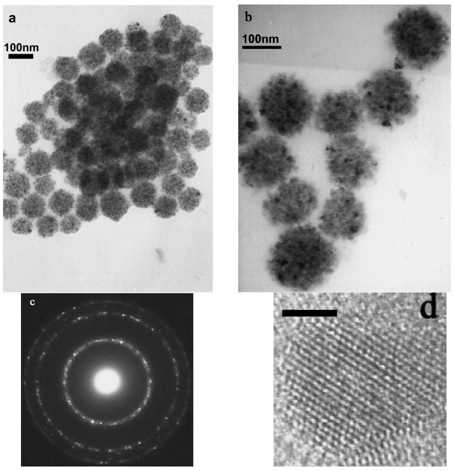

**Figure 2.** (a) Low-magnification TEM images of undoped ZnS nanospheres, (b) higher-magnification TEM image of ZnS nanospheres, (c) SAED image, (d) HRTEM image (bar scale = 5 nm).

(in Figure 2d). From Figure 2d, it is observed that the shape of each nanoparticle is close to spherical and the mean diameter is 10 nm, which is good agreement with calculated results from XRD patterns. The edges of nanoparticles are extremely clear. These crystallites built up to produce large nanospheres with an average diameter of 100 nm.

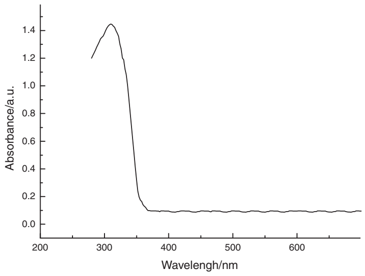

**Figure 3.** UV–vis absorption spectrum of the ZnS nanospheres.

Figure 3 shows UV–vis absorption spectrum of the ZnS nanospheres. The absorption spectrum shows an excitonic peak centered at around 310 nm, which is at a shorter wavelength than 340 nm for bulk ZnS. This structure in the absorption spectrum corresponds to the $1S_e$–$1S_h$ exctionic transitions in the ZnS nanospheres. It can be seen that the spectral shape is very simple. It means that the particle size distribution is relatively narrow and particle size is almost indentical. It is known that the absorption onset shifts to larger energy with decreasing nanoparticle size. Therefore, the blue shift of the absorption edge for the ZnS nanospheres results from decreasing particle sizes. The PL spectrum of the ZnS nanospheres using a 320-nm excitation is shown in Figure 4, which exhibits that the spectrum is Gaussian distribution. A strong peak at 450 nm (blue) in PL spectrum belongs to the ZnS defect luminescence which is caused by sulfur vacancies in the materials.[22]

For comparison with unannealed nanospheres, annealed nanospheres exhibit slightly strong PL properties (see solid line in Figure 4) at the same measurement condition. These results of PL spectra are consistent with those of XRD, which indicates that the particles of better crystallinity have higher PL intensities than those of poor crystallinity. Generally, it is known that the PL properties of particles are impacted by many factors, such as particle shape, size, size distribution, and so on. In particular, the effect of particle crystallinity can not be ignored. It is thought that nanospheres with higher crystallinity have low concentration of detects, which act as sites for nonradiative recombination of electron–hole pairs. As a result, the emission intensities can be enhanced. Therefore, post-treatment has an effect on improving the PL intensity of nanospheres.

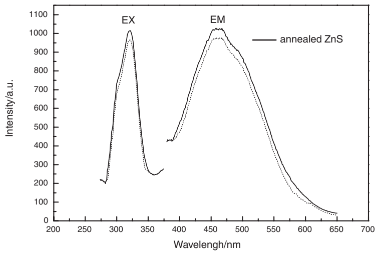

**Figure 4.** PL spectrum of the ZnS nanospheres with and without annealing.

In summary, highly monodisperse pure ZnS nanospheres with an average diameter of 100 nm were synthesized by a solvothermal route, which is easily controllable, safe, and convenient. The XRD and TEM observations demonstrate that ZnS nanospheres are highly crystalline. The absorption and photoluminescence spectra show the substantial shift compared to bulk ZnS. It is possible to extend this approach to the formation of other monodisperse transition metal sulfides. It is promising to satisfy the requirement for the future display technique development, such as flat screens, low operating voltage, high resolution, etc., using this kind of ZnS nanocrystals with monodisperse spherical morphology.

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