This chapter describes synthesis of larger size ZnS nanocrystals by anion control growth using different S precursors. Here thiourea and thioacetamide act as S precursors. Using this precursors, high quality Mn doped ZnS also can be synthesized.
4.1 Introduction

Fluorescing semiconductor nanocrystals with size tunable optical emissions\textsuperscript{1-3} have been extensively studied as light emitting source for LEDs,\textsuperscript{4} lasers,\textsuperscript{5} bar-coding,\textsuperscript{6} biological labeling\textsuperscript{2,7} and chemical sensing\textsuperscript{8} etc. These highly emissive nanocrystals with tunable, narrow and stable emission are mostly direct band gap inorganic semiconductors where the generated exciton relaxes within their valance and conduction bands.\textsuperscript{1-3,9} Apart from this direct exciton relaxation, introducing additional impurity or dopant states in between the valance and conduction band diverts the exciton relaxation process through these additional energy states leading to intense dopant related emission at host excitations.\textsuperscript{10-16}

These dopant related emission compete with tunable exciton emission for the comparable intensity, stability\textsuperscript{17} and other related photo-physical aspects for different applications.\textsuperscript{18,19}

One of the best suitable semiconductor hosts to dope different transition metal ions is ZnS, a heavy metal free and wide band gap material.\textsuperscript{13,20-22} When Mn\textsuperscript{2+} is doped in ZnS host nanocrystals exciton relaxes through $^4T_1(4G) \rightarrow 6A_1(6S)$ of Mn d-states leading to yellow-orange emission centered at ~585 nm.\textsuperscript{13,20,23} In last two decades enormous efforts have been done to synthesize high quality doped nanocrystals, to understand the doping mechanism and to get efficient dopant emission. Analyzing different doping processes, it has been observed that adsorption of dopant ions on to the surface of host nanocrystals remained the key and crucial step,\textsuperscript{11,24-27} and these surface adsorbed dopants are further needed to be shelled to prevent the dopant centre from surface photo-oxidation to get efficient emission.\textsuperscript{11,17,28} As adsorption of dopant ions on the surface of host nanocrystals simultaneously competes with the adsorption of different constituents of host nanocrystal during the growth, a slow growth process is expected to provide the dopant ions more opportunity for precipitation or adsorption on to the appropriate facets of host nanocrystals.\textsuperscript{27} Similarly, to keep the dopant centers away from the surface to allow better relaxation for the created defects, larger size host nanocrystals are essentially required.\textsuperscript{25} In high temperature colloidal synthesis of nanocrystals decoupling the nucleation and growth process has been mostly controlled by lowering the reaction temperature soon after the precursor/s injection.\textsuperscript{1,29} Additionally, the growth of semiconductor nanocrystals in colloidal synthesis has been associated with several other processes i.e. available ligands
and their binding strength on nanocrystals surface,\textsuperscript{30,31} hydrophobic interaction of surface binding ligands with solvent molecules,\textsuperscript{1,31} competition with possibility of new nucleations during growth and possible ripening during long time annealing.\textsuperscript{32} For the case of ZnS nanocrystals, it is less probable to grow beyond 5 nm particle size using the traditional colloidal synthetic method\textsuperscript{13} and forcefully attempts to grow ends up with their precipitation. Hence, to control the growth of nanocrystals need to overcome many simultaneously running different hindering processes which would help to grow the nanocrystals larger and would facilitate the doping process.

We report in this chapter a self-decoupled fast nucleation and slow growth process to synthesize relatively larger size ZnS nanocrystals and to dope Mn\textsuperscript{2+} ions during the favorable slow growth process. The synthetic process follows with suitable sulfur precursors at an optimized and fixed reaction temperature which automatically separates the growth from nucleation. Using different organo-sulfur compounds, for example carbon disulfide (CS\textsubscript{2}), thiourea (\text{NH}_2\text{CSNH}_2) and thioacetamide (\text{CH}_3\text{CSNH}_2), as sulfur source and zinc carboxylates as zinc source, ZnS nanocrystals up to 8 nm are synthesized. These sulfur reagents having >C=S functional group are very common reagent in metal-sulfide synthesis\textsuperscript{33-35} but these compounds are used mostly in low boiling polar solvents to get different metal-sulfide nanocrystals, in solvothermal synthetic process.\textsuperscript{34} We have used these “S” sources in high boiling non-polar solvent by dispersing them in calculated amount of polar long chain amines (hexadecylamine, octadecylamine etc) and found out that these can act as potential sulfur source to serve our purposes for allowing continuous growth of ZnS nanocrystals beyond its normal size barrier. Additionally, this slow growth process has been observed ideal to dope Mn\textsuperscript{2+} ions and to get efficient Mn dopant emission.
4.2 Experimental Section

4.2.1 Synthesis

(a) Materials
Zinc stearate (ZnSt2, tech), Octadecylamine (ODA, 97%), Oleyl Amine (90%), Octadecene (ODE, tech.), Mercaptopropionic acid (MPA), Cystaminehydrochloride, Stearic acid (SA, 95%), Thiourea (99%), Thioacetamide (99.9%) and Manganese(II)Chloride (MnCl2, 98%) were purchased from Aldrich. All the chemicals were used without further purification.

(b) Preparation of S stock solution
In a three necked flask 0.152 gm (2 mmol) thiourea, 2.69 gm (10 mmol) and 10 ml of ODE are taken and degassed it with purging argon for 10 min at 60 oC. Then the temperature is increased to 220 oC. Initially it is a colloidal solution, after 5-10 mins it was clear and transparent solution. Finally the mixture is cooled down to room temperature and collects in a vial under argon atmosphere.

(c) Preparation of manganese stearate
10 mmol Stearic acid was dissolved in methanol and heated to 40 °C to get a clear solution. 10 mmol TMAH was diluted by 5 ml methanol and added to the SA solution. The mixture was stirred for 20 minutes to complete the reaction. Next, 5 mmol of MnCl2 was dissolved in methanol and drop wise added to the above solution under vigorous stirring condition. White precipitate of manganese stearate flocculated which was collected and dried under vacuum.

(d) Synthesis of ZnS and Mn doped ZnS
In a typical synthesis process, 0.063 gm (0.1mmol) ZnSt2 and 10 ml ODE are loaded in a 50 ml three necked flask. The reaction mixture is degassed for 15 minutes by purging with Argon and heated to 260 °C. Previously made S precursor 2 ml stock is then injected to the reaction flask at 260 °C and annealed it 250 °C. For Mn doping the 0.002 g (0.03 mmol) Mn stearate in 1ml ODE was injected soon after the injection of S source. In a separate vial 0.325 g ZnSt2, 0.142 g Stearic acid and 4 ml ODE are mixed together and degassed by
purging Argon. Once the desire Mn d emission was noticed (~585 nm) then the ZnS\textsubscript{2} stock was injected by two phase in the reaction mixture at 250\degree C. In this step the reaction flask was kept for another ~30 mins at same temperature for further growth (up to 8 nm). Finally, nanocrystals were purified by addition of acetone and dispersed in chloroform for further characterization. The quantum yield (QY) of the nanocrystals was measured using a standard organic dye, quinine sulfate in 0.1N H\textsubscript{2}SO\textsubscript{4} solution. The QY of the nanocrystals after repeated purifications was usually found to be between 30-40%.

For carbon disulfide and thioacetamide as sulfur source the reaction temperature is maintained at 220 \degree C and 240 \degree C respectively.

(e) Water soluble Mn doped ZnS using cystaminehydrochloride

Purified doped nanocrystals were taken in a minimum volume of chloroform and excess cystaminehydrochloride in minimum volume of ethanol had been added until the solutions become cloudy. The mixture was then shaken for 20 minutes. The cystamine hydrochloride capped doped nanocrystals were flocculated and separated out by centrifugation. The precipitate was washed with ethanol to remove excess cystaminehydrochloride. Finally desired amount of water was added in the precipitated nanocrystals to transfer them in water.

4.2.2 Characterization

(a) Optical measurements

UV-Vis measurements were taken with a Agilent-8453 UV-Vis spectrophotometer. Photoluminescence spectra were collected using a Horiba Jobin Yvon Fluromax -4 spectrofluorometer. The QY was measured with respect to a dye quinine sulphate using a standard procedure.
(b) Transmission electron microscopy
TEM images were taken on a JEOL-JEM 2010 electron microscopy using 200kV electron source. Specimens were prepared by dropping a drop of nanocrystal solution in chloroform on a carbon coated copper grid, and the grid were dried under in air.

(c) Inductively coupled plasma atomic emission spectroscopy
The dopant percentage was determined by ICP using Perkin – Elmer Optima 2100 DV machine. At first, the D-dots were repeatedly purified to remove excess precursors. Then the purified nanocrystals were dissolved in chloroform. The chloroform was then evaporated and the dried nanocrystals were digested in concentrated HNO3. The nitric acid solution of the samples was diluted with double distilled water to do the measurements.

(d) X-ray diffraction (XRD)
XRD of the doped sample was taken by Bruker D8 Advance powder diffractometer, using Cu Kα (λ= 1.54 Å) as the incident radiation.

(e) Electron paramagnetic resonance (EPR)
EPR measurement was done using a 9.5 GHz JEOL spectrometer operated at X-band frequency. The g value (effective Zeeman factor) is dependent on the orientation of magnetic field.

4.3 Results and Discussion

4.3.1 Synthesis of ZnS and Mn doped ZnS nanocrystals
Traditional high temperature injection synthesis process for colloidal nanocrystals has been followed for ZnS nanocrystals. Typically, zinc precursors are dispersed in solvent ODE in a three necked flask and heated to desired reaction temperature. Depending on the selective sulfur precursors, synthesis temperature has been chosen with 240 °C to 260 °C for both nucleation and growth. Amines are initially not taken along with Zn-sterate in the mixture to avoid ZnO formation at higher temperature. Mn-stearate has been chosen as the dopant precursors and injected along with sulfur precursor. Figure 4.1 shows the schematic representation of the synthesis of ZnS and Mn doped ZnS nanocrystals.
Chapter 4: Doping Mn$^{2+}$ … slow growth process

Figure 4.1 Schematic presentation of synthesis of Mn doped ZnS nanocrystals. Initially Zn precursor was taken in ODE. At higher temperature the S precursor was injected along with fatty amine for synthesis of ZnS. For Mn doped ZnS case Mn precursor was injected soon after the injection of S.

Figure 4.2a shows the typical absorption and photoluminescence (PL) spectra of Mn doped ZnS nanocrystals synthesized by using thiourea as S precursor which is relatively stable compared to other selected sulfur sources. The PL spectrum is centered at wavelength (λ) 585 nm, which is characteristic of the Mn $^4T_1 \rightarrow ^6A_1$ phosphor transition with 320 nm excitation. The digital photographs of the nanocrystals with and without UV irradiation (Figure 4.2b) provide a visual indication of the emission color and transparency of the solution respectively. The reproducible quantum yield (QY) of the solution has been measured to be 35±5% using quinine sulfate as reference dye.

The growth of these nanocrystals is also supported from the transmission electron microscope (TEM) images. Figure 4.3a and 4.3b shows the TEM micrographs of ZnS nanocrystals taken out from the reaction flask at different time intervals where former one shows ~5 nm and later shows nearly ~11 nm diameter particle size. Figure 4.3c shows the electron diffraction pattern corresponding to Figure 4.3b and this supports (111), (220), (311) planes of cubic system. XRD in Figure 4.4a also supports cubic crystal structure. Following Debye-Scherrer equation the diameter of ZnS nanocrystals was calculated to be 10.8 nanometer and it agrees well with the size measured from the TEM image (Figure 4.3b).
Figure 4.2 (a) Typical UV-Visible and PL spectra of Mn doped ZnS. In PL spectra the center at 585 nm. (b) Digital picture of Mn doped ZnS in presence of day light (left panel) and UV light (excitation at 254nm).

Figure 4.3 (a) TEM images of small size Mn doped ZnS nanocrystals taken from before overgrowth sample. (b) TEM images of large size (~7.5nm) Mn doped ZnS particles taken from after overgrowth sample. (c) SAED pattern of Mn doped ZnS of the sample (b).

In addition to the emission at 585 nm originated from Mn centers at host excitation as a support of Mn doping, Electron Paramagnetic Resonance (EPR) spectra for large size Mn doped ZnS nanocrystals (Figure 4.4b) also supports the tetrahedral placement of dopant Mn$^{2+}$ ions inside ZnS host nanocrystals. The six line spectrum resulting from the hyperfine interaction of the unpaired electrons with $^{55}$Mn nuclear spin (I=5/2) provides evidence for well dispersed doping without any clustering of Mn$^{2+}$. The hyperfine splitting of $65G$ and $g$
= 2.003 determined from the EPR spectrum are in close agreement with the literature data for Mn$^{2+}$ ions in (tetrahedral sites) zincblende lattice.\(^{27}\)

**Figure 4.4** (a) XRD pattern of Mn doped ZnS (large size around 8nm). The 2θ positions at 28.37°, 47.49° and 56.42° are corresponds to (111), (220) and (311) plane of cubic (Zinc blende) ZnS (JCPDS No. 03-0524) (b) EPR spectra of Mn doped ZnS after overcoating with Zn precursors.

### 4.3.2 Associated chemical processes during synthesis

Our chosen sulfur precursors having (\(\equiv\text{C=S}\)) bonds act differently than commonly used S precursors in high temperature injection colloidal synthesis. These S precursors in long chain fatty amines form a complex and remains dispersed in amine and ODE mixture. Due to Lewis acid property of long chain amine, it attacks the electrophilic center of thiourea at higher temperature (above 200 °C) and produces the ammonia gas\(^{37}\) and 1-octadecylthiourea. This 1-octadecylthiourea intermediate is supported by C\(^{13}\) NMR spectra (Figure 4.5). The peak at 184 ppm in Figure 4.5 is due to C containing the thiourea moiety (-CSNH-) but it is red shifted compared to pure thiourea (~177 ppm). Other signals are due to alkyl chain of the fatty amines. This intermediate compound decomposes at higher temperature via a proposed Chugave type cyclic reaction (Figure 4.6) and produces H\(_2\)S gas in the reaction mixture.
Figure 4.5 C\textsuperscript{13} NMR spectra of intermediate state (thiourea complex) where R is C\textsubscript{18}H\textsubscript{39}.

Figure 4.6 Proposed reaction mechanism of thiourea with long chain amine.

Formation of H\textsubscript{2}S gas from the decomposition of 1-octadecylthiourea was also confirmed by its rotten egg smell and formation of PbS, after purging the gas in a solution of lead acetate. The decomposition of 1-octadecylthiourea in amine and ODE mixture varies with reaction temperature. At above 290 °C, the decomposition has been observed sharp and almost all of the compounds decomposed immediately after injection. But this decomposition rate has been found slow within 240 °C to 260 °C. This is confirmed by analyzing the samples in different time intervals at 250 °C and 290 °C and undecomposed
1-octadecylthiourea has been found even 20 minutes at 250 °C while it was almost decomposed at 290 °C. Once the 1-octadecylthiourea decomposes, the evolved H\textsubscript{2}S dissolves in the balanced ratio of fattyamine (octadecyl amine or oleyl amine) and ODE mixture present in the reaction flask. Amine plays a vital role both in formation as well as dissolution of H\textsubscript{2}S making reaction medium slightly polar. H\textsubscript{2}S cannot be dissolved in presence of nonpolar solvent and polar amines are essential to trap the gas in solution phase. We have confirmed this by taking 1-octadecylthiourea compound only in ODE without amine and heated it upto 250 °C and found out no dissolution of H\textsubscript{2}S occurs. Also this dissolution of H\textsubscript{2}S in presence of amine does not ensure complete solvation of gaseous H\textsubscript{2}S and there are always some gaseous H\textsubscript{2}S remains above the solution, in equilibrium with dissolved H\textsubscript{2}S. When the gas above the solution has been taken out by a carrier gas or by using a syringe, we have observed the ceasing of the growth leading smaller size particles at fixed temperature. This supports the role of H\textsubscript{2}S in gas phase in controlling the growth of nanocrystals. Hence, the whole reaction has been associated with simultaneously running different chemical processes (Figure 4.7); (1) Decomposition of 1-octadecylthiourea to evolve H\textsubscript{2}S gas, (2) Dissolution of this evolved H\textsubscript{2}S in the amine-ODE mixture, (3) Equilibrium between gaseous H\textsubscript{2}S and dissolved H\textsubscript{2}S. Each of these processes can control the formation of nucleations and their growth of ZnS nanocrystals in solution.

**4.3.3 Nucleation and growth processes**

As the rate of decomposition of the chosen sulfur precursor depends on the injection temperature, the formation of H\textsubscript{2}S gas and its dissolution in amine-ODE mixture and hence formation of ZnS nanocrystals is also controlled by the temperature. It has been observed that number of nucleations at higher temperature (290 °C) injection of 1-octadecylthiourea is more compared to that of 250 °C injection as reflected from their difference of OD (optical density) values (not given). Also, after the completion of the reaction, ZnS nanocrystals with smaller number of nucleations were grown to ~ 8 nm (as shown in Figure 4.3) and that one injected at higher temperature, remained smaller in diameter. This indicates that our chosen precursors and optimized reaction parameters help to control the
nucleation and allow them to grow larger with self-controlled supply of both zinc and sulfur precursors in the reaction system.

Figure 4.7 Schematic presentation of different chemical activities during the formation of ZnS nanocrystals. The sulfide ions for ZnS formation comes from dissolved H₂S gas in the polar amine and ODE mixture.

Nucleations of ZnS which were immediately formed by the injection of 1-octadecylthiourea, ceases once the concentration of sulfide ions decreases in the reaction mixture. To be stated here, the concentration of active sulfide source which is the dissolved H₂S gas in amine-ODE mixture depends on both the rate of decomposition of 1-octadecylthiourea and its equilibrium with gaseous H₂S. Once the growth starts, the concentration of this active sulfide source in the solution decreases which shift the equilibrium with gaseous H₂S towards dissolution. This decrease in the concentration in the active sulfide source also enhances the decomposition of 1-octadecylthiourea. Both these processes help to increase the active sulfide source in solution and the growth of ZnS nanocrystal continues without ripening even for more than 60 minutes annealing at 250 °C. The whole growth process has also been observed slower compared to normal colloidal ZnS synthesis\textsuperscript{13} which can be attributed for all these associated chemical process to control the supply of sulfide source in the solution.
Being slow, the growth process also facilitates the dopant ions effective adsorption on the surface of host nanocrystals. This is to inform here that using elemental S in ODE as sulfur source; we were able to synthesize 4.2 to 4.5 nm ZnS particles following identical reaction protocol.

4.3.4 Reactivity of different chosen precursors

As our chosen sulfur reagents have variable reactivity, we found different optimized decomposed reaction temperature for each of them. For thiourea, 260 °C is the best temperature for nucleation for both ZnS and Mn doped ZnS nanocrystals but for thioacetamide and CS₂, lower temperature (220 °C-240 °C) is preferred for slower growth to get larger size particle.

The formation of H₂S gas is more rapid for thioacetamide and CS₂ compared to thiourea and accordingly the availability of sulfide ions is also faster in case of CS₂ and thioacetamide. This causes less number of nuclei formations in case of thiourea in comparison with thioacetamide and CS₂ which has been proven by their optical density values for the same amount of the sample. Evolved H₂S gas allowed these nuclei to grow for larger extent. The maximum size of ZnS nanocrystals using thiourea was 8nm while in thioacetamide and CS₂ it remained within 5 nm which is similar to elemental S in ODE as sulfur source. The larger size in case of thiourea facilitated more the doping process with higher quantum efficiency compare to thioacetamide and CS₂.

4.3.5 Processibility of nanocrystals

These doped nanocrystals can be made water soluble with different surface functionalization processes using different ligands e.g. cystaminehydrochloride, mercaptocarboxylic acid, polyacrylamine etc. Emission efficiency for cystamine capped Mn doped ZnS nanocrystals in water is almost same as Mn doped ZnS in non-polar solvent. After ligand exchange the doped nanocrystals retains almost same quantum yield and remains stable for few months and under longtime UV irradiation. Additionally due to intense dopant emission, transparency and non-absorbance of visible light make this material a potential workhorse for the light emitting devices.
4.4 Conclusion

In conclusion, we report here the synthesis of larger size (~8nm) spherical ZnS particles using organosulfur compounds that has not been possible so far by existing high temperature colloidal methods in the literature. These larger size ZnS nanocrystals are shown to be an effective host for dopant Mn$^{2+}$ ions, leading to intense dopant emission. Our chosen organosulfur precursors helped to decouple the fast nucleation and slow growth process. This slow growth process is effective for the adsorption of dopant ions on the host surface to get enhance dopant emission. Finally we have also shown that Mn$^{2+}$ doped ZnS nanocrystals can be transferred in water without any perceptible effect on the Mn$^{2+}$ emission intensity, unlike many other systems, thereby suggesting possible applications as source of light emitting materials for today’s and tomorrow’s applications.
Chapter 4: Doping Mn$^{2+}$ ... slow growth process

Bibliography


Chapter 4: Doping $\text{Mn}^{2+}$ ... slow growth process


