Chapter 6

Effect of shape of confinement potential on blinking and emission behavior of Nanocrystals

Advanced single pot wet chemical method is employed to obtain graded CdZnSe nanocrystals (NCs) which show remarkably sharp single quantum dot spectra with average full width at half maximum (FWHM) around 50 meV at room temperature. These NCs show blinking suppression up to 95%. Blinking suppression is attributed to localization of exciton at the center of NC, thereby reducing effect of trap levels. Composition profile is further changed to reconfirm the dependence of emission on the shape of confinement potential.

Work Presented in this chapter is communicated for publication
6.1 Introduction

High photoluminescence (PL) quantum efficiency and size-tunable emission wavelength are two important features of semiconductor quantum dots which are proving useful in applications such as semiconductor lasers, biological markers, solar cells etc. Chemical synthesis routes allow one to form different configurations like doped, core/shell, different shaped quantum dots in bulk quantity and with rather ease. PL intensity fluctuations, most commonly referred as PL blinking\(^1\) and change in PL emission wavelength referred as spectral diffusion are the two restrictions in their use in application. The first theoretical model for blinking is proposed by Efros and Rosen.\(^2\) According to this model the “OFF” time in blinking is assigned to ionized state of the NC. When the NC is ionized the extra charge carrier in the NC assists the non radiative Auger recombination rate rendering the non emissive NC. Till date it is widely accepted model. The model is further modified to take in to account the experimental results.\(^3\) Reported work also indicate that the origin of blinking in NCs is not the non radiative Auger recombination.\(^4,5\) These reports support another model put forward by Frantsuzov and Marcus.\(^6\) This model does not evoke the Auger assisted non radiative recombination and does not need ionization of NC. According to this model, hole from the NC is trapped. The excess energy arising from trapping is transferred to the electron in 1S state to excite it to the higher state. The excited electron then recombines non-radiatively with the trapped hole rendering the emission from NC. Recent experiments indicate that both these mechanisms contribute to the blinking.\(^7,8\)

Blinking poses serious limitation in application of single NC where a constant and reliable luminescence is required. In order to suppress blinking, two different pathways are followed. One of the way-out is to eliminate the intrinsic trap sites in the NCs.\(^9,10,11\) Traps mainly arise from dangling bonds present at the surface. By removing the trapped charge carriers, extra charges would be absent and the nonradiative Auger processes will be suppressed. Hohng et al.\(^11\) flushed commercially available CdSe/ZnS NCs with β-mercaptoethanol (BME) to eliminate traps present on surface. The blinking is substantially suppressed after treating the NCs with BME. However removal of BME reverses the effect recovering blinking. Further, NCs need to be immersed continuously in BME solution to attain blinking suppression. This hinders use of these NCs for experiments as well as in applications. Alternate
approach is to grow a thick shell to completely isolate the charge carriers from the surface of the NCs. Mahler et al.\textsuperscript{9} and Chen et al.\textsuperscript{10} reported synthesis of such structure consisting of CdSe core covered with thick CdS displaying reduced blinking. However even after coating a thick shell only $\sim$ 20\% NCs were observed to be non blinking by Chen et al.,\textsuperscript{10} while 68\% NCs were found to be non blinking by Mahler et al.\textsuperscript{9} Moreover, forming a thick shell on the core NCs is a complex procedure and needs synthesis expertise.

Alternate approach to get rid of blinking is to eliminate or suppress the Auger recombination in NCs. Theoretical investigations by Cragg et al.\textsuperscript{12} suggest that, Auger rate depends on the smoothening of confinement potential. If the confinement potential is smoothly varying the Auger recombination rate is suppressed. The shape of confinement potential can be tuned by changing the microscopic composition within the NC from core to shell (graded core shell structure). Klimov’s group,\textsuperscript{13} used the theoretical proposition to explain the reduced Auger rate in giant core/shell NCs. In their case, composition grading of interface is speculated with fluorescence line narrowing (FLN) experiment. Wang et al.\textsuperscript{14} showed that the non-blinking nature of the NCs is due to reduced Auger rate. The NCs are considered to be compositionally graded in nature; however no experimental evidence regarding graded composition profile is provided.

In the present manuscript, blinking behavior of graded and alloyed CdZnSe nanocrystals is investigated at a single particle level. The nanocrystals were prepared by single pot synthesis method, thereby minimizing the interfacial defects between Cd-rich core and Zn-rich shell. The synthesis route is advanced to yield the smallest full width at half maximum (FWHM) at ensemble as well as single particle level with concomitant suppression in blinking up to 95\%. Shape of confinement potential is changed to reconfirm role of the same on blinking behavior.

Two different graded core/shell NCs with Cd concentration 48\% and 36\% (named as Sample A and Sample B respectively), and a uniform alloyed sample (with Cd concentration 36\% ) named as sample C are studied here.

\textbf{6.2 Results and Discussion}

Sample A, sample B and sample C has different composition profile. On the atomistic level, amount of Cd in sample A and B is smoothly decreasing from center
to the surface of NC, whereas, atomic concentration of Cd and Zn in sample C is uniform throughout the NC. Owing to different microscopic composition these NCs have different confinement potential. For graded structure the confinement potential is smoothly increasing from core to surface as shown in Fig. 6.1 (a) and 6.1 (b). The microscopic composition of alloyed NCs is homogeneous. This results in a flat confinement potential inside NC, which terminates abruptly at the interface [as shown in Fig. 6.1(c)]. Even though the confinement potential is smoothly varying in sample A and B, degree of smoothness in sample A and B is different and depends on the composition of these NCs. For sample B as amount of Cd is less than sample A, the difference in amount of Cd in adjacent atomic layers in sample B will be rapidly varying compared to sample A. As a result the confinement potential in sample B is less smoothly varying than sample A.

**FIG. 6.1** change in shape of confinement potential in (a) sample A, (b) sample B, and (c) Sample C. Optical absorption and PL spectra of (d) sample A, (e) sample B, and (f) sample C.

Figure 6.1 (d), 6.1 (e), and 6.1 (f) show ensemble optical absorption and PL spectra of samples A, B, and C respectively. Band gap measured from optical absorption of sample A and B is 2.19 eV and 2.24 eV respectively. The change in
band gap for sample A and B is attributed to change in the size of CdSe rich core.\textsuperscript{15} Approximate CdSe rich core size is estimated from absorption peak by using empirical formula suggested by Yu \textit{et al.}\textsuperscript{16} These sizes are indicated in Table 6.1. With annealing, slight increase in particle size is observed (Table 6.1). Blue shift in band gap of sample C (2.34 eV), compared to sample B (2.21 eV), is observed.\textsuperscript{9} Blue shift in band gap for sample C is caused by alloying. All these samples show defect free intense emission with FWHM $\sim$ 100 meV (Table 6.1) with high PL efficiency ($\sim$ 60\% for sample A and B, and 45\% for sample C). It is worthwhile to mention here that these NCs are prepared by single pot route to attain the lower defect density in NC. In graded structures strain induced defects are minimal making these samples highly luminescent.

**TABLE 6.1** Physical properties like particle size, band gap, ensemble and single particle emission energy and FWHM for samples A, B, and C.

<table>
<thead>
<tr>
<th>Measured Parameters</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
</tr>
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<tbody>
<tr>
<td>Total size of NC from TEM (nm)</td>
<td>4.9 ± 0.5</td>
<td>4.5 ± 0.5</td>
<td>4.9 ± 0.8</td>
</tr>
<tr>
<td>Ensemble optical absorption peak position (eV)</td>
<td>2.19</td>
<td>2.24</td>
<td>2.34</td>
</tr>
<tr>
<td>Ensemble PL peak position (eV)</td>
<td>2.13</td>
<td>2.21</td>
<td>2.32</td>
</tr>
<tr>
<td>Ensemble FWHM (meV)</td>
<td>106</td>
<td>105</td>
<td>103</td>
</tr>
<tr>
<td>Size of core CdSe-rich NC from optical absorption (nm)</td>
<td>3.4</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>Single NC mean PL peak position (eV)</td>
<td>2.13</td>
<td>2.23</td>
<td>2.32</td>
</tr>
<tr>
<td>Single NC mean FWHM (meV)</td>
<td>53</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td>% of NCs showing suppressed blinking</td>
<td>$\sim$ 95</td>
<td>$\sim$ 93</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>% of non-blinking NCs</td>
<td>$\sim$ 66</td>
<td>$\sim$ 50</td>
<td>&lt; 20</td>
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</table>

In order to study the effect of the shape of confinement potential on individual NC, blinking behavior of single particle emission was analysed with an epi-fluorescence set up. Figure 6.2 (a), 6.2 (b), and 6.2 (c) show blinking traces of individual NC from sample A, B, and C respectively. Observation of OFF state in the emission confirms that we are indeed looking at the single particle. It is quite clear
from the blinking traces that, sample A and B show suppressed blinking compared to sample C. The intensity histogram for each trace is depicted in Fig. 6.2(a), 6.2 (b) and 6.2 (c) right panel. Histogram indicates that NCs of sample A and B are in ON state for longer time while NCs of sample C are in OFF state for longer time Individual NC in each sample show different blinking behavior [see Fig. 6.2 (a), 6.2 (b), 6.2 (c)]. In order to arrive at statistically reliable data, more than 150 NCs from each sample are analyzed for blinking behavior. Figure 6.2 (d), 6.2 (e) and 6.2 (f) show the percentage of on-time distribution for sample A, B, and C respectively.

In order to analyze the data, NC remaining in ON state for more than 90% of total recording time (5 minutes) is said to show suppressed blinking, and NC remaining ON for more than 99% recording time is said to be 100% ON. In sample A, more than 95% NCs show suppressed blinking, where as approximately two third of analyzed NCs are 100% ON. Blinking trace with 100 ms time binning and 5 min recording time, for sample A is shown in Appendix IV. In sample B, 90-95% NCs show suppressed blinking, where as approximately half the particles are 100% ON. Statistical analyses indicate that even though sample A, and B show suppressed blinking the fraction of NCs showing suppressed blinking and non blinking behavior are different in both the samples. Sample C show the highest blinking. Statistical analysis of sample C indicate that less than 50% of NCs in sample C show suppressed blinking, and less than one fifth NCs are 100% ON.

It is clear from the preceding paragraph that samples A, B, and C show different emission pattern. The difference in the emission behavior of these samples lies in the different confinement potential seen by exciton in these samples. Recent studies on blinking in NC revealed two types of blinking mechanisms, viz. Auger assisted and trap assisted. As discussed previously sample A has smoother confinement potential, whereas confinement potential for sample B is less smoothly varying than sample A. This change in the shape of confinement potential is responsible for different blinking behavior in these samples. Smoothly varying confinement potential suppresses Auger rate in NCs. The degree of Auger rate suppression depends on smoothening of confinement potential. Reduced Auger recombination rate further suppresses blinking arising from Auger recombination. Moreover, sample A and B are grown by single pot protocol. Thus, defects and interfacial strain is minimal in the NCs. This assures that the trap density within NC
is negligible, and only trap levels available will be the one at the surface of the NC. The shape of confinement potential will confine the exciton within the core of the NCs.

FIG. 6.2 Blinking traces, and intensity histogram (right panel) of (a)Sample A, (b)Sample B, (c)Sample C. On time histogram plotted for more than 150 particles each from (d)Sample A, (e)Sample B, and (f) Sample C.
This will reduce the access of surface trap to the exciton. In short, the shape of confinement potential and quality of sample both assure that the trap assisted blinking in these NCs is also suppressed. The reduction of trap states and the confinement potential shape reduces the Auger assisted and trap assisted blinking in sample A and B. As a result blinking in these NCs is suppressed. As the shape of confinement potential in sample B is less smoothly varying, spatial spread of exciton wave function would be wider and the trap levels can be accessible for sample B, increasing trap assisted blinking in these NCs. The confinement potential for sample C is flat and terminates abruptly at the surface. The lack of smoothly varying confinement potential makes NCs of sample C prone to Auger recombination. Moreover over the exciton can now “see” the surface traps (as the exciton is no longer confined in the core region). As a result, the trap assisted blinking pathways will also be opened up. Subsequently, sample C shows substantial blinking. Even though, the effect of confinement potential shape on the blinking behavior is already discussed in literature,\textsuperscript{14} the emission from these NCs reveal multiple peaks attributable to shake up lines arising from charged exciton. Moreover, effect the change in shape of confinement potential on blinking and emission is not studied so far.

Figure 6.3 (a), 3 (b), and 3 (c) show emission spectra from sample A, B, and C respectively. The normalized sum of all individual NCs and normalized ensemble PL spectra are superimposed on each other and shown in the inset of figure. The inset of figure clearly indicates that the sum of individual NC spectra covers the entire emission region of the ensemble spectra. This assures that the range of particles contributing to ensemble emission is taken care of. Most interestingly the emission from individual NC is single peaked. In order to confirm that the single peaked emission is indeed arising from NC with suppressed blinking in sample A and B, energy-time-intensity plot of emission from individual NCs is extracted. These plots are depicted in the Appendix IV (See Fig. AIV.1). It is clear from this figure that indeed the single peaked nature is from individual NC. Earlier, multiple peaks were observed\textsuperscript{14} in graded NCs at single particle level and are attributed to shakeup line arising from charged exciton with suppressed Auger recombination. Auger assisted blinking require extra charge in the NC. If the blinking suppression is by means of Auger rate suppression then, the extra charge will change the emission of NC. The emission from charged NC is vivid from multiple peaks.\textsuperscript{14} Absence of multiple peaks
in the present case, indicate that the NC is neutral, and no extra charge is generated in the NC.

**FIG. 6.3** PL spectra of individual NCs in (a) sample A, (b) Sample B, and (c) sample C inset of each figure show ensemble PL (green) and sum of individual particle PL (red). Distribution of FWHM in (d) sample A, (e) sample B, and (f) sample C.
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The absence of extra charge will automatically terminate the possibility of Auger assisted blinking. This clearly indicates that what ever blinking we are observing in sample A and B is trap assisted. In other words, the shape of confinement potential not only suppresses the Auger recombination, but also prevents the possibility of extra charge generation.

The emission from individual NC from same sample is not exactly identical. Figure 6.3 (d), 6.3 (e), and 6.3 (f) show the full width at half maxima (FWHM) distribution in sample A, B, and C respectively. The mean FWHM of sample A, B, and C is 53, 49, and 47 meV respectively. However, the values of FWHM at single particle level are distributed over a range from 25 meV through 90 meV. Most commonly the FWHM of single NC at room temperature is between 50 and 70 meV. In the present study, considerable number of NCs shows narrow FWHM (~30 meV or less). To the best of our knowledge, such a narrow FWHM is not reported for individual NC at room temperature. In a recent article, Braam et al. correlated the spectral diffusion to line width. Spectral diffusion in NC arises from Stark effect of diffused charge around the NC. The line width of NC emission arises from charge carrier displacement of diffused charge carrier within the integration time. More is the charge carrier displacement wider will be the emission line. More over, the FWHM will be larger for the NC, with shifted energy position due to Stark effect of diffused charge. In our sample (sample A and B), the spectral diffusion is negligible (see Appendix IV Fig. AIV.2). The lack of spectral diffusion indicates the absence of extra charge around the NCs, which is also obvious from the blinking behavior. The diffused charge will be the one ejected from the NC. In our samples, the possibility of charge generation (or ejection of charge carrier) is minimized. So chances of having diffused charge will be minimal. And hence no spectral diffusion is observable causing the reduction in the FWHM of the emission line. In conclusion the shape of confinement potential not only controls the blinking of the NCs but also the spectral behavior of the NCs.

6.3 Conclusions

To summarize, the synthesis protocol is advanced to prepare NCs with varying shape of the confinement potential by single pot method. Effect of smoothening of the confinement potential on blinking and spectral properties of single NCs is studied.
Along with suppressed blinking of these NCs, single particle spectra show extremely narrow, single peaked emission line. The suppression of blinking and absence of multiple peaks in the PL spectra suggest the absence of extra charge in the NC. This has been explained on the basis of shape of confinement potential and the quality of sample. Shape of the confinement potential is varied to reconfirm the blinking suppression. Simultaneous recording of ensemble as well as single particle emission spectra indicate that the change in shape of the confinement potential can tune the optical behavior.
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