Photoluminescent Quantum-Dot Light Emitting Devices Controlled by Electric Field Induced Quenching

by

Melissa Li

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Abstract

Colloidal quantum dots (QDs) have been promising luminophores due to their bright,
pure, and tunable colors. The ability to control the emission properties of QDs
has far-reaching potential applications for a new generation of display and lighting
technologies. The emission control of QDs in a QD light-emitting device (LED) is
usually achieved by changing the injection current density. However, these devices
face issues with lifetime and stability as well as low external quantum efficiency (EQE)
at high biases. In this thesis, we demonstrate a unique approach in operating a QD
device that avoids these limitations. The device is a photoluminescent LED (PL-LED)
where the emission from the LED is from optical excitation. To tune the emission, we
apply a bias to intentionally dim or turn off the QD PL, using the PL quenching at
high biases to our advantage. We also study the field-induced quenching mechanisms
using capacitor structured PL-LEDs and QD-LEDs. Traditional electroluminescent
QD-LEDs can be used as a PL-LED when operated under reverse bias. We propose
that the electric-field induced quenching in our devices is due to exciton dissociation
and reduced band-edge exciton formation at high field strengths. The resulting QD
PL device exhibits voltage-controlled PL quenching up to 99.5%, corresponding to a
high contrast ratio of 200:1, and a sub-microsecond response time. Our demonstration
of PL tunability can lead to a new class of devices for fluorescent displays and voltage-
controlled devices.

Thesis Supervisor: Vladimir Bulović
Title: Professor
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Chapter 1

Introduction

Colloidal quantum dots (QDs) are solution processed nanoscale crystals of semiconducting materials. They emit bright, pure, and tunable colors and their saturated emission spans the visible spectrum. The ability to use colloidal synthesis techniques and their optical properties make them excellent candidates for low-cost light emitting devices (LEDs). Significant advances have been made in the synthesis of high-quality QDs, understanding QD photo-physics, and integrating QDs as emitters into thin film solid-state devices [6, 21]. While QDs have recently found applications as optically excited color enhancement films to improve the performance of conventional LCDs, commercially viable display technologies based solely on QD emission have yet to be developed. Substantial progress has been made toward electrically driven quantum dot light-emitting diodes (QD-LEDs), but challenges such as poor device stability [5] and efficiency droop at high biases [20] remain as hurdles toward commercialization. This quenching phenomenon at high biases is a problem that affects most types of LEDs, including OLEDs [20].

In this thesis, we attempt to deepen our understanding of this quenching phenomena and use it to our advantage through operating the QD-LED in an altogether different way. This proposed QD device is an optically excited photoluminescent LED (PL-LED), and the electric field is applied to intentionally turn off the device. By modulating the external field, we can in turn modulate the photoluminescence emission from the optically excited QD film and selectively turn on and off individual
devices [4]. Unlike the case with forward biased LEDs, where both QD excitation and emission intensity modulation are achieved through current injection into the QDs, the PL-LED decouples the two mechanisms. Moreover, we can dynamically modulate the emitted intensity without electrical injection of carriers that leads to the deterioration of QDs typically observed with electroluminescent QD-LEDs.

A PL display based on electric field induced quenching of PL-LEDs has many advantages over current display technologies. In an OLED display, to increase the brightness of a pixel, the current through the pixel and the voltage applied needs to be increased. This limits the maximum achievable brightness of OLEDs and other electroluminescent based devices since the device will break down after a certain voltage. With a PL-LED, the brightness is based on the intensity and wavelength of the excitation light source, which avoids the limitations of electrical breakdown. Additionally, a PL-LED does not need thick and conductive charge transport layers, allowing greater transparency.

Compared to LCDs displays, which operate under light filtering, a QD PL display ensures wider viewing angles since the QD emission profile is isotropic. The QD emission is also brighter and more stable than the phosphors in phosphor LCDs. Phosphor LCDs require the phosphors to have high PL quantum yields under UV excitation, which is extremely rare since most phosphors decompose under high energy UV light. Meanwhile, QD PL has been commercially proven to be extremely stable under continuous UV illumination, with PL quantum yields typically approaching unity.

1.1 Outline of Presented Work

The goals for this thesis are to study the quenching mechanisms in QD devices and to achieve PL quenching at low voltages to maximize on-off ratio of PL-LEDs. The general device structure is given in Chapter 3 and the following variations are made to the device to study the electric field effects on quenching in absence of charge injection:
• Using dielectric materials such as hafnium dioxide to form a capacitor structured PL-LED.

• Using a traditional QD-LED but operating the device in reverse-bias. Operating the device in reverse bias allows us to apply field without injecting charge. We use two QD-LEDs to study the dependence on the interfaces: monolayer of QDs (10 nm) and multilayer of QDs (30 nm).

We perform the following measurements to study the quenching mechanisms in the QD PL-LEDs.

• PL measurements using the photodetector with a steady state applied voltage to study the effects of voltage on PL.

• PL measurements using various waveforms to study transient effects of voltage on PL.

• Time-resolved PL to study the carrier dynamics. This gives us information on both the peak emission and the lifetime of the excitons involved in recombination.

• Differential absorption measurements to directly measure charge occupation and electric field in the QD film.

1.1.1 Thesis Organization

The structure of the thesis is as follows. Chapter 2 focuses on the basics of quantum dots, excitation mechanisms, and traditional electrically driven QD-LEDs. Chapter 3 gives an overview of optically excited PL-LEDs, device structure, and quenching mechanisms. Most of Chapter 3 can be found in [4]. Chapter 4 introduces the capacitor structured PL-LED where the quantum dot layer is sandwiched in between dielectrics. The capacitor structure is used as a proof of concept device that shows up to 80% quenching under a large applied bias of 40V. We also show similar results using a completely transparent device. However, the 80% quenching corresponds
to a low on-off ratio of 4:1, which is too low for displays. Moreover, the capacitor device shows transient PL dynamics when the device is under a constant bias. We attribute this to electric field screening from the photo-generated charges. To rapidly extract the photogenerated charges, we present a QD-LED operated as a PL-LED in Chapter 5, where we reverse bias the film to prevent charge injection. Through TRPL measurements we attribute the quenching to exciton dissociation and reduced band-edge exciton formation. The monolayered QD-LED shows a complete PL suppression of 99.5% at a constant 20V bias and a sub-microsecond response time, demonstrating it’s potential for display applications. The manuscripts covering the work in Chapter 5 are in preparation. Finally, Chapter 6 is the conclusion for this work and outlook for PL-LEDs. The future work includes improvements that could be made on the PL-LEDs presented in this work as well as preliminary data on a PL-LED controlled by charge induced quenching. The device structure is similar to the capacitor PL-LED, except one of the dielectric layers is swapped with a charge injection layer. This modified PL-LED can be used to study both the effects of charge induced quenching and carrier transport through quantum dot films.
Chapter 2

Background

2.1 Colloidal Quantum Dots

2.1.1 Physics of Quantum Dots

One of the greatest assets of quantum dots in light emitting applications is their size-tunable color emission. Their tunable band gap is governed by the quantum size effect. For a bulk semiconductor, the energy dispersion curve of a direct band gap semiconductor is shown in Figure 2-1a. When a semiconductor nanocrystal is smaller than its Bohr radius, the energy levels of the electron-hole pair (exciton) are altered due to boundary conditions. Thus, only the states that satisfy the boundary conditions are allowed (Figure 2-1b), leading to the quantization of bulk energy levels and atomic emission-like spectra. As a result, the band gap of the material is widened, allowing size-tunable band gap energies by simply changing the QD size. For example, cadmium selenide (CdSe), the most widely studied semiconductor for colloidal QDs, has a direct band gap energy of 1.73 eV, but CdSe QDs band gap can be tuned to up to 2.8 eV. This tunability is shown in Fig. 2-2, where solutions of colloidal QDs of varying size and composition exhibit PL under ultraviolet excitation. The PL spectra also exhibit a narrow linewidth of around 30 nm. Both the tunability and narrowband emission are advantages quantum dots have over organic dyes and inorganic phosphors.
Figure 2-1: (a) An energy band diagram of a direct bandgap semiconductor. (b) Only states that satisfy boundary conditions exist for QDs [10].

The energy levels of a QD can be analytically approximated by modeling the QD as a particle-in-a-sphere with infinite potential walls. This gives a confinement energy of,

$$E_{e,h}^{e,h} = \frac{\hbar^2 \phi_{l,n}^2}{2a^2 m_{e,h}},$$

where $\phi_{l,n}$ is the $n^{th}$ root of the spherical Bessel function of order $l$ and $m_{e,h}$ is the effective mass of the electron and hole, respectively. This can be viewed as the kinetic energy of a free particle, but with quantized wave vectors. We can apply the effective mass approximation and model the conduction and valence bands parabolically since the QDs are usually larger than the lattice constants of the constituent materials. We can also describe the particle wavefunctions as linear combinations of Bloch wavefunctions. The exciton energy (from [10]) is given by

$$E_{\text{exciton}} = E_g + \frac{\hbar^2}{2a^2} \left( \frac{\beta_{nle}^2}{m_e} + \frac{\beta_{nlh}^2}{m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon a},$$

where the first term, $E_g$, accounts for the dependence on the bulk band gap of the semiconductor, the second term is the quantum confinement term from equation 2.1.
Figure 2-2: Tunable and pure color light emission from colloidal quantum dots [2, 23].
that depends on the QD radius, $a$, and the third term is the Coulombic attraction between the electron and hole. The 1.8 results from assuming the electron and hole are both in their respective 1S state, i.e. lowest excited state. Therefore, the Coloumb energy can be calculated using first order perturbation theory, which gives:

$$\Delta E = \langle \psi_e, \psi_h | \frac{-q^2}{4\pi\epsilon|\vec{r}_e - \vec{r}_h|} | \psi_e, \psi_h \rangle.$$  \tag{2.3}$$

For the 1S state the electron or hole wavefunction, $\psi_{e,h}$, is given by

$$\psi_{e,h} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(\pi r/a)}{r}.$$  \tag{2.4}$$

However, the quantum confinement effect derived from the simple parabolic band approximation is only a model that accounts for the correlation between QD size and PL energy. Since this thesis focuses on QD PL operated in a device, it is worth noting that a more detailed multi-band effective mass approximation is required to explain some of the intricacies of QD PL spectra. As mentioned, lowest excited state of a QD is when the electron and the hole are in the 1S and $1S_{3/2}$ states respectively. This state is called the bandedge exciton state and is eight-fold degenerate. The degeneracy is a product of two-fold degenerate electron states and four-fold degenerate hole states. Many of the perturbation effects can lift this degeneracy and create an exciton fine structure [13]. The lowest energy exciton state is an optically inactive state, known as the dark exciton state, that lies below an optically active state, called the bright exciton state. The difference between the two states are generally less than $k_B T$ at room temperature, so the exciton in the dark state can be thermally excited to the bright state, making the QDs efficient at room temperature. In Chapter 5, we see this effect of this two sub-population emission.
2.1.2 Operating Mechanisms

Excitons in QDs

An exciton is a bound electron-hole pair that can be formed either optically or electrically. The pair is bound by Coulomb interaction between the electron and the hole. Excitons are typically categorized into two types: Wannier-Mott excitons and Frenkel excitons. Wannier-Mott excitons, or free excitons, are excitons observed in inorganic semiconductors and other materials with high dielectric constants ($\epsilon_r > 10$). The Coulomb interaction is weak in these materials due to screening. As a result, these excitons are large and extend over many atoms. They have low binding energies (around 0.01 eV) and are generally not observable at room temperature.

Frenkel excitons, or tightly bound excitons, are excitons often observed in organic molecules. Organic materials have a low dielectric constant ($\epsilon_r \sim 3$), resulting in strong Coulomb interaction. The excitons are localized to individual molecules and have high binding energies (0.1-1 eV), which make them observable at room temperature.

However, the excitons in QDs are different in nature from the above two excitons. QD excitons are generally bounded by physical confinement due to a potential well instead of Coulomb interactions. As shown in equation 2.2, the kinetic energy of the charge carrier becomes larger than the Coulomb interaction energy as the QD radius, $a$, gets smaller.

QD excitation mechanisms

As shown in Figure 2-3, there are four ways to generate excitons in QDs.

1. Optical excitation: Figure 2-3a, demonstrates optical excitation, where an exciton is formed in a QD by absorbing a photon.

2. Charge injection: Figure 2-3b shows an exciton forming through charge injection, where neighboring charge transport layers (CTL) inject charge carriers directly into the QD.
3. Energy Transfer: Figure 2-3c shows an exciton that is transferred from a nearby molecule through Förster resonant energy transfer (FRET). When the nearby molecule can emit a photon, it has a transition dipole. The dipole represents the strength of oscillating current and generates an oscillating near-field that can excite the QD.

4. Ionization: Figure 2-3d shows an electric field ionizing an electron from one QD to another and generating a hole. In a QD film, the generated electrons and holes can meet on the same QD to form excitons.

In all the four instances listed above, the exciton recombines (Figure 2-3e) and generates light. In electrically driven QD-LEDs, described in the next section, the dominating mechanisms are direct charge injection and FRET [22]. In PL-LEDs, described in detail in the next chapter, the excitation is driven by optical excitation.
2.2 Electroluminescent QD-LEDs

Electroluminescent QD-LEDs are electrically driven thin film light-emitting devices that uses QDs as luminophores. They are similar to organic light emitting diode (OLEDS), sharing many of the material sets and fabrication techniques. Figure 2-4 shows a typical QD-LED design and operation. It is typically comprised of a QD film sandwiched between an inorganic metal oxide electron transport layer and an organic hole transport layer.

2.2.1 Operating Mechanisms

These electrically driven QD-LEDs are mostly driven by direct charge injection and FRET. In the case of direct charge injection, shown in Figure 2-5 with green arrows, an electron and hole are injected from electron transport layers (ETL) and hole transport layers (HTL), respectively, into the quantum dot. In Figure 2-5 (blue arrows), an exciton is first formed on a luminescent CTL and then transferred to the QD via FRET.
In the past few years, substantial progress have been made toward EL QD-LEDs. However, as previously mentioned, there are many challenges facing these devices. Besides the quenching phenomena at high current densities, the constant current flow through the QDs also leads to intrinsic device degradation. Moreover, the complex device architecture with charge injection and transport layers are opaque to visible light. In the next chapter, we introduce a new device architecture that avoids these problems.
Chapter 3

Photoluminescent LEDs

To avoid the deleterious effects of charge and field from electroluminescent QD-LEDs, we propose an LED based on optical excitation of the QD, a photoluminescent LED (PL-LED). For this device, the electric field is applied only to intentionally dim or turn off the QD PL emission. This approach leverages the optical performance of QDs while avoiding the challenges of exciting them electrically. This chapter provides the device structure and operational mechanisms of the PL-LED.

3.1 Device Structure

Figure 3-1 shows the cross-sectional view of a PL-LED. In this device structure, a substrate made up of a transparent material such as glass or plastic is coated with the following layers and materials:

1. **Electrodes:** A conductive material, such as aluminum (Al), gold (Au), silver (Ag), etc. can be used as one of the two electrodes. However, one of the electrodes must be transparent in order for the PL to be collected through the face of the device. A number of transparent conducting materials could be used, including but not limited to indium tin oxide (ITO), fluorine-doped tin oxide (FTO), indium zinc oxide (IZO), etc.

2. **Barrier layers:** Depending on the quenching mechanism, the barrier layers could
be an insulating dielectric material or a charge transporting semiconductor. For electric-field induced quenching, an insulating dielectric material such as silicon dioxide, hafnium dioxide, etc. could be used to form a capacitor structure. For charge injection quenching, a charge transporting semiconductor such as zinc oxide, titanium oxide, etc. could be used. The quenching mechanisms are described in the next section.

3. **Emitter**: The emitter used in this thesis are colloidal quantum dots (QDs). As mentioned Chapter 2, the physical dimensions of these quantum-confined QDs could be varied to change the band gap and the wavelength of emission. However, other quantum-confined nanostructured materials like nanorods, nanowires, nanoplatelets, etc can also be used.

3.2 **Device Operation**

Figure 3-2 shows the cross-sectional view of a PL-LED in the "ON" and "OFF" state. The excitation light is provided by an external light source, e.g. an ultraviolet light emitting diode (UV-LED). In the "ON" state, no voltage is applied between the two electrodes so the emitter is excited by the excitation light and emits light in the visible spectrum. In the "OFF" state, a voltage is applied between the two electrodes. The
applied voltage quenches the emitter, i.e., decreasing the emitter intensity.

3.3 Quenching Mechanisms

From previous studies on single dots and QD films, there are primarily two known causes of bias-induced photoluminescence (PL) quenching: 1) applied electric field that results in exciton polarization or dissociation [3, 20], Fig. 3-3, and 2) charging of QDs, Fig. 3-4 [9].

3.3.1 Electric Field Induced

As shown in Figure 3-3c, an applied electric field partially polarizes excitons in the emitter by driving the electron and hole toward opposite directions and decreasing the electron and hole overlap. The electron and hole can be uniformly separated, (Fig. 3-3a) or completely delocalized (Fig. 3-3b). The radiative recombination rate is proportional to the wave-function overlap, thus the reduction in the overlap diminishes the PL. This process also often results in a red-shift of the PL spectrum, known as the quantum-confined stark effect (QCSE). For instance, studies performed on single CdSe QDs have showed substantial PL quenching and up to 40 meV shift in peak emission at 0.35 MV/cm [8, 14]. At strong enough fields, the exciton dissociation rate increases by lowering the inter-dot tunneling barrier for the electron or hole.
Figure 3-3: Electric field induced quenching through (a) exciton polarization and (b) exciton dissociation. (c) The electron and hole wave function overlap decreases as the applied field increases.

Figure 3-4: Quenching through Auger recombination. Instead of emitting a photon, the exciton transfers its energy to a nearby charge.

3.3.2 Auger Recombination

QD charging can efficiently quench QD luminescence by opening up the Auger recombination pathway. This mechanism has now been widely accepted as a dominant factor for efficiency loss in most QD-LEDs especially at high current density [19]. Auger recombination is a non-radiative exciton recombination mechanism that involves a third charge carrier (shown in Fig. 3-4). Instead of emitting a photon, the exciton transfers its energy to a nearby carrier and then enters back to its ground state after being excited.

Several studies have attempted to characterize PL quenching of QD films in ab-
Bozyigit et al. used a capacitor-structured QD device to show that the electric field strongly quenches the luminance of QD solids through spatial separation of electron and hole wavefunctions [3]. Adopting a similar capacitor structure, Rowland et al. utilized QD emission to track the action potential profile of a firing neuron and attributed the PL quenching to field driven exciton ionization [16]. However, despite these studies, the field-induced PL quenching mechanisms in QDs are still debatable.

In the following chapters, we show that the quenching in our devices is due to a combination of QCSE and field-induced hot electron extraction. We then demonstrate its potential for PL displays where we use the PL quenching to dim selective pixels. Previous work from Salihoglu et al. had demonstrated a color-variable PL display that uses QD PL quenching by directly injecting charges into the QDs through graphene [18]. However, the performance of their QD PL devices demonstrated so far is inadequate. In order to use their PL-LEDs for display applications, the contrast ratio (maximum fractional PL quenching achievable) and PL modulation speed require further improvements.
Chapter 4

Capacitor Structured PL-LED

4.1 Device Overview

A capacitor structure allows us to apply electric field without charge injection from electrodes. In a capacitor structured device, the QD film is sandwiched between two wide bandgap dielectric layers. The dielectric materials surrounding the QD film have to meet certain requirements: the layers should be a thin and transparent material with a high dielectric constant so that a large electric field can be placed across the QD to enable maximum quenching. Additionally, the materials need to be resistive so that they impede charge injection. It is also important that the QD PL quenching is minimized during the fabrication process, specifically when putting down the layers on top of the quantum dots.

4.1.1 Device Fabrication

The general structure of the capacitor structured PL-LEDs used in this chapter is shown in Fig. 4-1: Glass/ITO/Hafnium Dioxide (50 nm)/QD (20-50 nm)/Parylene (10 nm)/Hafnium Dioxide (50 nm)/Aluminum or ITO (100 nm). Fabrication of QD PL-LEDs require successions of thin film depositions and the fabrication method of each layer depends on the material being deposited and the material of the previous layer. The materials used in thin film optoelectronic devices are generally sensitive
4.2 Results

4.2.1 Steady-State Measurements

To study the effect of electric field on QD PL in our capacitor structured PL-LED, we first perform steady-state PL measurements by applying the bias to the device under optical excitation while measuring the PL intensity and spectrum. The resulting
integrated PL intensity as a function of bias is shown in Fig. 4-2. The PL intensity (normalized to the integrated intensity at zero bias) monotonically decreases with the applied field and shows fluorescence quenching up 80%.

The resulting spectrum and image of the device under the operation is shown in Fig. 4-3. The observed ~80% quenching under 40V corresponds to a contrast ratio of 4:1. The pixel image in Fig. 4-3b clearly shows the distinction when the field is off (pixel on) and when the field is applied (pixel off), successfully demonstrating the ability to use electric field quenching to control PL pixels. However, 40V is unreasonable high and the contrast ratio of 4:1 is too low for display applications, which usually start from 200:1 [1]. Chapter 5 will discuss an alternative device structure that significantly improves these results.

4.2.2 Transient Measurements

To study the PL quenching dynamics, we apply an extended voltage pulse and monitor the temporal evolution of PL. Here we use the term "VON transient" to refer to the transient behavior and recovery of PL intensity while a bias is held constant, and use "VOFF transient" to describe the restoration of PL after the bias is removed. Note that for applications such as displays, we want a slow or no VON transient since the
Figure 4-3: PL spectrum and image of the capacitor structured device. (a) PL spectrum when no voltage applied (black) and when 40V is applied (red). The spectrum under 40V shows $\sim80\%$ quenching. (b) Image of the device and pixel with 0V and 40V applied.

PL should be held constant without recovery at a constant applied voltage, but a fast VOFF transient where the PL should quickly recover to its original value once the voltage is turned off.

The resulting PL intensity time traces under 1s and 1ms square 40V pulses are plotted in Fig 4-4a. From the 1s time trace (blue), we see the VON transient where the PL recovers quickly even under an applied bias (this effect is on the order of milliseconds and is hard to see in Fig. 4-4a due to the time scale, but Fig 4-5b shows a zoomed in image at this VON edge that clearly illustrates this recovery). Ideally, the PL should be held constant during the .5 s when the device is under bias. If we apply a higher frequency pulse (1 ms shown in green in Fig 4-4a), we suppress the VON transient recovery and the PL quenching appears to be held constant. Since these
dynamics occur on a time scale of hundreds of milliseconds to seconds, we suspect there is charge trapping in the device. While we do not expect charge injection, since we use a capacitor structure, previous single particle blinking experiments have demonstrated that an isolated QD may become spontaneously charged through an ionization process where a photo-generated charge is ejected from the bulk of the nanocrystal into the surface states or the surrounding matrix and becomes trapped [7]. Either the trapped charge or the opposite charge left on the QD may be able to screen the external electric field, thereby reduce the amount of field-induced quenching. The underlying physical processes are further examined using differential absorption spectroscopy in Chapter 5. In addition to these VON transient dynamics, the VOFF transient (PL recovery when bias is turned off), shown in Fig 4-4b, is extremely slow and doesn’t recover to it’s original value until minutes after the bias is turned off. For display applications, the transition times where the device turns on and off with the field is too slow. This should be on the order of milliseconds for pixels in a display [1]. The device structure in Chapter 5 will also address these issues.

**Transient Measurements with Transparent Top Electrode**

The measurements above were tested using an aluminum top electrode. To demonstrate the potential of the device to be completely transparent, we replace the alu-
minimum top electrode with sputtered ITO. The resulting time trace of the device under a 40V square bias is shown in Fig 4-5. When we zoom in on the edge where the voltage switches from 0V to 40V (Fig. 4-5b), we observe ∼80% quenching. We also clearly see the VON transient PL recovery that happens on the order of milliseconds.

4.2.3 Testing Methods

All of the steady-state PL measurements are performed on encapsulated devices in air. A 405 nm pulsed laser with 80 MHz repetition rate is used as a quasi-CW source. For measurements where the excitation is synchronized to the bias, the laser is electrically gated but with the leading and trailing edge of the laser pulse shifted by about 5us toward the middle of the bias pulse, so that the measured PL is not affected by any electrical transients. The laser is incident on the device at approximately 20 degrees from normal through the glass/ITO, while the PL is collected and delivered to an imaging spectrometer. A long-pass filter between the relay lens filters out the scattered 405nm light. For PL time trace measurements, the spectra are collected continuously.

4.3 Summary

We demonstrate that a capacitor structured PL-LED allows us to modulate the QD emission by applying an electric field to quench the PL without current injection. The device structure and operation method of the PL-LED has many advantages over electroluminescent LEDs. Our device architecture, where the QD layer is sandwiched between dielectrics, is much simpler than traditional LEDs, where charge transport layers need to be carefully chosen for proper band alignment. We can also more easily make our device transparent by choosing transparent dielectrics and conductors, like HfO$_2$ and ITO. The operation mechanism of a PL-LED is also better for device stability since the lack of charge injection prevents electrical degradation.

However, the proof of concept device has its limitations. We are able to show up to 80% quenching under a 40V bias, corresponding to a contrast ratio of 4:1. For
Figure 4-5: (a) Time traces of PL under 40V square wave bias for transparent PL-LED. (b) Zoomed in trace for when voltage is switched on
display applications, the contrast ratio is too low and the voltage applied is too high. Moreover, the transition time where the PL turns on and off with the field is too slow and should be on the order of milliseconds for displays. Finally, the electric field screening effect from photo-generated charges severely limits the PL quenching. To address these issues of low on-off ratio, slow transition time, and electric field screening, we use an alternative device structure in Chapter 5, which is a traditional quantum dot LED device but operated under reverse bias.
Chapter 5

Reverse biased QD-LED as a PL-LED

5.1 Device Overview

The challenges of limited contrast ratio and slow response times for the devices in Chapter 4 are both associated with electric field screening by charges that reside in delocalized band-edge states, defect states on the nanocrystal, or electronic states in the surrounding matrix. We significantly improve the electric field induced quenching of QD PL in this chapter by operating a highly efficient QD-LED under reverse bias. The electroluminescence performance under forward bias of the QD-LED is shown in Fig. 5-1b. The device exhibits an EL emission centered at 635 nm with peak external quantum efficiency of 15.9% at 2.9 V. Assuming an outcoupling efficiency of 20%, the internal photoluminescence quantum yield of the QD film is at least 80%. This highly efficient QD-LED can be operated as a PL-LED by optically exciting the film but applying a reverse bias to control the PL emission. Reverse biasing the device allows both the application of electric field without external charge injection from electrodes and the rapid extraction of the unwanted photo-generated charges.

5.1.1 Device Fabrication

The structure and energy band diagram of the QD-LEDs used in this chapter are shown in Fig. 5-1a. Our QD-LEDs are comprised of CdSe/ZnCdS core-shell QDs
sandwiched between a ZnO ETL and a tris(4-carbazoyl-9-ylphenyl)amine (TCTA) HTL. Thin films of Al, molybdenum oxide (MoO$_3$), and ITO are used as the anode, hole injection layer, and cathode, respectively.

Since the materials used in the QD-LED differ from the ones used in the capacitor devices in Chapter 4, the fabrication method differs slightly. Prior to device fabrication, pre-patterned ITO glass substrates are cleaned following the procedure in Appendix A. Then, ZnO nanoparticles dissolved in a mixture of methanol and isopropanol are spin-coated onto the ITO substrates at 2000 rpm for 45 s and annealed at 100 °C for 45 min in a nitrogen-filled glovebox. Next, the QD solution is spin-coated at 2000 rpm for 45 s followed by successive thermal evaporation of TCTA, MoO$_3$, and Al at deposition rates of 1 Å/s, 0.5 Å/s, and 2-3 Å/s, respectively. Further details about material synthesis and fabrication methods are discussed in Appendix A.
5.2 Results

5.2.1 Steady-State PL measurements

To study the effect of electric field on QD PL in our QD-LEDs, we first perform steady-state PL measurements by reverse biasing the device under optical excitation while measuring the PL intensity and spectrum. We apply 2 ms duration square voltage pulses at 100Hz repetition rate with amplitudes from 0V to -20V, corresponding to electric fields up to 3.3 MV/cm. The waveform is selected to minimize the effect of charge trapping in the initial characterization. The field strength in the QD film is estimated by dividing the applied bias by total thickness of the QD and HTL, which have similar dielectric constants of $3^{19}$. Two devices with QD films thickness of 10nm (monolayer) and 30nm are used in this study. As shown in Fig.5-2, both devices exhibit PL quenching with increasing electric field strength. In addition to the expected PL decrease, the PL spectra in Fig.5-2a show significant red-shift as well as broadening, both signatures of QCSE. The integrated PL intensity, normalized to the intensity at zero bias, of the two devices is shown in Fig 5-2b. Under same field strength, the device with thinner QD exhibits a higher degree of PL quenching up to a maximum of 99.5% at around 3MV/cm, corresponding to a contrast ratio of 200:1. No further improvement on PL quenching is observed beyond -20V, at which point leakage current reaches 20nA. The CCD camera image of the QD-LED under the microscope in Fig.5-3 starts to show residual electroluminescent emission from the area under -24V, which is suggestive of dielectric breakdown. The residual emission is also possibly due to EL generated through QD ionization, where an electron can transfer from the valence band of one QD to the conduction band of a neighboring QD when the applied voltage exceeds the bandgap energy. This process has been previously used to demonstrate AC driven QD-LEDs [23].
Figure 5-2: Steady state PL spectra of devices with (a) 10nm and 30nm of QD both exhibit a decrease in PL intensity and a red shift in peak wavelength with increasing electric field. (b) Integrated PL intensity (normalized) as a function of applied electric field shows more significant quenching for device with thinner QD layer.

5.2.2 Transient measurements

To study the effects of electric field screening by charges, we apply an extended voltage pulse and monitor the temporal evolution of the PL. The time response at the start and end of a 10V pulse for the monolayered device is measured using an APD and is shown in Fig. 5-4b. The device shows a fast response time of about 300 ns, which is sufficient for displays. This response time is much faster than the capacitor device (Fig. 4-4b), which occurs on the order of seconds.

The resulting PL intensity time traces under 10s square voltage pulses of different
amplitudes are shown in Fig. 5-4a. The amplitude of the voltage pulses here also range from 0 to -20V, corresponding to a maximum field strength of 2.5 and 3.3 MV/cm for the 30nm and 10nm QDs respectively. We observe a slow VON transient PL recovery in the intensity while the voltage is held constant. This VON transient is more prominent at lower applied fields and for the thicker QD device (shown in blue in Fig. 5-4a), but is almost completely suppressed at -20V for the monolayer device (red in Fig. 5-4a. The slow or lack of recovery under bias is particularly attractive for displays or probes where the PL should be tunable and held constant at a given voltage. As mentioned, these dynamics are likely due to charge trapping in the device that screens the electric field, reducing the amount of quenching. The underlying physical processes are further examined using differential absorption spectroscopy in the next section to quantify the degree of charging when the device is under reverse bias.

5.2.3 Differential Absorption Measurements

We use the differential absorption measurements to measure charge occupation and electric field on the QD film at various points during the VON and VOFF transients, as shown in Fig. 5-5. As mentioned earlier, the VON transients are more significant for thicker QD films and lower electric field. Thus a device with 30 nm QD film at -10V bias is used for the measurements. We first note that the VON transient is
Figure 5-4: (a) Modulation of PL intensity under different applied fields. (b) PL intensity measured at the start (bottom) and the end (top) of a 10V pulse for device with 10nm QD, showing a fast response time on the order of hundred nanoseconds.
concomitant with a blue shift toward the zero-field value. This suggests either lower electric field resulting from reduced QCSE, or the presence of delocalized electrons, which under photoexcitation leads to the formation of negative trions with lower electric field polarizability [11]. Differential absorption shows that the QD electron population remains minimal during the entire reverse bias pulse. We therefore attribute the VON transient to electric field screening by trapping of photo-generated charges, although we are unable to pinpoint which carrier is trapped. When the bias is removed, PL intensity does not immediately return to the initial zero-bias value, but rather does so over seconds, similar to the capacitor device. Differential absorption measurements show a sharp, immediate increase in $1S_e$ electron population when the bias is removed. We attribute the rush of electrons into the QD film to the existence of trapped holes that remain in the device when bias is turned off, which shifts the vacuum level of the QD film.

5.2.4 Time-resolved PL

In order to study the mechanisms behind PL quenching, we investigate exciton decay dynamics at different applied electric field using time-resolved photoluminescence (TRPL) measurements. Fig.5-6 shows the TRPL at different electric fields up to 1.7MV/cm for the device with a monolayer of QD. The normalized traces in the inset clearly illustrate the changes in the exciton lifetime. We extract three exciton lifetimes: the short lifetime $\tau_1$, long lifetime $\tau_2$, and $\tau_{1/e}$ where the PL intensity has decreased to $1/e$ of its initial value. The lifetimes, given in Fig. 5-6b, show a marked decrease from 15.7 to 5.5 ns when the electric field increases from zero to 1.7MV/cm. Unexpectedly, this trend differs from multiple earlier investigations in which PL lifetime remain constant with electric field [20, 3, 16]. To explain this, we note that the primarily difference between our device and those in the earlier works is the two interfaces sandwiching the monolayer of QD film. A favorable band-alignment between the QDs and ZnO or TCTA under reverse bias lowers the energy barrier for exciton dissociation, leading to observed lifetime decrease with increasing field.

While exciton dissociation qualitatively agrees with the reduction in PL intensity,
it does not explain why the peak height of the TRPL curves immediately following photo-excitation decreases with increasing field. If the exciton dissociation were the only effect of the applied field, the instantaneous radiative rate just after photoexcitation would remain constant. We explore two distinct possibilities that could give rise to the observed trend: a decrease in radiative recombination rate due to reduced spatial overlap of the electron and hole wavefunctions (QCSE), and a reduction in the number of band-edge excitons formed due to hot carrier trapping.
Figure 5-6: (a) Time-resolved PL decays of QD-LED with 10nm QD reverse biased with increasing electric field from 0 up to 2.0 MV/cm. Inset: normalized decay traces. (b) Lifetimes from biexponential fit.

**Decrease in Radiative Recombination Rate**

The possibility of a strong QCSE is consistent with the large observed redshift of the PL spectrum. The ZnCdS shell provides an intermediate confinement potential for the 1$S_e$ electron, between that of CdS and ZnS, and allows partial wavefunction leakage into the shell. This can result in a significant reduction in the optical transition matrix element for the lowest exciton. Bozyigit et. al. estimated that an electric field of 1.7MV/cm, corresponding to -8V bias in our device, could lead to a 1.6x and 5x increase in the radiative lifetime of a 4nm core-diameter CdSe QD coated with 2.1nm
thick CdS and ZnS shells respectively [3]. A similar conclusion was reached in an analytical calculation that takes into account of the fine structure of band-edge hole states [13], which also showed that the nearly eightfold degenerate $1S_e 1S_{3/2}$ zero-field exciton ground state is split into a doublet by a large electric field. From the PL spectra of our device (Fig. 5-2a), we see a clear second peak developing as bias is increased to beyond -10V. The second peak is split from the main peak by more than 100 meV at -16V in the 30nm QD device. The PL spectra of the 10nm QD device and the 30nm QD device exhibit different shapes at similar field, with the thicker device showing a larger contribution from the low energy peak as well as higher total intensity. This can be explained by the fact that charge carriers on QDs in the thinner device can be ionized more easily. Exciton dissociation from the higher energy state competes with the relaxation to the exciton ground state, hence reduce the ground state PL emission intensity. The disappearance of ground state emission as the bias is increased to -20V is likely due to a further decrease in both the relative relaxation rate and the ground state radiative recombination rate.
Hot Carrier Trapping

Next, we consider the process of hot carrier trapping or extraction that could occur prior to a photo-excited electron or hole relaxing to a low energy state. This would decrease the number of emissive excitons formed and lead to the drop in peak TRPL intensity. At high excitation energy, photo-excited carriers are delocalized over the entire shell. These hot carriers can be trapped by localized surface states on a time scale of hundreds of femtoseconds to picoseconds. Reports have shown that the relative rate of charge trapping versus relaxation to the band-edge depends on the excitation energy, thereby leading to an excitation energy dependence of the PLQY if the trapped charges are ultimately extracted by the electrodes or recombine through non-radiative channels [17, 15]. Given the high PLQY of our QD film at 405 nm excitation, we do not expect a significant amount of hot carrier trapping at zero field. However, it could be induced by a large electric field, which modifies both charge-phonon coupling and interaction of charge carriers with defect states. To check whether this mechanism plays a role, we measure the steady-state PL quenching at different excitation wavelengths from 460nm to 590nm, shown in Fig. 5-7. At -20V bias, PL quenching of 460nm excitation is 3.5x more efficient than quenching of 590nm excitation, confirming the role of hot carriers in field-induced PL quenching.

5.2.5 Testing Methods

The steady-state and transient PL measurements are taken following the procedure from Section 4.2.3. Time-resolved photoluminescence (TRPL) data is taken using a silicon detector and a time-correlated single photon counting module. The samples are excited using a 405nm pulsed laser at a repetition rate of 2.5MHz. The instrument response of the system at the detected wavelength is measured to have a FWHM of less than 0.5ns. The QD-LEDs are driven using square pulses of 1ms duration and 10ms period to limit photo-charging effects. Both the laser and the detector are gated such that the laser pulses are produced and photons are collected only when the bias pulses are high. Excitation wavelength dependent PL measurements are taken using a laser
with an acousto-optic tunable filter as the excitation source. At each bias, excitation wavelength is changed every 50ms. The entire list of excitation wavelengths is cycled through and repeated an integer number of times until the desired signal-to-noise ratio is reached. Finally, the differential absorption measurement set up is given by Zhu [24].

5.3 Summary

In this chapter, we demonstrate that traditional QD-LEDs can be operated as an efficient PL device when operated in reverse bias. We show quenching up to 99.5% and a sub-microsecond response time. Using a combination of field-dependent TRPL and differential absorption measurements, we identify that exciton dissociation and decreased band-edge exciton formation are the sources of reduced PL intensity with increasing applied field. In addition, by analyzing the transient behaviors in PL quenching, we infer that there is surface charge trapping by the transport layers surrounding the QD under large external field. Under a large enough reverse bias, we can extract these unwanted charges in the monolayered QD-LED and suppress the transient behavior. Since no modification to the QD-LED structure for forward bias operation is required, this can be a highly efficient dual-functioning device. A similar structure could potentially be integrated into an optical cavity for dual operation as a laser or electro-optic modulator.
Chapter 6

Conclusion

6.1 Thesis Summary

The results presented in this thesis open up exciting possibilities of using QD PL device in display application as well as offering a platform of studying the physical processes governing QD emission in solid state devices. Using optical spectroscopy, we show that a large electric field can strongly modify hot carrier dynamics in a nanos- tructure. The stable and repeatable quenching is accomplished by a combination of hot carrier trapping or extraction, QCSE, and exciton dissociation.

In Chapter 4, we introduce a capacitor structured PL-LED that shows 80% quenching under a 40V bias. However, we observe transient behaviors while the device is under a constant bias and a long PL recovery time when the bias is turned off. Using a monolayered device in Chapter 5, we are able to show strong PL reduction up to 99.5% under a 20V bias along with fast sub-microsecond response times, giving us the best performing QD PL device to date. The monolayer device shows improvements in the VON transients over the capacitor device and the 30nm QD device, where differential absorption measurements suggest trapped photogenerated charges screen the electric field. By reverse biasing the monolayer QD-LED, we can rapidly extract these unwanted charges, thus improving both the degree of quenching and the transient behavior.
Figure 6-1: Device structure and time trace of a PL-LED enabled by charge induced quenching

6.2 Future Work

6.2.1 Improvements on Capacitor Structured Device

Despite the improvements on the PL quenching and transient behavior using a reverse biased monolayer QD-LED, there are advantages of using the capacitor structure. For example, the capacitor architecture, where the QD layer is sandwiched between dielectrics, is simpler than for the traditional QD-LEDs. The charge transport layers need to be carefully chosen for proper band alignment in a QD-LED in order for us to extract the photogenerated charges. For a capacitor PL-LED, we do not have to worry specifically about band alignment as long as the QD is sandwiched between dielectric layers. Improvements in the capacitor structure can be made by replacing quantum dots with 1D or 2D nanostructures (i.e. nano-rods or nano-platelets) with an extended dimension parallel to the electric field. This could enhance the QCSE, enable greater quenching at lower biases. Moreover, the transient behavior caused by electric field screening by trapped photogenerated charges can be minimized by doing further experiments to identify the exact origins of the trapped states.
6.2.2 PL-LED Controlled by Direct Charge Injection

In this thesis, we focus on studying the electric field induced quenching in QD. However, we can also implement a device based on charge induced quenching. Using a charge transporting semiconductor such as zinc oxide on one side of the QD film and a dielectric on the other side, we can intentionally inject electrons through the film to quench the dots. This would allow us to study the charging effect on quenching. As a proof of concept of this method, we adopt the structure of the capacitor PL-LED (Fig. 4-1) but swap out the bottom dielectric with sputtered ZnO to inject electrons.

The device structure and PL time traces of the device is shown in Fig. 6-1. The square voltage waveform (green) is varied between -2.5V to 2.5V. It is important to note here that the voltage is being applied to the ITO electrode and the Al electrode is grounded. When the voltage transitions from negative to positive, we see a large momentary quenching of $\sim 90\%$ at only 2.5V. When the voltage switches from positive to negative, the PL also momentarily decreases but only to $\sim 10\%$. To explain this result, we use the following picture: when a negative voltage is applied to the ITO, electrons are being stochastically being injected from the ZnO through the quantum dots. However, since the electrons cannot pass through the dielectrics, the electrons pile up at the quantum dot-parylene interface. When the voltage switches from negative to positive, these piled up electrons then simultaneously pass through the QD device, which explains the high degree of momentary quenching. These results have promising applications other than displays. For example, this simple device structure could potentially be implemented as a method to measure drift velocity through the QD film. However, more characterizations such as PL spectrum and TRPL, need to be taken in order to realize its potential applications.
Appendix A

Fabrication Methods

A.1 Deposition Methods

This appendix introduces the fabrication procedures of PL-LEDs. Fabrication of thin film optoelectronic devices that contain materials sensitive to $O_2$ and $H_2O$, such as organic materials and QDs, usually takes place in a high vacuum chamber or a glove box filled with $N_2$. The devices used in this thesis were fabricated and tested at the Organic and Nanostructured Electronics Laboratory (ONE Lab).

A.1.1 Solution Processing

Solution processing is a method that dissolves the material into a solution before depositing it onto a substrate. The usefulness of this technique is in its simplicity and applicability to many materials and it can be performed at a low cost. The solution-processing technique that is used in this thesis is spin-coating.

Spin-coating

Spin-coating involves depositing a solution with the desired material onto a substrate and then rotating the substrate. Rotating the substrates leaves a uniform film of the material as the solvent evaporates off during the rotation. The thickness of the film depends on the rotation speed of the substrate, the concentration of the
solution, and the kind of solvent. The thickness is generally controlled by changing the concentration of the solution since the film thickness scales proportionally with the concentration. However, the thickness of the spin-coated films are not as well controlled as some of the other techniques and are limited to materials that can be easily dissolved.

A.1.2 Physical Vapor Deposition

Physical vapor deposition (PVD) allows for the deposition of materials that are not solution processable, such as metals and metal oxides. This technique is a vacuum deposition method that produces a film by vaporizing the material and allowing it to condense onto a substrate. PVD allows better control of the film thickness compared to solution processing, but cannot be used for some materials like QDs. The two kinds of PVD techniques used is thermal evaporation and sputtering.

Thermal Evaporation

Thermal evaporation vaporizes the material by heating the desired material and evaporating it onto a substrate. A schematic and a picture of a thermal evaporator is shown in Figure A-1. It consists of tungsten crucibles that hold the materials, which are in powder or pellet form. When an AC current is delivered to the crucibles, they heat the materials inside, and the rate of deposition is controlled by adjusting the current. This deposition technique provides nanometer precision for film thickness. However, its limitations include not being able to deposit materials that have high sublimation temperatures like polymers.

Sputtering

Sputtering allows for deposition of materials with high boiling points that can not be evaporated. This technique deposits a film by bombarding ionized inert gas, such as argon, into a disk of the desired material, which ejects the atoms from the disk and deposits it onto a substrate. The setup of the system, shown in Figure A-2 is...
similar to the thermal evaporator except the crucibles are replaced with sputtering guns. The sputtering guns consist of two electrodes, which form the electric field to ionize the gas and form a plasma, and two magnets, which form the magnetic field to localize the plasma over the target. The rate of film deposition can be controlled by adjusting the power delivered to the electrodes. Similar to the thermal evaporator, sputtering also allows for nanometer precision for film thickness. However, the plasma can damage organic films on the substrate, so sputtering directly on top of a QD layer is usually avoided.
A.2 Material Synthesis and Preparation

A.2.1 QD solution

QD solutions are purified three times by precipitation with butanol and methanol and then redispersion in octane. As shown in Fig. A-3, the synthesized CdSe/ZnCdS QDs exhibit an emission wavelength centered at 625 nm with a full width half maximum (FWHM) of 30 nm. Deposition of QD solution is done through spin coating. The thickness is dependent on the spin speed and/or QD concentration.

A.2.2 ZnO Nanoparticle Synthesis

The ZnO nanoparticles synthesis was adapted from a previously published protocol [12]. In a typical synthesis, 1.5 g of zinc acetate dihydrate was dissolved in 100mL of 2-methoxyethanol. The solution was stirred for 3h under room temperature. 25g of tetramethylammonium hydroxide (TMAH) dissolved in 10mL of 2-methoxyethanol was prepared and added to the zinc acetate solution. Afterwards, the solution was washed with toluene and hexane then re-dispersed in a mixture of methanol and isopropanol. The solution was filtered with PTFE 0.2μm filters and stored in the
A.3 Substrate Cleaning Procedure

The substrates used to make the PL-LED and QD-LEDs are ITO (150 nm) coated glass substrate acquired from commercial companies. They are cleaned with the following procedure.

1. Sonicate in 1% Micro-90 (or other detergent) in de-ionized (DI) water for 5 minutes
2. Sonicate in de-ionized (DI) water for 5 min
3. Repeat step (2) using fresh DI water
4. Sonicate in acetone for 2 minutes
5. Repeat previous step using fresh acetone
6. Immerse substrates in boiling isopropanol for 2 minutes and then repeat using fresh isopropanol
7. Blow dry the substrates with N2 gas
8. Use oxygen plasma to treat the substrate for 10 min
Bibliography


