Synthesis and Luminescent Modulation of ZnS Crystallite by a Hydrothermal Method

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ABSTRACT: Pure and Eu3+-doped zinc sulfide (ZnS) crystallites were synthesized through a hydrothermal method using water and ethanol (W/E) as the solvent. The powder samples have been characterized systematically using a number of characterization techniques such as X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy, photoluminescence spectroscopy, and UV–vis absorption spectroscopy. The band gap of ZnS and ZnS/Eu3+ was calculated according to absorption spectroscopy, and an obvious red shift with the increasing molar fraction of Eu3+-doped ions was found. The luminescent mechanism of ZnS was explored by measuring the emission spectra of ZnS with different ratios of Zn and S. The emission spectra of ZnS/Eu3+ included the characteristic emission peak of ZnS and Eu3+ ions. The CIE chromaticity coordinates of the ZnS/Eu3+ sample varied with the molar fraction of Eu3+ ions. The emission intensity and morphology changed with the ratio of W/E in the process of hydrothermal reaction. The results indicate that the luminescence of the ZnS crystallite can be modulated by doping a certain amount of Eu3+ ions, changing the ratio of Zn and S, or adding moderate ethanol as the reaction medium.

1. INTRODUCTION

In recent years, as one of the representative II–VI group semiconductors, zinc sulfide (ZnS) with a wide band gap of 3.6 eV has been used as an attractive material for a UV–blue semiconductor laser device or quantum dot light-emitting devices.1,2 Compared with CdS and CdSe, ZnS has a lower toxicity and better biocompatibility, which causes broad applications in a biological fluorescence detection field.3 Besides, ZnS is also a kind of luminescence material and could produce different emissions corresponding to defect levels. Because of the various interface structures and larger specific surface areas of ZnS, there exist a lot of dangling bands and defects in the surface. Actually, emissions rooting from the recombination of electron–hole pairs are few and mainly occur at the defect in the lattice.

There are two kinds of methods for the preparation of ZnS materials including oil-phase and aqueous-phase method, which leads to different features of the obtained nanoparticles.4,5 The crystallite material obtained by the oil-phase method has high quantum yield, narrow half-peak width, controllable particle size, good monodispersity, and stability. However, the process of its preparation is highly toxic, costly, and dangerous. The aqueous-phase method is environmentally friendly owing to its use of water as the solvent and inorganic salt as the reaction precursor. Therefore, the operation is simple, and the reagent is nontoxic and cheap. As one of the aqueous-phase methods, the hydrothermal method is wildly used, and the obtained crystal has high purity and good dispersion. Its advantage follows from higher stability, and the process itself is fast and requires only a low thermal supply. Recently, there have been a series of reports about ZnS materials synthesized by the hydrothermal method, and the results are satisfactory.6–8

When ZnS is doped with different impurities such as transition-metal elements and rare-earth (RE) elements, it can also achieve in the region of visible and near-infrared fluorescence because of the production of new energy level. Moreover, the doped materials have unique electric and magnetic properties and could be used in many fields. The study of transition-metal element doping is relatively mature, and its luminescence property has been improved in intensity and color and so forth.9,10 Because of the similar charge and ionic radius of Zn2+ ions and transition-metal ions, the doped ions could enter the lattice of ZnS easily. Compared with the common element, RE has more electronic energy levels, spectral line, and longer excited-state lifetime. In the same way, RE doping in ZnS could add a new energy level between the valence and conduction bands, and their characteristic peaks would appear in the spectra, which could produce a new color

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after combining with the ZnS emission. Therefore, nanomaterials doped with RE have been viewed as a promising candidate for fabricating a new type of light-emitting diodes (LEDs). Nowadays, there are a lot of reports concerning the preparation and properties of the doped ZnS nanoparticles by the hydrothermal method, and most of the doping ions are transition-metal ions such as Mn$^{2+}$, Cu$^{2+}$, and Co$^{2+}$.

Certainly, there exist a series of reports about RE doping such as Eu$^{3+}$, Gd$^{3+}$, Pr$^{3+}$, and so on, which are worth our consideration. Among the REs, Eu$^{3+}$ is a common red-light activator because of its simplest energy-level structure and excellent emission at the red region and thus becomes a preferred candidate for red-emitting materials. However, there is little investigation on the Eu$^{3+}$-ion-doped ZnS by the hydrothermal method.

In this paper, we employed a hydrothermal route to synthesize ZnS$_x$/Eu$^{3+}$ crystallite. The obtained crystallite showed pure cubic phase and was spherical and monodispersed, and the emission spectra were rooted from the transition of $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, and $^5D_0 \rightarrow ^7F_4$ of Eu$^{3+}$, which could indicate that the Eu$^{3+}$ ions enter into the lattice of the ZnS crystallite preliminarily.

2. RESULTS AND DISCUSSION

The powder X-ray diffraction (XRD) patterns of the as-prepared ZnS crystallite are shown in Figure 1, in which the diffraction peaks are in well agreement with the standard JCPDS card no. 05-0566. The main diffraction peaks are located at $2\theta = 28.56^\circ$, $47.52^\circ$, and $56.29^\circ$ corresponding to the reflection from (111), (220), and (311) planes, respectively, which confirms the cubic zinc blende ZnS crystals. No impurity peaks were detected, revealing the single-phase ZnS products.

Figure 2 depicts the UV absorption spectrum of the ZnS crystalline, and we could find that the absorption region is from 300 to 400 nm and the direct band gap energy ($E_g$) was approximated from a Tauc plot, that is, a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$), using the relationship

$$ah\nu = A(h\nu - E_g)^n$$

where $h\nu$ is the photon energy, $A$ is a constant, $\alpha$ represents the absorption coefficient, $\alpha = 4nk/\lambda$ ($k$ is the absorption index), $\lambda$ is the wavelength, and $n = 1/2$ for the allowed direct band gap. It can be clearly seen from the inset that the direct band gap value is 3.452 eV by extrapolating the absorption edge of ZnS.

![Figure 1. XRD patterns of ZnS.](image)

![Figure 2. UV–vis absorption spectrum of ZnS.](image)

The excitation and emission spectra of the ZnS sample are given in Figure 3. As shown in this figure, all of the emission spectra have two peaks at around 483 and 586 nm, which could be ascribed from a trap-state emission arising from surface defect sites. The intensities of the two peaks vary from different excitation wavelengths, and the ratio of their intensities is shown in the inset. In addition, the excitation spectra monitored for 483 nm are composed of a main peak located at 347 nm and a shoulder peak at 360 nm, whereas the excitation spectrum monitored for 586 nm has three peaks at 309, 337, and 400 nm. It can be seen from Figure 3 that the emission dominates at 483 nm when the excitation wavelengths are 309 and 400 nm. However, the relative intensity of the peak at 586 nm is stronger when the ZnS sample is excited by 337, 347, and 360 nm light. The results indicated that the emission peaks at 483 and 586 nm correspond to different defects.

To explore the luminescence mechanism, a series of ZnS samples with different values of Zn/S have been synthesized, and their XRD patterns are shown in Figure 4. The three main diffraction peaks of the samples with Zn/S = 1.5:1 and 1:1.5 are coincident with the JCPDS card no. 05-0566, which reveals that the cubic zinc blend structure of the ZnS crystallite could be obtained even when the ratio of Zn and S is adjusted in the fabrication process.

![Figure 3. Excitation and emission spectra of ZnS.](image)

The emission spectra excited at 400 nm of ZnS samples with different values of Zn/S are shown in Figure 5. It can be seen that the shape of the emission spectra changes considerably when the ratio varies from 1.5:1 to 1:1.5. The peak at the orange region is observed at 608 nm resulting from the red shift...
of 586 nm, and the peak located at 498 nm is shifted from 483 nm. When the ratio is 1.5:1, Zn is relatively excessive so that the sulfur vacancy dominate on the surface, which results in a stronger peak at 498 nm, whereas when the ratio is 1:1.5, S is excessive and the zinc vacancy is much more than the sulfur vacancy, which leads to a stronger peak at 608 nm. Therefore, we could conclude that the peak located at 498 nm (483 nm) belongs to the transition of sulfur vacancy, whereas the peak at around 608 nm (586 nm) belongs to the transition of zinc vacancy.

The decay behaviors of the ZnS sample with different values of Zn/S (1.5:1, 1:1.5, and 1:1) are measured. The decay curves excited at 400 nm are shown in Figure 6, and they can be well-fitted using a first-order exponential decay formula

\[ I = I_0 \exp(-t/\tau) \]  

(2)

It can be calculated that \( \tau \) is 4.68, 4.05, and 3.26 ns, respectively. The variation of lifetime that could be attributed to the peak at 483 nm is a result of sulfur vacancy transition, and the sample with Zn/S = 1.5:1 has more sulfur vacancy.

Figure 7 shows that the CIE chromaticity coordinates of the sample prepared with different values of Zn/S 1:1, 1.5:1, and 1:1.5 are (0.26, 0.40), (0.33, 0.44), and (0.40, 0.45), respectively, which shows the change of color from green to orange. In addition, the luminescence photography is obtained under the irradiation of a UV lamp. The result revealed that the ratio of Zn and S has a bigger effect on the emission properties of the ZnS crystallite.

As we all know, it is significant to adjust the ratio of water and ethanol (W/E) in the reaction process of the hydrothermal reaction. Therefore, we have prepared a series of samples with different W/E and their XRD patterns, and the emission spectra excited by 400 nm are given in Figures 8 and 9, respectively. The XRD patterns revealed that the obtained materials all belong to the cubic zinc blend structure. From Figure 9 and its inset, we could find that the emission intensities of the samples vary with W/E. When W/E is 1:1, the intensity of emission spectrum reaches the maximum, and the full width at half-maximum is the narrowest, which indicates that the optimal
reaction condition is half water and half ethanol, and in this case, the obtained particles have a good size distribution.

To investigate the reason of various spectra, a series of SEM images of ZnS with different ratios of W/E are obtained and given in Figure 10. Meanwhile, the calculated diameters of the particles are shown in Figure 10, and (a–e) correspond to the ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 and (f) shows the various curves of crystal size and difference with the W/E. The histograms of diameter distribution are shown in Supporting Information. From the SEM images, we could find that the ZnS nanoparticles are spherical, and the diameters vary from 1.39 to 2.25 μm, which match with the change of the peak position in Figure 9 because of the quantum size effect. The crystallite size and its variance are the minimum when the W/E ratio is 1:1, which verify what we mentioned in the last paragraph. As a kind of solvent, ethanol could dissolve oleic acid in the process of preparation. Therefore, the content of ethanol would have influence on the solubility of oleic acid, which acts as a surfactant. Then, the surface state will be changed, and the coating thickness is optimal when the ratio is 1, which led to better morphology and performance.

A series of Eu³⁺-ion-doped ZnS samples with different concentrations have been synthesized, and their powder XRD patterns are shown in Figure 11. It could be observed that both Eu³⁺-doped samples maintain the same crystal phase with undoped ZnS, which indicates that the doping of Eu³⁺ does not change the structure of the ZnS crystallite. No diffraction peaks associated with any other impurity material are detected.

To verify the presence of Eu in the doped samples, the EDS spectrum is measured and analyzed. Figure 12 shows the EDS spectrum of 3.5% Eu³⁺-doped ZnS crystallite, and it revealed the emission peak corresponding to Eu along with the characteristic peaks of Zn and S. Table 1 summarizes the estimated atomic percentages of Zn, S, and Eu in different samples. In addition, the doped samples show an improved
stoichiometry with Zn and S ratio close to 1:1. It is worthy to note that with the increasing doping concentration, there is a systematic increase in the atomic percentage of Eu along with a simultaneous decrease in the Zn content, indicating a possible replacement of Zn by Eu in the ZnS host lattice. However, there must be a part of Eu\(^{3+}\) occupying the gap position of ZnS.

The UV absorption spectra of the ZnS/\(x\)Eu\(^{3+}\) (\(x = 0.025, 0.030, 0.035, 0.040, 0.045,\) and 0.050) crystallite is shown in Supporting Information, and it could be found that the absorption region is before 390 nm, which leads to a red shift as a result of the increase of the Eu\(^{3+}\)-doped concentration. The band gaps of ZnS doped with different molar fractions of Eu\(^{3+}\) are shown in Figure 13, and it indicates that the band gap became more and more small with the increase of the doping dosage of Eu\(^{3+}\) ions, and their values are shown in the inset of Figure 13. Compared with pure ZnS, the calculated band gaps of the doped crystallite are 3.295, 3.279, 3.257, 3.224, 3.213, and 3.141 eV with the molar fraction of Eu\(^{3+}\) varying from 0.025 to 0.05. Both the shift of absorption and the band gap are the result of Eu\(^{3+}\) present in the conduction and valence band of the ZnS crystallite.

The emission spectra of different concentrations of the Eu\(^{3+}\)-doped ZnS crystallite are shown in Figure 14 under a single excitation wavelength of 395 nm. It can be seen from the figure that except the peak of ZnS, there are three peaks which are located at 395, 622, and 701 nm corresponding to the \(^{3}D_0 \rightarrow ^{3}P_0\), \(^{3}D_0 \rightarrow ^{3}P_2\), and \(^{3}D_0 \rightarrow ^{3}F_4\) transition of Eu\(^{3+}\), respectively. Moreover, when the molar fraction is 0.035, the intensities of the peak of ZnS/Eu\(^{3+}\) reach the maximum.

To further investigate the site occupancy information, the decay behaviors of the ZnS/Eu\(^{3+}\) sample with different Eu\(^{3+}\) concentrations (0.030, 0.035, and 0.040) are measured. The decay curves under 395 nm monitoring at 621 nm are shown in Figure 15, and they can be well-fitted using a second-order exponential decay formula:

\[
I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]

It can be calculated that \(\tau\) is 0.450, 0.676, and 1.832 mS when the molar fraction of Eu\(^{3+}\) is 0.030, 0.035, and 0.040, respectively. The result reveals that Eu\(^{3+}\) ions mainly occupy two types of site, and \(\tau\) changes with the dosage of Eu\(^{3+}\) ions.

Figure 16 shows the CIE chromaticity coordinates of the ZnS/Eu\(^{3+}\) sample at (0.27, 0.39), (0.27, 0.38), (0.26, 0.38), (0.26, 0.39), and (0.39, 0.42) corresponding to the molar fraction of 0.025 to 0.050, respectively. Also, the results indicate that the doping of Eu\(^{3+}\) into ZnS makes the chromaticity coordinates vary in the green region.

3. CONCLUSIONS

We have reported a series of pure and Eu\(^{3+}\)-doped ZnS crystallites obtained by a simple hydrothermal route. The XRD pattern indicates the cubic zinc blend structure of ZnS and ZnS/Eu\(^{3+}\) crystallite was prepared under different conditions. The emission spectrum shows that the ZnS crystallite could be excited by different wavelengths, and there are two emission peaks corresponding to the sulfur and zinc vacancies. In addition, the optimal ratio of W/E is 1:1. The UV−vis absorption spectroscopy and the calculated band gap show that the band gap became smaller and smaller with the increase of the doped concentration. The emission spectra of ZnS/Eu\(^{3+}\)
included the blue and red emission peak corresponding to ZnS and Eu$^{3+}$ ions, and the two emission peaks induce the samples taking on white. In a word, the emission of the ZnS crystallite can be modulated by changing the excitation wavelength, by changing the ratio of water/ethanol or Zn/S, and by adding some Eu$^{3+}$ ions.

4. EXPERIMENTAL DETAILS

The ZnS and ZnS/Eu$^{3+}$ crystallites were synthesized by a hydrothermal method. The starting materials including Zn-(CH$_3$COO)$_2$, Na$_2$S, oleic acid, and Eu(CH$_3$COO)$_2$·6H$_2$O are the analytical reagents without further purification. A certain amount of Na$_2$S was put into a beaker with deionized water and stirred by a magnetic stirrer (solution A). Zn(CH$_3$COO)$_2$ and moderate deionized water were put into another breaker and stirred by a magnetic stirrer (solution B). When Na$_2$S was taken on white. In a word, the emission of the ZnS crystallite can be modulated by changing the excitation wavelength, by changing the ratio of water/ethanol or Zn/S, and by adding some Eu$^{3+}$ ions.

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Powder XRD data were measured on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. The room-temperature photoluminescence spectra were measured by a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W Xe lamp as the excitation source. A Hitachi U-4100 ultraviolet and visible spectrophotometer was used to measure the UV–vis absorption spectra. The measurement of luminescence lifetime was conducted by utilizing a Horiba FL-1057 luminescence spectrometer with an excitation source of 375 nm pulse laser radiation (nano-LED). SEM images were obtained using an FEI NOVA NANOSEM 450. All of the measurements were identified at room temperature.

Figure 16. CIE chromaticity coordinates of ZnS/Eu$^{3+}$ with different x.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01574.

Histogram of diameter distribution of ZnS prepared with different ratios of W/E (3:1, 2:1, 1:1, 1:2, and 1:3) and absorption spectra of ZnS/Eu$^{3+}$ (x = 0.025, 0.030, 0.035,0.040, 0.045, and 0.050) crystallite (PDF)

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Notes
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