Pristine and Mn$^{2+}$-Activated (Zn$_{1-x}$Cd$_x$)S Nanoparticles: Synthesis, Microstructure and Photoluminescent Properties

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Abstract

Nanoparticles of pristine and Mn$^{2+}$-activated (Zn$_{1-x}$Cd$_x$)S (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) have been synthesized via a simple chemical colloid route. The size of as-prepared (Zn,Cd)S or (Zn,Cd)S:Mn$^{2+}$ nanoparticles was determined to be ca. 5-10 nm in diameter with a narrow size distribution, as indicated by bright-field TEM imaging investigations. With increasing x the X-ray diffraction (XRD) peaks were found to be broadened with their intensity weakened and the corresponding diffraction angles were observed to shift toward lower $2\theta$ for nanocrystalline (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ and (Zn$_{1-x}$Cd$_x$)S phases.

The $\lambda_{\text{ex}}$ was found to exhibit a blue shift from 362 to 325 nm and $\lambda_{\text{em}}$ was observed to exhibit also a blue shift from 460 to 425 nm, as indicated by the comparison of PLE and PL spectra for the nanocrystalline and bulk (Zn,Cd)S phases. In the nanocrystalline (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases the absorption of (Zn,Cd)S dominates and no absorption due to Mn$^{2+}$ was observed, as indicated by the PLE spectra. On the other hand, the emission of Mn$^{2+}$ dominates and $\lambda_{\text{em}}$ was observed to exhibit a blue shift from 596 nm to 584 nm with x increasing from 0 to 0.8, as indicated by the PL spectra for (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases. The effect of synthetic routes on the PLE and PL spectra and the fluorescence decay life time for ZnS:Mn$^{2+}$ has also been investigated and reported.

Key Words: Nanoparticles, (Zn,Cd)S:Mn$^{2+}$, Photoluminescence, Chemical Colloid Synthesis, Solvothermal Synthesis, TEM and SEM Imaging

1. Introduction

ZnS has been reported to crystallize into two modifications, namely, zinc blende (cubic $\beta$-phase) and wurtzite (hexagonal $\alpha$-phase) structures and both were found to exhibit luminescence [1]. Bulk ZnS has been used as a host lattice of phosphors for applications of cathode ray tube (CRT) and electroluminescent displays (ELDs). Furthermore, (Zn,Cd)S has long been known as a host material used in monochrome and color CRTs in the 1960’s. In recent years the researches on the synthesis and optical properties of semiconductor quantum dots of ZnS [2], CdS [3], PbS [4] and ZnO [5] have attracted much interests because of the well-known quantum confinement effect. In general, as a consequence of the large number of
surface atoms and the space confinement of the electrons in quantum dots, novel optical properties for semiconductor nanoparticles have been observed [2-5]. In particular, the optical properties of ZnS:Mn$^{2+}$ nanocrystals were first reported by Bhargava et al. [6] and Bol et al. [7], respectively, to exhibit high luminescent efficiency and lifetime shortening. On the other hand, the preparation of ZnS or ZnS:Cu nanoparticles has also been reported via different routes, i.e., rapid expansion of supercritical solutions [8], AOT/isoctane reverse micelle [9], solvothermal [10], coprecipitation [11] and sol-gel [12] methods. However, chemical colloid method has been proven to be an efficient route to prepare nanocrystalline ZnS:Mn$^{2+}$ at ambient temperature [13]. Furthermore, the size of nanocrystallites can be controlled by temperature, mixing rate of reagents, and by the concentration of stabilizers, as reported Rossetti et al. [14], Alivisatos et al. [15], and Eychmuller et al. [16]. Recently, a systematic substitution of Zn by Cd in the phosphor such as ZnGa$_2$O$_4$ has been shown to exhibit tuning effect on the luminescence of self-activated ZnGa$_2$O$_4$ [17]. Therefore, this work was especially motivated by the attempts to investigate the effect of quantum confinement effect as well as to study the variation of host compositions on the photoluminescent properties of (Zn,Cd)S and (Zn,Cd)S:Mn$^{2+}$ nanoparticles derived from a simple chemical colloid method.

2. Experimental

Nanocrystalline pristine and Mn$^{2+}$-activated (Zn$_{1-x}$Cd$_x$)S phases with $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$, respectively, were precipitated from an aqueous solution of stoichiometric Zn(NO$_3$)$_2$, Cd(NO$_3$)$_2$ or/and Mn(NO$_3$)$_2$ (all from Aldrich Chemicals Co., U.S.A.) at ambient temperature via a simple chemical colloid route by employing Na$_2$S as a precipitant and (NaPO$_3$)$_6$ as a dispersing agent as described by Sun et al. [13]. The synthetic methodology is briefly summarized as a flow diagram and shown in Figure 1. Furthermore, samples derived from the solvothermal method are prepared by dissolving stoichiometric amount of Zn(NO$_3$)$_2$·4H$_2$O or/and Cd(NO$_3$)$_2$ and 1 mol% Mn(NO$_3$)$_2$·4H$_2$O in a solvent mixture of thiourea and ethanol. The solution was then transferred to a teflon-lined autoclave and heated at 200 ℃ for 5 h. Then, the (Zn,Cd)S:Mn$^{2+}$ nanoparticles were obtained by centrifugation from the obtained solution and the nanoparticles were then washed with dry ethanol and dried prior to measurements.

To investigate the effect of temperature on the stability and phases transition of nanocrystalline (Zn$_{1-x}$Cd$_x$)S and (Zn$_{1-x}$Cd$_x$)S: Mn$^{2+}$ samples, we have annealed the as-prepared samples at temperature ranging from 400 ℃ to 800 ℃ under nitrogen atmosphere. The phase purity and homogeneity of the as-prepared as well as post-annealed (Zn$_{1-x}$Cd$_x$)S and (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ nanoparticles were investigated by X-ray diffraction (XRD) technique. The XRD profiles for nanocrystalline (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases were collected by using a MAC Science MXP-3 automatic diffractometer with a graphite-monochromatized and Ni-filtered CuK$_\alpha$ radiation. Special caution was taken to observe the changes of crystallinity and polymorphic forms as a function of synthetic temperature in the XRD profiles for both pristine and Mn$^{2+}$-activated (Zn$_{1-x}$Cd$_x$)S phases.

The ambient temperature photoluminescence (PL) spectra in the spectral region of 400 to 800 nm and excitation spectra (PLE) in the spectral region of 250 to 500 nm were measured by using a Spex Fluorolog-3 spectrofluorometer equipped with a 450W Xenon lamp. An UV-35 cut-off filter was used to eliminate the second-order emission from the excitation source. The measurements of fluorescence decay curves and lifetime for ZnS:Mn$^{2+}$ phases derived from different synthetic routes were carried out by exciting the samples by using a Lamda Physik LPX150T excimer laser (λ = 248 nm) with pulse duration of 25 nsec and the detector was equipped with a Hamamatsu R928 type photomultiplier.
Aqueous solution of stoichiometric Zn(NO$_3$)$_2$ or/and Cd(NO$_3$)$_2$

and 1 mol% Mn(NO$_3$)$_2$ • 4H$_2$O

0.5 M (NaPO$_3$)$_3$ added as a dispersant

1 M aqueous solution of Na$_2$S • 9H$_2$O
slowly added (1 mL/min)

Stirred and thoroughly mixed

Centrifugation

Colloids of ZnS and (Zn,Cd)S (white) or/ and CdS (yellow-orange)

Dried at 80 °C

Nanoparticles of (Zn$_{1-x}$Cd$_x$)S or (Zn$_{1-x}$Cd$_x$)S: Mn$^{2+}$ ($0 \leq x \leq 1$)

Figure 1. Flow diagram for the synthesis of (Zn$_{1-x}$Cd$_x$)S and (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ nanoparticles

3. Results and Discussion

Nanoparticles of both pristine and Mn$^{2+}$-activated (Zn$_{1-x}$Cd$_x$)S ($x = 0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) have been synthesized at ambient temperature via a simple chemical colloid route by precipitating stoichiometric amount of Zn$^{2+}$ or/and Cd$^{2+}$, and Mn$^{2+}$ cations from aqueous solutions by reacting with excess amount of Na$_2$S. In order to understand the effectiveness of the chemical colloidal synthesis, we have determined the cation loss to be $1.61 \times 10^{-1}$ mol%, $8.73 \times 10^{-2}$ mol%, and $2.62 \times 10^{-1}$ mol% for Zn$^{2+}$, Cd$^{2+}$, and Mn$^{2+}$ in the preparation of ZnS, CdS and ZnS:Mn$^{2+}$ nanocrystals, respectively, by using ICP/MS technique.

The as-prepared sulfide nanoparticles were found to be unstable when exposed to the air and must be stored under inert atmosphere. However, surface passivation or capping of the nanoparticles has been reported to enhance luminescence intensity effectively by coating of polyvinyl alcohol or poly(methacrylic acid) [18] and the capping of (Zn,Cd)S and (Zn,Cd)S:Mn$^{2+}$ phases is currently under investigations in our laboratory.

Furthermore, the XRD profiles for (Zn$_{0.6}$Cd$_{0.4}$)S:Mn$^{2+}$ were investigated when subjected to post-annealing at different temperatures and the results are summarized in Figure 2(a). The as-prepared (Zn$_{0.6}$Cd$_{0.4}$)S:Mn$^{2+}$ phase was found to be poorly crystalline and exhibit diffraction peak broadening when thermally treated below 400 °C, which indicates the poorly nanocrystalline nature of the product. As the temperature increases up to 700 °C, ZnO starts to appear in the product as an impurity, as indicated by XRD profile analysis. Interestingly, we have also observed a phase transition from cubic to hexagonal symmetry for (Zn,Cd)S at ca. 500 °C. Furthermore, the effect of Cd$^{2+}$ dopant content ($x$) on the XRD profiles for nanocrystalline cubic (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases was also investigated and the results are summarized in Figure 2(b). With increasing $x$ the diffraction peaks attributed to reflections of (111), (220), and (311), respectively, were found to be broadened and their intensity weakened and the corresponding diffraction angles were observed to shift toward lower 2θ which is consistent with the expected host lattice expansion.

To compare the microstructure of different ZnS:Mn$^{2+}$ samples prepared from solid-state and chemical colloidal routes, we have measured and shown the SEM and TEM imaging micrographs in Figures 3(a) and 3(b), respectively. As indicated in Figure 3(a), the grain morphology for bulk ZnS:Mn$^{2+}$ appears to be irregularly spherical with diameter ranging from 0.1 to 2.5 µm and the average grain size was estimated to be 0.6 µm. On the other hand, the size of as-prepared (Zn,Cd)S:Mn$^{2+}$ nanoparticles was determined to be ca. 5-10 nm in diameter with a narrow size distribution, as indicated by bright-field TEM imaging shown in Figure 3(b).
The PLE and PL spectra for nanocrystalline (Zn$_{1-x}$Cd$_x$)S phases are represented in Figure 4. We have observed that as $x$ varies from 0 to 1.0 both the $\lambda_{\text{ex}}$ and $\lambda_{\text{em}}$ for (Zn$_{1-x}$Cd$_x$)S host were observed to exhibit an apparent red shift, as indicated by the comparison of PLE and PL spectra for the nanocrystalline (Zn$_{1-x}$Cd$_x$)S with different Cd$^{2+}$ dopant content. The trend of $\lambda_{\text{ex}}$ and $\lambda_{\text{em}}$ shifting is consistent with those reported in the literature and the observation can be attributed to the decrease in band gap energy ($E_g$) and increase in covalency of the host with increasing Cd$^{2+}$ dopant content.
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The PLE and PL spectra for nanocrystalline (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases are represented in Figures 5(a) and 5(b). In the nanocrystalline (Zn$_{1-x}$Cd$_x$)S: Mn$^{2+}$ phases the absorption of (Zn,Cd)S host dominates and no absorption due to Mn$^{2+}$ was observed, as indicated by the PLE spectra. On the other hand, as indicated by the PL spectra for (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases, the emission of Mn$^{2+}$ dominates and $\lambda_{em}$ attributed to Mn$^{2+}$ $^4T_1$-$^6A_1$ transition was observed to exhibit a blue shift from 596 nm to 584 nm when $x$ increases from 0 to 0.8. These observations can be rationalized by the weakening of crystal field strength and the corresponding Tanabe-Sugano diagram for a tetrahedral Mn$^{2+}$ with $d^5$ configuration, and for tetrahedral Mn$^{2+}$ ion upon Cd$^{2+}$ substitution. However, we have also noticed that with increasing Cd$^{2+}$ dopant content for nanocrystalline (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ phases, both the absorption and emission intensities were found to decrease drastically, which can presumably be attributed to the impurity effect introduced by Cd$^{2+}$ doping.

To investigate the effect of synthetic routes on the self-activated luminescence of host, we have measured the PLE and PL spectra for ZnS derived from solid-state and chemical colloid preparations, respectively, and the results are shown in Figure 6. The $\lambda_{ex}$ was found to exhibit a blue shift of 37 nm from 362 to 325 nm and $\lambda_{em}$ was observed to exhibit also a blue shift of 35 nm from 460 to 425 nm, as indicated by the comparison of PLE and PL spectra for the nanocrystalline relative to the buck ZnS. The observation can be attributed to the quantum confinement effect similar to that observed by Bhargava et al. and Bol. et al. in MnS:Mn$^{2+}$ nanoparticles [6].
On the other hand, the comparison of PLE and PL spectra for ZnS:Mn$^{2+}$ phases synthesized from solid-state, chemical colloid and solvothermal routes, respectively, is also represented in Figure 7. We have observed that the bulk ZnS:Mn$^{2+}$ sample synthesized by solid-state method exhibits absorption multiplets at 338 nm (attributed to ZnS host), and 392, 425, 468, and 493 nm, which are attributed to $^6\text{A}_1 \rightarrow ^4\text{T}_2$, $^4\text{E}(^5\text{D})$, $^6\text{A}_1 \rightarrow ^4\text{A}_1$, $^4\text{E}(^4\text{G})$, $^6\text{A}_1 \rightarrow ^4\text{T}_2 (^4\text{G})$, and $^6\text{A}_1 \rightarrow ^4\text{T}_1 (^4\text{G})$ transitions of Mn$^{2+}$, respectively. On the contrary, the nanocrystalline ZnS:Mn$^{2+}$ samples derived from both chemical colloid and solvothermal routes, respectively, exhibit absorption due to ZnS host and weak Mn$^{2+}$ ion absorption, which may be attributed to different energy absorption and energy transfer mechanisms. In the PL spectra the emission due to Mn$^{2+}$ $^4\text{T}_1 \rightarrow ^6\text{A}_1$ transition dominates and the corresponding $\lambda_{\text{em}}$ was found to be 578, 596, and 597 nm for samples prepared by solid-state, chemical colloidal and solvothermal methods, respectively. However, the self-activated emission from ZnS expected to occur at 425 nm (nanoparticles) and 460 nm (bulk) was found to be too weak to be observed.

Furthermore, the comparison of fluorescence decay for ZnS:Mn$^{2+}$ phases is represented in Figure 8 and the life time for ZnS:Mn$^{2+}$ nanoparticles derived from different synthetic routes was also compared and summarized in Table 1. We have observed that both the lifetime for ZnS host as well as Mn$^{2+}$ activator for bulk samples synthesized by solid-state method are much shorter than that found for nanocrystalline ZnS:Mn$^{2+}$ prepared via the chemical colloid route, as indicated by the analysis of decay lifetime shown in Table 1. The shortening of decay lifetime for both host and activator luminescence has also been observed and discussed by Bhargava et al. [6] and Bol et al. [7].
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4. Conclusions

Nanoparticles of pristine and Mn$^{2+}$-doped (Zn$_{1-x}$Cd$_x$)S ($x = 0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) phases have been synthesized via a chemical colloidal or a solvothermal route. The average size of as-prepared (Zn,Cd)S and (Zn,Cd)S:Mn$^{2+}$ nanoparticles was determined to be ca. 5-10 nm in diameter, as indicated by bright-field TEM imaging investigations. The $\lambda_{\text{ex}}$ was found to exhibit a blue shift from 338 to 345 nm, whereas $\lambda_{\text{em}}$ was observed to exhibit a red shift from 578 to 597 nm for nanocrystalline relative to bulk ZnS:Mn$^{2+}$, as indicated by the PLE and PL spectra. An apparent red shift in $\lambda_{\text{em}}$ and $\lambda_{\text{ex}}$ attributed to the host was also observed with increasing $x$ for (Zn$_{1-x}$Cd$_x$)S nanoparticles, whereas an opposite trend in the shifting of $\lambda_{\text{em}}$ attributed to Mn$^{2+}$ for (Zn$_{1-x}$Cd$_x$)S:Mn$^{2+}$ nanoparticles can be rationalized by Tanabe-Sugano diagram for a tetrahedral Mn$^{2+}$ with $d^5$ configuration.

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References


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