Chapter 5

Energy levels engineering by composition tuning of Zn\textsubscript{1-x}Cd\textsubscript{x}Se NCs

Single pot method is employed to obtain systematically varying amount of Zn across Zn\textsubscript{1-x}Cd\textsubscript{x}Se nanocrystals (NCs) which are free of any interfacial defects. Further Zn distribution within NCs is strategically made uniform by annealing. Electron energy levels mapped by the optical techniques reveal reduced energy level spacing due to Zn incorporation. The Stokes shift also attains remarkably lower value in alloyed Zn\textsubscript{1-x}Cd\textsubscript{x}Se NCs. Radiative decay time measurements indicate that the reduction in Stokes shift is caused by the reduced dark bright gap in alloyed NCs. First principles electronic structure calculations (performed in collaboration) indicate enhanced hybridization of Zn $d$ levels with Se $p$ levels in comparison to that of Cd $d$ levels in homogeneously alloyed NCs leading to decreasing energy difference between the occupied electron energy levels. Essentially notable fact is that alloyed NCs concomitantly exhibit blue shift in the forbidden gap but red shift in higher energy transitions.

Work Presented in this chapter is communicated for publication,
5.1 Introduction

The study of nanometer size semiconductors is rigorously initiated since last two decades. By the end of the previous century, control on the excitonic transition energy in semiconductor nanocrystals (NCs) due to quantum size effects was realized in various materials.\(^1\)-\(^4\) Variety of preparation routes emerged in due course of time with better control on the size, the size dispersion and moreover on the shape.\(^5\) Studies on core/shell nanocrystals received special attention due to enhanced stability and improved luminescence efficiency.\(^5\)-\(^7\) Doped semiconductor NCs emerged as different branch in the field of nanoscience.\(^5\) Core/shell nanocrystals are formed by overcoating semiconductor NCs with smaller band gap, by layers of another semiconductor having larger value of the band gap. These hetero-nanocrystals suffer from the problem of interfacial defects. Subsequent attempts to vary the composition of the nanocrystals was successful in minimising the lattice strain and hence the trap levels. Interestingly, composition graded semiconductor quantum dots also show suppressed blinking in the single particle spectra.\(^8\)

Composition variation of NCs open up another degree of freedom to control the properties.\(^9\)-\(^12\) For example, graded type I core/shell structure exhibit a superior PL efficiency as compared to normal core/shell NCs.\(^9\),\(^10\) Some properties, like blue emission in CdSe, is possible only by reducing the size. Reduction in size almost always leads to increased defect density in NCs.\(^13\) Effectively defect free NCs could be obtained by graded composition.\(^13\)

Although the change in band gap with composition is discussed in the literature,\(^13\)-\(^14\) the electron energy levels of varying composition in different sized NCs are not unravelled. We study composition graded Zn\(_{1-x}\)Cd\(_x\)Se NCs grown by single pot method. The present synthesis protocol minimizes the lattice stresses involved. At single particle level, very sharp features are observed from the graded NCs. Blinking analysis reveal that the graded structure show suppressed blinking, discussion on which is presented in next chapter. This paper discusses the energy level structure of such a system. Electron energy levels are mapped using photoluminescence excitation (PLE) spectroscopy. The Stokes shift of graded NCs is seen to be considerably smaller and can attain minimal value on alloying the NCs. The separation between first few excited states monotonically decreases on alloying.
5.2 Results and Discussion

Room temperature optical absorption and PL spectra of graded core/shell, and alloyed Zn$_{1-x}$Cd$_x$Se NCs are shown in Fig. 5.1. Band gap of these NCs is quite smaller than bulk ZnSe, implying that the ZnCdSe-I NCs are more or less CdSe like. As Cd is more reactive than Zn toward TOP-Se, faster reaction of Cd is anticipated, resulting in CdSe seed formation. Subsequently, Zn ions participate in the reaction to form a graded structure with CdSe rich core and ZnSe rich shell. These NCs show PL efficiency of 60%. Such a high efficiency indicates effective passivation of cationic and anionic site without interfacial defects.

In order to facilitate diffusion of ions, sample is annealed. Annealing graded nano-structure at 290 °C for longer time duration, typically up to 180 minutes yields uniform alloy NCs. Fig. 5.1 depicts absorption and PL spectra (recorded at RT) of the annealed NCs. Annealing causes blue shift in the absorption feature from 539 nm to 498 nm. Concomitant blue shift in PL spectra is also observable from 547 nm through 501 nm. Such a blue shift in band gap, without reduction in size, indicates formation of alloy structure (See Appendix III for NC size). Further blue-shift is not observed in the PL spectra after time duration of 180 min. Annealing NCs cause diffusion of Zn from shell in to Cd rich core and out diffusion of Cd in the shell region. The overall process results in formation of alloy, thereby blue shifting the band gap by 41 nm. PL measurements reveal subtle deterioration in quantum efficiency. Even after alloy formation the PL efficiency is ~45%. Such a high efficiency is comparable to conventional core/shell structure. Progressive alloy formation leads to decrease in the Stokes shift (from 8 to 3 nm) as shown in Fig. 5.1 (a). Stokes shift arises due to the exchange interaction between electron and hole in NC and decreases with increasing size. Exchange interaction splits the lowest energy level in to two levels with net spin projection J=1 and 2. Energy level with net spin projection J=2 is optically forbidden and called as dark state where as level with spin projection J=1 is optically active and called as bright state. The difference in these levels leads to Stokes shift in NCs. Here, Stokes shift reduces as one increases concentration of Zn in the core [Fig. 5.1(a)]. The reduced Stokes shift in alloyed NCs suggest that the dark and bright gap , responsible for Stokes shift in NCs, is reducing compared to graded core/shell NCs.
FIG. 5.1 (a) Room temperature optical absorption and (b) PL spectra of alloyed Zn$_{1-x}$Cd$_x$Se NCs recorded with the excitation wavelength 425 nm. The Stokes shift is mentioned in figure (a).
To analyze the effect of Zn incorporation on energy levels, PL and PLE measurements are carried out at 10 K. Figure 5.2 (a) shows PL spectra of ZnCdSe-I NCs recorded at 10 K. Blue shift (~15-19 nm) in emission maxima is observed at low temperature (10 K). The blue shift is consistent with the dependence of band gap on temperature. It is worth noting here that even though particle size (ZnCdSe-I) is ~4.3 nm, optical absorption of these NCs (ZnCdSe-I) matches with that of CdSe NCs with nominal size of 3.2 nm. In order to analyze the energy levels in these NCs PLE spectra are recorded at 10K [Fig. 5.3 (a)]. The recorded PLE spectra for ZnCdSe-I is compared with that of CdSe of size 3.2 nm. Peak position of ZnCdSe-I and CdSe of size 3.2 nm matches. This clearly indicates that the emission is caused by CdSe like core. Even with increasing the annealing time the PLE spectra does not show overlap of any energy levels [See Fig. 5.3 (a)]. However a continuous blue shift in energy of all the peaks is observed. The PLE spectra is fitted with Gaussian fit as discussed in ref. 1 [Fig. 5.3 (b)]. The peak positions are assigned as in case of CdSe. The energy levels are extracted from PLE and assigned as in CdSe.1 Figure 5.2 (b) shows the variation in energy levels as a function of annealing time. With increasing annealing time, difference between adjacent energy levels progressively decreases. Subsequently, energy levels of alloyed NCs are located closer to each other. Energy level spacing in NCs goes on increasing as size is reduced.1 Particle size of NCs is not changing appreciably, even though energy levels are coming closer to each other. Notably the forbidden gap in alloyed NCs goes on increasing with Zn incorporation in the core. The increase in band gap is a property of smaller NCs. While reduced spacing in the energy levels is a property of larger NCs. Alloyed NCs combine both the properties. The present experimental findings thus identify spatial distribution of composition as the parameter to control the physical properties. The change in the microscopic composition of the NCs is changing the energy level spacing. The composition might also be changing the dark bright energy gap, which in turn is reducing the Stokes shift for alloyed NCs. To shed light on the dark and bright gap in these NCs TRPL measurements were carried out.
**FIG. 5.2** (a) 10 K PL spectra of alloyed Zn$_{1-x}$Cd$_x$Se NCs recorded with the excitation wavelength 425 nm. (b) Plot depicting change in energy levels with annealing of Zn$_{1-x}$Cd$_x$Se NCs.
FIG. 5.3 (a) PLE spectra recorded on ZnCdSe-I, ZnCdSe-Ia, ZnCdSe-Ib, ZnCdSe-Ic, and ZnCdSe-Id. (b) Fitting of PLE spectra and assignment of the peak.
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Figure 5.4 depicts TRPL spectra of graded and alloyed NCs. Alloying is responsible for shortening PL life time. TRPL spectra of semiconductor NCs can be understood\textsuperscript{25} on the basis of three level model (Fig. 5.5). In semiconductor NCs, confinement enhances electron hole exchange interaction. Exchange interaction split the lowest energy level into two levels with net spin projection $J=1$ and $2$. Energy level with net spin projection $J=2$ is optically forbidden and called as dark state. Energy level with net spin projection $J=1$ is optically active and called as bright state.\textsuperscript{25} Dark state is lower in energy than bright state. Occupancy of level depends on Boltzmann factor. The decay rate of exciton in dark and bright states is given by\textsuperscript{25}

$$\tau = \frac{(\tau_d + \lambda \tau_b)}{(1 + \lambda)};$$

Where $\tau_d$ and $\tau_b$ are decay rates of dark and bright energy levels respectively and $\lambda$ is defined as

$$\lambda = e^{-\Delta/kT},$$

with $\Delta$ is the dark-bright gap and $k$ is the Boltzmann constant. Change in $\Delta$ can be inferred without knowledge of $\tau_d$ and $\tau_b$.

Reducing $\Delta$ will increase $\lambda$ (as at particular temperature $T$, it is exponentially decaying function of $\Delta$), and hence the contribution from bright state will also increase (as it is scaled by $\lambda$). Overall at a particular temperature, reducing $\Delta$ will increase the decay rate and hence reduce the life time $\tau^{-1}$. In other words, if $\Delta$ is greater than the thermal energy, electron in dark state has to decay through the same state. However if $\Delta$ is less than the thermal energy then the electron can move to bright state and decay through that state, increasing the total decay rate. The probability of electron going from dark state to bright state strongly depends on $\Delta$ at a given temperature. Reducing $\Delta$ increases the probability of transition from dark to bright state, and hence increases the total decay rate. TRPL spectra clearly demonstrate reduction in $\Delta$ in alloyed NCs. Reduction in $\Delta$ is further responsible for reduction in the Stokes shift of these NCs.
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**FIG. 5.4** TRPL spectra of Zn$_{1-x}$Cd$_x$Se NCs annealed at different time. Diffusion of Zn from shell to core causes the reduction in the life time.

**FIG. 5.5** Three level diagram for TRPL spectra. (a) In graded core shell structure $\Delta$ gives a finite probability of transition from dark to bright state. (b) Reduction in $\Delta$ increases the probability of dark to bright transition. Increased number of electrons in bright state increases the bright decay rate and hence reduces the life time.
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In order to understand the origin of reduction in energy level spacing, first principles electronic structure calculations are performed in collaboration with Mr. Mr. Laxman Tatikondewar, and Prof. Anjali Kshirsagar, Department of Physics, University of Pune. Total density of state plot indicates reduced spacing in adjacent states in alloy as compared to abrupt and graded core/shell structure. The partial charge density study on these structure indicates that the HOMO states are composed of Se $p$ state hybridized with cation $d$ state. The difference in atomic energy of Se $p$ and Zn $d$ level is less as compared to that of Cd $d$ state. Because of this Zn hybridization in graded and alloyed structure is enhanced. This enhanced hybridization of the Zn level with Se level is responsible for the reduced energy level spacing in alloyed structure.

Conclusions

The electron energy levels of compositionally graded Zn$_{1-x}$Cd$_x$Se and alloyed NCs are determined by optical means. Progressive incorporation of Zn in core region results into reduced energy difference in higher transitions along with blue shift in forbidden gap. First principles calculations performed on prototype Zn$_{1-x}$Cd$_x$Se NCs shed light on the underlying phenomena. The calculations indicate enhanced hybridization of Zn levels with Se levels compared to those of Cd levels. Subsequently, energy spacing between occupied energy levels reduces with Zn incorporation in the core region.

Interestingly reduction is also observed in Stokes shift of alloyed NCs as compared to graded NCs. Radiative life time as estimated from time resolved PL spectroscopy reveal that the gap between dark and bright exciton energy levels is reduces as zinc diffuses in NCs, thus corroborating with the reduced value of Stokes shift.

Size variation provides a tool to tune the optical transitions monotonically. However, present findings clearly demonstrate electron energy level engineering by tuning the composition profile of NCs. To the best of our knowledge, this is the first report indicating feasibility of tuning higher energy transitions by varying composition in NCs.
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