

Simplified hydrothermal synthesis and optical properties of core-shell ZnS microspheres

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Zinc acetylacetonate and thiourea are reacted in a 30:10 mixed water: glycerin solvent for 12 hours at 130°C to synthesize “core-shell” ZnS microspheres. The ZnS microspheres are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray (EDX), high-resolution transmission electron microscopy (HRTEM); and selected area electron diffraction (SEAD). Ultraviolet-visible spectra (UV-vis) and photoluminescence spectroscopy (PL) were used in an optical study of the product. The results show that the synthesized ZnS microspheres have a diameter of 3–5 micrometers, a smooth shell surface, and an inner core structure. The existence of glycerin is crucial to the formation of spherical ZnS. no spherical particles are obtained in reaction systems without glycerin, and a decrease in glycerin content of the system reduces the yield of spherical products.

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1. Introduction

Zinc sulfide is an important II–VI semiconductor with a bandgap of 3.7 eV [1] at room temperature. Due to its unique electrical and optical properties, ZnS has been widely used in light-emitting diodes, solar cells, sensors, lasers, photocatalysts, and infrared windows [2-5]. Researchers have found that semiconductor materials with unique morphologies, sizes, and structures possess outstanding physical and chemical properties compared to ordinary bulk semiconductor materials [6-8]. Thus, the synthesis of semiconductor materials with unique morphologies, including ZnS, has become widespread in the field.

So far, many types of ZnS materials with unique morphologies and structures have been synthesized, such as hollow spherical nanorods, [9] nanoplates, [10] nanowires, [11] quantum dots, [12] etc. There are various synthetic methods for making ZnS materials with diverse morphologies, [13-16] and among them hydrothermal methods are especially prominent due to their mild reaction conditions and their simple and readily available experimental setup. During hydrothermal synthesis, templating agents are usually added to the system to control the morphologies of the materials. However, these additives not only increase the cost but also require additional product separation steps, which significantly

reduce the methods' appeal as a large-scale production technique.

The use of self-produced soft templates in the reaction system has become an important technique in the synthesis of materials with special morphologies. It has been demonstrated [17-19] that some polar alcohols (e.g., isopropanol) and ketones (e.g., acetone) can easily aggregate in aqueous media and form heterogeneous micro-emulsion droplets. These droplets can then be used as soft templates for the synthesis of spherical materials. Glycerol is another attractive candidate for this synthesis technique because it under hydrothermal conditions it may be partly polymerized. This would give rise to emulsified spheres serving as soft templates for subsequent deposition of the shell structure. Although ZnS materials with various morphologies have been successfully prepared, there has not been much work reported on “core-shell” ZnS microspheres. In this work, we applied a hydrothermal method with a processing temperature under 130°C and successfully synthesized “core-shell” ZnS microspheres. We used zinc acetylacetonate and thiourea as the zinc and sulfur sources, respectively, and a mixed water/glycerin solvent, which forms a micro-emulsion soft template. It is shown that the glycerin plays a crucial role in the formation of the core-shell structure morphology.

2. Experimental

2.1 Materials

Zinc acetylacetonate were obtained from Aldrich chemicals Ltd. Thiourea and glycerin was obtained from sinopharm Chemical Co. Ltd. All the chemicals were of analytical grade and used as received without further purification.

2.2 Synthesis of ZnS microspheres

In a typical experiment, Zinc acetylacetonate (0.006 mmol) was weighed and dissolved in a beaker with 40 mL of a 30:10 water:glycerin mixture. This mixture was then sonicated for 30 min in an ultrasonic bath. Next, thiourea (0.006 mmol) was added, followed by one hour of intense stirring. The solution was transferred to a 50 mL steel reactor with a PPL lining and held for 12 hours in an incubator at 130°C. The reactor was naturally cooled to room temperature after completion of the reaction. The product was then centrifuged and washed several times with distilled water and dehydrated ethanol. Finally, a grey-white ZnS powder was obtained after 24 hours in a vacuum drying oven at 40 °C.

X-ray diffraction (XRD) patterns of the product were obtained using a D/Max-III A diffractometer with Cu K α radiation ($\lambda=1.54056 \text{ \AA}$) at a $0.07^\circ \text{ s}^{-1}$ scanning rate with 2θ ranging from 5° to 80° . Field-emission scanning electron microscopy (FESEM) images and energy-dispersive x-ray (EDX) spectrographs were obtained with a HITACHI-S4800 apparatus, operating at 5.0 kV. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SEAD) patterns were obtained with a JEM-2010 instrument at 200 kV. The x-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer. Photoluminescence spectra were measured by PerkinElmer LS 55 with 450W Xe lamp. UV-visible diffuse reflectance was obtained by UV-2600 (SHIMADZU) ultraviolet-visible spectrophotometer with the integrating sphere.

3. Results and discussions

The x-ray diffraction (XRD) pattern collected from the synthesized ZnS sample is shown in Fig. 1. The three peaks with 2θ values of 28.74° , 48.08° , and 56.96° correspond to the (111), (220), and (311) crystal planes of ZnS, respectively. this pattern closely matches that of the Sphalerite (cubic) pattern (JCPDS 05-0566). Other than these three sharp peaks, the XRD pattern has wide peaks, which indicates that the prepared ZnS has a polycrystalline structure with small particles. The average crystallite size of 9.36 nm was calculated based on the full width at half-maximum of the (111) crystal planes using the Scherrer equation [20]: $D = K\lambda / (\beta \cos\theta)$. The absence of

additional peaks representing other phases indicates good purity and growth of the ZnS crystals.

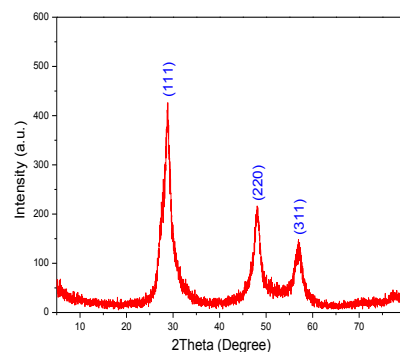


Fig. 1. The XRD spectrum of obtained ZnS in water and glycerin (30:10) system.

EDX analysis, Fig. 2, shows that the sample mainly consisted of S and Zn in an atomic ratio of 1:1. The O in the spectrum originated from oxygen in the air, and the small amounts of Al and Si may have come from substrate impurities introduced during EDX measurements. No other elements were observed in the spectrum, which proves that the product mainly consists of the ZnS.

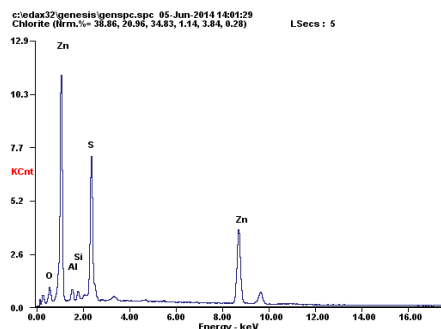


Fig. 2. The EDX spectrum of obtained ZnS in water and glycerin (30:10) system.

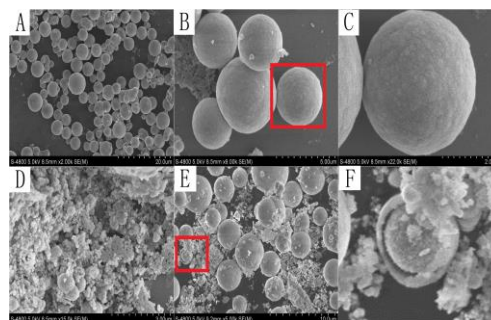


Fig. 3. (A-C): SEM images of the ZnS obtained in water and glycerin (30:10) mixture system. (D): SEM images of the ZnS obtained in water syatem. (E-F): SEM images of the ZnS obtained in water and glycerin(35:5) mixture system.

The morphology of the synthesized sample was determined with SEM, these results are seen in Fig. 3. As

shown in Fig. 3A, the synthesized ZnS particles all have spherical shapes with nonuniform sizes. From a magnified electron micrograph Fig. 3B, we observe that the spherical structures are 3–5 micrometers in diameter. The surface of the ZnS spheres exhibited many densely placed micro-protrusions, as seen in Fig. 3C. The ZnS sphere sizes determined by SEM are far larger than the 9.36 nm calculated from the Scherrer equation, and this fact demonstrates that the micro-spherical ZnS particles described in this paper are assembled from nanoscopic crystals. In order to reveal the growth mechanism of the ZnS microspheres, we replaced the glycerin in the reaction system with purified water while maintaining unchanged all other conditions. This substitution resulted in messy and disorganized ZnS products, as shown in Fig. 3D. There were no spheres produced, which indicates that the glycerin-aggregated micro-emulsion droplets have a crucial templating function in the hydrothermal process [21]. When we reduced the glycerin volume from 10 mL to 5 mL (while maintaining all other conditions), a significant decrease in the yield of spherical ZnS particles was apparent, as shown in Fig. 2E. There was a large amount of ZnS powder produced that did not assemble into spherical ZnS particles. We infer that the formation of micro-emulsion droplets was hindered by the decrease in the glycerin content in the system, which led to a decrease in the quantity of the spherical products. Broken ZnS microspheres were found in the product of the reduced-glycerin reaction, as seen in Fig. 3F, which show the interior structure of the core-shell.

In order to explore the interior structure of our synthesized ZnS particles, we used TEM to observe the ZnS products as shown in Fig. 4.

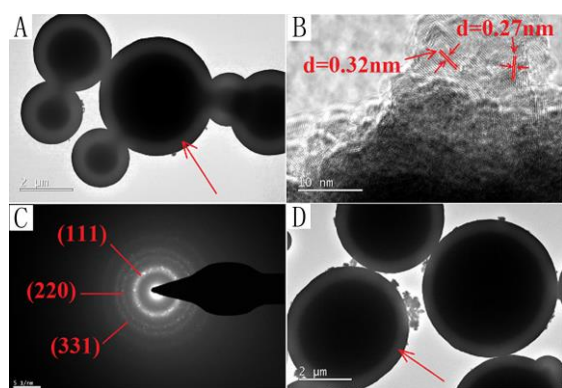


Fig. 4. The TEM images (A), HR-TEM images (B) and SEAD pattern (C) of the ZnS obtained in water and glycerin(30:10) mixture system; The TEM images (D) of the ZnS obtained in water and glycerin (35:5) mixture system.

The “core” and “shell” regions are clearly seen in Fig. 4A, as indicated by the red arrows. These micrographs are entirely consistent with the core-shell structure of broken spherical ZnS particles shown in Fig. 4F. Clear lattice

fringes can be observed in the partially magnified figures of the HERM measurements, the lattice spacing measurement data are 0.27 and 0.32 nm as shown in Fig. 4B, respectively. The SEAD pattern obtained by focusing the electron beam on the ZnS shows diffuse rings corresponding to the (111), (220) and (331) crystal planes in Fig. 3(C), which indicates a good crystallinity of our synthesized ZnS. In Fig. 4D, we observe core-shell structures in the products of low-glycerin processing and unassembled ZnS powder distributed around the spherical particles, which is consistent with the observations from Fig. 3E. From the Fig. 3(A and E), we found despite that changed the content of the glycerol in system, still get the same core-shell structure of ZnS just only changed the yield rate.

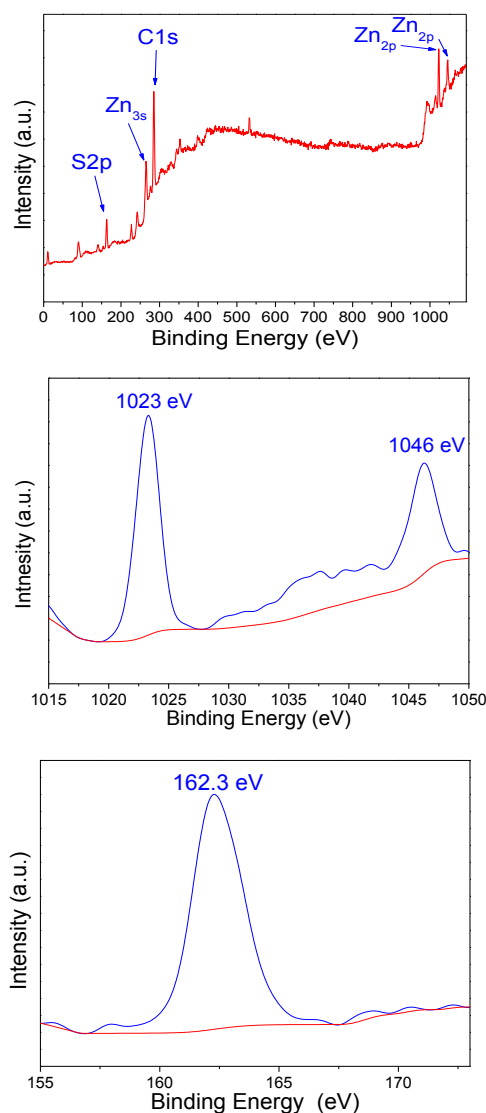


Fig. 5. XPS spectra of the as-obtained ZnS in water and glycerin(30:10) mixture system.

An XPS analysis of the sample is shown in Fig. 5. It shows two strongly absorbing peaks at 1023 eV and 1046

eV corresponding to $\text{Zn}:2p_{3/2}$ and $\text{Zn}:2p_{1/2}$, respectively. These peaks are associated with the Zn^{2+} ions in zinc sulfide. The absorbent peak at 162.3 eV, corresponding to $\text{S}:2p$, belongs to the S^{2-} ions in zinc sulfide. There is no absorbent peak of any other compound in the spectrum, which is consistent with the literature [22], indicating that the product was pure ZnS.

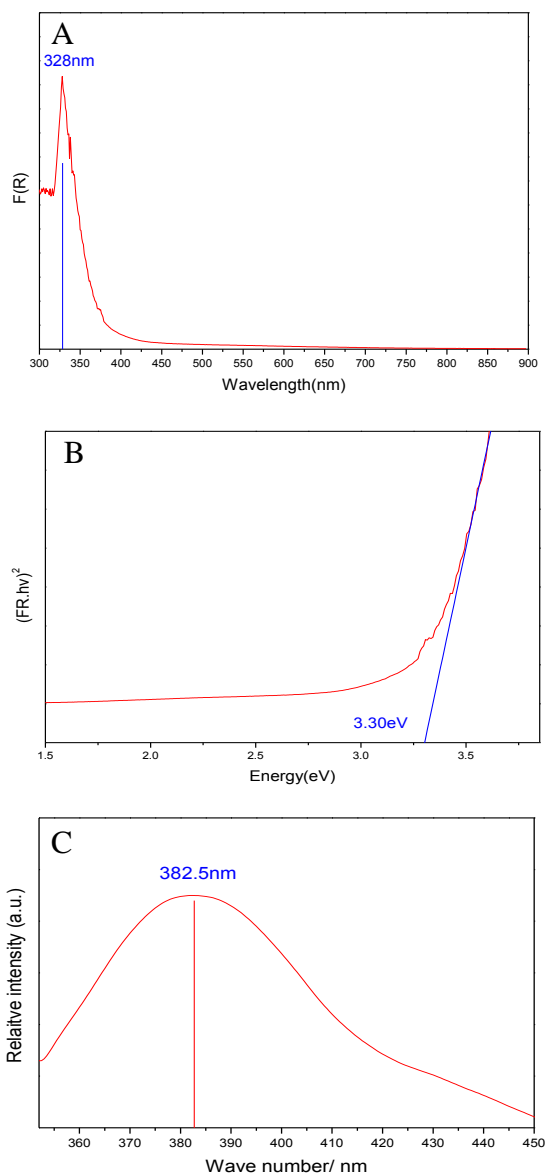


Fig. 6. *UV-vis spectra (A and B) and PL spectra (C) of ZnS microspheres.*

The room temperature UV-visible diffuse reflectance spectrum of the sample is shown in Fig. 6A. According to the figure, the sample has strong absorption in the 200–400 nm UV wavelength region. Within this range, the wavelength of the highest absorption was 328 nm. The band energy gap E_g of the sample can be calculated with [23,24]:

$$ahv = A (hv - E_g)^{1/2} \quad (1)$$

$$F(R) = (1 - R)^2 / 2R \quad (2)$$

$$hv = 1240 / \lambda \text{ (in nm)} \quad (3)$$

where α in equation (1) is the absorption coefficient, The value of a can be calculated from diffuse reflectance data using the K-M function, the Kubella-munk functions can be expressed as the equation (2), in which R is the reflectivity in the diffuse reflection spectrum and $h\nu$ can be deduced from equation (3). In a plot of $[F(R) \times hv]^2$ vs. $h\nu$, the region between the x -intercept and extended tangent line of the linear portion of the curve is the E_g . Using this plot, we calculated that our synthesized ZnS has an $E_g = 3.30$ eV as shown in Fig. 6 B. Compared to the E_g value of most reported ZnS materials (3.7eV), [25] the E_g of our material was red shifted [26]. It's very similar with the ZnS microspheres prepared by Zhao [27], which also have a red shift ($E_g=3.35$ eV). Therefore, we speculated that the special solid microspheres micrometer-scale spherical structures may be the reason for the reduced energy gap.

The optical properties of the sample were analyzed using photoluminescence (PL) measurements, these data are in Fig. 6C. It is widely known that the fluorescence excitation process in ZnS crystals is very complicated and that it is strongly influenced by the synthetic method, morphology, and particle size [28-30]. According to the literature, most ZnS materials show fluorescence absorption near 400–500 nm, the blue light absorption band, which is commonly believed to have originated from the surface defect states in the sample [31,32]. However, the strongest fluorescence emission peak of our synthesized ZnS sample was at 382.5nm ($\lambda_{ex}=325$ nm), According to the related literature, the fluorescence emission peak shift to the lower wavenumbers region may be due to the sulfur vacancies formed from the recombination processes [33-35].

4. Conclusions

In this paper, zinc acetylacetonate and thiourea were mixed in a solvent of water/glycerin in a simplified hydrothermal reaction (at 130°C) to successfully synthesize ZnS microspheres. SEM characterizations reveal that the products have diameters ranging about 3-5 micrometers and with a “core-shell” structure. The experimental results show that the micro-emulsion droplets produced by glycerin in the system served as “soft templates” in the production of the spherical products and that the glycerin content of the system affected the yield of spherical products. The UV-vis absorption spectrum reveals that there is a obvious absorption peak at about 328nm. The E_g of our synthesized ZnS microspheres has a obvious red-shift. Room temperature PL spectrum reveals that the obtained ZnS solid microspheres has a strong emission band centered at about 382.5 nm and have a obvious shift towards the lower wavenumbers region.

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