Chapter 5

Luminescence of ZnO quantum-dot assemblies

Assemblies of ZnO nanocrystals can be charged with electrons; the average electron number can be varied in a controlled way between zero and ten. The luminescence of such charged assemblies due to UV excitation has been studied and compared with the luminescence of quantum-dot suspensions. The luminescence of ZnO assemblies depends on the electron number and the nature of the interpenetrating electrolyte. Remarkably, with increasing electron number, the green (defect) luminescence quenches, while the exciton luminescence increases. Thus, quenching of the exciton luminescence by an Auger-type process is unimportant in charged ZnO quantum dots. This forms a strong contrast with results obtained with Si and CdSe quantum dots.
5.1 Introduction

ZnO has been known as a luminescent material for a century, and some fifty years ago it was discovered that firing ZnO powder in a reducing atmosphere gives a particularly efficient blue-green phosphor. Green light has an energy smaller than the band gap of ZnO and corresponds to an electronic transition via a defect. Green-emitting ZnO is usually denoted as ZnO:Zn because of the loss of oxygen during the reducing treatment [1]. This material has a high efficiency as a low-voltage phosphor and has been used in vacuum fluorescent displays (VFD’s) and field emission displays (FED’s) [2]. Because of the important applications luminescent ZnO has been the subject of much research aimed at finding the origin of the visible emission.

Recent work has indicated that oxygen vacancies are the most likely candidates for the recombination centers involved in the visible luminescence of ZnO [3–8]. In the past, most work has been done on micron-sized single-crystalline materials. Van Dijken et al. investigated ZnO nanocrystals and deduced from the size-dependent visible emission that a hole in a deep trap and an electron in the conduction band must be responsible for the visible emission [4]. The deep hole trap was assigned to oxygen vacancies in ZnO.

Besides the visible luminescence an ultraviolet emission is also found in many cases; this is due to the radiative recombination of excitons. This emission is relatively narrow and located at around 3.25 eV for a bulk ZnO crystal. Both the visible and the exciton emission was observed in ZnO quantum-dot assemblies. It was found that the intensity of the visible and the exciton emission depended on the electrochemical potential of the system [9, 10].

In this chapter, we compare the luminescence of assemblies of ZnO quantum dots with that of suspensions. We make use of the fact that, in our experiments, the average electron number $\langle n \rangle$ is known with a reasonable accuracy. In particular, we investigate the effect of an increasing occupation of the conduction orbitals on the defect and exciton luminescence.

5.2 Experimental

The suspensions and assemblies of ZnO nanocrystals were prepared by the method described in Chapter 2. The electrodes used in this work were made with fluoride-doped tin oxide (TFO) on glass substrates. The average number of electrons per quantum dot $\langle n \rangle$ was determined as described in Section 2.5. The results de-
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scribed in this chapter were obtained with ZnO assemblies made from 4.3 nm quantum dots, unless otherwise mentioned.

The photoluminescence measurements were performed on a SPEX Fluorolog spectofluorometer model F2002 equipped with a double-grating 0.22 m SPEX 1680 monochromators and a 450 W xenon lamp as the excitation source. UV irradiation of the suspensions and the assemblies was carried out inside the spectrophotometer using the excitation beam (at 300 nm). The emission light was transported through a fibre optics cable to a 0.3 m monochromator (Acton Pro SP-300i, 150 lines/mm grating, blazed at 500 nm).

The suspensions in ethanol were measured in a quartz cuvette. The excitation beam had a rectangular cross section of about 1 cm by 1 mm. The penetration depth of the UV radiation was such that absorption took place over the entire width of the cuvette.

The ZnO assemblies were investigated in an electrochemical cell with quartz windows. The aqueous electrolyte was an argon-purged 0.2 M phosphate buffer (pH = 8) and was made by adding pure NaOH to a phosphoric acid solution. Here the reference electrode was a Ag/AgCl electrode, and the counter electrode a platinum sheet. Otherwise, anhydrous propylene carbonate (PC) with 0.1 M tetrabutylammonium perchlorate (TBAClO$_4$) was used. In this electrolyte a silver rod served as a quasi-reference electrode (see also Chapter 3).

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In Figure 5.1 typical emission and absorption spectra of a ZnO suspension are shown, taken after the sol was purged with nitrogen for 10 minutes. A broad band emission is observed in the visible region extending from 1.5 eV to 3.0 eV with a maximum at 2.2 eV. This is called the visible emission of ZnO. A much sharper peak is observed in the UV region with a maximum at 3.4 eV and extending from 3.0 to 3.5 eV. This is called the exciton emission of ZnO.

The exciton and visible emission of ZnO are found to be size dependent and from this size dependence the mechanism for the luminescence was derived by Van Dijken et al. [3, 4]. The mechanism for the exciton and visible emission of ZnO is taken from these references and briefly summarized.

Figure 5.2 gives a schematic overview of the radiative relaxation processes that take place upon photoexcitation of a ZnO dot. The non-radiative recombination processes which occur after photoexcitation of a ZnO quantum dot are omitted from this scheme. The band edges are shown as well as a deep trap level.
Figure 5.1: Room-temperature emission and absorption spectra of a suspension of nanocrystalline ZnO quantum dots in ethanol. The emission spectrum was obtained with 4.1 eV excitation after the ZnO suspension was purged with nitrogen for 10 minutes. A broad band is observed in the visible region with a maximum at 2.2 eV. A much sharper peak is observed in the UV region with a maximum at 3.4 eV. The onset of absorption is at about 3.4 eV.

in the bulk of the dot, $V_{O^\cdot}$. At the surface of the dot, the energy distribution of an $O^{2-}/O^-$ state is shown. The arrows indicate the electronic transitions. If a ZnO quantum dot is excited with a photon with an energy larger than the band gap, an exciton is created. This exciton can decay to the quantum-dot ground-state by emission of a UV-photon ($A$). The hole can be trapped in a surface state $O_S^{2-}$ which is oxidized to $O_S^-$ ($B$). The trapped hole is transferred to the oxygen vacancy $V_{O^\cdot}$ which is oxidized to $V_{O^{\cdot\cdot}}$ ($C$). The electron in the conduction band recombines with the trapped hole to give the visible emission ($D$).

Electron paramagnetic resonance (EPR) studies have shown that oxygen vacancies containing one electron ($V_{O^\cdot}$) are the predominant paramagnetic defects [5–7]. In macrocrystalline ZnO these defects are represented by a level approximately 2 eV below the conduction band edge [11] and they are often assumed to be the recombination centers for the visible emission in ZnO. The $V_{O^\cdot}$ center can only serve as the recombination center for the visible emission after formation of a $V_{O^{\cdot\cdot}}$
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A schematic overview of the radiative relaxation processes that take place upon photoexcitation of a ZnO dot [4]. The band edges are shown as well as a deep trap level in the bulk of the particle. At the surface of the dot, an energy distribution of an $O^{2-}/O^-$ state is shown. A The exciton relaxes to its ground-state emitting a UV-photon. This is the exciton emission. B The hole gets trapped in a surface state $O_S^{2-}$ which is oxidized to $O_S^-$. C The trapped hole is transferred to the oxygen vacancy $V_O^-$ which is oxidized to $V_O^{**}$. D The electron in the conduction band recombines with the trapped hole which gives rise to the visible emission.

Figure 5.2: A schematic overview of the radiative relaxation processes that take place upon photoexcitation of a ZnO dot [4]. The band edges are shown as well as a deep trap level in the bulk of the particle. At the surface of the dot, an energy distribution of an $O^{2-}/O^-$ state is shown. A The exciton relaxes to its ground-state emitting a UV-photon. This is the exciton emission. B The hole gets trapped in a surface state $O_S^{2-}$ which is oxidized to $O_S^-$. C The trapped hole is transferred to the oxygen vacancy $V_O^-$ which is oxidized to $V_O^{**}$. D The electron in the conduction band recombines with the trapped hole which gives rise to the visible emission.

center as was shown by Van Dijken et al. [4] (Figure 5.2).

Figure 5.3 shows the effect of purging the suspension with nitrogen and irradiation with UV light. Spectra were taken at different times after purging with nitrogen had started. Upon UV irradiation the visible emission quenches while the intensity of the exciton emission increases. The width of the exciton emission increases slightly (from 100 to 150 meV) and the peak maximum shifts to somewhat lower energies (3.36 to 3.34 eV) as the intensity increases, on the other hand, the width of the visible emission peak is constant (approximately 600 meV) and the peak maximum does not shift significantly.

The photochemical charging of the ZnO quantum dots with electrons was found to be responsible for the increased exciton emission [8]. Van Dijken showed
that admission of oxygen into the colloidal suspension restored the initial emission properties. The quenching of the visible emission was accounted for by assuming that oxygen scavenges photogenerated electrons. In the absence of oxygen, excess photogenerated electrons are present resulting in a passivation of $V^*_O/V^{**}_O$ centers, which are involved in the visible emission process [3, 4, 8] (see Figure 5.2). A $V^{**}_O$ center changes into a $V^*_O$ center by accepting an electron. The $V^*_O$ center can trap an additional electron to form a $V^*_O$ center which is located just below the conduction band edge [3, 4, 11]. Thus, in the presence of conduction electrons, the defect center for the green emission is removed. By performing measurements on an assembly, we hoped to obtain more detailed information on the role of conduction electrons in the defect and exciton luminescence.
5.4 Potential-dependent luminescence

5.4.1 Phosphate buffer

In Figure 5.4 room-temperature emission spectra are shown of a ZnO assembly permeated with a deaerated phosphate buffer. The numbers in the figures refer to the potential in V vs. Ag/AgCl. The total potential range is divided into four domains to emphasize the changes in the visible and exciton emission. The visible emission increases by a factor of about three when the potential is decreased from 0 to -0.5 V (A). The exciton emission is very weak and nearly constant in this potential domain. Changing the potential to more negative values leads to a strong decrease of the visible emission, while the exciton emission is increased (B). In the third domain (C), the visible emission has almost vanished. The exciton emission increases further with decreasing potential. The width of the exciton emission peak increases from about 0.1 to 0.3 eV in this domain. The width of the visible emission peak is broad (0.6 eV) and does not change much from 0 to -1 V. In the fourth domain from -1 to -1.2 V, the visible emission is completely quenched. The exciton emission decreases slightly at more negative potentials.

From the results presented in Figure 5.3 and 5.4 for the ZnO assembly and the ZnO suspension respectively, it is obvious that decreasing the potential (from -0.50 to -0.75 V) has the same effect on the luminescence as purging the UV-irradiated suspension with nitrogen.

The same potential-dependent luminescence characteristics were obtained by changing the potential back to more positive values. This shows that the assemblies are chemically stable in this potential range. Changing the potential to values more negative than -1.2 V leads, however, to irreversible damage of the ZnO layer; the assemblies of ZnO nanocrystals become turbid and less charge can be stored. The ZnO dots and the underlying TFO are known to be reduced in this potential range [12].

In Figure 5.5 the results from Figure 5.4 are summarized. The maximum intensity of both the visible and the exciton emission peaks are plotted versus the electrochemical potential. It can be clearly seen that the visible emission increases from an almost constant value to a maximum at -0.5 V about three times as high. At more negative values the visible emission is quenched. From Chapter 2 we know that -0.6 V is the onset potential for electron injection into the atom-like conduction levels of the ZnO quantum dots. At this potential the exciton emission starts to increase strongly and the visible emission is quenched.

With the results obtained from the charging experiments in Chapter 2 we can
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**Figure 5.4:** Room-temperature emission spectra of a ZnO assembly permeated with a phosphate buffer. The numbers in the figures refer to the potential in V vs. Ag/AgCl. The potential is changed in 50 mV steps. The total potential range is divided into four characteristic regions:  
- **A** From 0 to -0.5 V; the visible emission peak increases and the exciton emission is small and does not change.  
- **B** From -0.5 V to -0.75 V; the visible emission quenches gradually (by a factor of 20 at -0.75 V) and the exciton emission starts to increase at almost the same potential (from -0.6 V).  
- **C** From -0.75 V to -1.0 V; The visible emission is quenched almost completely and the exciton emission increases further and becomes the most intense emission.  
- **D** From -1.0 V to -1.2 V; the visible emission is quenched and the exciton emission decreases slightly.
Figure 5.5: Peak intensity of the visible and exciton emission as a function of the potential. The visible emission increases between 0 and -0.5 V from an almost constant value to a value 3 times higher and is quenched at more negative potentials. At -0.8 V the intensity has decreased to only 2% of the maximum value. The exciton emission has an almost constant value for the potential range from 0 to -0.55 V. At -0.6 V the exciton emission increases but is quenched at potentials higher than -1.05 V.

plot the maximum intensities of Figure 5.5 against the average number of electrons per quantum dot $\langle n \rangle$ (see Figure 5.6). It is clear that the visible emission is quenched as soon as electrons are injected into the conduction levels of the ZnO dots. The intensity has decreased by a factor of eight for $\langle n \rangle = 1$ and the visible emission has almost vanished for $\langle n \rangle = 2$. These results strongly suggest that on average there is at most one green luminescent defect center per quantum dot. The exciton emission increases almost linearly with $\langle n \rangle$ to a value of an average of six electrons per quantum dot. This shows that Auger recombination is not important in ZnO. In contrast, Auger recombination was found to be a dominant process in other quantum-dot systems, such as porous Si [13–15] and CdSe [16, 17]. In the case of Auger recombination an exciton can recombine non-radiatively by transferring its energy to an electron in a conduction level (or another exciton). The Auger-excited electron will relax by non-radiative processes. This leads to a decreasing luminescence with an increasing concentration of electrons in the conduction levels. It is not clear why Auger recombination is unimportant in ZnO and
why the luminescence intensity increases with $\langle n \rangle$. A possible explanation could be that the probability for radiative recombination is proportional to the number of electrons in the conduction levels. Further (theoretical) work is needed to answer these important questions.

In Chapter 2 and 3 we can find that at -0.8 V only about half the quantum dots have $N = 1$; at -0.8 V the maximum of the $S$-type energy level distribution is reached. This would suggest that the largest dots in the assembly are predominantly responsible for the visible emission. That could also be an explanation for the small shift in the energy of the visible and exciton peak maxima in Figure 5.7 are plotted versus the potential. The visible peak maximum shifts from around 2.12 to 2.10 eV in the same potential range in which the visible emission increases to its maximum value at -0.5 V. At more negative potentials the peak shifts to higher energy (approximately 2.3 eV at -1.15 V). In the potential range from 0 to -1 V we find an increase in the peak maximum energy of approximately 180 meV. For comparison, Hoyer et al. observed a much stronger increase of the energy of approximately 400 meV [9]. The shape of their visible emission peak also changed strongly in this potential range. They observed asymmetrical and ir-
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![Graph showing the relationship between potential (in V vs Ag/AgCl) and emission peak maximum energies for visible (VIS) and UV emission.](image)

**Figure 5.7:** Visible and exciton emission peak maximum energies. The visible peak maximum energy decreases from approximately 2.12 to 2.10 eV if the potential is changed from 0 to -0.5 V. If the potential is further decreased, the energy shifts to a maximum value of approximately 2.25 eV at -1.0 V. The exciton emission peak maximum energy shifts to lower energies from approximately 3.35 to 3.25 eV in the potential range of -0.6 to -1.2 V. Because of the irregular shape of the exciton emission peak at potentials more negative than -1 V we took the maximum energy of the best Gaussian fit.

The increasing intensity of the visible emission and the decreasing energy of this emission in the potential range of 0 to -0.5 V are not understood. The decrease in the visible emission, starting negative of -0.5 V is due to the loss of V\textsubscript{O} / V\textsubscript{O} centers caused by the occupation of these centers by electrons. The energy shifts to somewhat higher values because the largest dots are filled with electrons first, before the smaller ones. The upward shift by 180 meV is in line with the dispersion of the conduction energy levels deduced from independent optical and
Figure 5.8: Peak intensities of the visible and exciton emission as a function of the potential. The results are shown for a ZnO quantum-dot assembly permeated with PC. The visible emission increases by a factor 2 from 0 to -0.2 V and is quenched on going to more negative potentials. At -0.6 V the maximum intensity has decreased to only 5% of the maximum value. The exciton emission increases strongly at potentials more negative than -0.2 V but is quenched at potentials more negative than -0.9 V.

5.4.2 Propylene carbonate electrolyte

Here, we consider the role of conduction electrons on the defect and exciton luminescence for assemblies in an aprotic solvent (PC). In this case, fewer electrons can be stored per dot than in an assembly permeated with the phosphate buffer (see Chapter 3).

In Figure 5.8 the maximum peak intensities for the visible and exciton emission are shown as a function of the electrochemical potential of a ZnO quantum-dot assembly permeated with PC. The maximum intensities do not significantly differ from the values found with the phosphate buffer. We observe a similar potential dependence for the increase and quenching of the two emission peaks. The visible emission increases by a factor of 2 from 0 to -0.2 V and is quenched at
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Figure 5.9: Emission peak intensity of the visible and exciton emission as a function of the average electron occupation number $\langle n \rangle$. The visible emission intensity is almost completely quenched at $\langle n \rangle = 2$. The exciton emission increases almost linearly up to $\langle n \rangle = 2$.

more negative potentials. At -0.6 V the intensity has decreased to only 5% of the maximum value. The exciton emission increases strongly from -0.2 V to -0.9 V. Negative of -0.9 V, there is a slight decrease in intensity. This decrease is probably due to chemical degradation of the ZnO surface.

In Figure 5.9 the results from Figure 5.8 are replotted as intensity versus $\langle n \rangle$. The visible emission goes down as soon as electrons are injected into the ZnO assembly and this emission is almost completely quenched at $\langle n \rangle = 2$. The exciton emission increases as electrons are injected into the assembly. The increase is almost linear up to $\langle n \rangle = 2$. If we take $\langle n \rangle = 1$ as a reference we can compare the results in PC and water. The intensity of the visible emission has decreased to 7 and 13% of its maximum value for PC and the phosphate buffer, respectively. Thus, it seems that less electrons per quantum dot are needed in PC than in the phosphate buffer to get the same degree of quenching. A possible explanation is that the visible emission originates mainly from the larger quantum dots in the assembly. The Coulomb repulsion in the PC electrolyte causes the electrons to occupy mainly the larger quantum dots, in contrast to the situation without Coulomb repulsion (see Section 3.3.1). This is due to the increase of the electrochemical
potential for electron injection caused by the Coulomb repulsion.

In Figure 5.10 the energy maxima of the visible and exciton emission are shown as a function of the potential. The visible peak maximum decreases from approximately 2.15 to 2.10 eV as the potential is changed from 0 to -0.15 V. As the potential is further decreased, the peak energy increases gradually to a maximum value of approximately 2.25 eV at -1.15 V. The exciton emission peak maximum energy shifts to lower energies from about 3.33 to 3.28 eV in the potential range of -0.30 to -1.05 V. Because of the irregular shape of the exciton emission peak at potentials more negative than -0.9 V we took the peak energy of the best Gaussian fit. These results for PC are similar to the results obtained with the phosphate buffer in the same potential range as can be seen from Figure 5.7 and 5.10.
5.5 Conclusions

ZnO quantum dots show in general two types of emission: a broad-band emission in the visible range and a relatively narrow ultraviolet emission (the exciton emission). A change from predominantly visible to completely ultraviolet emission is observed on purging a ZnO suspension with nitrogen or inserting electrons electrochemically into ZnO assemblies. We found a strong decrease in the visible emission and a strong increase in the exciton emission with decreasing potential. The interpenetrating electrolyte had a clear effect on the emission characteristics. With PC much fewer electrons were needed to produce the same exciton emission intensity. The stability of the ZnO in the specific electrolyte solution seemed to be the limiting factor in the increase of the exciton emission.

References


