Temperature dependent photoluminescence (PL) studies were carried out on Cd$_x$Zn$_{1-x}$S/ZnS alloy core graded shell nanocrystals with varying composition. The effect of grading on the emission line width and hence exciton-phonon coupling is studied. Contrary to the consensus that narrow emission line width is observable with reduction in size (due to increased exciton-acoustic phonon coupling coefficient $\sigma$), an increased value is noted with size. Based on a theoretical report on graded core-shell NCs, the relationship between electron hole wave function overlap and exciton lifetime was invoked to understand this anomaly. Smaller sized alloy core-shell NCs (CdZnS/ZnS-I) have larger lifetime than that of larger NCs (CdZnS/ZnS-II) as determined from time-resolved spectroscopy. Thus, CdZnS/ZnS-I NCs should have smaller electron hole wave function overlap giving larger effective size of NCs even though the actual size, estimated from TEM, was smaller. Experimental evidence of graded core-shell nanocrystals reveal an additional functionality to control the emission linewidth in NCs.
4.1 Introduction:

Optical properties of nanocrystals (NCs) can be tuned by varying size or by doping impurity inside the NCs. Although such size tunable NCs are technologically important, small sized NCs are prone to defects, especially surface defects. The surface to volume ratio of NCs is very high, and with smaller size increases further. As a result, the photoluminescence (PL) is adversely affected in the small NCs. Luminescence behavior can be tuned over a wide range of energies without getting affected by these surface defects in alloy NCs [1–3]. For example, smaller sized CdSe NCs emit in blue region but are associated with surface defects as well [4,5]. When Cd$_{1-x}$Zn$_x$Se alloy is formed by diffusing Zn ions into CdSe blue emission can be achieved. Similarly in case of CdS, defects are prominent in almost all the sizes. These defects can be minimized by making an alloy of CdS with Se or with Zn [6,7]. Moreover, band gap engineering can be attained without changing the size of the NCs. The alloy NCs are classified in two sub-types: (i) homogeneous alloy NCs and (ii) graded NCs. In graded NCs, composition of constituent elements is changed gradually. Graded NCs are different than core-shell NCs where a shell of different material is coated on top of a core semiconductor. The interfacial strain in abrupt core-shell NCs is reduced in the graded NCs. The concentration of one material decreases from shell to core while that of the other material increases from core to shell. This allows one to have better crystallinity and hence higher PL efficiency. Variation in the reactivity of the precursors can be effectively used to form graded NCs [8–11]. In such reactions, one of the precursors is more reactive than the others and hence grows faster to form core of the NC whereas the slowly reacting precursor forms the shell. Bae et al. [8] allowed the reaction to proceed at elevated temperatures in chemical bath so that the shell precursors diffuse inside the core to form graded interface. Synthesis of homogeneous alloy of CdTeSe and graded structure of CdTe-CdSe NCs were reported by changing the concentration of Cd [12]. By varying the concentration of precursors, composition as well as morphology of graded NCs can be controlled [13].

In general, the luminescence line width (FWHM) of graded NCs is observed to be narrow at room temperature [2,8,10,14,15], and is attributed to the small size distribution (or reduced inhomogeneous broadening). Homogeneous broadening that originates due to scattering of excitons with optical and acoustic phonons is not addressed. Exciton–
phonon studies are important to understand energy relaxation pathways and thermal transport processes. None the less, some reports do address homogeneous broadening of the line width. For instance, the temperature dependent PL studies on CdSe QDs coated with CdS/CdZnS/ZnS multishells [22] and CdSe/ZnS QDs indicate different line widths due to the change in electron and hole overlap.

Increased coupling between exciton-acoustic phonon with decrease in size of CdSe due to quantum confinement effects is also noted [17]. Recently, it is reported [18] that the exciton-phonon coupling increases with decreasing size of CdTe which results in broadened emission line and is attributed to the quantum confinement. On the other hand, the temperature dependent PL study of CdTe [26] showed that the emission line width decreases with size due to enhanced exciton-acoustic phonon coupling constant. Theoretical calculations [27] also predict increased coupling between exciton–phonon in small particles. On the similar lines, in case of epitaxially grown CdSe/ZnCdSe quantum structures [28] confinement is observed to reduce LO-phonon coupling strength and increase interaction with acoustic phonons.

In alloyed CdSeS NCs, it is observed [29] that acoustic phonon contributes for broadening of the line width up to 130 K, while LO-phonon exciton interaction dominates beyond it. On the contrary, decreased exciton-phonon coupling with increase in CdSe core [30] is conjectured as a surface related phenomenon, rather than quantum confinement effect. Similar finding is reported in case of a single CdSe/CdZnS NCs [23] as well. Presence of trapped charges enhances coupling with LO-phonons and thereby linewidth in NCs. From temperature dependent PL studies on CdSe-CdTe graded NCs [31], it was observed that the graded core/shell interface is instrumental in efficient charge separation than the abrupt core/shell interface.

In the present work, effect of size and composition of NCs on the emission line width is explored with the aid of temperature dependent photoluminescence spectroscopy along with time resolved photoluminescence spectroscopy. Experimentally observed narrow line width (140 meV) in alloy graded core-shell Cd$_x$Zn$_{1-x}$S/ZnS NCs is not only a manifestation of exciton-phonon coupling, but also governed by the spatial overlap of electron and hole wave function in the nano-hetero-structure.
4.2 Results and discussions:

Figure 4.1. X-ray diffraction pattern for alloy core and core-shell NCs with two different sizes of alloy core. CdS and ZnS bulk pattern are shown for reference.

Figure 4.1 shows x-ray diffraction pattern for CdZnS NCs, diffraction pattern for bulk cubic CdS and ZnS are also depicted for comparison. It can be seen that the diffraction pattern matches with cubic zinc-blende phase with (111), (220) and (311) planes. In a uniform alloy, XRD features are governed by the Vegard’s law [3] and are located in between that of CdS and ZnS. The diffraction features are closer to CdS in case of CdZnS-II sample whereas those are more ZnS like in CdZnS-I sample. This indicates that CdZnS-II NCs have higher Cd concentration while CdZnS-I NCs have smaller Cd concentration. On ZnS cladding, the peaks shift towards ZnS, indicating graded interface formation. The details about the composition and structure of these NCs is reported earlier [8]. Transmission electron micrographs (TEM) (Figure AII.1) shows spherical NCs with sizes 8.1± 0.5 nm and 9.0± 0.4 nm for CdZnS/ZnS-I and CdZnS/ZnS-II NCs respectively which match with the reported values. Cubic zinc-blende phase is reconfirmed from electron diffraction patterns.

Optical absorption spectra (Figure 4.2) depict features at 437 nm (2.84eV) and at 451 nm (2.74eV) for CdZnS-I and CdZnS-II respectively. Shell formation leads to the
blue shift in forbidden gap. The absorption feature for CdZnS/ZnS-I and CdZnS/ZnS-II were at 430 nm (2.88eV) and 445 nm (2.79eV) respectively. In general, on shell formation, a red shift in the forbidden gap is observed in Type-I core-shell structures [32–34]. In the core-shell NCs, owing to smaller effective mass, the electron wave function is delocalized and spreads in to the shell. The leakage of electron wave function attributes to the red shift in the optical absorption [35]. The observed red shift is also partially due to the loss of quantum confinement on shell cladding [34,35]. On the contrary, in the present case, a blue shift in forbidden gap is observed. The observed blue shift is due to diffusion of Zn ions inside the core alloy samples at higher temperature (here 310 °C) [8], that tends the forbidden gap towards ZnS, which is higher than that of CdS. Consequently, the optical absorption shifts to the higher energy than core CdZnS alloy NCs and also in graded alloy samples [8,36].

**Figure 4.2.** Room temperature photoluminescence and optical absorption spectra for (a) CdZnS-I NCs, (b) CdZnS/ZnS-I NCs, (c) CdZnS-II NCs, and (d) CdZnS/ZnS-II NCs.

Room temperature photoluminescence (PL) spectra of core-shell NCs are also depicted in Figure 4.2. PL spectrum shows a hump at lower energy side for core NCs whereas this feature is suppressed on cladding. Moreover, the PL intensity enhances from
~ 5% to 80% for the core-shell NCs. The band-edge PL emission was observed at 453 nm (2.74 eV) with line width (FWHM) ~ 0.25 eV and 447 nm (2.77 eV) (FWHM ~ 0.14 eV) for CdZnS-I and CdZnS/ZnS-I NCs respectively. On the other hand, the emission for CdZnS-II and CdZnS/ZnS-II NCs is seen at 468 nm (2.65 eV) (FWHM ~ 0.2 eV) and 460 nm (2.69 eV) (FWHM ~ 0.15 eV) respectively. By extending the analogy given above, the emission energy values also reaffirm formation of graded shell. Interestingly emission from core-shell structure is associated with very narrow line width (FWHM). Such a narrow FWHM is noted in the earlier reports [12,37,23,38,39] and attributed to smaller inhomogeneous broadening, due to fluctuations in size, shape, composition etc, and homogeneous broadening such as coupling of excitons with phonons. From TEM, one can conclude the narrow size distribution in alloyed core and core-shell NCs. Moreover, in both the cases, NCs are spherical in shape. In other words, inhomogeneous broadening may not be playing a vital role in reduction of FWHM on shell formation. It would be interesting to probe the effect of interfacial grading on line broadening. It is demonstrated, by theory [40,41] and by experiments [17,18,28] that for smaller size, or for confined nanostructures the exciton-acoustic phonon has a larger value and the emission line width is smaller.

The exciton-phonon coupling can be found out from temperature dependent PL spectroscopy (Figure AII.2). The line width as a function of temperature can be fitted with empirical equation, given below [17,18,42].

\[
\Gamma(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} (e^{E_{LO}/k_B T})^{-1}
\]

Here, \(\Gamma_{inh}\) is the inhomogeneous broadening parameter, which is temperature independent and is due to fluctuations in size, shape, and composition of the NCs; \(\sigma\) is the exciton-acoustic phonon coupling coefficient. \(\Gamma_{LO}\) represents the exciton-LO phonon coupling coefficient and \(E_{LO}\) is the LO-phonon energy. FWHM as a function of temperature was measured for each sample and presented in Figure 4.3.
Figure 4.3. Emission line width as a function of temperature. The solid line represents the fitting curve.

Qualitative information regarding exciton-phonon coupling can be obtained by fitting the data with semi-empirical equation 4.1 to deduce parameters such as exciton-acoustic phonon coupling coefficient, LO-phonon energy. As mentioned above, the exciton-acoustic phonon coupling coefficient determines the FWHM of the PL peak. It has been reported that with decrease in size the exciton-acoustic phonon coupling coefficient increases [17,18], causing reduction in FWHM. Interestingly, here, the exciton-acoustic phonon coupling coefficient decreased with reducing size, in contrast to the literature reports. The estimated parameters are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (nm)</th>
<th>Exciton-acoustic phonon coupling coefficient (μeV/K)</th>
<th>Exciton-LO-phonon coupling coefficient (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdZnS-I</td>
<td>4.7</td>
<td>5.6</td>
<td>35</td>
</tr>
<tr>
<td>CdZnS/ZnS-I</td>
<td>8.1</td>
<td>39</td>
<td>43</td>
</tr>
<tr>
<td>CdZnS-II</td>
<td>5.4</td>
<td>12.4</td>
<td>29</td>
</tr>
<tr>
<td>CdZnS/ZnS-II</td>
<td>9.0</td>
<td>76.5</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 4.1. Exciton-acoustic phonon coupling coefficient for alloyed core and core-shell NCs.
It is worthwhile to note that $\sigma$ for CdZnS/ZnS-I NCs is 39 $\mu$eV/K whereas that for CdZnS/ZnS-II is 76.5 $\mu$eV/K. These results are contradicting to the reported size dependence as smaller size shows reduced $\sigma$. The usual size dependence depict that reduction in size increases exciton-acoustic phonon coupling. Confinement is stronger by size reduction hence one can say that if confinement increases exciton-acoustic phonon coupling also increases.

To shed light on the confinement of the charge carriers, time resolved photoluminescence measurements were performed at room temperature (Figure 4.4).

![Figure 4.4. Room temperature time resolved photoluminescence spectra for alloyed core and core-shell NCs](image)

The lifetime values obtained by fitting the curves to equation 4.2 are given in Table 4.2.

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$$  \hspace{1cm} 4.2

Where, $t_1$ and $t_2$ are the lifetimes and $A_1$ and $A_2$ are the amplitudes.

The NCs show two lifetimes, shorter lifetimes are due to band-edge transition while surface traps are responsible for longer lifetimes [33,43]. The average lifetimes are almost similar (25 ns for CdZnS-I and 26 ns CdZnS-II) for core-only NCs, suggesting comparable confinement in the alloyed core NCs. However, on ZnS shell cladding, the lifetimes increases, albeit more so for CdZnS-I NCs.
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<table>
<thead>
<tr>
<th>Sample</th>
<th>Lifetime (ns)</th>
<th>Average Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_1 )</td>
<td>( \tau_2 )</td>
</tr>
<tr>
<td>CdZnS-I</td>
<td>22.9</td>
<td>140</td>
</tr>
<tr>
<td>CdZnS/ZnS-I</td>
<td>33</td>
<td>79</td>
</tr>
<tr>
<td>CdZnS-II</td>
<td>24</td>
<td>120</td>
</tr>
<tr>
<td>CdZnS/ZnS-II</td>
<td>26</td>
<td>85</td>
</tr>
</tbody>
</table>

**Table 4.2.** Lifetimes for alloyed core and core-shell NCs

The average lifetime for CdZnS/ZnS-I is 36 ns which is appreciably different than that of CdZnS/ZnS-II which is 29.5 ns. The lifetime in core-shell NCs is related \([44,45]\) to the effective overlap of electron and hole wave functions. In type–II NCs where electron and hole wave function is confined exclusively in core or shell, the lifetime is larger. The lifetime is inversely proportional to electron hole wave function overlap and can be understood from Fermi’s golden rule \([45,46]\),

\[
\frac{1}{\tau} = \frac{4e^2 \omega_{ij}^3}{3\hbar c^3} n |\langle i | r | j \rangle|^2
\]

4.3

Where, \( \tau \) is the radiative lifetime, \( |i\rangle \) and \( |j\rangle \) are the initial and final states respectively, \( \omega_{ij} \) is the emission frequency, \( \hbar \) is the reduced Planck’s constant, \( c \) is the velocity of the light in vacuum, \( n \) is the refractive index of the system and \( \langle i | r | j \rangle = M_{ij} \), the overlap function.

Hence a smaller lifetime depicts effective overlap of electron and hole wave function. As is clear from Table 4.2, CdZnS/ZnS-II NCs have smaller lifetime compared to CdZnS/ZnS-I NCs indicating that electron and hole are effectively confined to CdZnS/ZnS-II NCs. The role of confinement effect on carrier lifetime is elucidated by the first principle calculations on CdS/ZnS system \([45]\). Accordingly, in case of CdS/ZnS NCs, the electron hole wave functions are strongly confined and thus have higher overlap than CdSe/CdS NCs which have smaller electron hole wave-function overlap. The faster decay rates in case of CdS/ZnS NCs than that of CdSe/CdS NCs are attributed to differential spatial spreading of the wave function. The lifetime is inversely proportional to the electron hole wave function overlap \([31,36,44,45,47]\). In a core-shell structure, the bulk band-offsets determine the electron hole localization/delocalization. A smaller
conduction band-offset will delocalize the electron wave function and it will spread towards the shell of the NC which reduces the overlap of the wave functions. Moreover, smaller valence band offset will spread the hole wave function and thus reduce the wave function overlap. Hole being heavier, spreading of the hole wave function will be smaller and restricts the larger change in the wave function overlap. It has been reported that with graded structure at the interface of the NCs, the electron and hole wave functions will be confined towards the core giving higher wave function overlap. As mentioned above, CdZnS-I have 58% Cd and CdZnS-II has 76% composition. Thus the band offsets of these two systems are different. With higher amount of Cd, CdZnS-I has smaller conduction band offset whereas that of CdZnS-II has larger conduction band offset. Thus electron hole wave function overlap will be larger in case of CdZnS-I case. However, one has to consider the grading effect in these systems. With graded interface the electron hole wave functions is strongly confined in the core resulting in to the increase in overlap for CdZnS-II structure. In other words, whenever electron hole wave function overlap is larger, the effective size is smaller in case of NCs. This explains the anomaly in the exciton-acoustic phonon coupling coefficient with size, which states that with changing the composition of the NCs with grading, the electron hole wave function overlap changes and this account for the change in the exciton-acoustic phonon coupling. The coupling strength affects the emission line width of the NCs. In short, the emission line width can be controlled by yet another parameter, composition with graded structure.

**4.3 Conclusions:**

Highly luminescent CdZnS/ZnS graded core-shell NCs were prepared by reported method with two different sizes and Cd composition. The NCs reveal narrow emission line width. The exciton-acoustic phonon coupling parameters were estimated from low temperature photoluminescence measurements. Surprisingly these estimates contradict the established size dependence. Rather than increase in exciton-acoustic phonon coupling coefficient for larger NCs, the reduction in the coefficient is observed with decrease in size. In case of core-shell semiconductors, the effective size may be estimated on electron hole wave function overlap, which was determined from the excitonic lifetimes. Based on a theoretical report on graded core-shell NCs, the
relationship between electron hole wave function overlap and exciton lifetime was invoked to understand this anomaly. Time resolved photoluminescence measurements show that the smaller sized alloy core-shell NCs (CdZnS/ZnS-I) have larger lifetime than that of bigger NCs (CdZnS/ZnS-II). Thus, CdZnS/ZnS-I NCs should have smaller electron hole wave function overlap giving larger effective size of NCs even though the actual size, estimated from TEM, was smaller. This explains the anomaly in the exciton-acoustic phonon coupling coefficient with size. Thus it was shown here that composition with graded structure can be utilized to control the emission line width in NCs.
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References: