

Generation and Optical Properties of Monodisperse Wurtzite-Type ZnS Microspheres

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Monodisperse wurtzite-type ZnS microspheres have been prepared by using glutathione (GSH) as a sulfur source at low reaction temperatures ranging from 160 to 210 °C. The diameter of the ZnS microspheres can be tuned from ~254 to ~597 nm by changing the reaction parameters such as temperature, molar ratio of reactants (GSH/Zn²⁺), and reaction medium (ethylenediamine or ammonia). Our results demonstrate that monodentate amines (ammonia) play the same role as that of bidentate amines (ethylenediamine) in the formation of the wurtzite-type ZnS microspheres. The formation process of the monodisperse ZnS microspheres consists of a GSH-dominated nucleation process and an amine-dominated assembly process. The as-synthesized monodisperse ZnS microspheres readily self-assemble into ordered hexagonal patterns and thus have potential applications as colloidal crystalline materials. Blue fluorescence emission peaks at 415 and 466 nm in wavelength, attributed to deep-trap emission, are observed at room temperature.

1. Introduction

The controllable sizes of certain monodisperse particles have been demonstrated to obviously affect their physical and chemical properties, which provides a route by which their electronic, optical, and magnetic properties can be tailored.¹ Methods for the generation of monodisperse micro- and nanostructures with controllable sizes and shapes are of key importance in inorganic and material chemistry. For example, it allows people to explore the collective properties of an assembly of particles, and monodisperse particles are also an important requirement for the application in 2D or 3D arrays and photonic crystals.² Monodisperse semiconductors with micrometer diameters have important applications, which require a controllable size and a narrow size distribution.³ Much interest has been aroused recently in the generation of monodisperse micro- and nanospheres.⁴ However, the ability to synthesize monodispersed micro- and nanospheres remains a challenge. It was regarded that control of the shape of nanoparticles was achieved in two ways: with a template⁵ or an appropriate capping agents.⁶ Understanding

of the reaction parameters governing the generation of nanoparticle assemblies would allow the design of the desired micro- and nanospheres for optical, microelectronic, and biological applications.⁷

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As one of the most important semiconductors, ZnS ($E_g = 3.74\text{--}3.88$ eV for hexagonal wurtzite phase of ZnS and $E_g = 3.66$ eV for cubic zinc blended phase of ZnS)⁸ has been extensively investigated.^{2c,6d,6e,9} The cubic zinc-blend structure is a stable phase at low temperatures for ZnS, while the hexagonal (wurtzite) phase is the high-temperature polymorph of ZnS which can be generated at temperatures higher than 1296 K.^{8b,10} Many efforts have been devoted to the synthesis of wurtzite-type ZnS with different sizes and shapes in solution at low temperature.^{8b,9c,9n,9p,10–15} Monodisperse ZnS spheres of tunable size may be of great application in the preparation of semiconductor photonic crystals as a complementary system for currently popular polymer and silica-based photonic crystals.¹⁶

The tripeptide glutathione (GSH, γ -Glu-Cys-Gly) is widely distributed in living plant and animal cells, where it plays a

crucial role in the protection of intracellular components against oxidative damage and in the capture or removal of toxic heavy metal ions through the thiol group.¹⁷ GSH has, therefore, been considered to be an ideal sulfur source and an appealing candidate for the preparation of novel materials.¹⁸ Herein, we report a simple synthesis by using a low-temperature self-assembly synthetic route to generate ZnS microspheres with several hundred nanometer diameters which are composed of hexagonal wurtzite ZnS nanocrystals. Our strategy is to use biomolecular GSH as the sulfur source in the formation of ZnS where GSH functions both as a ligand to zinc ions and as source of sulfur in the formation of ZnS, which is different from GSH being used as capping agent as reported by Mehra et al.^{6d,6e}

2. Experimental Section

Microspheres Preparation. In a typical synthesis, biochemical grade (>98% pure) glutathione (0.500 g, 1.626 mmol) was added to a stirred solution of ZnCl₂ (0.074 g, 0.542 mmol) in deionized water (35 mL). Analytical grade ethylenediamine (en, ~5 mL) was then added to the reaction mixture and stirred for 15 min (~34 °C). The resulting solution was transferred to and sealed in a Teflon-lined autoclave, heated to 160 °C for 10 h, and finally allowed to cool to room temperature. The effects of reaction parameters on the size and shape of the products were studied through the alteration of the time, temperature, reactant molar ratio (GSH/Zn²⁺), and reaction medium. When en was replaced with ammonia or sodium hydroxide (NaOH) solutions, the pH values of reaction system were adjusted to the same as that with en. The precipitate was collected by centrifugation (10 000 rpm, 5 min), washed alternately with small amounts of deionized water and ethanol, and dried in air at 50 °C for 1 h.

Characterization. Products were characterized by power X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) and operating at 40 kV \times 40 mA. The Raman spectra of the ZnS products were directly recorded with a RM2000 Microscopic Confocal Raman spectrometer (Renishaw Corp., U.K.) using the 514.5 nm line of an Ar ion laser in air at room temperature. Transmission electron microscopy (TEM) images were obtained with a JEOL TEM-1200EX transmission electron microscope using an accelerating voltage of 120 kV. TEM samples were prepared by spreading one drop of the ZnS colloid suspended in an ethanol–water solution (at a volume ratio of 1:1) at a concentration of 0.1 mg/mL onto standard copper grids covered with perforated carbon films, and they were dried in the air overnight. FT-IR spectra were measured with a NICOLET 560 Fourier transform infrared spectrophotometer. High-resolution TEM (HRTEM) measurement was carried out on a JEM 2010 high-resolution transmission electron microscope using an accelerating voltage of 200 kV. UV–vis spectra were recorded on a UV–vis spectrophotometer (UV-2102 PC, UNICO Corp., China). PL spectra were recorded using a FP-6500 fluorescence spectrophotometer (JASCO Corp., Japan).

3. Results and Discussion

Monodisperse ZnS particles could be prepared using the ZnCl₂/GSH (glutathione)/aqueous amine under hydrothermal

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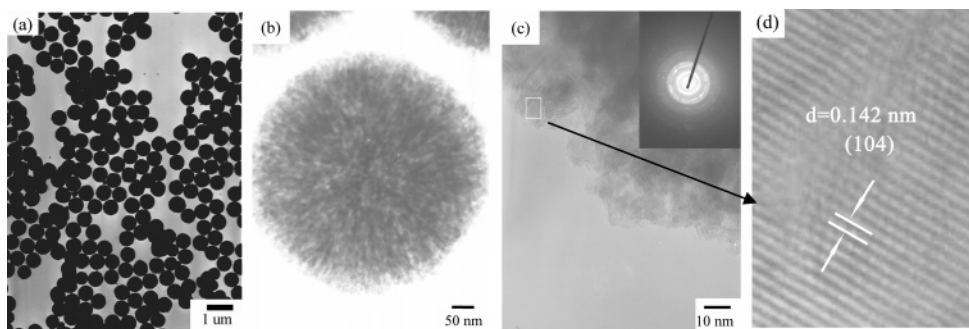


Figure 1. (a–c) TEM images and (d) HRTEM image of **ZnS-1** microspheres prepared at a GSH/Zn²⁺ molar ratio of 3:1 with $T = 160\text{ }^{\circ}\text{C}$ and $t = 10\text{ h}$ in en–aqueous solution.

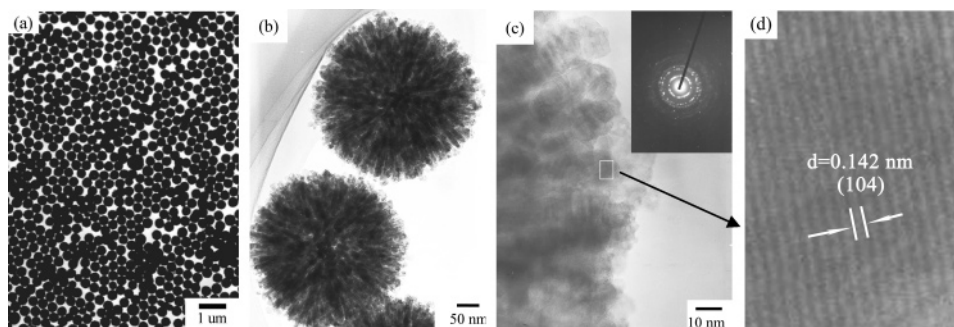


Figure 2. (a–c) TEM images and (d) HRTEM image of **ZnS-2** microspheres prepared at a GSH/Zn²⁺ molar ratio of 1.5:1 with $T = 210\text{ }^{\circ}\text{C}$ and $t = 10\text{ h}$ in en–aqueous solution.

Table 1. Reaction Conditions and Sizes of the As-Synthesized Samples

	GSH/Zn ²⁺ molar ratio	solvent	temp (°C)	time (h)	sphere size (nm)
ZnS-1	3:1	en–aqueous	160	10	~597
ZnS-2	1.5:1	en–aqueous	210	10	~377
ZnS-3	1.5:1	NH ₃ –aqueous	160	10	~254
ZnS-4	1.5:1	NaOH–aqueous	160	10	nanoparticles

conditions where GSH acts as a zinc chelating agent and sulfur donor. A summary of the results of the experiments is given in Table 1. As can be seen from the Table 1 and Figures 1–3, the sizes of the microspheres can be tuned by variation of the different parameters of the experiment, including the GSH/Zn²⁺ molar ratio, solvent, reaction temperature, reaction time, etc. Figure 1 shows the TEM and HRTEM images of the as-prepared **ZnS-1** microspheres. The average diameter of ZnS spheres obtained from the TEM images is ~597 nm. It is noticeable that the surface of the spheres is not smooth but rough (Figure 1b). The electron diffraction (ED) pattern (the inset of Figure 1c) confirms the **ZnS-1** microspheres to be polycrystalline. The lattice fringes ($d = 0.142\text{ nm}$) agree well with the separation between the (104) lattice planes (Figure 1d, the boxed area in Figure 1c). These data confirm that the **ZnS-1** microspheres consist of particles.

Figure 2 shows the TEM and HRTEM images of the **ZnS-2** microspheres with an average diameter of ~377 nm, which were synthesized with a GSH/Zn²⁺ molar ratio of 1.5:1 in the en aqueous solution at 210 °C for 10 h. The two-dimensional ZnS microsphere arrays can be obtained by spreading one drop of the **ZnS-2** colloid suspended in ethanol–aqueous solution (volume ratio of ethanol to water = 1:1) onto standard copper grids covered with carbon films,

which were dried in the air overnight; this suggests that these ZnS microspheres can be applied to construct two- and three-dimensional photonic crystalline materials.¹⁹

To investigate the function of en in the synthesis of ZnS microspheres, we also adjust the pH of the reaction system using aqueous ammonia (NH₃·H₂O) and sodium hydroxide (NaOH) solutions, respectively. **ZnS-3** microspheres with an average diameter of ~254 nm were obtained when ammonia was used (Figure 3), while **ZnS-4** nanoparticles, not microspheres, were generated when NaOH (aq) was employed (Figure 4). These facts suggest that both organic (en) and inorganic bases (ammonia) play similar roles in the formation of ZnS microspheres.

The phase characteristics of the products were examined by powder X-ray diffraction. Figure 5a–c shows the XRD patterns of as-synthesized **ZnS-1**, **ZnS-2**, and **ZnS-3** microspheres, respectively. The diffraction peaks at 28.5, 47.5, and 56.4° can be indexed to the (002), (110), and (112) planes of hexagonal wurtzite-type ZnS, respectively (JCPDS Card No. 36-1450). These results suggest that the wurtzite-type ZnS can be synthesized at temperatures ranging from 160 to 210 °C in the presence of either en or ammonia.

The structural information of the as-prepared ZnS microspheres synthesized in the organic base (en) and inorganic base (ammonia) systems was further investigated using Raman spectroscopy (Figure 6). A characteristic property of the wurtzite-type ZnS is that the vibrational modes are highly isotropic (i.e., A₁(transverse) = E₁(transverse) and A₁(longitudinal) = E₁(longitudinal)).²⁰ Figure 6a and b shows the Raman spectra of **ZnS-1** and **ZnS-3** microspheres,

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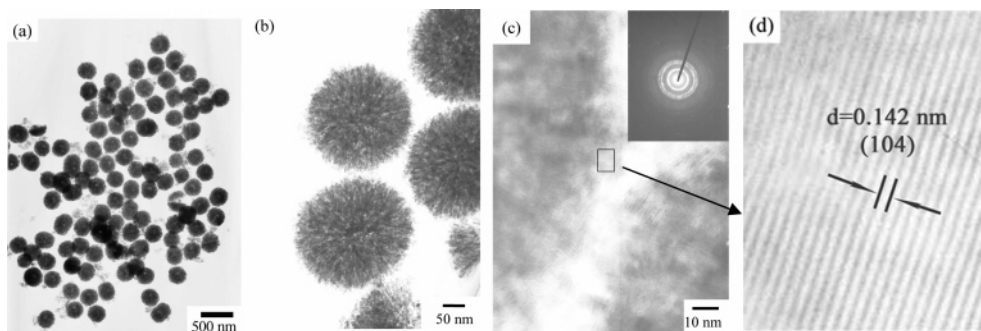


Figure 3. (a–c) TEM images and (d) HRTEM image of **ZnS-3** microspheres prepared at a GSH/Zn²⁺ molar ratio of 1.5:1 with $T = 160\text{ }^{\circ}\text{C}$ and $t = 10\text{ h}$ in ammonia–aqueous solution.

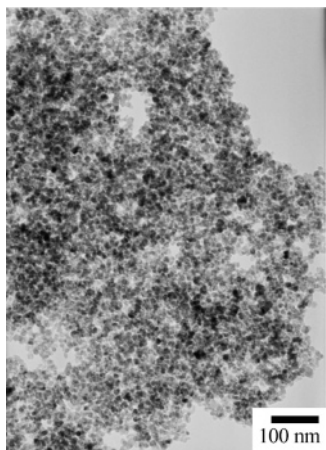


Figure 4. TEM image of **ZnS-4** nanoparticles prepared in NaOH aqueous solution with GSH/Zn²⁺ molar ratio = 1.5:1, $T = 160\text{ }^{\circ}\text{C}$, and $t = 10\text{ h}$.

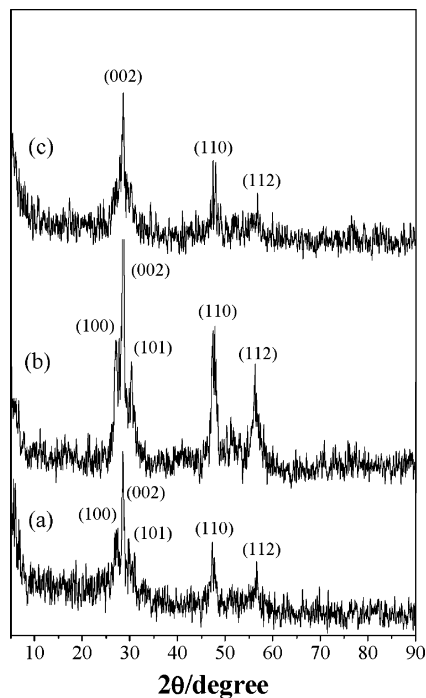


Figure 5. XRD patterns of ZnS microspheres: (a) **ZnS-1**, (b) **ZnS-2**, and (c) **ZnS-3**.

respectively. As shown in Figure 6a, there are two intense peaks at $346\text{ and }255\text{ cm}^{-1}$, which do not exactly match the corresponding longitudinal (LO) and transverse (TO) phonon modes of wurtzite ZnS ($352\text{ and }274\text{ cm}^{-1}$, respectively).²⁰

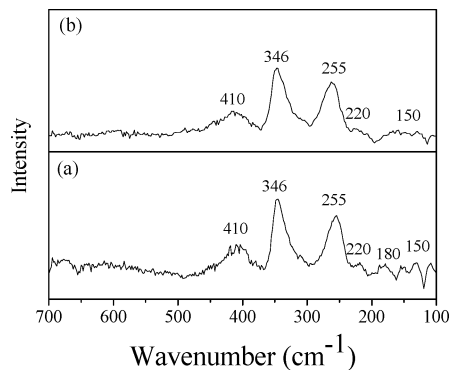


Figure 6. Raman spectra of ZnS microspheres (a) **ZnS-1** and (b) **ZnS-3** recorded in the air using the 514.5 nm line of an Ar ion laser as the excitation source.

It was reported that small particles could result in frequency shifts of the maxima lines as compared with the massive crystals.²¹ In the case of a large surface-to-volume ratio, surface scattering contributes more to the Raman signal than the volume scattering. Therefore, the frequency shifts of the LO and TO modes observed in the present study may be attributed to the smaller size and larger surface-to-volume ratio compared with the bulk ZnS. Several weak bands around 150 , 180 , 220 , and 410 cm^{-1} may also be explained by the small size of the as-synthesized ZnS.²⁰ When en was replaced with ammonia (Figure 6b), two identical intense Raman peaks appear at the same positions as those shown in Figure 6a, which suggests that the same structure is obtained independently of the nature of the added base. A slight difference exists in the weak bands between Figure 6a and 6b, which may be a consequence of the different sizes of the products. Thus, the Raman spectra provide further evidence that the wurtzite-type ZnS can be prepared using en or ammonia to control the pH.

The as-prepared ZnS microspheres with different diameters were also characterized using the FT-IR spectrophotometer (Figure 7). The sharp peak near 1620 cm^{-1} is assigned to the N–H deformation vibration that demonstrates the existence of en or ammonia on the surface of microspheres. In the case of en, the as-prepared ZnS microspheres with a $-\text{NH}_2$ group adsorbed on the surface can be used as a

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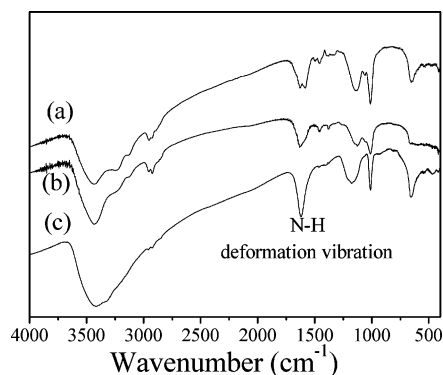
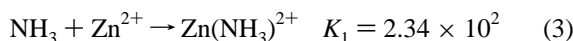
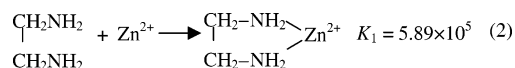
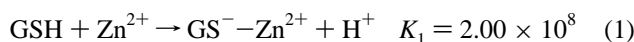


Figure 7. FT-IR spectra of ZnS microspheres: (a) ZnS-1, (b) ZnS-2, and (c) ZnS-3.

favorable matrix for the immobilization of $-\text{NH}_2$ -containing biomolecules through covalent binding.²²

On the basis of the results mentioned above, we speculate that the present synthesis of wurtzite-type ZnS microspheres consists of a GSH-dominated nucleation process and en/ammonia-dominated assembly process. The formation constants (K_1) of the $\text{GS}^- - \text{Zn}^{2+}$ and the $\text{en} - \text{Zn}^{2+}$ (or ammonia- Zn^{2+}) complexes are as follows:²³



It is obvious that the $\text{GS}^- - \text{Zn}^{2+}$ complex is more stable than $\text{en} - \text{Zn}^{2+}$ or ammonia- Zn^{2+} because of its larger formation constant. The GSH ligand also functions as the source of sulfur. ZnS nuclei can be formed after decomposition of the $\text{GS}^- - \text{Zn}^{2+}$ complex. This means that the nucleation process is controlled by GSH. Subsequently, the second ligand, such as en or ammonia, is adsorbed onto the surface of the incipient ZnS nuclei and thereby hinders further growth of the nuclei. The en/ammonia-coated ZnS nanoparticles were assembled into the larger monodisperse ZnS spheres. Thus, the monodispersity of ZnS microspheres is primarily determined by ligands such as en and ammonia.

An adjustment of the content of en without changing other reaction parameters will directly determine the morphology of the products (TEM images are shown in Supporting Information, Figure S1). In the absence of en (the pH value of the reaction system is 3.0), the unprotected ZnS nanoparticles agglomerated into irregular bulk structures (Figure S1a), while ZnS nanoparticles were obtained when the pH value of reaction system was neutral (pH = 7.0, by adding ~0.2 mL en) or weakly basic (pH = 9.0, by adding ~0.26 mL en) (corresponding to Figure S1b and c, respectively). The monodisperse ZnS microspheres can be obtained when

the pH value of reaction system is ~11.40 (by adding 5 mL en). The increase of the content of en further to pH = 13.0 (by adding 20 mL en) led to irregular bulk structures being obtained again (Figure S1d). According to the TEM and FT-IR data, this further suggests that the hydrogen-bond interactions between N-H in ligands en or ammonia adsorbed on the ZnS particles favor the assembly and formation of microspheres.

The optical properties of semiconductor materials are directly determined by the size and shape of the particles. We investigated the optical properties of ZnS microspheres using a combination of UV-vis and photoluminescence (PL) technologies. The UV-vis absorption properties of the ZnS samples were investigated by ultrasonically dispersing the ZnS microspheres into aqueous solutions (Figure 8). For example, the absorption spectrum of ZnS-1 microspheres (Figure 8(a) shows a very broad adsorption peak between 340 and 800 nm in wavelength which consists of several shoulder peaks centered at 390, 425, 475, and 555 nm in wavelength: a feature likely to reflect the change in the scattering efficiency of the spheres as a function of wavelength.²⁴ According to Mie theory, dielectric spheres, with a radius comparable to the wavelength of light, are efficient scatters, and the scattering cross section exhibits a number of resonances for a given particle.²⁵ The observation of a resonance peak in the UV-vis spectrum also provides strong evidence for the narrow size distribution of the ZnS microspheres because the short-range Mie resonance features are only observed when the spheres are sufficiently monodisperse.^{24,26} Similar resonance peaks are also observed for ZnS-2 microspheres (Figure 8(b): a main band centers at 352 nm in wavelength which is consistent with data reported in the literature,²⁵ accompanied by a shoulder at 388 nm in wavelength. When en was replaced with ammonia, the absorption maximum of the ZnS microspheres (ZnS-3) shifts to 338 nm in wavelength, accompanied by a weak shoulder in a shorter wavelength (~215 nm, Figure 8c). The differences between the UV-vis absorption spectra of the three samples prepared under different conditions may be attributed to the different sizes and dispersivities of the ZnS microspheres.²⁵

The stability of the ZnS microspheres was assessed by ripening the products for different times (i.e., original time, 5 days, and 10 days). There are no significant changes in peak positions after storage of the aqueous suspensions for 10 days at room temperature (Figures 8). Only minor changes of absorbance are observed which can be attributed to the ripening process.

The PL properties of the as-prepared ZnS-1, ZnS-2, and ZnS-3 microspheres were measured at room temperature (shown in Figure 9). A blue emission peak at ~415 nm in wavelength, accompanied by two weaker peaks at ~355 and ~466 nm in wavelength, was observed when the sample was

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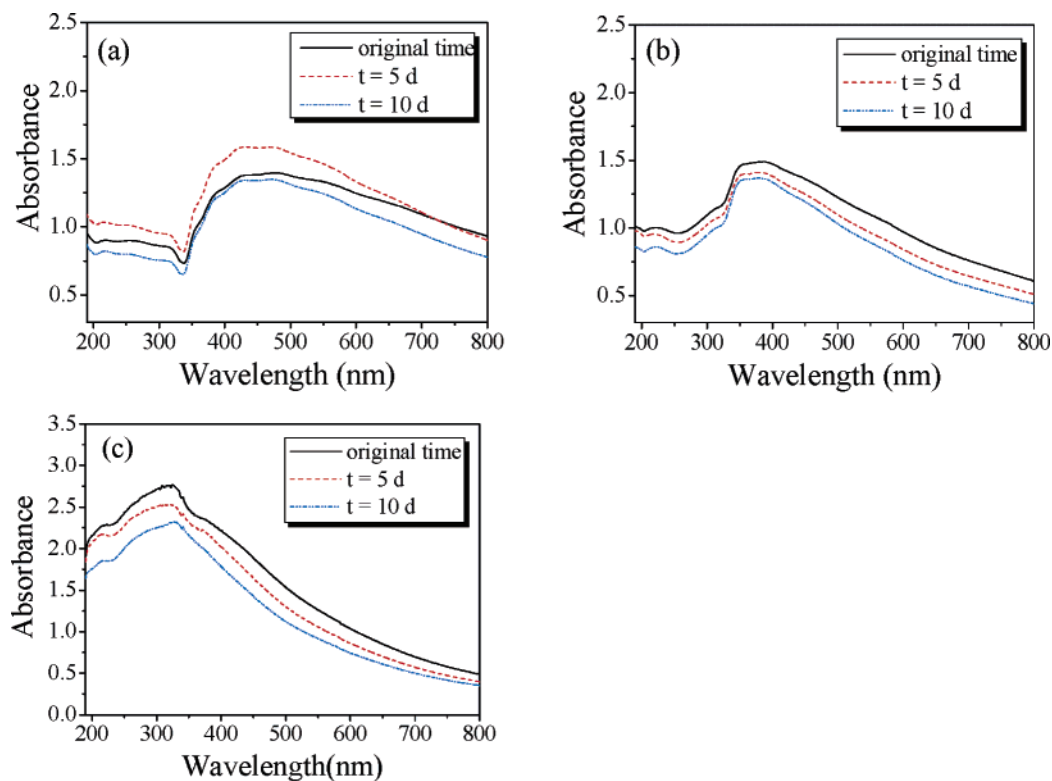


Figure 8. UV-vis spectra of ZnS microspheres (a) ZnS-1, (b) ZnS-2, and (c) ZnS-3 in aqueous solution.

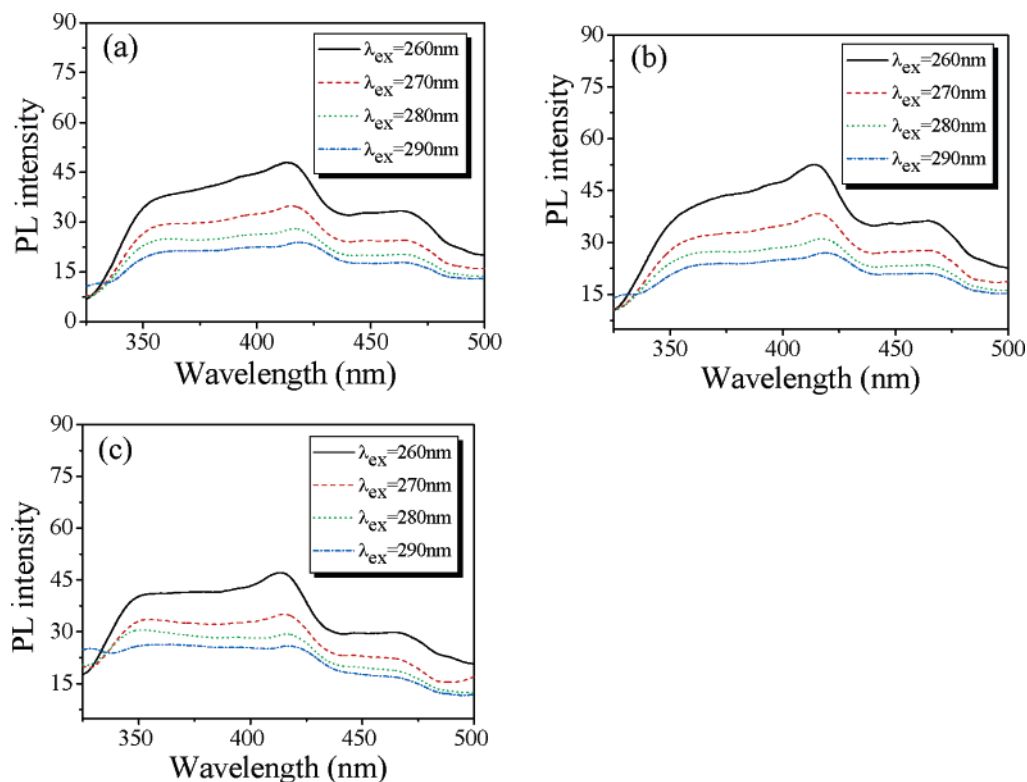


Figure 9. Photoluminescence spectra of ZnS microspheres (a) ZnS-1, (b) ZnS-2, and (c) ZnS-3 in aqueous solution.

excited with a wavelength of 260 nm. A slight red-shift (~ 6 nm) is observed when different excitation wavelengths are employed ($\lambda_{\text{ex}} = 260, 270, 280,$ and 290 nm); this is attributed to the coupling action among the ZnS microspheres and interactions between the ZnS microspheres and their

surrounding environment.⁹ⁱ Hu and co-workers have reported ZnS nanobelts that display fluorescence emission at 401 nm and also present shoulder peaks at 470 nm when excited with a 250 nm light source.²⁷ Kar and Chaudhuri have recently reported the synthesis of wurtzite-type ZnS nanowires and

nanoribbons that show an intense blue emission consisting of two bands at 394 and 456 nm in wavelength when excited also at 250 nm.²⁸ Moreover, it has also been reported that ZnS colloidal dispersions present blue emission peaks centered at 428 and 418 nm in wavelength, which were attributed to the sulfur vacancy and interstitial lattice defects.²⁹ On the other hand, the emission bands located around 480 nm in wavelength have traditionally been ascribed to the well-known luminescence of zinc vacancies.^{27,30} In our studies, the strong blue emission bands around 415 nm in wavelength can be assigned to the sulfur vacancies or interstitial lattice defects, whereas the zinc vacancies could be responsible for the weaker peaks around 466 nm in wavelength. An additional weak peak appearing near 355 nm in wavelength (3.49 eV in photon energy) can be assigned to the near-band-edge (NBE) emission.³¹ The observed blue fluorescence emission of the monodisperse wurtzite-type ZnS microspheres could provide an interesting application in the development of novel luminescent devices.

4. Conclusion

In summary, monodisperse wurtzite-type ZnS microspheres have been synthesized by using GSH as sulfur source

at a relatively low temperature range (160–210 °C). ZnS microspheres with an average diameter between ~254 and ~597 nm can be obtained by altering reaction parameters such as the reaction temperature, reactant molar ratio (GSH/Zn²⁺), and reaction medium. Our results suggest that the monodentate ammonia ligand plays a role comparable to that of the bidentate en ligand in the formation of wurtzite-type ZnS microspheres. The wurtzite-type ZnS microspheres, exhibiting blue fluorescence emission bands centered at 415 and 466 nm in wavelength, have potential applications as substrates for biomolecule immobilization and building blocks for the construction of two- and three-dimensional photonic crystalline materials.

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Supporting Information Available: Figure S1, showing TEM images of ZnS prepared in en-aqueous solution with different pH values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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