Synthesis and Characterization of Doped Core/Shell Quantum Dots

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SYNTHESIS AND CHARACTERIZATION OF DOPED CORE/SHELL QUANTUM DOTS

by

Elizabeth J. Sodt

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Elizabeth J. Sodt
SYNTHESIS AND CHARACTERIZATION OF DOPED CORE/ SHELL QUANTUM DOTS

Elizabeth J. Sodt, M.S.
Western Michigan University, 2007

The central theme of the research performed is the systematic modification of the optical properties of quantum dots by the formation of a shell of another quantum dot of a different band gap energy. Core/shell quantum dots such as CdS:Mn/CdS, CdS:Mn/ZnS, and ZnS:Mn/CdS with various concentrations of dopant Mn$^{2+}$ in the core and shell concentrations have been synthesized under mild conditions in the aqueous phase using stoichiometric amounts of the surfactant stabilizer dodecyl sulfate. These quantum dots exhibit UV-vis, emission, and electron paramagnetic resonance (EPR) spectral behavior that is dependent on the concentration of the shell and the dopant Mn$^{2+}$ in the core. The emission intensities of the core quantum dots do not exhibit a systematic variation with Mn$^{2+}$ concentration. When a shell is added a systematic variation in the emission intensity and lifetime that are inversely proportional to the concentration of the shell is observed. When the large band gap ZnS is added as a shell to the small band gap CdS, the Mn$^{2+}$ ions migrate from the core to the shell which is manifested in the emission and EPR spectra. Additionally the mixing of the valence and conduction band energy states of the large and small band gap shell and core respectively is also manifested in the emission spectra. In the reverse case, namely when CdS is added as a shell to ZnS the migration is not observed and the mixing of the valence and conduction band energy levels is minimum. The tunable optical properties of these core/shell quantum dots make them excellent platforms for the generation of nanosensors for nerve gas analogs.
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Quantum dots are semiconductor nanoparticles that are 1-10 nm in diameter. Quantum dots have become a very active area of research because of their improved and size dependent optical properties over their bulk counterparts. As the size is reduced down to the nanoscale quantum dots begin to exhibit quantum confinement in all three dimensions. Quantum confinement is when an electron-hole pair (exciton) can be trapped in one or more dimensions. The emission can be tuned by controlling the size of the quantum dots. The smaller a quantum dot becomes, the greater the blue-shift in the emission. This phenomenon makes quantum dots extremely important for applications in such diverse fields as optics, bioimaging, sensors, and electronics (1-11).

When an electron is excited from the valance band to the conduction band a positively charged hole is left behind (10). The electron and hole are considered to be a bound pair due to the attraction between the negatively and positively “particles”, creating an exciton. Both the electron and the hole are considered to have their own masses. At the 1-10 nm scale the quantum dots become smaller than the Bohr radius and therefore the distance between the electron and the hole can be calculated using the Bohr approximation, equation 1.1.
Where \( r \) is the radius of the sphere, \( \varepsilon \) is the dielectric constant of the semiconductor, \( m_r \) is the reduced mass of the electron-hole pair, \( h \) is Planck’s constant, and \( e \) is the charge of an electron. The distance between the electron and the hole is dependent on the size of the quantum dot, and hence, by controlling the size of the quantum dot it is possible to control the quantum confinement effects. As the size of the quantum dot is reduced there is an increase in the bandgap energy increasing the probability of radiative recombination of excitons.

Doping is when an impurity is intentionally introduced into the lattice of a semiconductor material (12). This technique is important for the controlled modification of bulk semiconductor properties. Doping thus offers the possibility of introducing new and interesting properties to the system. By doping with \( \text{Mn}^{2+} \) it is possible to understand how dopants are incorporated by characterization with luminescence and electron paramagnetic resonance spectroscopy. The emission intensity can also be manipulated by changing the concentration of the dopant.

Though much research has been performed on quantum dots their surface properties are still complex and have a profound influence on their behavior (13-15). Surface properties become extremely important when dealing with particles in the nanoscale
as the surface-to-volume ratio is very large. With such a large portion of the particle’s atoms on the surface and associated defects, such as dangling bonds, are detrimental to the chemistry of the particle because they attract impurities to the surface. Surface defects can also trap excitons decreasing the emission of the quantum dots. One possible approach to minimizing surface defects is the formation of a shell on the core quantum dot. Surface modification is also referred to as surface passivation as it tends to minimize defects and dangling bonds.

Surface passivation can be achieved with either organic ligands or by adding a shell of inorganic material with a smaller or larger bandgap. While passivating the surface with organic ligands improves the surface defects it does not completely rectify the problem because it is difficult to simultaneously passivate both the anionic and cationic sites (16-18). However, passivating the surface with a material that has a band gap different from the core has been shown to be much more effective than with ligands and in fact offers the possibility of electron and energy transfer from the wider bandgap material to the core and vice versa.

The central hypothesis of this research is that optical properties of doped quantum dots can be significantly modified by the addition of a shell of the same or different quantum dot (same or different band gap energy). The addition of a shell resulting in core/shell quantum dots could lead to: (i) the mixing of the conduction and valence band energies when the band gaps of the core and shell are different resulting in
changes in the absorption and emission properties; (ii) the migration of the dopant from the core to the shell and vice versa depending on the affinity of the dopant for the individual crystal lattices; (iii) such a migration resulting in changes in the absorption and emission spectra and emission lifetimes and spectral properties of the dopant itself; (iv) the shell with a smaller band gap than the core can compete for the exciton energy with the dopant and result in reduced emission intensity and lifetime characteristic of the dopant; and (v) the x-ray diffraction pattern of the core-shell quantum dots could also exhibit significant shift from one that is characteristic of the core to one that is characteristic of the shell depending on the concentration of the shell added.

Quantum dots are often synthesized at high temperatures in organic solvents from organometallic precursors and require the use of capping ligands to prevent their aggregation (17, 19, 20). Such synthetic procedures also do not readily lend themselves to doping with magnetic nuclei such as Mn$^{2+}$ and trivalent lanthanide ions. These quantum dots also cannot be dispersed in an aqueous medium for a variety of applications such as biological imaging and sensor fabrication. Most importantly, these synthetic routes involve very toxic and costly solvents. Previous attempts to synthesize quantum dots in an aqueous medium employed a large excess of phosphates and polyphosphates and surfactants to stabilize the quantum dots as colloids. This invariably led to the irreversible adsorption of the stabilizers on the quantum dots rendering further surface modifications such as the systematic addition
of a shell or other ligands difficult and challenging. Some aqueous based techniques have been developed that involve elemental-direct-reactions and photon irradiation (21, 22).

This research was performed along the objectives listed below:

1. Develop a green synthetic method for core and core/shell quantum dots in the aqueous phase under mild conditions.

2. Introduce various concentrations of the dopant Mn$^{2+}$ in the core and shell and characterize them by UV-vis absorption spectroscopy, luminescence, electron paramagnetic resonance, x-ray diffraction, transmission electron microscopy, and scanning electron microscopy. Understand the spectral properties as a function of the concentration Mn$^{2+}$ and the shell.

3. Add the shell to the core quantum dot sequentially in the same synthesis (one pot method, Method I) or from the shell separately in a different reaction vessel and add to the previously formed core quantum dots (mixture method, Method II). Compare the properties of the core/shell quantum dots from Method I and Method II.

4. Test the central hypothesis by employing the quantum dots ZnS and CdS interchangeably as the core and shell. The core will be doped with varying concentrations of Mn$^{2+}$ to determine the effects (i)-(iv) listed above by monitoring the emission intensity and lifetime of the $^{4}T_{1} - ^{6}A_{1}$ transition of
Mn$^{2+}$ arising from the exciton energy transfer from the quantum dot in the core and the characteristic six line EPR spectrum of Mn$^{2+}$. Additionally XRD and TEM will be employed to characterize the core/shell quantum dots.
CHAPTER II

EXPERIMENTAL AND INSTRUMENTATION PROCEDURES

2.1 Reagents

The compounds Cadmium acetate hydrate (99.99%), Aldrich (CAS 89759-80-8)
Cadmium sulfate (99%), Sigma-Aldrich (CAS 10124-36-4)
Manganese (II) sulfate hydrate (99.99%), Aldrich (CAS 15244-36-7)
Sodium dodecyl sulfate (SDS, 99.0%), Sigma-Aldrich (CAS 151-21-3)
Sodium sulfide nonahydrate (99.99%), Aldrich (CAS 1313-84-4)
Zinc acetate dihydrate (98+%), Sigma-Aldrich (CAS 5970-45-6)
Zinc sulfate heptahydrate (99.999%), Sigma-Aldrich (CAS 7446-20-0) were used as
received except SDS and Na₂S which were purified as described.

Sodium dodecyl sulfate was recrystallized by dissolving 12 g into 200 mL of ethanol
heated to 70-80 °C while stirring in a beaker. After the volume was reduced to 100
mL the solution was allowed to cool to room temperature. The solids were then
filtered using a Buchner funnel and Whatman filter paper.

Sodium sulfide was dried/kept in a vacuum dessicator. Due to the hygroscopic nature
of the reagent it was difficult use the same amount of Na₂S from synthesis to
synthesis. The weight was determined by monitoring the weight loss of a small sample over a time period. The original sample was nonahydrated and once it was assumed all the water was absent the new formula weight was taken to be 78 g/mol.

Water was purified by a Milli-Q water purification system (resistance 18.2 kΩ).

2.2 Instrumentation

2.2.1 UV-Visible Spectrophotometer

UV-Vis absorption was taken either with a Perkin-Elmer Lambda 20 (Figure 2.1) or a Shimadzu UV-2101 PC UV-Vis Scanning Spectrophotometer (Figure 2.2). The software employed for the Perkin-Elmer was WinLab and UVProbe for the Shimadzu.

Figure 2.1 Perkin-Elmer Lambda 20 UV-Visible Spectrophotometer.
2.2.2 Photoluminescence Spectrometer

Emission, excitation, and lifetime data were obtained using an Edinburgh Instruments sub-nanosecond lifetime and steady state fluorescence spectrometer (Figure 2.3). The data collection and analysis was performed using F900 software. The following conditions were employed in the emission and excitation data. The parameters were the same for most experiments and will be noted if otherwise.

Excitation wavelength for emission spectra: 400 nm

Emission wavelength for excitation spectra: 650 nm

Excitation slit: 3 nm
Emission slit: 10 nm
Emission filter: 455 nm
Excitation filter: 550 nm
Step: 1 nm
Dwell time: 0.500 s

The lifetime and time-resolved emission spectroscopy data were obtained using a 370 nm light emitting diode laser.

Figure 2.3 Edinburgh Instruments sub-nanosecond lifetime and steady state fluorescence spectrometer.
2.2.3 Transmission Electron Microscope (TEM)

The transmission electron microscope images were obtained using a JEOL JEM 1230 instrument operated at 80 kV. The aqueous colloidal samples were dispersed on a Cu grid and allowed to dry.

2.2.4 High Resolution Transmission Electron Microscope (HRTEM)

The high resolution transmission electron microscope images were obtained using a JEOL 2200FS 200 kV field emission TEM at Michigan State University in Lansing, Michigan.

2.2.5 X-Ray Diffractometer

The XRD data was recorded using a Rigaku Ultima III (Figure 2.4) at Altair Nanotechnologies in Reno, Nevada. The instrument is equipped with a thin film state and cross beam optics which allow for focusing and parallel beam optics. On the receiving side is a graphite monochromator. The slits are auto-variable and are set during the scan. The slits used for the various samples and will be indicated in the text.
2.2.6 Electron Paramagnetic Resonance Spectrometer

A JEOL JES-TE100 ESR Spectrometer (Figure 2.5) was employed to obtain electron paramagnetic resonance data at room temperature. The powder samples were analyzed in 250 mm length round bottom Norell S-4-EPR-250S quartz EPR tubes. The experiments were performed using the following parameters:

Modulation width: 0.32 mT
Modulation frequency: 100 kHz
Center field: 323.00 mT
Sweep time: 0.5 min
Frequency: 9.06043 GHz
Power: 2.00 mW

The sample data was recorded using EWWin software Version 1.04 4.0.

Figure 2.5 JEOL JES-TE100 ESR Spectrometer.
2.2.7 Scanning Electron Microscope (SEM)

The SEM images were recorded using a Hitachi S-4700 scanning electron microscope (Figure 2.6) at Altair Nanotechnologies in Reno, Nevada. The instrument is equipped with a cold field emission gun capable of producing high brightness (~ $2 \times 10^9$ A/cm$^2$/sr) with little energy spread (0.2 - 0.3 eV).

Figure 2.6 Hitachi S-4700 Scanning Electron Microscope.
2.3 Synthesis of Manganese Doped Cadmium Sulfide and Zinc Sulfide Quantum Dots with Various Shells

2.3.1 Synthesis of Cadmium Dodecyl Sulfate Precursor Salt

The cadmium dodecyl sulfate was prepared using a modified procedure from the literature (23). An 11.52 g quantity of recrystallized sodium dodecyl sulfate was dissolved in 200 mL of ethanol at 70-80°C. A 5.34 g quantity of cadmium acetate was dissolved in 50 mL methanol/10 mL water mixture. Cadmium acetate solution was then added to the boiling sodium dodecyl sulfate solution. The resulting mixture was reduced in volume to 100 mL by heating and then cooled to room temperature. The Cd(DS)₂ crystals that precipitated were washed three times with ethanol and filtered using a Buchner funnel and Whatman #1 filter paper. The crystals were dried in a vacuum dessicator and stored in a glass vial for future use.

2.3.2 Synthesis of Manganese Doped Cadmium Sulfide Quantum Dots

The nanoparticles were synthesized by arrested precipitation in water, using Cd(DS)₂ precursor salt. An appropriate amount of Mn²⁺SO₄·xH₂O was added to 400 mL aqueous solution containing dissolved Na₂S (0.480 g, 2 mmol) at room temperature, which was followed by the addition of Cd(DS)₂ (1.288 g, 2 mmol), as either a solid or from a stock solution, to form the CdS:Mn²⁺ colloidal solution. A small portion of the sample (~20 mL) was kept aside for solution analysis. The remaining bulk of the
The sample was cooled to -20°C overnight and brought back to room temperature to obtain solids. The solution was centrifuged, the supernatant decanted, and the solids were isolated. The obtained yellow solids were dried overnight in a vacuum desiccator over anhydrous CaCl2. The solids were then stored in glass vials to be used for elemental, XRD, and EPR analysis.

2.3.3 Synthesis of Manganese Doped Cadmium Sulfide Core/Shell Quantum Dots by One-Pot Method (Method I)

The manganese doped cadmium sulfide core was synthesized using the same procedure as above. The core solution was then allowed to stir for 10 min at room temperature. After the formation of the core, a shell was formed using various core:shell ratios namely, 1:1, 1:1/2, 1:1/4, 1:1/8, and 1:1/16. For the 1:1 core:shell synthesis, a solution of Na2S (0.480 g, 2 mmol) and a solution of CdSO4 (0.416 g, 2 mmol) were then added separately but simultaneously; dark orange solids immediately formed. After about 15 min of stirring at room temperature, a small portion (20 mL) was kept for solution data and the remaining bulk of the sample was stored at -20°C overnight and brought back to room temperature in order to obtain solids. The solution was then centrifuged, the supernatant decanted, and the solids were isolated. The obtained dark orange solids were dried overnight in a vacuum desiccator over anhydrous CaCl2 and were then stored in glass vials. The dried core/shell nanoparticles were used in elemental, XRD, and EPR analysis.
2.3.4 Synthesis of Manganese Doped Cadmium Sulfide with Zinc Sulfide Shell by One-Pot Method (Method I)

The manganese doped cadmium sulfide quantum dots with zinc sulfide shell were synthesized in the same manner as the manganese doped cadmium sulfide core/shell quantum dots except ZnSO$_4$ was used in place of CdSO$_4$, in the appropriate amount. For the 1:1 core/shell synthesis the amount of ZnSO$_4$ used was 0.568 g (2 mmol). Again after the resulting core/shell solution was stirred for 15 min, it was stored at -20 °C overnight, brought back to room temperature, and the solids were isolated by centrifugation.

2.3.5 Synthesis of Manganese Doped Cadmium Sulfide Core/Shell Quantum Dots by Mixture Method

The core/shell quantum dots were also synthesized by mixing, separately synthesized CdS:Mn$^{2+}$ core and CdS shell. An appropriate amount of Mn$^{2+}$SO$_4$.xH$_2$O was added to 300 mL aqueous solution containing dissolved Na$_2$S.9H$_2$O (0.480 g, 2 mmol) at room temperature followed by the addition of Cd(DS)$_2$ (1.288 g, 2 mmol), as either a solid or from a stock solution, to form the CdS:Mn$^{2+}$ core solution. The CdS shell was synthesized separately in 100 mL H$_2$O containing 0.288 g of SDS. For the sample with the shell concentration the same as the core concentration, 0.480 g of Na$_2$S.9H$_2$O and 0.416 g of CdSO$_4$ were added to the SDS solution. After approximately 15 min. of stirring the shell solution was added to the core solution making a total volume of
400 mL containing excess SDS which should not affect the overall reaction. The solids were then isolated using the same procedure as previously described.

2.3.6 Preparation of Cadmium Sulfide Shelled Manganese Doped Zinc Sulfide by Mixture Method

ZnS:Mn$^{2+}$ and CdS were synthesized separately and then added together using the same procedure as CdS:Mn$^{2+}$/CdS synthesized by the mixture method. The appropriate amount of Zn(DS)$_2$ was added to make a 0.005 M core solution (1.19 g, 2 mmol). The rest of the procedure is the same as the CdS:Mn$^{2+}$/CdS synthesis.

2.4 Elemental Analysis

Elemental analysis was performed by Desert Analytics in Tucson, Arizona. The samples were digested by weighing 5 to 25 mg of solid sample on a Sartorius microbalance into a 25 mL digestion flask. The amount of sample that was weighed was dependent upon the amount of sample that was available for analysis. Several of the samples (ES20 and ES54) were very small and only 0.2 mg of sample was available for analysis.

The digestion process involved adding 5 mL of concentrated HNO3 and heating the sample to near dryness on a hotplate. The digested sample was allowed to cool and then 1 mL of 30% H$_2$O$_2$ was slowly added and heated on the hotplate as a final
oxidation step. The combination of HNO₃ and H₂O₂ completely oxidized the organic components in the samples. To ensure that the metals were completely dissolved, 1 mL of concentrated HCl was added and the digested sample was again heated to near dryness. The sample was then allowed to cool and then transferred to plastic sample containers and brought to 10.0 mL final volume with rinses of 5% HCl/1% HNO₃. The digested batch included prep blank, two Laboratory Control Samples, and a set of duplicate samples.

Finally, the samples were analyzed for cadmium, zinc, or manganese depending on the desired elements using a Thermo Jarrell Ash 61E Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) at the following wavelengths: 257.6 nm for manganese and 226.4 nm for cadmium. Zinc was analyzed by Flame Atomic Absorption Spectrometry (Flame AAS) using a Perkin-Elmer model 3100 using the wavelength of 213.9 nm.
3.1 Overview

Quantum dots are semiconductor nanoparticles in the 1-10 nanometer size regime (10). Scientists have become increasingly aware of quantum dots over the past few years because of their interesting chemical, physical, and optical properties. Quantum dots exhibit quantum confinement in all three dimensions unlike quantum wires or quantum wells which display quantum confinement in one- and two-dimensions, respectively. Unlike their bulk counterparts semiconductor nanomaterials can be manipulated in order to demonstrate different properties. Most importantly, they are optically tunable due to quantum confinement effects. The optical properties can be altered by changing their size, passivating their surface with a different material, or by doping their lattice with other metal ions.

In the bulk form, both the valance and conduction bands have a continuous structure. As the size is reduced down to the nanoscale discrete energy levels develop in the conduction and valence regions. These energy levels resemble the lowest unoccupied molecular orbital and highest occupied molecular orbital of a molecule. If the sizes of the quantum dots surpass ten nanometers the energy levels are very close and less
quantum confinement effects are seen. The band gap is the energy difference between the valence and conduction bands and the mid point of the band gap is known as the Fermi level. When an electron is excited from the valance band to the conduction band, it leaves a positively charged hole in the valence band and a negatively charged electron in the conduction band resulting in an exciton or electron-hole pair. The minimum energy it takes to excite the electron to the conduction band is the band gap. Furthermore, the absorbance maximum is the optimum energy that is needed to excite an electron to the conduction band (generate an exciton).

The excitons like electronic excited states in molecules can relax to the ground state either by nonradiative or radiative processes. The radiative process results in an emission of photons over a characteristic range of wavelengths for quantum dots depending on their composition and size. This emission is generally termed luminescence to account for both allowed and forbidden transitions including those of dopants. The excitation of the electron occurs in the ultraviolet region of the electromagnetic spectrum for the systems investigated here and the emission occurs in the visible. For example, CdS:Mn$^{2+}$ has an excitation maximum of 400 nm and an emission maximum of 650 nm, while for ZnS:Mn$^{2+}$ these occur at 320 nm and 590 nm, respectively.

There are two methods used to synthesize quantum dots, top-down and bottom-up methods (24). The top-down method uses a template to build nanoscale materials
either on or in itself. The bottom-up approach builds the particles atom-by-atom by a controlled synthesis. Using the bottom up approach allows for smaller particles than the top down approach. Quantum dots are typically synthesized by employing the bottom-up approach either by vapor deposition or by colloidal synthesis.

Colloidal synthesis is the most popular method because it allows for exceptional control over the nucleation and growth of the particles (25-30). In order to ensure that the quantum dots are below 10 nm and are monodisperse it is important that the nucleation process occurs slowly followed by minimal growth. It is equally important that the quantum dots are stable in solution and do not re-dissolve and cause Ostwald ripening. Ostwald ripening is when re-dissolved species precipitate out of solution onto larger particles. This causes large size distributions and low quantum yields in emission. Due to this effect surfactants are often used to control growth. The most popular stabilizers are thiols, polyphosphate, TOP/TOPO, sodium dodecyl sulfate, and amphiphilic phospholipids (20).

The quantum dots in this study were stabilized by sodium dodecyl sulfate a readily available surfactant. Unlike with many stabilizers that are taken in excess the dodecyl sulfate (DS) is employed in stoichiometric amounts of the primary metal ions Cd$^{2+}$ and Zn$^{2+}$ by employing their dodecyl sulfate salts as precursors for the quantum dots. The cadmium dodecyl sulfate and zinc dodecyl sulfate precursor salts were prepared using a modified procedure from the literature (23). The synthesis is discussed in
Chapter II. Addition of Cd(DS)₂ precursor salt to an aqueous solution containing the appropriate amount of Na₂S and Mn²⁺ ions yields a transparent yellow colloidal solution, while addition of the Zn(DS)₂ precursor salt renders a clear solution. The quantum dots begin to aggregate and precipitate several days to weeks after preparation. A TEM image of re-dispersed CdS:Mn^{2+} quantum dots can be seen in Figure 3.1.

Figure 3.1 TEM image of CdS:Mn^{2+} re-dispersed in H₂O.
3.2 Optical Properties of CdS:Mn$^{2+}$ Quantum Dots

3.2.1 Absorption Spectra and Bandgap Calculations

Quantum confinement of nanoscale semiconductor particles causes the bandgap energy to blue-shift in comparison to bulk counterparts. The bandgap energies of bulk CdS and ZnS are 2.4 eV and 3.6 eV, respectively (31, 32). Bhattacharyya et al reported that the bandgap energy can be found by taking the derivative of the plot of absorbance versus $h\nu$ (eV) (29). This was determined by employing the equation

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^m$$  \hspace{1cm} (3.1)

where $A$ is a constant that is dependent upon $m$, which indicates the type of transition, $E_g$ is the bandgap energy, and $h\nu$ is the incident photon energy. The values of $m$ depend on the type of transition, specifically, 1/2, 3/2, 5/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect, respectively. Rearranging equation 3.1 and taking the derivative yields equation 3.2

$$\frac{d(\ln \alpha)}{d(h\nu)} = \frac{1}{h\nu} + \frac{m}{(h\nu - E_g)}$$  \hspace{1cm} (3.2)
By taking the derivative of the plot of absorbance versus $hV$ (eV) (Figure 3.2) it is possible to determine the bandgap energy. The peak maximum is the corresponding bandgap energy, as can be seen in Figure 3.3. The bandgap energy determined for CdS:Mn$^{2+}$ was 2.63 eV and 3.84 eV for ZnS:Mn$^{2+}$ which are higher than the values for the bulk semiconductors. It is also worth noting that the bandgap energy increases slightly as the concentration of Mn$^{2+}$ increases.

![Absorption spectra of CdS:Mn$^{2+}$ with 0.026% Mn$^{2+}$](image)

Figure 3.2 Absorption spectra of CdS:Mn$^{2+}$ with 0.026% Mn$^{2+}$ (Sample ES49).
Figure 3.3 Plot of $d(lna)/d(hv)$ versus $hv$ for sample ES49. Peak maximum indicates bandgap energy of 2.63 eV, which is approximately 0.21 eV above bulk CdS.

3.2.2 Particle Size Determination from Absorbance Data

The radius of the quantum dots can also be determined from the absorption spectra by the Brus equation (33). This equation takes into account the bandgap energy, ($E_g$), of the bulk semiconductor (first term), the crystal radius, ($r$), and effective electron, ($m_e$), and hole, ($m_h$), masses (second term), and the effects from Coulomb interactions (third term; $\varepsilon_0$ = permittivity of vacuum; $\varepsilon_r$ = dielectric constant of the medium). The last term is due to corrections to the equation and can be ignored in most cases. The equation is given as follows

$$E_g(r) = E_g(r \rightarrow \infty) + \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_r r} + O(r^{-3}) \tag{3.3}$$
Assumptions that must be made are that the electrons and holes behave freely within the particle and have different masses (effective mass approximation). This equation fails for very small particles that have less than 100 atoms because not all crystals in this size regime are stable due to large distortion in the band structure. In these cases, only quantum-chemical calculations can be used to determine the band structure. It is also assumed that the particles are spherical and have an infinite energy barrier. Rearrangement and solving for the appropriate constants gives the following equation for CdS which yields the radius of the quantum dots based on the bandgap energy for a given sample

\[
r(E_g) = 1.54 \frac{\sqrt{E_g - 2.48} - 0.094}{E_g - 2.485} \tag{3.4}
\]

A similar equation was derived previously by Suijver et al for ZnS and is equation 3.5 (34).

\[
r(E_g) = \frac{0.29 - 2.91\sqrt{E_g - 3.49}}{2(3.50 - E_g)} \tag{3.5}
\]

It is important to note that these equations are only first order approximations. Non-perfectly spherical quantum dots will differ from these approximations but it is useful
to compare the findings from the absorbance data to the particle sizes found from TEM images and XRD data (Scherrer’s Equation, 35). The average particle radius was determined to be 2.75 nm for CdS:Mn\(^{2+}\) from the Brus equation, which is in good agreement with Scherrer’s equation (method explained in section 3.4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn(^{2+})</th>
<th>(E_{\text{g}(\text{eV})})</th>
<th>(r(E_g)) (nm)</th>
<th>(d) (nm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES48</td>
<td>0.03</td>
<td>2.63</td>
<td>3.10</td>
<td>2.33</td>
</tr>
<tr>
<td>ES49</td>
<td>0.026</td>
<td>2.64</td>
<td>3.06</td>
<td>2.29</td>
</tr>
<tr>
<td>ES50</td>
<td>0.159</td>
<td>2.65</td>
<td>2.96</td>
<td>2.22</td>
</tr>
<tr>
<td>ES51</td>
<td>3.49</td>
<td>2.74</td>
<td>2.51</td>
<td>1.88</td>
</tr>
<tr>
<td>ES52</td>
<td>11.7</td>
<td>2.87</td>
<td>2.12</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Table 3.1 Comparison of particle sizes for CdS:Mn\(^{2+}\) derived from Brus equation and Scherrer’s equation. Please note the sizes calculated from Scherrer’s equation are smaller because of crystal strain introduced during the drying process used to prepare solid samples for XRD. Also note the bandgap energy increases and size decreases with increasing Mn\(^{2+}\) concentration.

3.2.3 Luminescence of CdS:Mn\(^{2+}\) Quantum Dots

Upon irradiation of light at a particular energy an electron is excited from the valance band to the conduction band. Once in the excited state the excitons can deactivate radiatively or non-radiatively. The non-radiative pathways result from surface defects or from vacancies in the crystal lattice. The excitons can deactivate by transferring energy to the \(^4T_1\) state of Mn\(^{2+}\) which relaxes to the \(^6A_1\) state resulting in an emission with a maximum at 650 nm. The \(^4T_1 \rightarrow ^6A_1\) is a more favored process; therefore non-
radiative processes become less prominent upon doping with Mn\(^{2+}\). This process can be seen in Figure 3.4 (36, 37).

![Figure 3.4 Mechanism of energy transfer between CdS crystal lattice and Mn\(^{2+}\) dopant sites upon irradiation with 400 nm wavelength photons resulting in a 650 nm wavelength emission maximum.](image)

The solutions used for the studies were aged for approximately 24 hours prior to the luminescence studies. The samples were normalized to a 0.2 absorbance at 400 nm. Excitation spectra for CdS:Mn\(^{2+}\) were taken by fixing the emission wavelength at 650 nm and scanning from 250 nm to 520 nm. The excitation maxima are around 370 nm and the peak position is independent of Mn\(^{2+}\) dopant concentration. In order to avoid an instrument artifact seen when excited at 370 nm, the emission spectra were obtained by excitation at 400 nm. The excitation spectra can be seen in Figure 3.5. The intensity changes with variation in Mn\(^{2+}\) impurity concentration, however, the change is not systematic. The broadness of the excitation spectra could be attributed to the polydispersity of the nanocrystals and aggregation.
Figure 3.5 Excitation spectra for CdS:Mn$^{2+}$ with various Mn$^{2+}$ dopant concentrations indicated in the legend. Emission wavelength was set to 650 nm prior to scan.

As with the excitation spectra the emission spectra, Figure 3.6, do not change systematically with a systematic change in the Mn$^{2+}$ dopant concentration. This could be either due to surface Mn$^{2+}$ being oxidized or due to Mn$^{2+}$ being incorporated randomly in CdS crystal lattice sites instead of tetrahedral sites. Electron paramagnetic resonance studies were performed to understand the incorporation of Mn$^{2+}$ further.
3.3 Electron Paramagnetic Resonance Studies of CdS:Mn

Electron paramagnetic resonance, or EPR, is a crucial tool in understanding the environment of Mn$^{2+}$ in quantum dot systems (38-52). Previous studies indicate that Mn$^{2+}$ replaces the cation in the crystal lattice, in this case Cd. There are four signal contributions that are indicative of the position of Mn$^{2+}$ in the crystal lattice. The contributions are due to Mn$^{2+}$ replacing the host cation in tetrahedral sites of the crystal lattice, Mn$^{2+}$ located at surface or interstitial sites, Mn$^{2+}$-Mn$^{2+}$ dipole interactions, and exchange-coupled Mn$^{2+}$ clusters. Mn$^{2+}$ in the surface sites and Mn$^{2+}$ clusters quench the luminescence of the quantum dots. Consequently, only Mn$^{2+}$ ions...
that are incorporated into the cation sites of the quantum dots can be attributed to the $^4T_1 \rightarrow ^6A_1$ transition.

CdS:Mn$^{2+}$ was synthesized using various concentrations of Mn$^{2+}$ and EPR spectra were recorded for all samples, see Figure 3.7. As the concentration of Mn$^{2+}$ increases there is an increase in Mn$^{2+}$-Mn$^{2+}$ dipole interactions and a subsequent broadening of the EPR signal occurs. Comparable results were found by Beerman et al in ZnS:Mn$^{2+}$ quantum dots (44, 45). At lower concentrations of Mn$^{2+}$, the Mn$^{2+}$ ions are located further apart in the crystal lattice and the characteristic six-line pattern can be seen due to Mn$^{2+}$ in tetrahedral sites. In both the CdS:Mn$^{2+}$, shown here, and ZnS:Mn$^{2+}$ cases, the presence of the ten weak forbidden transitions between the six-line pattern can be seen at the lower concentrations of Mn$^{2+}$. The characteristic six-line pattern is due to $M_s = -1/2$ to $M_s = 1/2$ transitions for the six values of $M_I$. Purely cubic centers have zero probability for forbidden transitions; therefore it is likely that the $T_d$ sites are slightly distorted. The intermediate samples show complex spectra due to the contribution of Mn$^{2+}$ in multiple sites.
Figure 3.7 EPR spectra of CdS:Mn$^{2+}$ with various concentrations of Mn$^{2+}$, indicated on the left. As the concentration of Mn$^{2+}$ in the crystal lattice increases there is a loss of the characteristic six-line pattern due to an increase in Mn$^{2+}$-Mn$^{2+}$ dipole interactions.

In order to understand the spectra one needs to use the spin Hamiltonian used to represent the spin states of the S=5/2, I=5/2 system of Mn$^{2+}$ given by equation 3.6 (45).

$$
\hat{H} = \beta_s \hat{S} \cdot \mathbf{g} \cdot \mathbf{H} + D(\hat{S}_z^2 - \frac{1}{3} S(S+1)) + E[\hat{S}_x^2 - \hat{S}_y^2] + \hat{S} \cdot \mathbf{A} \cdot \hat{I} - g_s \beta_n \hat{I} \cdot \mathbf{H} + Q(\hat{I}_z^2 - \frac{1}{3} I(I+1))
$$

(3.6)

The first term is the electron Zeeman term, the second and third terms are due to the zero field spin-spin interaction, and the further term is the electron spin-nuclear spin interaction. The last two terms are the nuclear Zeeman and nuclear quadrupole terms. The EPR parameters are useful for computer simulation of the EPR spectra. In our
case we are more interested in the shape of the spectra; however the parameters are listed for future reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>X2</th>
<th>X1</th>
<th>X2-X1</th>
<th>B</th>
<th>G</th>
<th>A (mT)</th>
<th>A (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES48</td>
<td>0.026</td>
<td>341.27</td>
<td>305.93</td>
<td>35.34</td>
<td>323.60</td>
<td>2.00</td>
<td>5.89</td>
<td>58.90</td>
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<td>306.13</td>
<td>35.34</td>
<td>323.80</td>
<td>2.00</td>
<td>5.89</td>
<td>58.90</td>
</tr>
<tr>
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<td>0.159</td>
<td>341.07</td>
<td>305.73</td>
<td>35.34</td>
<td>323.40</td>
<td>2.00</td>
<td>5.89</td>
<td>58.90</td>
</tr>
<tr>
<td>ES51*</td>
<td>3.490</td>
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</tr>
<tr>
<td>ES52*</td>
<td>11.700</td>
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</table>

*Spectra were too broad to calculate parameters.

Table 3.2 EPR parameters calculated from EPR spectra.

3.4 X-Ray Diffraction Analysis of CdS: Mn$^{2+}$

X-Ray diffraction, or XRD, is a powerful tool used to determine both the crystal lattice structure and size of nanoparticles. XRD is unique because it is capable of providing both quantitative and qualitative information about a solid sample by the position and intensity of the diffraction pattern. The diffraction angle, $2\theta$, is dependent upon the spacing between a set of planes. The line intensities are determined by the number and type of atomic reflection centers in each set of planes.

The particle size can be determined using Scherrer's equation (34), which is given by

$$L = \frac{0.9\lambda}{\beta \cos(\theta)}$$ (3.7)
Where \( L \) is the coherence length, \( \lambda \) is the wavelength of x-ray radiation, \( \beta \) is full width at half max in radians, and \( \theta \) is the angle of diffraction in radians). For spherical nanoparticles the diameter \( d = \frac{1}{4} L \). The parameters can be calculated by fitting the initial curve in a XRD pattern to a Gaussian curve as shown in Figure 3.8. Table 3.2 lists the diameters of the CdS:Mn\(^{2-}\) samples calculated from Scherrer’s equation.

![Figure 3.8 Determination of parameters for particle size calculation using Scherrer’s equation.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn(^{2-})</th>
<th>Xc (radians)</th>
<th>FWHM, ( \beta ) (radians)</th>
<th>( L )</th>
<th>( d ) (nm)</th>
</tr>
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<tr>
<td>ES48</td>
<td>0.026</td>
<td>0.464</td>
<td>0.0491</td>
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<td>2.368</td>
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<tr>
<td>ES49</td>
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<td>0.464</td>
<td>0.0502</td>
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<td>2.316</td>
</tr>
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<td>ES50</td>
<td>0.159</td>
<td>0.465</td>
<td>0.0508</td>
<td>3.053</td>
<td>2.29</td>
</tr>
<tr>
<td>ES51</td>
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<td>0.466</td>
<td>0.0525</td>
<td>2.956</td>
<td>2.217</td>
</tr>
<tr>
<td>ES52</td>
<td>11.7</td>
<td>0.466</td>
<td>0.0605</td>
<td>2.565</td>
<td>1.924</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>2.22 ± 0.18</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3 Particle sizes determined for CdS:Mn\(^{2-}\) from Scherrer’s equation.
All XRD of CdS:Mn$^{2+}$ in Figure 3.9 indicated the particles to have a zinc blende lattice structure. Both zinc blende and wurtzite lattice structures of CdS:Mn$^{2+}$ have been reported in the literature (53, 54). The lattice structure is dependent upon the procedure used to synthesize the quantum dots. This procedure consistently yields quantum dots with zinc blende structure for all systems studied.

Figure 3.9 XRD pattern of CdS:Mn$^{2+}$ samples ES48-ES52. Dashed lines represent the actual angles of diffraction for CdS.

3.5 Major Conclusions Drawn from CdS:Mn$^{2+}$ Study

Complete characterization of CdS:Mn$^{2+}$ synthesized using the procedure outlined in Chapter II yields complex results. While the EPR spectra show a systematic change as a function of the dopant concentration, this is not reflected in the emission spectra.
The emission spectral intensities are nonsystematic and the emission maxima at the higher Mn$^{2+}$ concentrations are blue-shifted and red-shifted for 11.7% and 3.49% Mn$^{2+}$, respectively. The average particle size calculated using Scherrer's equation is $2.22 \pm 0.18$ nm, which is in good agreement with sizes calculated using the Brus approximation $2.75 \pm 0.42$ nm.
4.1 Overview

Due to the large surface to volume ratio of quantum dots it is reasonable to expect that the surface sites play a significant role in the optical properties. As seen in the previous chapter, as the amount of dopant concentration is systematically changed there is not a systematic change in emission of un-passivated CdS:Mn$^{2+}$. This is most likely due to a surface charge left behind due to sulfur or cadmium vacancies and a subsequent attraction of the Mn$^{2+}$ and other impurities to the surface resulting in unpredictable emission behavior. As discussed previously, Mn$^{2+}$ adsorbed onto the surface of quantum dots quenches the luminescence and only Mn$^{2+}$ in tetrahedral sites can be attributed to the characteristic 650 nm emission. It is difficult to employ these quantum dot systems in applications such as optical sensors, when their optical properties are irreproducible. So an investigation of the surface properties is essential to understand the influence of surface sites on the optical properties of quantum dots.

Much research has been performed on quantum dot systems but little is known about their surface properties (55). By adding a shell or by passivating with organic ligands, the surface properties can be better understood. Organic capping is disadvantageous.
because it is difficult to simultaneously passivate both anionic and cationic sites with this method. Many groups have focused on the development of a core/shell procedure in which an inorganic material with a larger bandgap is applied as a shell around a smaller bandgap material in order to facilitate energy transfer due to the potential offset (11, 56-59). This technique has advantages of both eliminating surface defects, such as dangling bonds, and also ensuring that all energy is being transferred to the host lattice. The photogenerated excitons are confined to the host lattice by the larger bandgap material resulting in an increase in emission (56, 57).

Efforts in the epitaxial growth of a shell around the core to create a uniform shell have been largely unsuccessful. Another shortcoming of many of the procedures used to synthesize core/shell quantum dot systems is that they involve high temperatures and harsh solvents. While high temperatures help to anneal surface defects it adds to the cost and toxicity of manufacturing these materials. Here we introduce a procedure in which water is the solvent and shell formation can be accomplished at room temperature. Unfortunately there is not a way to eliminate the toxicity of CdS, however, we have discovered a way to isolate and dry the solids to reduce waste, see Chapter II. The drying process also eliminates most of the SDS in solution which causes aggregation. Figure 4.1 is a TEM comparison of a CdS:Mn$^{2+}$/CdS sample before and after the removal of SDS. Large aggregates can be seen in 4.1 (a) due to SDS. Particles are slightly aggregated in 4.1 (b) possibly due to the some remaining SDS.

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Many core/shell quantum dot systems have been characterized such as CdSe/CdS, CdSe/ZnS, and CdS:Mn$^{2+}$/ZnS (11, 15, 56-59). While CdSe core/shell systems have been extensively studied in the literature, there is little information regarding the mechanism of luminescence in doped core/shell systems (1, 60-65). The problem is further complicated by the ability of Mn$^{2+}$ to migrate within the nanocrystal. Electron paramagnetic resonance studies shed some light on this effect.

The effect of Mn$^{2+}$ dopant concentration on a CdS core/shell system was studied to discern the role of the shell in luminescence properties by blocking the surface defects and to ensure that the luminescence was from the doped core and not the shell. By
comparing the optical properties of the CdS:Mn$^{2+}$ core solution and the optical properties of the core solution following addition of CdS shell, we can conclude that the new optical properties are indeed due to an interaction between CdS and CdS:Mn$^{2+}$.

4.2 Optical Properties of CdS:Mn$^{2+}$/CdS Quantum Dots

The CdS:Mn$^{2+}$/CdS quantum dots were prepared using the procedure outlined in Chapter II. Here, we studied two different systems; one in which the shell was synthesized by direct addition to the core material (Method I; one-pot synthesis), and another that was synthesized by making the core and shell separately and then adding them together (Method II; mixture synthesis) which will be discussed in the next chapter. The core samples were prepared using the same procedure described in Chapter III. Following the preparation of the core, a shell was added using the appropriate amounts of CdSO$_4$ and Na$_2$S, depending on the extent of shell desired. First, the optical properties of Mn$^{2+}$ doped CdS core/shell quantum dots were studied with various amounts of Mn$^{2+}$ dopant. The effect of Mn$^{2+}$ concentration was studied for various core:shell ratios; 1:1, 1:1/2, 1:1/4, and 1:1/8. For example for 1:1, one mole of shell material was added per one mole of core. The various core-to-shell ratios were then studied at 0.01% Mn$^{2+}$ to show the effect of shell formation on the CdS:Mn$^{2+}$/CdS. The systems were studied using the same characterization techniques as in Chapter III.
4.2.1 Absorption Spectra, Bandgap Calculations, and Particle Size Determination

The absorption maximum of CdS:Mn$^{2+}$ remains unchanged following the addition a CdS shell. The absorption maximum remains at 450 nm, Figure 4.2. Calculation of particle sizes using Brus equation shows that the sizes do not differ from CdS:Mn$^{2+}$. This is an indication that addition of the shell slows the growth process by filling the missing anionic and cationic sites on the particle surface and subsequent shell growth follows. To further demonstrate this, particle sizes were calculated from the Brus method for the 1:1 and 1:1/2 series, Table 4.1. The particle sizes do not change as a function of the shell concentration, the sizes remain relatively unchanged. Furthermore, unlike CdS:Mn$^{2+}$, Mn$^{2+}$ concentration does not play a role in the particle size or the bandgap energy in the core/shell case. This is perhaps due to Mn$^{2+}$ resting in less distorted tetrahedral sites and thereby contributing less to the size of the quantum dots.
Figure 4.2 Absorbance spectra of CdS:Mn$^{2+}$/CdS (1:1) with varying Mn$^{2+}$ concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>$E_g$ (eV)</th>
<th>$r(E_g)$ (nm)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES20</td>
<td>12.70</td>
<td>2.636</td>
<td>3.070</td>
<td>*</td>
</tr>
<tr>
<td>ES18</td>
<td>0.393</td>
<td>2.622</td>
<td>3.183</td>
<td>2.387</td>
</tr>
<tr>
<td>ES16</td>
<td>0.032</td>
<td>2.635</td>
<td>3.074</td>
<td>2.306</td>
</tr>
<tr>
<td>ES15</td>
<td>0.034</td>
<td>2.619</td>
<td>3.205</td>
<td>2.404</td>
</tr>
<tr>
<td>ES17</td>
<td>0.006</td>
<td>2.726</td>
<td>2.567</td>
<td>1.925</td>
</tr>
</tbody>
</table>

1:1/2

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>$E_g$ (eV)</th>
<th>$r(E_g)$ (nm)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES25</td>
<td>5.75</td>
<td>2.729</td>
<td>2.555</td>
<td>1.916</td>
</tr>
<tr>
<td>ES24</td>
<td>0.602</td>
<td>2.636</td>
<td>3.069</td>
<td>2.302</td>
</tr>
<tr>
<td>ES23</td>
<td>0.185</td>
<td>2.621</td>
<td>3.185</td>
<td>2.389</td>
</tr>
<tr>
<td>ES22</td>
<td>0.009</td>
<td>2.622</td>
<td>3.182</td>
<td>2.387</td>
</tr>
<tr>
<td>ES21</td>
<td>0.003</td>
<td>2.635</td>
<td>3.074</td>
<td>2.305</td>
</tr>
</tbody>
</table>

Average 3.016 ± 0.247 2.258 ± 0.185

Table 4.1 Comparison of particle sizes calculated from the Brus Equation and from Scherrer’s Equation for the 1:1 and 1:1/2 series. The particle sizes are similar to those calculated for CdS:Mn$^{2+}$, (Chapter II). (* Indicates there was not enough solid sample for XRD analysis). Concentration of Mn$^{2+}$ was determined by elemental analysis.
4.2.2 Luminescence Spectra of CdS:Mn\textsuperscript{2+}/CdS Quantum Dots with Various Core:shell Ratios as a Function of Mn\textsuperscript{2+} Concentration

The luminescence of Mn\textsuperscript{2+}-doped QDs strongly depends on the surface properties and surrounding environment. Coverage of CdS:Mn\textsuperscript{2+} with a CdS shell should reduce the surface defects, and consequently, the surrounding environment should have less effect on the optical properties of the QDs. The luminescence of CdS:Mn\textsuperscript{2+}/CdS with various core/shell concentrations (1:1, 1:1/2, 1:1/4, and 1:1/8) were studied as a function of Mn\textsuperscript{2+} concentration. It was found that the luminescence did not change systematically as the amount of Mn\textsuperscript{2+} was changed, Figures 4.3-4.6. Figure 4.7 is a plot of emission intensity versus Mn\textsuperscript{2+} concentration. It appeared that the highest emission seemed to consistently come from samples that were synthesized using a theoretical Mn\textsuperscript{2+} concentration of 0.01\% (0.003\% by elemental analysis). Emission from this Mn\textsuperscript{2+} concentration employed in doping was studied as a function of core/shell concentration as shown in Figures 4.4–4.6.
Figure 4.3 Luminescence spectra of CdS:Mn$^{2+}$/CdS (1:1) with various Mn$^{2+}$ concentrations, excitation λ 400 nm.

Figure 4.4 Luminescence spectra of CdS:Mn$^{2+}$/CdS (1:1/2) with various Mn$^{2+}$ concentrations, excitation λ 400 nm.
Figure 4.5 Luminescence spectra of CdS:Mn$^{2+}$/CdS (1:1/4) with various Mn$^{2+}$ concentrations, excitation $\lambda$ 400 nm.

Figure 4.6 Luminescence spectra of CdS:Mn$^{2+}$/CdS (1:1/8) with various Mn$^{2+}$ concentrations, excitation $\lambda$ 400 nm.
4.2.3 Luminescence of CdS:Mn$^{2+}$/CdS Quantum Dots Studied as a Function of Core:shell Concentration

While the emission of CdS:Mn$^{2+}$/CdS cannot be easily tuned by systematically changing the dopant concentration there seems to be a direct correlation between the emission intensity and the level of shell material. Figure 4.8 shows the emission of CdS:Mn$^{2+}$/CdS at a theoretical Mn$^{2+}$ concentration of 0.01% (the amount taken in the synthesis; the actual dopant amount was determined by elemental analysis is indicated on the individual core/shell system emission spectra in 4.2.2). As the amount of shell material is decreased the emission increases with 1:1/8 being the most emissive. At the higher shell concentrations it is likely that CdS:Mn$^{2+}$, CdS:Mn$^{2+}$/CdS, and CdS are all contributing to the emission. As the amount of shell is decreased there is less
CdS in the system and the CdS:Mn\(^{2+}\)/CdS emission is enhanced. Since CdS:Mn\(^{2+}\)/CdS, CdS:Mn\(^{2+}\), and CdS all emit at the same wavelength it is difficult to differentiate the individual contributions to the emission. This was further investigated by generating the core/shell quantum dots by Method II (mixture method) and these studies are detailed in Chapter 5.

![Luminescence spectra of CdS:Mn\(^{2+}\)/CdS](image)

**Figure 4.8** Luminescence spectra of CdS:Mn\(^{2+}\)/CdS with a 0.01% theoretical doping of Mn\(^{2+}\) doping at varying core/shell concentrations.
Figure 4.9 Plot of emission intensity as a function of shell concentration of CdS:Mn$^{2+}$/CdS with a theoretical doping of 0.01% Mn$^{2+}$.

4.2.4 Emission Lifetimes of CdS:Mn$^{2+}$/CdS

Determination of the emission lifetimes of the CdS:Mn$^{2+}$/CdS systems were extremely difficult due to the low quantum yields of the samples. Time-resolved emission spectroscopy (TRES) was used to determine that the 650 nm emission was indeed due to luminescence and not due to light scattering. A CdS:Mn$^{2+}$/CdS (1:1/16, 0.01% Mn$^{2+}$) sample was synthesized and the TRES data was compared to the emission spectra, Figure 4.10. The TRES has intensity maximum at 650 nm like the emission spectrum indicating that the luminescence is real and not scattered light. The spike in the TRES after the 650 nm maximum is due to $2\lambda$ from the excitation wavelength. The lifetime was estimated to be about 7 ns from these studies.
4.3 Electron Paramagnetic Resonance (EPR) Studies of CdS:Mn\(^{2+}\)/CdS with Various Core:shell Ratios

The various core/shell systems were analyzed using electron paramagnetic resonance spectroscopy. Similar to CdS:Mn\(^{2-}\), the EPR spectra changed systematically with increasing amounts of Mn\(^{2-}\). At small Mn\(^{2-}\) concentrations, the characteristic 6-line for Mn\(^{2+}\) was observed. As the amount of Mn\(^{2+}\) was increased a loss of hyperfine structure and a broadening of the spectra occurred due to Mn\(^{2-}\)-Mn\(^{2+}\) dipole-dipole interactions. This was consistent with all CdS core/shell systems. The results are displayed in Figures 4.11-4.14 and summarized in Tables 4.2-4.5.
Figure 4.11 EPR spectra of CdS:Mn\textsuperscript{2+}/CdS (1:1) with varying Mn\textsuperscript{2+} concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn\textsuperscript{2+}</th>
<th>X2</th>
<th>X1</th>
<th>X2-X1</th>
<th>B</th>
<th>g</th>
<th>A (mT)</th>
<th>A (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES15</td>
<td>0.034</td>
<td>339.67</td>
<td>305.26</td>
<td>34.41</td>
<td>322.47</td>
<td>2.00</td>
<td>5.74</td>
<td>57.35</td>
</tr>
<tr>
<td>ES16</td>
<td>0.032</td>
<td>339.86</td>
<td>305.35</td>
<td>34.51</td>
<td>322.61</td>
<td>2.00</td>
<td>5.75</td>
<td>57.52</td>
</tr>
<tr>
<td>ES17</td>
<td>0.006</td>
<td>339.86</td>
<td>305.35</td>
<td>34.51</td>
<td>322.61</td>
<td>2.00</td>
<td>5.75</td>
<td>57.52</td>
</tr>
<tr>
<td>ES18</td>
<td>0.393</td>
<td>339.64</td>
<td>305.18</td>
<td>34.46</td>
<td>322.41</td>
<td>2.00</td>
<td>5.74</td>
<td>57.43</td>
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<tr>
<td>ES20*</td>
<td>12.7</td>
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<td></td>
</tr>
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</table>

Table 4.2 EPR parameters of CdS:Mn\textsuperscript{2+}/CdS (1:1) with varying Mn\textsuperscript{2+} concentrations. *Indicates that spectrum was too broad to calculate parameters.
Figure 4.12 EPR spectra of CdS:Mn$^{2+}$/CdS (1:1/2) with varying Mn$^{2+}$ concentrations.

Table 4.3 EPR parameters of CdS:Mn$^{2+}$/CdS (1:1/2) with varying Mn$^{2+}$ concentrations. * Indicates that spectrum was too broad to calculate parameters.
Figure 4.13 EPR spectra of CdS:Mn$^{2+}$/CdS (1:1/4) with varying Mn$^{2+}$ concentrations.

Table 4.4 EPR parameters of CdS:Mn$^{2+}$/CdS (1:1/4) with varying Mn$^{2+}$ concentrations. * Indicates that spectra were too broad to calculate parameters.
Figure 4.14 EPR spectra of CdS:Mn$^{2+}$/CdS (I:1/8) with varying Mn$^{2+}$ concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>X2</th>
<th>X1</th>
<th>X2-X1</th>
<th>B</th>
<th>g</th>
<th>A (mT)</th>
<th>A (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES26</td>
<td>0.042</td>
<td>341.27</td>
<td>305.93</td>
<td>35.34</td>
<td>323.6</td>
<td>2.00</td>
<td>5.89</td>
<td>58.90</td>
</tr>
<tr>
<td>ES27</td>
<td>0.311</td>
<td>340.9</td>
<td>305.42</td>
<td>35.48</td>
<td>323.16</td>
<td>2.00</td>
<td>5.91</td>
<td>59.13</td>
</tr>
<tr>
<td>ES28*</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES29*</td>
<td>3.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES30*</td>
<td>11.06</td>
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</table>

Table 4.5 EPR parameters of CdS:Mn$^{2+}$/CdS (1:1/8) with varying Mn$^{2+}$ concentrations. * Indicates that spectra were too broad to calculate parameters.

It may be seen from the EPR spectra of CdS:Mn$^{2+}$/CdS core/shell quantum dots that only at very low Mn$^{2+}$ dopant concentrations well resolved six line pattern is observed and becomes featureless at concentrations as low as 0.2% Mn$^{2+}$. The Mn$^{2+}$-Mn$^{2+}$ interactions and doping in multiple sites (tetrahedral, distorted, and surface sites on the shell) contribute to the broadening of the features and eventual loss of resolution.
4.4 X-Ray Diffraction Analysis of CdS:Mn$^{2+}$/CdS

The various CdS:Mn$^{2+}$/CdS systems were analyzed using x-ray diffraction to determine if the lattice structure would change upon addition of a CdS shell. The QDs maintained their zinc blende structure as seen in Figures 4.15-4.18. The particle sizes were calculated using Scherrer’s Equation and the results are summarized in Tables 4.6-4.9.

Figure 4.15 XRD patterns of CdS:Mn$^{2+}$/CdS (1:1) with varying Mn$^{2+}$ concentrations.
### Table 4.6 Particle sizes of CdS:Mn$^{2+}$/CdS (1:1) calculated from Scherrer’s Equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>Xc (radians)</th>
<th>FWHM (radians)</th>
<th>L</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES20</td>
<td>12.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES18</td>
<td>0.393</td>
<td>0.468</td>
<td>0.05</td>
<td>2.85</td>
<td>2.14</td>
</tr>
<tr>
<td>ES16</td>
<td>0.032</td>
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<td>0.05</td>
<td>2.95</td>
<td>2.21</td>
</tr>
<tr>
<td>ES15</td>
<td>0.034</td>
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<td>0.05</td>
<td>2.94</td>
<td>2.20</td>
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<tr>
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<td>0.006</td>
<td>0.467</td>
<td>0.06</td>
<td>2.82</td>
<td>2.12</td>
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</table>

Average $2.17 \pm 0.05$

Table 4.6 Particle sizes of CdS:Mn$^{2+}$/CdS (1:1) calculated from Scherrer’s Equation.

Figure 4.16 XRD patterns of CdS:Mn$^{2+}$/CdS (1:1/2) with varying Mn$^{2+}$ concentrations.
Table 4.7 Particle sizes of CdS:Mn$^{2+}$/CdS (1:1/2) calculated from Scherrer’s Equation.

![XRD patterns of CdS:Mn$^{2+}$/CdS (1:1/4) with varying Mn$^{2+}$ concentrations.](image-url)
Table 4.8 Particle sizes of CdS:Mn\(^{2+}\)/CdS (1:1/4) calculated from Scherrer’s Equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$%\text{Mn}^{2+}$</th>
<th>Xc (radians)</th>
<th>FWHM (radians)</th>
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<th>d (nm)</th>
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<tbody>
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<td>0.05</td>
<td>2.90</td>
<td>2.17</td>
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<td>ES33</td>
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<td>3.12</td>
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</tr>
<tr>
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<td>0.05</td>
<td>3.25</td>
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</tr>
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<td>ES31</td>
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<td>0.05</td>
<td>3.27</td>
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</table>

Average $2.30 \pm 0.16$

Figure 4.18 XRD patterns of CdS:Mn\(^{2+}\)/CdS (1:1/8) with varying Mn\(^{2+}\) concentrations.
<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn^{2+}</th>
<th>Xc (radians)</th>
<th>FWHM (radians)</th>
<th>L</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES30</td>
<td>11.06</td>
<td>0.467</td>
<td>0.06</td>
<td>2.61</td>
<td>1.96</td>
</tr>
<tr>
<td>ES29</td>
<td>3.24</td>
<td>0.467</td>
<td>0.06</td>
<td>2.79</td>
<td>2.10</td>
</tr>
<tr>
<td>ES28</td>
<td>1.24</td>
<td>0.465</td>
<td>0.05</td>
<td>3.09</td>
<td>2.32</td>
</tr>
<tr>
<td>ES27</td>
<td>0.311</td>
<td>0.466</td>
<td>0.05</td>
<td>3.17</td>
<td>2.38</td>
</tr>
<tr>
<td>ES26</td>
<td>0.042</td>
<td>0.466</td>
<td>0.05</td>
<td>3.11</td>
<td>2.33</td>
</tr>
</tbody>
</table>

**Average**  

\[ 2.22 \pm 0.18 \]

Table 4.9 Particle sizes of CdS:Mn\(^{2+}\)/CdS (1:1/8) calculated from Scherrer's Equation.

4.5 Major Conclusions for CdS:Mn\(^{2+}\)/CdS Quantum Dot Studies

It was discussed in Chapter 3 that CdS:Mn\(^{2+}\) quantum dots lack a definite emission pattern when systematically changing the dopant concentration. It was hypothesized that this could be due to their surface properties leading to the study of CdS:Mn\(^{2+}\)/CdS core/shell quantum dots. This hypothesis was tested by systematically adding varying concentration of the CdS shell after the CdS:Mn\(^{2+}\) core was formed for a given Mn\(^{2+}\) dopant concentration and varying the Mn\(^{2+}\) dopant concentration at a constant shell concentration. These reactions were carried out sequentially in the same reaction vessel (Method I; one pot synthesis). If surface defects were a major factor in affecting the emission intensity of the CdS:Mn\(^{2+}\) quantum dots we should have observed an increase in emission intensity as increasing concentrations of the shell was added to the CdS:Mn\(^{2+}\) core. However the exact opposite was observed, namely the emission intensity was inversely proportional to the concentration of the shell with the lowest concentration of the shell exhibiting the highest emission...
intensity. The dependence of emission intensity on Mn$^{2+}$ concentration for all shell concentrations was complex with generally intensity decreasing with increasing concentration of Mn$^{2+}$. When the Mn$^{2+}$ concentration is low and the shell concentration is increased, the decrease in emission intensity may be due to some of the Mn$^{2+}$ in the core migrating to the shell maintaining their tetrahedral environment as indicated by EPR. The $^4T_1$ states of Mn$^{2+}$ in the shell most likely get deactivated nonradiatively more rapidly compared to when they are in the core due to interaction with the solvent. When the Mn$^{2+}$ concentration was increased at a given shell concentration it distributed into various sites (tetrahedral, distorted) and the shell. The $^4T_1$ states of Mn$^{2+}$ in the shell are deactivated nonradiatively by the solvent water. In addition the Mn$^{2+}$-Mn$^{2+}$ interaction is also extensive as indicated by the broadening of the EPR features of Mn$^{2+}$ eventually becoming broad and featureless. These conclusions have been further tested by synthesizing the CdS:Mn$^{2+}$/CdS quantum dots where the core and shell were synthesized separately (Method II; mixture synthesis) and then mixed. These results are discussed in the following chapter.

The quantum yields of CdS:Mn$^{2+}$/CdS and CdS:Mn$^{2+}$ were extremely low (<0.0001%) making it difficult to determine the lifetimes. Following TRES analysis the lifetime of CdS:Mn$^{2+}$/CdS (1:1/16, 0.01% Mn$^{2+}$) was determined to be approximately 7 ns, concluding that the $^4T_1 \rightarrow ^6A_1$ is an efficient process.
CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF CdS:Mn\textsuperscript{2+}/CdS QUANTUM DOTS (METHOD II)

5.1 Overview

The CdS:Mn\textsuperscript{2+}/CdS quantum dots synthesized by Method I (one pot synthesis) exhibited an inverse relationship between emission intensity and the concentration of the shell added. In order to understand this phenomenon better and to determine if the emission was the result of a mixture of three types of quantum dots CdS:Mn\textsuperscript{2+}, CdS, and CdS:Mn\textsuperscript{2+}/CdS a different synthetic approach to CdS:Mn\textsuperscript{2+}/CdS quantum dots was adopted. Method II was developed in which the CdS:Mn\textsuperscript{2+} core and CdS shell were synthesized separately and portions were kept for spectroscopic analysis. Following the formation of the core and shell quantum dots the two were mixed together and then characterized as a whole. Results clearly indicate that there is some extent of shell formation occurring resulting in an increase of emission. The emission intensity increases as the shell concentration decreases. Figure 5.1 is a scanning electron micrograph image of CdS:Mn\textsuperscript{2+}/CdS quantum dots (ES43) synthesized using Method II. It is difficult to determine the particle sizes due to the limits of the instrument but aggregation is evident.

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5.2 Optical Properties of CdS:Mn$^{2+}$/CdS (Method II)

5.2.1 Absorption Spectra, Bandgap Calculations, and Particle Size Determination

Prior to the addition of the CdS shell solution to the CdS:Mn$^{2+}$ core solution a small portion of each was kept aside for spectroscopic analysis. The absorbance was measured for the CdS:Mn$^{2+}$ core solutions (Figure 5.2), CdS shell solutions (Figure 5.3), and CdS:Mn$^{2+}$/CdS mixture solutions (Figure 5.4). The band gap energies and particle sizes were determined using Brus’ equation, Table 5.1. It was found that the
band gap energy for all three solutions were about 2.60 eV before and after mixing. There is little particle growth following addition of the shell solution to the core. Table 5.4 is a comparison of all the particle sizes calculated from Brus' Equation.

Figure 5.2 Uv-vis absorbance spectra of CdS:Mn$^{2+}$ core solutions used for the various core/shell solutions indicated by the line color.
Table 5.1 Band gap energies and particle sizes for CdS:Mn$^{2+}$ core solutions calculated from Brus’ Equation.

<table>
<thead>
<tr>
<th>Core</th>
<th>$E_g$ (eV)</th>
<th>$r (E_g)$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>2.63</td>
<td>3.13</td>
</tr>
<tr>
<td>1:1/2</td>
<td>2.64</td>
<td>3.02</td>
</tr>
<tr>
<td>1:1/4</td>
<td>2.63</td>
<td>3.09</td>
</tr>
<tr>
<td>1:1/8</td>
<td>2.64</td>
<td>3.07</td>
</tr>
<tr>
<td>1:1/16</td>
<td>2.64</td>
<td>3.06</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.07 ± 0.04</strong></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.3 Uv-vis absorbance spectra of CdS shell solutions used for the various core/shell solutions indicated by the line color.
Table 5.2 Band gap energies and particle sizes for CdS shell solutions calculated from Brus’ Equation.

<table>
<thead>
<tr>
<th>Shell</th>
<th>$E_g$ (eV)</th>
<th>$r$ ($E_g$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>2.60</td>
<td>3.41</td>
</tr>
<tr>
<td>1:1/2</td>
<td>2.68</td>
<td>2.77</td>
</tr>
<tr>
<td>1:1/4</td>
<td>2.64</td>
<td>3.01</td>
</tr>
<tr>
<td>1:1/8</td>
<td>2.59</td>
<td>3.49</td>
</tr>
<tr>
<td>1:1/16</td>
<td>2.66</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Average $3.12 \pm 0.32$

Figure 5.4 Uv-vis absorbance spectra of CdS:Mn$^{2+}$/CdS solutions after mixing individual core and shell solutions together. Percentages indicate percent Mn$^{2+}$ in each sample determined by elemental analysis.
Table 5.3 Band gap energies and particle sizes for CdS:Mn$^{2+}$/CdS mixture solutions calculated from Brus’ Equation and Scherrer’s Equation.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$E_g$ (eV)</th>
<th>$r(E_g)$ (nm)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>2.60</td>
<td>3.41</td>
<td>2.37</td>
</tr>
<tr>
<td>1:1/2</td>
<td>2.62</td>
<td>3.19</td>
<td>2.34</td>
</tr>
<tr>
<td>1:1/4</td>
<td>2.63</td>
<td>3.09</td>
<td>2.44</td>
</tr>
<tr>
<td>1:1/8</td>
<td>2.63</td>
<td>3.09</td>
<td>2.48</td>
</tr>
<tr>
<td>1:1/16</td>
<td>2.63</td>
<td>3.14</td>
<td>2.16</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.13 ± 0.13</strong></td>
<td><strong>2.36 ± 0.13</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4 Comparison of particle sizes calculated from Brus’ Equation for the core, shell, and core/shell solutions following mixing.

<table>
<thead>
<tr>
<th>Core</th>
<th>Shell</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$ (nm)</td>
<td>$r$ (nm)</td>
<td>$r$ (nm)</td>
</tr>
<tr>
<td>1:1</td>
<td>3.13</td>
<td>3.41</td>
</tr>
<tr>
<td>1:1/2</td>
<td>3.02</td>
<td>2.77</td>
</tr>
<tr>
<td>1:1/4</td>
<td>3.09</td>
<td>3.01</td>
</tr>
<tr>
<td>1:1/8</td>
<td>3.07</td>
<td>3.49</td>
</tr>
<tr>
<td>1:1/16</td>
<td>3.06</td>
<td>2.91</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.07 ± 0.04</strong></td>
<td><strong>3.12 ± 0.32</strong></td>
</tr>
</tbody>
</table>

5.2.2 Luminescence of CdS:Mn$^{2+}$/CdS Quantum Dots with Various Core:shell Ratios

An interesting phenomenon was found when studying the luminescence spectra of the core, shell, and mixture solutions. There was a direct correlation between the level of shell material and the emission intensity using Method II. There was a systematic increase in emission intensity as the amount of shell material was decreased. In contrast, the core solutions and the shell solutions lacked any systematic change in
emission intensity. In other words, Figure 5.5 shows the emission spectra for the core solutions used for the core/shell system (indicated by line color), at 650 nm the emission pattern is: \(1:1/2 > 1:1/16 > 1:1 > 1:1/8 > 1:1/4\). For the shell solutions the emission pattern is \(1:1/16 > 1:1/4 > 1:1/2 > 1:1/8 > 1:1\), Figure 5.6. When the two solutions are mixed together the emission pattern becomes \(1:1/16 > 1:1/8 > 1:1/4 > 1:1/2 > 1:1\), Figure 5.7. Figure 5.8 is a plot of emission intensity as a function of shell concentration.

![Image](image_url)

**Figure 5.5** Luminescence spectra of CdS:Mn^{2+} core solutions used for the various core/shell solutions indicated by the line color. Concentration on Mn^{2+} for each core is given in Table 5.5.
Figure 5.6 Luminescence spectra of CdS shell solutions used for the various core/shell solutions indicated by the line color.

Figure 5.7 Luminescence spectra of CdS: Mn\(^{2+}\)/CdS solutions after mixing individual core and shell solutions together. Concentration of Mn\(^{2+}\) is given in Table 5.5.
5.3 Electron Paramagnetic Resonance Studies of CdS:Mn$^{2+}$/CdS with Various Core:Shell Ratios

EPR of CdS:Mn$^{2+}$/CdS quantum dots synthesized using Method II shows the characteristic 6-line pattern indicative of Mn$^{2+}$ resting in slightly distorted tetrahedral sites, Figure 5.9. The EPR spectra are in agreement with those of CdS:Mn$^{2+}$/CdS synthesized using Method I. Table 5.5 shows the EPR parameters calculated for Method II samples.
Figure 5.9 EPR spectra of CdS:Mn$^{2+}$/CdS with various core:shell concentrations synthesized using Method II. Concentrations of Mn$^{2+}$ are given in Table 5.5.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>%Mn$^{2+}$</th>
<th>X2</th>
<th>X1</th>
<th>X2-X1</th>
<th>B</th>
<th>G</th>
<th>A (mT)</th>
<th>A (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.013</td>
<td>341.69</td>
<td>306.41</td>
<td>35.28</td>
<td>341.69</td>
<td>2.00</td>
<td>5.88</td>
<td>58.80</td>
</tr>
<tr>
<td>1:1/2</td>
<td>0.005</td>
<td>341.54</td>
<td>306.41</td>
<td>35.13</td>
<td>341.54</td>
<td>2.00</td>
<td>5.855</td>
<td>58.55</td>
</tr>
<tr>
<td>1:1/4</td>
<td>0.006</td>
<td>341.99</td>
<td>306.86</td>
<td>35.13</td>
<td>341.99</td>
<td>2.00</td>
<td>5.855</td>
<td>58.55</td>
</tr>
<tr>
<td>1:1/8</td>
<td>0.010</td>
<td>342.14</td>
<td>306.86</td>
<td>35.28</td>
<td>342.14</td>
<td>2.00</td>
<td>5.88</td>
<td>58.80</td>
</tr>
<tr>
<td>1:1/16</td>
<td>0.035</td>
<td>341.27</td>
<td>305.93</td>
<td>35.34</td>
<td>341.27</td>
<td>2.00</td>
<td>5.89</td>
<td>58.90</td>
</tr>
</tbody>
</table>

Table 5.5 EPR parameters for CdS:Mn$^{2+}$/CdS with varying core:shell concentrations.

5.4 X-Ray Diffraction Analysis of CdS:Mn$^{2+}$/CdS

The crystal lattice structure of CdS:Mn$^{2+}$/CdS QDs synthesized using Method II was determined to be zinc blende powder from x-ray diffraction pattern as shown in
Figure 5.10. This is in agreement with CdS:Mn$^{2+}$/CdS QDs synthesized using Method I. Table 5.6 shows the particle sizes determined using Scherrer’s Equation.

Figure 5.10 XRD patterns of CdS:Mn$^{2+}$/CdS with varying core:shell concentrations synthesized using Method II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core:shell</th>
<th>% Mn$^{2+}$</th>
<th>$\theta$ (radians)</th>
<th>FWHM (radians)</th>
<th>$L$</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES39</td>
<td>1:1</td>
<td>0.01</td>
<td>0.47</td>
<td>0.05</td>
<td>3.16</td>
<td>2.37</td>
</tr>
<tr>
<td>ES40</td>
<td>1:1/2</td>
<td>0.00</td>
<td>0.47</td>
<td>0.05</td>
<td>3.12</td>
<td>2.34</td>
</tr>
<tr>
<td>ES41</td>
<td>1:1/4</td>
<td>0.01</td>
<td>0.47</td>
<td>0.05</td>
<td>3.25</td>
<td>2.44</td>
</tr>
<tr>
<td>ES42</td>
<td>1:1/8</td>
<td>0.01</td>
<td>0.47</td>
<td>0.05</td>
<td>3.31</td>
<td>2.48</td>
</tr>
<tr>
<td>ES43</td>
<td>1:1/16</td>
<td>0.03</td>
<td>0.46</td>
<td>0.05</td>
<td>2.88</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Average $2.36 \pm 0.13$

Table 5.6 Particle sizes of CdS:Mn$^{2+}$/CdS with varying core:shell concentrations synthesized using Method II calculated by Scherrer’s Equation.
5.5 Major Conclusions Drawn from CdS:Mn\textsuperscript{2+}/CdS (Method II)

The CdS:Mn\textsuperscript{2+}/CdS quantum dots synthesized by Method I (one pot synthesis) and Method II (mixture synthesis) yielded nanoparticles with similar properties. The latter showed a clear inverse correlation between the concentration of the shell and the Mn\textsuperscript{2+} centered emission intensity corresponding to the \( ^4A_1 - ^6T_1 \) electronic transition when the dopant concentration was low. This correlation was evident despite the fact that the Mn\textsuperscript{2+} concentration was not constant for the various shell concentrations. In the core/shell system obtained Method II the emission intensity was thus more sensitive to the shell concentration than the concentration of Mn\textsuperscript{2+}. This supports the conclusion arrived at for the quantum dots obtained by Method I, namely that as the shell concentration is increased the Mn\textsuperscript{2+} migrates to the shell from the core resulting in greater nonradiative deactivation of the \( ^4A_1 \) Mn\textsuperscript{2+} excited state by the solvent molecules resulting in emission intensity decrease. The difference in the emission properties of quantum dots obtained by one pot and mixture synthesis may stem from the fact that the former yields shells which are not uniform but are patchy while the latter yields more uniform shells. Efforts to obtain TEM images to confirm this possibility were unsuccessful as the quantum dots melted under the electron beam. In both systems the emission appears to be more sensitive to Mn\textsuperscript{2+} concentration than the EPR spectra. A systematic change in Mn\textsuperscript{2+} concentration results in a systematic change in EPR spectra but not for emission. Investigation of other quantum dot
systems such as CdS:Mn$^{2+}$/ZnS and ZnS:Mn$^{2+}$/CdS could provide a better understanding of the cores/shell systems.
CHAPTER VI

SYNTHESIS AND CHARACTERIZATION OF CdS:Mn$^{2+}$/ZnS QUANTUM DOTS (METHOD I)

6.1 Overview

CdS:Mn$^{2+}$/ZnS core/shell quantum dots were first reported by Holloway using a reverse micelle synthetic approach (66-68). Before this, research on core/shell quantum dots was concentrated on undoped systems such as CdSe/ZnS, ZnSe/ZnS, and CdSe/CdS (11, 56-59). The introduction of a dopant adds new and interesting properties to the nanocrystals such as dopant centered emission and magnetic properties which can be monitored to gain a fundamental understanding of such systems. The role of the shell depending on the nature of the shell could be envisioned as minimizing surface defects, surface passivation, and confining excitons to the host core lattice. We have investigated the CdS:Mn$^{2+}$/CdS quantum dots as discussed in Chapters 4 and 5 and have extended these studies to the CdS:Mn$^{2+}$/ZnS quantum dots to gain a better understanding of the doped core/shell quantum dots. A series of CdS:Mn$^{2+}$/ZnS quantum dots were synthesized using Method I (one pot synthesis). Various core/shell ratios were employed and the quantum dots were characterized by uv-vis absorbance, luminescence, and EPR spectroscopy and X-ray powder diffraction.
Figure 6.1 TEM image of CdS:Mn$^{2+}$/ZnS (1:1/4, 0.01% Mn$^{2+}$) with samples on Formvar grid and electron beam energy of 200kV.

6.2 Optical Properties of CdS:Mn$^{2+}$/ZnS Quantum Dots (Method I)

6.2.1 UV-Vis Absorption Spectra

Absorbance spectra of CdS:Mn$^{2+}$/ZnS shows new absorbance maxima at 310 nm due to the ZnS shell. The quantum dots with small shell concentrations, 1:1/16 and 1:1/8, exhibited two shoulders at 310 nm and 450 nm. The 320 nm peak is due to the ZnS shell and the 450 nm peak is due to the CdS core. Bandgap energies and particle sizes
are given in Table 6.1. As the shell concentration decreases the bandgap energy decreases. The quantum dots with 1:1 core:shell ratio has a slightly larger bandgap than 1:1/2 which could be due to the presence of individual ZnS nanoparticles in solution.

Figure 6.2 Uv-vis absorbance spectra of CdS:Mn^{2+}/ZnS with varying core/shell ratios. Absorbance was set to 0.2 at 320 nm before performing emission studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn^{2+}</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES59</td>
<td>0.004</td>
<td>4.069</td>
</tr>
<tr>
<td>ES60</td>
<td>0.006</td>
<td>4.065</td>
</tr>
</tbody>
</table>
Table 6.1 Comparison of band gap energies of CdS:Mn$^{2+}$/ZnS with various core/shell ratios. As the amount of shell is reduced so is the band gap energy.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ES61</td>
<td>0.011</td>
<td>4.042</td>
<td></td>
</tr>
<tr>
<td>ES62</td>
<td>0.015</td>
<td>3.959</td>
<td></td>
</tr>
<tr>
<td>ES63</td>
<td>0.045</td>
<td>4.011</td>
<td></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>4.029 ± 0.046</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2.2 Luminescence spectra of CdS:Mn$^{2+}$/ZnS Quantum Dots with Various Core:shell Ratios

The luminescence of CdS:Mn$^{2+}$/ZnS was measured for the various core:shell ratios. The excitation is very broad due to the presence of the two semiconductors as seen in Figure 6.3. The emission wavelength was set to 590 nm for the excitation scan. The quantum yield was considerably higher following addition of the ZnS shell. Only one scan was needed to obtain spectra with good signal to noise ratio whereas with the CdS:Mn$^{2+}$ and CdS:Mn$^{2+}$/CdS quantum dots averaging ten scans was necessary. The emission spectra were obtained using both excitation maxima, 320 and 400 nm, and are shown in Figures 6.4 and 6.6, respectively.

Following the addition of the ZnS shell the emission maximum blue-shifts from 650 nm to 590 nm. Some of this shift may arise due to the addition of a shell of higher bandgap material ZnS to the lower band gap core CdS:Mn$^{2+}$ thereby confining the excitons to the core lattice. However, the major contribution is due to the migration of the Mn$^{2+}$ cations to the ZnS as shown by EPR spectra, section 6.3. The ZnS:Mn$^{2+}$ quantum dots emit at 590 nm providing the rationale for the emission maximum
shifting form 650 nm to 590 nm as the ZnS shell concentration is increased. The inverse relationship between the shell concentration and emission intensity stems from the Mn$^{2+}$-Mn$^{2+}$ interactions and the nonradiative deactivation of the Mn$^{2+}$ $^4T_1$ excited state by the solvent molecules.

Figure 6.3 Excitation spectra of CdS:Mn$^{2+}$/ZnS quantum dots with various core/shell ratios. Emission wavelength was set to 590 nm.
Figure 6.4 Emission spectra of CdS:Mn$^{2+}$/ZnS with various core/shell ratios. Excitation wavelength was set to 400 nm.

Figure 6.5 Plot of emission intensity (at 590 nm) versus shell concentration of CdS:Mn$^{2+}$/ZnS with theoretical Mn$^{2+}$ concentration of 0.01% (excitation wavelength 400 nm).
Figure 6.6 Emission spectra of CdS:Mn$^{2+}$/ZnS with various core:shell ratios. Excitation wavelength was set to 320 nm.

Figure 6.7 Plot of emission intensity (at 590 nm) versus shell concentration of CdS:Mn$^{2+}$/ZnS with theoretical Mn$^{2+}$ concentration of 0.01% (excitation wavelength of 320 nm).
6.2.3 Emission Lifetimes of CdS:Mn$^{2+}$/ZnS Quantum Dots

Since the quantum yield of CdS:Mn$^{2+}$/ZnS is much improved over CdS:Mn$^{2+}$ and CdS:Mn$^{2+}$/ZnS it was easier to obtain convincing lifetime data. Following original reports of lifetimes of Mn$^{2+}$ doped QDs by Bhargava further research has discounted that originally reported by Bhargava (43). Bhargava originally reported that as the size of the semiconductor is reduced down to the nanoscale there is a subsequent increase in the rate of energy transfer between the ZnS host and the 3d energy states of the Mn$^{2+}$ dopant. The group claimed that at the nanoscale the process was more efficient thereby decreasing the lifetime. However, other groups claimed that as the size was reduced the decrease in lifetime was due to Mn$^{2+}$-Mn$^{2+}$ interactions (56). Our data supports the latter claims. Keeping the dopant concentration constant and increasing the shell concentration there was a subsequent increase in emission lifetime. This further supports evidence that the Mn$^{2+}$ is migrating to the ZnS shell. As the shell becomes larger the Mn$^{2+}$ active sites are further apart decreasing the extent of Mn$^{2+}$-Mn$^{2+}$ interactions and thereby increasing the lifetime as shown in Figure 6.8 and summarized in Table 6.2. It may be seen from the table there is a distribution of lifetimes due to the presence of Mn$^{2+}$ in various sites. The lifetime with the maximum contribution ($\geq 80\%$) is plotted as a function of shell concentration in Figure 6.8. While the lifetime increases with the concentration of the shell, the emission intensity decreases due to lowered quantum yield from increased nonradiative decay of the Mn$^{2+}$ $^4T_1$ excited state.
Figure 6.8 Lifetime with maximum contribution versus core/shell concentration of CdS:Mn\(^{2+}\)/ZnS. Lifetime contributions are given in Table 6.1.

<table>
<thead>
<tr>
<th>Sample CdSMn(^{2+})/ZnS</th>
<th>(\tau_1 (\mu s))</th>
<th>(f (%))</th>
<th>(\tau_2 (\mu s))</th>
<th>(f (%))</th>
<th>(\tau_3 (\mu s))</th>
<th>(f (%))</th>
<th>(\tau_4 (\mu s))</th>
<th>(f (%))</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1.04</td>
<td>96.9</td>
<td>47.0</td>
<td>3.06</td>
<td>11.0</td>
<td>3.98</td>
<td>63.0</td>
<td>3.09</td>
<td>1.06</td>
</tr>
<tr>
<td>1:1/2</td>
<td>0.748</td>
<td>87.9</td>
<td>4.17</td>
<td>5.08</td>
<td>11.0</td>
<td>3.98</td>
<td>63.0</td>
<td>3.09</td>
<td>1.00</td>
</tr>
<tr>
<td>1:1/4</td>
<td>0.723</td>
<td>5.76</td>
<td>0.723</td>
<td>80.0</td>
<td>9.56</td>
<td>5.00</td>
<td>86.0</td>
<td>9.25</td>
<td>1.07</td>
</tr>
<tr>
<td>1:1/8</td>
<td>0.010</td>
<td>5.68</td>
<td>0.233</td>
<td>92.1</td>
<td>16.0</td>
<td>0.321</td>
<td>120</td>
<td>1.94</td>
<td>1.04</td>
</tr>
<tr>
<td>1:1/16</td>
<td>0.268</td>
<td>91.4</td>
<td>0.296</td>
<td>2.34</td>
<td>2.35</td>
<td>3.04</td>
<td>120</td>
<td>3.14</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 6.2 CdS:Mn\(^{2+}\)/ZnS lifetimes obtained by excitation at 320 nm and emission at 650 nm.
6.3 Electron Paramagnetic Resonance Studies of CdS:Mn$^{2+}$/ZnS with Various Core:shell Ratios

Unlike the CdS:Mn$^{2+}$/CdS quantum dots that were also synthesized using Method I all of the CdS:Mn$^{2+}$/ZnS core/shell systems did not show the characteristic 6-line pattern attributed to Mn$^{2+}$ present in the tetrahedral lattice sites in their EPR spectra displayed in Figure 6.9. In fact, only the lowest concentration of shell material displayed the 6-line pattern and the forbidden transitions which indicate that as the concentration of shell increases the behavior of CdS:Mn$^{2+}$/ZnS system is very different from that of CdS:Mn$^{2+}$/CdS system. This difference can be attributed to the greater migration of Mn$^{2+}$ from the CdS:Mn$^{2+}$ core lattice to the ZnS shell compared to the CdS shell. This is manifested in broadening of the EPR signal which indicates Mn$^{2+}$-Mn$^{2+}$ dipole-dipole interactions. As the Mn$^{2+}$ migrates towards the ZnS shell the cations move in closer vicinity of each other. Given the extremely small size of QDs even a slight migration will result in peak broadening. The ionic radii of Mn$^{2+}$ (0.80 Å) and Zn$^{2+}$ (0.74 Å) are closer in value than those of Mn$^{2+}$ and Cd$^{2+}$ (0.97 Å) (69). Therefore, the Mn$^{2+}$ will be more likely to migrate to the ZnS lattice replacing a Zn$^{2+}$ cation because the crystal lattice will be less distorted. This is further evidenced by the results given in Chapter 7. Other groups have reported Mn$^{2+}$ migration within nanocrystal systems as well (12, 70).
Figure 6.9 EPR spectra of CdS:Mn$^{2+}$/ZnS with various core:shell ratios. The Mn$^{2+}$ concentrations are given in Table 6.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>X2</th>
<th>X1</th>
<th>X2-X1</th>
<th>B</th>
<th>G</th>
<th>A (mT)</th>
<th>A (G)</th>
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<td></td>
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<tr>
<td>ES63</td>
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<td>341.84</td>
<td>306.86</td>
<td>34.98</td>
<td>341.84</td>
<td>2.00</td>
<td>5.83</td>
<td>58.30</td>
</tr>
</tbody>
</table>

Table 6.3 EPR parameters calculated for CdS:Mn$^{2+}$/ZnS with various core:shell ratios. *Indicates that the peaks were too broad to calculate the EPR parameters.

6.4 X-Ray Diffraction Analysis of CdS:Mn$^{2+}$/ZnS

As the shell concentration increases the XRD diffraction pattern moves from that of CdS to ZnS as seen in Figure 6.10. This can be rationalized as XRD is a surface sensitive technique and at the smaller shell concentrations it is likely that there are
patches of ZnS on the CdS:Mn$^{2+}$ core and not a complete shell. The 1:1/16 sample has diffraction planes for both ZnS and CdS. As the shell is increased to 1:1/8 the ZnS diffraction peaks begin to dominate. Finally in the 1:1 sample there is no evidence of CdS diffraction planes indicating a complete shell formation with ZnS. If there was no shell growth than CdS diffraction planes would still be apparent because the concentrations of CdS and ZnS would be the same.

![Figure 6.10 XRD patterns of CdS:Mn$^{2+}$/ZnS with various core:shell ratios. The black and red lines represent the lines of diffraction of CdS and ZnS, respectively.](image-url)
Table 6.4 Particle sizes calculated from Scherrer's Equation of CdS:Mn$^{2+}$/ZnS with various core:shell ratios.

6.5 Major Conclusions Drawn from CdS:Mn$^{2+}$/ZnS

Following complete characterization of CdS:Mn$^{2+}$/ZnS it is concluded that the Mn$^{2+}$ impurity moves from the host CdS lattice to the ZnS shell for which it has greater affinity. This is evidenced by lifetime, luminescence, and EPR data. There is complete shell growth of ZnS on the CdS core according to XRD results. Our reports contradict those originally reported by Holloway et al (59, 60).
CHAPTER VII

SYNTHESIS AND CHARACTERIZATION OF ZnS:Mn\(^{2+}\)/CdS QUANTUM DOTS (METHOD II)

7.1 Overview

ZnS:Mn\(^{2+}\)/CdS quantum dots were synthesized using Method II. The objective was to study the effect of adding a CdS shell to the ZnS:Mn\(^{2+}\) core. We found as discussed in Chapter 6 that in CdS:Mn\(^{2+}\)/ZnS the Mn\(^{2+}\) cation migrated from the CdS:Mn\(^{2+}\) core to the ZnS shell as Mn\(^{2+}\) has higher affinity for the ZnS lattice than the CdS lattice. It is important and interesting to determine if in the reverse situation of CdS shell on ZnS:Mn\(^{2+}\) the Mn\(^{2+}\) will be essentially confined to the core with minimum migration to the shell. This was investigated by examining luminescence and EPR spectra, and lifetime measurements. The TEM images shown in Figure 7.1 revealed extremely uniform shell formation around a completely spherical core. The particles were isolated and re-dispersed via sonication. They were then depositing on Cu grids. The particles are of varying size as seen from Figure 7.1 (a), (b), (c). Smaller particles (< 5 nm) can be seen in Figure 7.1 (d).
Figure 7.1 HRTEM image of ZnS:Mn$^{2+}$/CdS quantum dots synthesized using Method II.
7.2 Optical Properties of ZnS:Mn\(^{2+}\)/CdS (Method II)

7.2.1 UV-Vis Absorption Spectra and Bandgap Calculations

UV-vis absorption spectra were obtained for ZnS:Mn\(^{2+}\)/CdS with various core/shell concentrations and are displayed in Figure 7.2. Addition of a ZnS shell in increasing concentrations on a CdS:Mn\(^{2+}\) core resulted in a systematic increase in bandgap energy. This is however not seen with ZnS:Mn\(^{2+}\)/CdS. When a larger band gap shell is added to the smaller band gap core, the valence and conduction bands of the small bad gap core is affected through mixing of the energy states resulting in a higher band gap for the core/shell quantum dot compared to the core. This mixing depends on the concentration of the shell indicating that it is not an efficient process. Such an energy mixing leads to minimum perturbation of the band gap of the core with the higher energy when a lower band gap energy shell is added. The bandgap energy is approximately 2.61 eV for all of the samples as seen in Table 7.1. In the 1:1/16 sample there is the appearance of a second bandgap of 3.839 eV as seen in Figure 7.3. This indicates that at very small concentrations of CdS shell incomplete shell formation and free ZnS:Mn\(^{2+}\) without shell are likely present. As with CdS:Mn\(^{2+}\)/ZnS, the particle sizes of ZnS:Mn\(^{2+}\)/CdS could not be calculated using the Brus equation because the equation takes into account the bandgap of the bulk semiconductor. The presence of two band gaps leads to mixing of energy states and the Brus model cannot be employed.
Figure 7.2 Uv-vis absorption spectra of ZnS:Mn$^{2+}$/CdS with varying core/shell concentrations.

Table 7.1 Comparison of bandgap energies of ZnS:Mn$^{2+}$/CdS with various core/shell and Mn$^{2+}$ concentrations. The Mn$^{2+}$ concentrations were determined by elemental analysis.
Figure 7.3 Derivative of absorbance plot of ZnS:Mn$^{2+}$/CdS. Appearance of second bandgap due to incomplete shell formation and possibly individual ZnS:Mn$^{2+}$ quantum dots.

7.2.2 Luminescence Spectra of ZnS:Mn$^{2+}$/CdS Quantum Dots with Various Core to Shell Ratios

Emission spectra were recorded for both the core and the core/shell solutions in water. As with the CdS:Mn$^{2+}$ quantum dots prior to the addition of shell the emission intensity did not exhibit a systematic change with Mn$^{2+}$ concentration and the ZnS:Mn$^{2+}$ core synthesized with the same concentration of Mn$^{2+}$ exhibited different emission intensities from different synthesis as shown in Figure 7.5. The Mn$^{2+}$ concentrations for each given in Table 7.1 indicate that the same concentration of Mn$^{2+}$ does not get incorporated in the ZnS lattice even though the same concentration is taken in the synthesis. The main contributing factor to the variation in the emission intensity for the various quantum dots appears to stem from the difference in their
Mn\textsuperscript{2+} concentrations. Following addition of the CdS shell the same phenomena was seen as with CdS:Mn\textsuperscript{2+}/CdS and CdS:Mn\textsuperscript{2+}/ZnS, Figure 7.7. The 1:1/16 sample was the most emissive and the 1:1 sample was the least emissive. As can be expected the smaller bandgap material limited the amount of energy transfer to the ZnS:Mn\textsuperscript{2+} core and instead of increasing the emission instead quenched it. The emission maximum of CdS:Mn\textsuperscript{2+} blue shifted from 650 nm to 590 nm due to the migration of Mn\textsuperscript{2+} to the ZnS shell. Here the emission maximum stays at 590 nm indicating that there is no Mn\textsuperscript{2+} migration. More evidence for this can be seen in the EPR section, 7.3.

Figure 7.4 Excitation of ZnS:Mn\textsuperscript{2+} core solutions prior to addition of CdS shell. The core used for each core/shell solution is indicated by the line color.
Figure 7.5 Emission of ZnS:Mn$^{2+}$ core solutions prior to addition of CdS shell. The core used for each core/shell solution is indicated by the line color.

Figure 7.6 Excitation of ZnS:Mn$^{2+}$/CdS with various core/shell ratios.
Figure 7.7 Emission of ZnS:Mn\(^{2+}\)/CdS with various core/shell ratios.

Figure 7.8 Plot of emission intensity versus core:shell ratio of ZnS:Mn\(^{2+}\)/CdS.
7.2.3 ZnS:Mn$^{2+}$/CdS Lifetimes

The lifetime data of ZnS:Mn$^{2+}$/CdS supports our lifetime data of CdS:Mn$^{2+}$/ZnS. Figure 7.9 shows the decay curve for ZnS:Mn$^{2+}$/CdS (1:1). As the shell concentration decreases there is a subsequent increase in emission lifetime as listed in Table 7.2. At the larger shell concentrations the emission is quenched by the smaller bandgap CdS shell leading to shortening of the emission lifetime. As the shell concentration increases the small bad gap CdS shell competes for the energy of the ZnS exciton with Mn$^{2+}$ leading to decreased emission intensity and lifetime.

![Emission lifetime decay curve of ZnS:Mn$^{2+}$/CdS (1:1).](image-url)

Figure 7.9 Emission lifetime decay curve of ZnS:Mn$^{2+}$/CdS (1:1).
Table 7.2 ZnS:Mn\(^{2+}\)/CdS emission lifetimes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_1) ((\mu)s)</th>
<th>(f) (%)</th>
<th>(\tau_2) ((\mu)s)</th>
<th>(f) (%)</th>
<th>(\tau_3) ((\mu)s)</th>
<th>(f) (%)</th>
<th>(\chi^2)</th>
</tr>
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<tbody>
<tr>
<td>ZnS:Mn(^{2+})</td>
<td>410</td>
<td>89.1</td>
<td>0.148</td>
<td>9.04</td>
<td>16.0</td>
<td>1.86</td>
<td>1.23</td>
</tr>
<tr>
<td>ZnS:Mn(^{2+})/CdS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>380</td>
<td>62.1</td>
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<td>26.1</td>
<td>0.00045</td>
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<td>1:1/4</td>
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<td>47.0</td>
<td>4.73</td>
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<td>4.33</td>
<td>5.14</td>
<td>0.56</td>
<td>1.07</td>
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</table>

7.3 Electron Paramagnetic Resonance Studies of ZnS:Mn\(^{2+}\)/CdS with Various Core to Shell Ratios

As anticipated following formation of a CdS shell on ZnS: Mn\(^{2+}\) there was no migration of Mn\(^{2+}\) from the ZnS lattice to the CdS shell. The characteristic 6-line pattern attributed to Mn\(^{2+}\) resting in slightly distorted tetrahedral sites was seen in all five samples as shown in Figure 7.10. This indicates that the Mn\(^{2+}\) do not migrate to the CdS shell from the ZnS core to which these ions have a higher affinity. Extensive migration of Mn\(^{2+}\) from the CdS core to the ZnS shell was observed in the CdS:Mn\(^{2+}\)/ZnS core/shell quantum dots. The EPR parameters for ZnS:Mn\(^{2+}\)/CdS quantum dots are listed in Table 7.3.
Figure 7.10 EPR spectra of ZnS:Mn$^{2+}$/CdS with various core/shell ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn$^{2+}$</th>
<th>X2</th>
<th>X1</th>
<th>X2-X1</th>
<th>B</th>
<th>g</th>
<th>A (mT)</th>
<th>A (G)</th>
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<tr>
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<td>0.011</td>
<td>341.07</td>
<td>305.83</td>
<td>35.24</td>
<td>341.07</td>
<td>2.00</td>
<td>5.87</td>
<td>58.73 ± 0.37</td>
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<td>ES54</td>
<td>0.09</td>
<td>341.07</td>
<td>305.83</td>
<td>35.24</td>
<td>341.07</td>
<td>2.00</td>
<td>5.87</td>
<td>58.73 ± 0.37</td>
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<td>ES55</td>
<td>0.034</td>
<td>341.17</td>
<td>305.93</td>
<td>35.24</td>
<td>341.17</td>
<td>2.00</td>
<td>5.87</td>
<td>58.73 ± 0.37</td>
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<td>ES56</td>
<td>0.033</td>
<td>341.07</td>
<td>305.83</td>
<td>35.24</td>
<td>341.07</td>
<td>2.00</td>
<td>5.87</td>
<td>58.73 ± 0.37</td>
</tr>
<tr>
<td>ES57</td>
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<td>341.07</td>
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<td>2.00</td>
<td>5.79</td>
<td>57.90 ± 0.37</td>
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</table>

Table 7.3 EPR parameters calculated for ZnS:Mn$^{2+}$/CdS with various core/shell ratios.

7.4 X-Ray Diffraction Analysis of ZnS:Mn$^{2+}$/CdS Quantum Dots

As the shell concentration increases the XRD diffraction pattern of ZnS:Mn$^{2+}$/CdS moves from that of ZnS to that of CdS as can be expected and displayed in Figure 7.11. This is similar to the results of CdS:Mn$^{2+}$/ZnS in which the diffraction pattern
shifted from that of CdS to that of ZnS. This is evidence for complete shell formation of CdS on the ZnS:Mn$^{2+}$ core. If there was incomplete shell formation than the diffraction pattern of ZnS would still be apparent. Particle sizes were calculated using Scherrer’s formula and are shown in Table 7.4.

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**Table 7.4 ZnS:Mn$^{2+}$/CdS particle sizes calculated using Scherrer’s equation.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Mn$^{2+}$</th>
<th>Xc (radians)</th>
<th>FWHM (radians)</th>
<th>L</th>
<th>d (nm)</th>
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<td>0.052</td>
<td>2.78</td>
<td>2.09 ± 0.16</td>
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<td>ES54</td>
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<td>2.25</td>
<td>1.69 ± 0.16</td>
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<td>2.07 ± 0.16</td>
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<td>ES56</td>
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<td>0.055</td>
<td>2.62</td>
<td>1.97 ± 0.16</td>
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<td>0.018</td>
<td>0.316</td>
<td>0.056</td>
<td>2.59</td>
<td>1.94 ± 0.16</td>
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---

Figure 7.11 XRD patterns of ZnS:Mn$^{2+}$/CdS with various core/shell ratios.
7.5 Major Conclusions Drawn from ZnS:Mn$^{2+}$/CdS

Complete characterization of ZnS:Mn$^{2+}$/CdS allows us to further confirm our CdS:Mn$^{2+}$/ZnS results. The addition of ZnS shell on CdS:Mn$^{2+}$ results in the migration of Mn$^{2+}$ to the ZnS shell. Addition of a smaller bandgap material such as CdS to ZnS:Mn$^{2+}$ results in competitive energy transfer from the ZnS core to the shell and the Mn$^{2+}$ dopant. There is no Mn$^{2+}$ migration to the from the ZnS core, with which it has higher affinity, to the CdS shell with which it has less affinity. The emission maximum does not shift from 590 nm characteristic of ZnS:Mn$^{2+}$ to 650 nm characteristic of CdS:Mn$^{2+}$ emission. Luminescence intensity and lifetime for the Mn$^{2+}$ centered emission ($^4A_1 - ^4T_1$ transition) decrease with increasing CdS shell due to competition with Mn$^{2+}$ for the energy transfer from ZnS core. As the shell concentration increases the XRD diffraction pattern shifts from that of ZnS to that of CdS indicating complete shell formation. Complete shell formation can also be seen in the TEM images of the larger particles.
CHAPTER VIII

CONCLUSIONS AND FUTURE DIRECTIONS

8.1 Conclusions

The central hypothesis of this research is that optical properties of doped quantum dots can be significantly modified by the addition of a shell of the same or different quantum dot (same or different band gap energy). The addition of a shell resulting in a core/shell quantum dots could lead to: (i) the mixing of the conduction and valence band energies when the band gaps of the core and shell are different resulting in changes in the absorption and emission properties; (ii) the migration of the dopant from the core to the shell and vice versa depending on the affinity of the dopant for the individual crystal lattices; (iii) such a migration resulting in changes in the absorption and emission spectra and emission lifetimes and spectral properties of the dopant itself; (iv) the shell with a smaller band gap than the core can compete for the exciton energy with the dopant and result in reduced emission intensity and lifetime characteristic of the dopant; and (v) the x-ray diffraction pattern of the core/shell quantum dots could also exhibit significant shift from one that is characteristic of the core to one that is characteristic of the shell depending on the concentration of the shell added.
The central hypothesis was tested employing the quantum dots ZnS and CdS interchangeably as the core and shell. The core was doped with varying concentrations of Mn$^{2+}$ to determine the effects (i)-(iv) listed above by monitoring the emission intensity and lifetime of the $^4T_1 - ^6A_1$ transition of Mn$^{2+}$ arising from the exciton energy transfer from the quantum dot in the core and the characteristic six line EPR spectrum of Mn$^{2+}$. Additionally XRD patterns and TEM images were also to confirm the formation of a uniform shell. Then main conclusions from these studies are summarized and future research directions based on these studies are suggested.

In order to test the central hypothesis a novel green synthetic method for the core/shell quantum dots was developed. Quantum dots are often synthesized at high temperatures in organic solvents from organometallic precursors and require the use of capping ligands to prevent their aggregation. Such synthetic procedures also do not readily lend themselves to doping with magnetic nuclei such as Mn$^{2+}$ and trivalent lanthanide ions. These quantum dots also cannot be dispersed in an aqueous medium for a variety of applications such as biological imaging and sensor fabrication. Previous attempts to synthesize quantum dots in an aqueous medium employed a large excess of phosphates and polyphosphates and surfactants to stabilize the quantum dots as colloids. This invariably led to the irreversible adsorption of the stabilizers on the quantum dots rendering further surface modifications such as the systematic addition of a shell or other ligands difficult and challenging. In addition the use of phosphates presents a challenge for doping with trivalent lanthanides due to
the affinity of these ions for phosphates leading only to surface doping and not doping of the crystal lattice and often precipitation of the lanthanide phosphates.

A novel synthetic method at room temperature in the aqueous phase employing dodecyl sulfate (DS) salts of Zn and Cd, namely Zn(DS)$_2$ and Cd(DS)$_2$ was developed in this research. This has the advantage that the surfactant stabilizer dodecyl sulfate is only present in stoichiometric amounts as the core metal ion Zn$^{2+}$ and Cd$^{2+}$ and the quantum dots obtained from this synthesis can be isolated by precipitation resulting in minimum adsorption of the surfactant on the surface of the quantum dots. Employing the DS salt as precursor the core quantum dots ZnS:Mn and CdS:Mn with varying concentrations of Mn$^{2+}$ and core/shell quantum dots CdS:Mn/CdS, CdS:Mn/ZnS, and ZnS:Mn/CdS with varying concentrations of the shell and Mn$^{2+}$ were synthesized and characterized by absorption and emission spectroscopy, emission lifetime, EPR spectroscopy, XRD and TEM. Two synthetic procedures for the addition of the shell were developed, namely the addition of the shell at the desired concentration in relation to the core subsequent to the formation of the core quantum dots in the same reaction (one pot synthesis, Method I) and the formation of the core and shell quantum dots separately and mixing the desired concentration of the shell quantum dot to the core quantum dot (mixture synthesis, Method II). Significant results and conclusions of these studies are:
1. While EPR of CdS:Mn shows a systematic change as a function of Mn dopant concentration, this is not reflected in the emission spectra. The emission intensities vary in a random manner as a function of Mn concentration and the emission maximum blue-shifts at higher Mn concentrations. This could be due to the surface properties and doping occurring both in the crystal lattice and the surface of the quantum dots. This provided the impetus for the investigation of the core/shell quantum dots to gain an understanding of surface modification on their spectroscopic properties.

2. The Mn doped CdS core/shell systems were studied both as a function of Mn concentration and as a function of shell concentration employing synthesis Method I. When the Mn concentration was increased at a given shell concentration EPR indicated distribution of Mn into various sites and migration to the shell. Again, emission intensity did not exhibit a systematic change with Mn concentration. However, there was a direct correlation between the emission intensity and the shell concentration. As the shell concentration increased there was a systematic decrease in emission intensity. At low concentrations of Mn (theoretically 0.01%) EPR of CdS:Mn/CdS showed characteristic 6-line pattern indicative of Mn in slightly distorted tetrahedral sites. Following migration of Mn to the shell emission intensity is decreased due to nonradiative collisional deactivation of Mn $^4T_1$ states by the solvent water. Following TRES analysis the
lifetime was determined to be approximately 7 ns concluding that $^4T_1 \rightarrow ^6A_1$ is an efficient process.

3. CdS:Mn/CdS quantum dots studied using synthetic Method II (mixture synthesis) yielded similar results as those synthesized by Method I. The core/shell systems synthesized by Method II the emission intensity was more sensitive to the shell concentration than was to the concentration of Mn$^{2+}$. This supports the conclusion arrived at using Method I that the Mn migrates from the core to the shell resulting in nonradiative deactivation of the Mn excited state by the solvent molecules causing an emission decrease.

4. The emission intensity of CdS:Mn/CdS synthesized by both Methods I and II is more sensitive to Mn concentration than the EPR spectra.

5. The CdS:Mn/ZnS quantum dots were synthesized using Method I to further understand the role of the shell in doped quantum dot systems. Following complete characterization using a combination of lifetime, luminescence and EPR spectroscopy it was concluded that Mn was migrating to the ZnS shell. This migration along with the mixing of the energy levels of the small band gap core CdS with a large band gap shell ZnS resulted in a shift in the emission maximum from 650 nm characteristic of CdS:Mn to 590 nm characteristic of ZnS:Mn. XRD indicated complete shell growth of ZnS on the CdS core. This was discerned from the gradual disappearance of CdS diffraction pattern and the emergence of ZnS diffraction pattern as the shell
concentration increased. At the highest core/shell concentration only the ZnS diffraction pattern could be observed.

6. ZnS:Mn/CdS quantum dots were synthesized using Method II. Addition of a smaller bandgap material such as CdS to ZnS:Mn$^{2+}$ results in competitive energy transfer from the ZnS core to the shell and the Mn$^{2+}$ dopant. As indicated by EPR, there is no Mn$^{2+}$ migration from the ZnS core with which it has higher affinity to the CdS shell with which it has less affinity. This could be due to the larger difference in ionic radii of Mn$^{2+}$ (0.80 Å) and Cd$^{2+}$ (0.97 Å) and similarity in the ionic radii of Mn$^{2+}$ and Zn (0.74 Å). The emission maximum does not shift from 590 nm characteristic of ZnS:Mn$^{2+}$ to 650 nm characteristic of CdS:Mn$^{2+}$ emission also indicating that the Mn$^{2+}$ does not migrate from the core to the shell. Luminescence intensity and lifetime for the Mn$^{2+}$ centered emission ($^4T_1 - ^6A_1$ transition) decrease with increasing CdS shell due to competition with Mn$^{2+}$ for the energy transfer from ZnS core. As the shell concentration increases the XRD diffraction pattern shifts from that of ZnS to that of CdS indicating complete shell formation. Complete shell formation can also be seen in the TEM images of the larger particles.
8.2 Future Directions

The central hypothesis has been tested and supported employing the ZnS and CdS quantum dots interchangeably as core and shell and doping the core with Mn\(^{2+}\) ions. This has yielded core/shell systems with modified optical and other spectroscopic properties. The following future research directions are suggested to build on this research and understand better these core/shell systems:

1. Synthesize Mn doped core/shell quantum dots in nonaqueous media such as methanol to determine if the Mn migration is dependent on the environment.

2. Synthesize core/shell quantum dots with silica shell to eliminate the deactivation of the Mn \(^{4}T_1\) state by the solvent water and study the emission as a function of Mn concentration. Silica also has much higher band gap energy compared to CdS and ZnS which could result in minimum mixing of valence and conduction band energies.

3. Synthesize CdS:Mn/ZnS using Method II (mixture synthesis) to determine if similar TEM images can be obtained as with ZnS:Mn/CdS. Shell formation is difficult to discern when core and shell are the same material, such as CdS:Mn/CdS, because the core and the shell have the same density and transmission of electrons.

4. Dope the core/shell system with different metal ions such as trivalent lanthanides which have distinct metal centered emission and study the effect of dopant concentration and shell concentration.
5. Investigate the role of these core/shell quantum dots in applications such as sensors and bioimaging.
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