The Mechanism of Thermally-Activated Photoluminescence Quenching and Its Correlation with Transport in Electronically-Coupled PbS Quantum Dot Arrays

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The Final Copy of This Thesis Has Been Examined by the Signatories, and We Find That Both the Content and the Form Meet Acceptable Presentation Standards of Scholarly Work in the above Mentioned Discipline.
ABSTRACT

Zhang, Jing (M.S., Chemistry and Biochemistry)

The Mechanism of Thermally-Activated Photoluminescence Quenching and Its Correlation with Transport in Electronically-Coupled PbS Quantum Dot Arrays

Thesis Directed by Professor Arthur J. Nozik

We have measured the temperature-dependent photoluminescence (PL) and quantum yield (QY) of a series of alkanedithiol-treated PbS quantum dot (QD) films as a function of QD size and the length of the alkane chain. These films have PLQYs ranging 2% - 40% at 20 K, with the lowest values measured for shorter ligands and larger QD sizes. All films show PL quenching and shifting/narrowing with increased temperature characterized by exponential (Urbach) band tail behavior. The PLQY vs temperature takes a form derived from an Arrhenius-like dependence of activated charge separation. We also find temperature-dependent photoconductivity (\(\sigma\)), showing an Arrhenius relationship with inverse temperature (\(T^{-0.5}\) at lower temperature matching variable-range hopping model and \(T^{-1}\) at higher temperature corresponding to near-neighbor hopping model), is inversely related with temperature-dependent PL. This indicates that temperature-dependent PL is a relevant measure of transport properties in the presence of deep trap states and reasonably high charge carrier mobilities.
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1. INTRODUCTION

Strong quantum confinement and the possibility of multiple exciton generation (MEG) have attracted significant interest for applications of quantum dot solar cells (QDSCs).\(^1\) So far the highest power conversion efficiency of a QDSC is approximately 7\%.\(^2\) However, a poor understanding of the mechanisms of charge transport in chemically treated colloidal lead chalcogenide (PbX, X=S, Se) QD thin films hinders their photovoltaic (PV) performance.\(^3\)

To date, studies demonstrate that Coulomb charging effects, intersite coupling, and the presence of deep traps play important roles in charge transport.\(^4\) Charge transport behaviors vary from Arrhenius to hopping to metallic behavior, even to superconductivity.\(^5\) Most transport measurements are now done using field-effect transistors (FETs) for dark, trap-free mobility without any spectroscopic identification of quantum state occupations.\(^6\) Photoconductivity is also a valuable tool to probe charge separation/trapping and carrier recombination mechanisms.\(^7\)

1.1. Quantum Dot (QD) Thin Film Basics

The actual active element of most devices made of chemically synthesized nanoparticles is macroscopic arrays, not individual nanoparticles. The nanoparticle assemblies should conduct charge carriers and perform useful functions such as light absorption and carrier generation and separation in solar cells, light emission in LEDs, etc. Tailoring the properties of individual QDs such as composition, size, shape, capping ligand and surface chemistry as well as the degree of superlattice order should provide routes for better electronic and optoelectronic applications.\(^8\)

The intrinsic carrier concentration depends on semiconductor parameters such as band gap, doping and Fermi levels, the bandedge electron and hole effective masses, and
temperature. The valence and conduction band density of states (DOS) are shown in Figure 1; $f(E)$ is the Fermi function. $N_h(E)$ and $N_e(E)$ are the hole and electron DOS. $p$ and $n$ are the population distribution of holes and electrons as a function of energy.

\[ p = \int_{-\infty}^{E_v} (1-f(E)) N_h(E) \, dE \]
\[ n = \int_{E_c}^{\infty} f(E) N_e(E) \, dE \]

Figure 1. Schematic of DOS of the Conduction and Valence Bands. [9]

1.2. Charge Transport Basics

Figure 2 shows the most common radiative and nonradiative transitions in a semiconductor. The occupation of the conduction band by free electrons, the valence band by free holes, and shallow and deep trap states within the forbidden gap are shown in the Figure 2. Energy emissive transitions are divided into 3 categories: (1) Interband transitions; (2) Transitions involving impurities or defects or traps; and (3) Hot carrier intraband transitions.

Transition 2(a) shows the fundamental band-to-band absorption; Transitions 2(b) and 2(c) are known as bound-to-free and free-to-bound transitions, respectively, which dominate at sufficiently low temperatures as carriers are frozen in relatively shallow impurity states. At room temperature or higher, bound electrons or holes in shallow states have a high probability of being released into the conduction band or valence band. Figure 2(d) shows transitions between bound electron-hole pair states when both are present and they are
usually deeper than the shallow states of Figure 2 (b) and (c); these states are also termed donor-acceptor pair states and Coulomb interactions can modify their transition energy.

Figure 2(e) shows an excitonic recombination where the Coulomb attraction between photogenerated electrons and holes leads to the formation of coupled electron-hole pair producing a hydrogen-like state called an exciton. In bulk materials the excitons can move in the crystal lattice and become free excitons.

In Figure 2(f) if only the single electron and hole recombine, this is the bandedge radiative recombination, but if multiple electrons and holes are present in high density, an Auger transition (non-radiative) transition can occur whereby the bandedge transition energy is instantly transferred to either a neighboring electron or hole, exciting it to a higher state. \[10\]

Figure 2(g) is non-radiative recombination of free electrons/holes via a deep-level trap state.

\[\text{Figure 2. Common Radiative and Non-Radiative Transitions in Semiconductors.}^{[9]}\]

1.3. Photoluminescence Basics

Luminescence is the emission of light that occurs after excited electrons and holes recombine via radiative recombination. It can be divided into 5 types based on different
external energy sources. If the material absorbs and then re-emits light the resulting emission is called photoluminescence (PL). If an external current is applied and the carriers are injected the emission is called electroluminescence. If the excitation is created by the absorption of energy-rich electrons the emission is called cathodoluminescence. If the energy is provided from an exoergic chemical reaction the emission is called chemoluminescence. Finally, if the energy is provided as thermal energy (heat) the emission is called thermoluminescence. PL is the most commonly studied type of emission, which is a nondestructive method with very high sensitivity to investigate electronic structure and optical process by optical characterization that does not require electrical contacts.\textsuperscript{[9]}

The excitation energy and intensity for PL can be chosen to probe different excitation types and regions of the sample. PL can be used to determine energy levels, concentration of impurities, defects, passivation, reproducible synthesis, and overall quality. PL involves three main processes as indicated in Figure 3 (a) (b) (c); these are: (a) Excitation: An electron absorbs a photon, for example from a laser, a arc-discharge lamp, or a bulb, and is promoted from the valence band to the conduction band; (b) Thermalization: The electron cools down to the bottom of the conduction band by emitting phonons; and (c) Recombination: The photogenerated electron recombines with the photogenerated hole resulting in emission of light with energy $h\nu$. This process could be radiative or non-radiative.\textsuperscript{[9]}

![Figure 3. Photoluminescence Schematic.\textsuperscript{[9]}](image-url)
1.4. Temperature Dependence of Photoluminescence

The effect of temperature on both the variation of emission intensity and the fundamental gap energy $E_g$ is discussed below.

The variation of emission intensity can take the form

$$ I(T) = \frac{I(0)}{1 + A e^{-E_a/k_B T}} \quad (1) $$

where $A$ is a fitting parameter, $E_a$ is the thermal activation energy of the transition and $k_B$ is Boltzmann’s constant. At high temperature the following condition is satisfied,

$$ A e^{-E_a/k_B T} \gg 1 \quad (2) $$

Then $I(T)$ can behave as:

$$ I(T) \propto e^{E_a/k_B T} \quad (3) $$

Thus, $E_a$ value can be deduced from the slope of the plot of Log $(I)$ versus $1/T$. With the use of $E_a$, one can determine the energy levels of the semiconductor.

The temperature dependence of $E_g$ can be experimentally determined by the form

$$ E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (4) $$

where $E_g(0)$ is the bandgap at 0 K, $\alpha$ and $\beta$ are fitting parameters. $E_g$ of a semiconductor is generally determined by two factors, one is the electron-phonon interaction and the other is the thermal expansion of the crystal lattice. The first one gives a major contribution. As $T$ gets higher, the second term in the Equation (4) behaves like $-\alpha T$. For bulk PbS and PbSe, the bulk parameters $\alpha$ are negative showing that the band gap is increased upon increasing temperature. This is opposite to the behavior of most semiconductors. Furthermore, for PbS and PbSe QDs, the parameters $\alpha$ change as a function of QD size, making the band gap shift smaller as QD size decreases.
1.5. **Our Model of Carrier Dynamics**

Here we have measured the temperature-dependent photocurrent and PL of a series of alkanedithiol-treated PbS quantum dot (QD) films as a function of QD size and the length of the alkane chain. We proposed the model of carrier dynamics depicted in Figure 4.

![Figure 4. Model of Carrier Dynamics in a Coupled QD Film.](image)

In this model, we postulate that:

1. Upon photoexcitation, quantum-confined excitons are initially formed.
2. Relaxation of electrons occurs to band tail states, which are due to film disorder.
3. Radiative recombination (PL) from band tail states to the ground state is observed. As temperature increases, electrons can be activated to the transport level.
4. Electrons can be thermally excited to the transport level and undergo multiple-trapping processes. This quenches the PL.
5. Shockley-Reed-Hall (SHR) recombination via deep-trap level states can also occur. Thus the PL can also be quenched and a shift observed.
The energy of the emitted photon is dependent on the change in the energy state of the electron-crystal system. In highly coupled systems, non-radiative recombination and charge trapping could be competitive with radiative decay. By studying the nature of these trap states, we can resolve the impurity or defect information.\textsuperscript{[11-13]} In QDs with high surface to volume ratios, the termination of lattices represents an opportunity for defect state formation, even in the absence of any foreign impurities. Although we cannot determine the nature of dark traps from our PL studies, the PL quantum yield value significantly less than 100\% for untreated QD films under low light excitation suggests that they are present and can be related to mid-gap bands.\textsuperscript{[3,9]}

Our results will establish a deeper understanding of how charges percolate in PbS QD films by correlating photocurrent and PL trends, with comparison to high-performance QD-based optoelectronic devices fabricated by similar methods in our laboratory.
2. EXPERIMENTAL SECTIONS

2.1. Photoluminescence (PL) Setup

PL experiments were conducted under vacuum (<$10^{-5}$ Torr) in a closed-loop Helium flow cryostat ranging 20-300 K at intervals of 10-30 K. Films were excited with 15-40 mW Argon ion laser at 488 nm chopped at 1 kHz. The resulting PL spectra were detected with a Si, Ge, or InSb photodiode (varying with the needed wavelength range) routed to a lock-in amplifier. The luminescence was resolved with a monochromator (PTI, Quantamaster) and detector efficiencies were determined using a calibrated lamp. The spectra were collected starting from the lowest temperature and warming up to the highest.\textsuperscript{[14]} The experimental setup was designed such that the PL can be collected at the same time as photo-current.

2.2. Photoconductivity Measurements

For the photoconductivity measurements, the devices were biased using a Keithley 2636A source-measure unit. The photocurrent was measured with and without illumination with the laser and the voltage stepped in 4 V increments from 4 V to 20 V. The photocurrent shows some transient behavior, so a minimum time delay is used for measuring the photocurrent after the voltage change.\textsuperscript{[15]}

2.3. Photoluminescence Quantum Yield (PLQY)

PL quantum yield (PLQY) and the PL lifetime can often determine the associated radiative and non-radiative rates and thus establish time scales for electron transfer. A LabSphere integrating sphere is used for measuring the absolute PLQY. Samples are excited by monochromatic light selected from a xenon lamp passed through a monochromator (PTI) mechanically chopped at 22 Hz. The excitation and emission spectra were fiber coupled to the emission monochromator of the fluorescence spectrometer and measured with a two-stage thermoelectrically-cooled InGaAs photodiode amplified by an Stanford Research
Systems (SRS) SR530 lock-in amplifier. A calibrated lamp is used for grating, fiber, sphere, and detector efficiency corrections.

Determination of the PLQY consists of integrating spectral scans of the sample and of the reference sapphire substrate.

\[
PLQY = \frac{\int I_{\text{sample}}(\lambda) - r \cdot I_{\text{ref}}(\lambda) \, d\lambda}{\int E_{\text{ref}}(\lambda) - E_{\text{sample}}(\lambda) \, d\lambda}
\]  

(5)

where \(E_{\text{ref}}\) is the intensity of the excitation light measured with the reference substrate, \(E_{\text{sample}}\) is the intensity of the transmitted and reflected excitation light with the test fluorophore, and \(I_{\text{sample}}\) is the intensity of the emitted light. Optionally, for weak emissions, we remove background effects by normalizing by \(r\) and subtracting the background emission spectrum \(I_{\text{ref}}\). This same technique has been employed in QD photoluminescence measurements, and we have found that this approach yields reasonable results for all samples.\[^{16}\] Drop-cast films were measured at room temperature using this method and then transferred to the temperature-dependent setup for use as a reference for treated QD films. Due to inhomogeneous films, the possibility of short-term oxidation, and sample positioning repeatability, there is some uncertainty in this procedure, estimated to be about 15% for each measured PLQY based on repeated measurements.

Room-temperature absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. All sample preparation was conducted in an inert atmosphere in a glove box to prevent oxidation and transported for measurements in a sealed capsule. Films were sandwiched between two sapphire substrates, spaced by an O-ring, and tightly screwed into a copper tube with a retaining ring.\[^{14}\]
3. RESULTS

3.1. PLQY for Three Batches of PbS QD Treated Films

The studied PbS QD films treated with varying dithiol ligands (HS (CH₂)ₙSH, with n=2-8) have PLQY from about 2% through 40% at 20 K.; the relative error was determined to be around 15% based on experiments repeated two to three times to give a standard deviation. The PLQY of the QDs in solution at room temperature is 30%-40%. These results are summarized in Table 1. A dropcast film refers to the film that have not receive any treatment but just have oleic acid capped on the QD surface from the synthesis.

<table>
<thead>
<tr>
<th>Treatment (Abbreviation)</th>
<th>Formula</th>
<th>Ligand Length /Angstroms</th>
<th>1.78 eV PLQY</th>
<th>1.39 eV PLQY</th>
<th>1.12 eV PLQY</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Oleic Acid Capped)</td>
<td>C₁₈H₃₄O₂</td>
<td>19.70</td>
<td>0.39</td>
<td>0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>1,2-Ethanedithiol (EDT)</td>
<td>C₂H₆S₂</td>
<td>4.25</td>
<td>0.10</td>
<td>0.11</td>
<td>0.021</td>
</tr>
<tr>
<td>1,3-Propanedithiol (PrDT)</td>
<td>C₃H₈S₂</td>
<td>5.50</td>
<td>0.11</td>
<td>0.039</td>
<td>0.022</td>
</tr>
<tr>
<td>1,4-Butanedithiol (BDT)</td>
<td>C₄H₁₀S₂</td>
<td>6.75</td>
<td>0.17</td>
<td>0.22</td>
<td>0.019</td>
</tr>
<tr>
<td>1,5-Pentanedithiol (PeDT)</td>
<td>C₅H₁₂S₂</td>
<td>8.00</td>
<td>0.24</td>
<td>0.36</td>
<td>0.054</td>
</tr>
<tr>
<td>1,6-Hexanethiol (HDT)</td>
<td>C₆H₁₄S₂</td>
<td>9.25</td>
<td>0.17</td>
<td>0.37</td>
<td>0.074</td>
</tr>
<tr>
<td>1,8-Octanethiol (ODT)</td>
<td>C₈H₁₈S₂</td>
<td>11.75</td>
<td>0.18</td>
<td>0.36</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 1. PLQY for All PbS Film Treated with 1mM Dithiol Solution.

The PLQY has an apparent dependence on the QD size and ligand length. The most dramatic trend we see is that smaller QD size and longer ligand lead to higher PLQY. As discussed in Reference 16, a decreasing PLQY with increasing QD size results from: (1) enhanced non-radiative multiphonon transitions into a dark trap state with a size-dependent depth ("energy gap law"); and (2) energy transfer to oleic acid capping ligand vibrations. Longer dithiol ligands tend to have a larger energy barrier for electron transfer, so more electrons remain localized and produce PL which leads to higher QY. Propanedithiol treated films with strongly coupled QDs consistently exhibit a very low PLQY which indicates that the way two thiols may connect with QDs is not linear but instead does so through a
bidentate attachment that decreases the inter-QD distance and produces tunneling, while for longer chains it is much less likely.

What is novel about the values in Table 1 is that we have shown that low temperature PL in coupled QD films is not a rare event from a minute fraction of QDs but rather represents a significant portion of the excited state decay and thus reports on how a large portion of the carriers in the film are behaving. Thus, the PL quenching behavior as temperature is raised shows how the carriers are moving upon thermal activation.

3.2. **PL Quenching Spectrum-Temperature**

Figures 5 and 6 show a representative spectral series vs temperature ($T$) for a QD dropcast film and QDs treated with 1,2-ethanediethiol (EDT).

**Figure 5. PL vs $T$ of 1.39 eV Bandgap PbS Dropcast Film.**

**Figure 6. PL vs $T$ of 1.39 eV Bandgap PbS EDT Film.**
From Figure 5, we see the PL peak blue shift vs increasing temperature for untreated film with oleic acid, which is due to no charge transport and thus is mostly dictated by the increase in fundamental gap $E_g$ as the temperature is raised.\textsuperscript{[11,14]}

While for dithiol treated films, Figure 6 shows that the PL peak shift vs increasing temperature is red shift instead. Initially as temperature is raised, the carriers in shallow band tail states are thermally activated to the transport levels and thus the PL is quenched. From prior work \textsuperscript{[14]}: PL quenching occurs when carriers are activated from band tails to the transport edge, indicating loss of localization and a regime of multiple trapping, leading ultimately to charge separation or non-radiative recombination at deep trap states, possibly via Auger recombination. Increasing the temperature further successively activates the carriers from deeper and deeper traps to the transport levels, quenching their emission and causing a red shift in the PL because the remaining localized carriers are at lower energy.\textsuperscript{[17]}

Thus, the PL shifting is a unique signature of the sub bandgap density of states.

### 3.3. Global Fit for All Dithiol-Treated PbS QD Films

Data for 1.12 eV first exciton PbS QDs treated with EDT through ODT are shown in Figure 7. All treated films show quenching and shifting/narrowing characterized by band tail behavior, matching previous work.\textsuperscript{[14]}

![Graph EDT](image_url)

![Graph PrDT](image_url)

*EDT*  
*PrDT*
With the longer ligand ODT we usually see very little quenching and instead temperature-dependent behavior that is not related to thermally-activated charge separation. In principle we should see the quenching at $T > 350$ K for the longer ligands but such heating is likely to cause film morphology changes and annealing that also changes PL. The quenching behavior is size-dependent, with QDs with first exciton in the range 1.03 eV to 1.65 eV showing strong emission at low $T$, but larger QDs being essentially dark at all temperatures. We hypothesize that this is due to a change in the QD surface chemistry such that fast hole trapping at surface sulfur sites outpaces the initial trapping in band tails and leads to very little emission, but the effect needs to be investigated in more detail.
We then fitted the data sets globally using Equation 6.3 derived from Equations 6.1 and 6.2,

\[
PLQY(T) = \frac{\frac{k_{RR}}{k_{RR} + \sum k_{NR}}}{1 + \alpha e^{-\frac{E_a}{T}}} \quad (6.3)
\]

Equation 6.1 is a general relationship for the rate competition between non-temperature dependent processes \((k_{RR})\) and the temperature-dependent nonradiative process \((k_{NR})\). The summation means that the nonradiative recombination could involve different kinds of recombination, such as SHR recombination, Auger recombination, or energy transfer to the ligand vibration, etc.\(^{[16]}\) Equation 6.2 is the Arrhenius equation for the charge separation rate constant \((k_{CS})\), which we hypothesize is the dominant mode of PL quenching in our treated samples, hence \(\sum k_{NR} = k_{CS}\). \(E_a\) is the activation barrier, which is temperature-independent in this model. The variable \(\alpha\) is a pre-factor that is often considered to be the intrinsic (high temperature) “attempt frequency” for charge separation. Here we recognize that other processes also quench PL \((PLQY\) is not 100% at low temperature), but we assume that these other quenching processes and the rate constant \(k_{RR}\) are not strongly temperature dependent. Another assumption is that once carriers are released from band tail states, their eventual fate is always non-radiative recombination via SRH recombination at deep traps.

With three variables and only 10-14 data points for one film, such a fit can exhibit covariance between parameters. Therefore, we employed a fit in which all data sets for one size with six ligands are fitted simultaneously with some variables linked which means it is allowed to vary but taking on just one global value for the entire data set. \(A\) typically takes a value near one in our data because the curves are normalized at low temperature and PL is usually fully quenched at room temperature. Therefore we have two natural choices for the
linked variable using this global fit function: either $E_a$ or $\alpha$. The physical significance of this choice will be discussed below.

Figure 8 shows a global fit result for 1.12 eV PbS treated with six different ligands of EDT, PeDT, BDT, PeDT, HDT and ODT, linking $E_a$ and thus assuming that it is a global variable for the data set. Figure 9 shows the fit when $\alpha$ is linked, and $E_a$ is allowed to adopt a different value for each individual ligand. The variable-linking procedure works equally well for both types of fits ($E_a$ and $\alpha$ linked) for ligands EDT through about HDT, but for ODT linking $E_a$ provide a better fit. Deviations from perfect fits may be indication that $E_a$ is not temperature-independent but rather changes as the bandgap shifts higher with higher $T$. The other possibility is a temperature-dependent $\alpha$, which could be tested with a more advanced model.

Figure 8. Global Fit $\alpha$ ($E_a$ Linked) for 1.12 eV Bandgap PbS Treated Films.
Figure 9. Global Fit $E_a$ ($\alpha$ Linked) for 1.12 eV Bandgap PbS Treated Films.

3.4. $\alpha$-d Relationship for All Treated Films

From Liu et al. [15], we see that an equation for the temperature-dependence of the charge separation rate (hopping/tunneling) can be formulated using a prefactor and an Arrhenius activation term: [15]

$$k_{CS} (T) \propto e^{-2\beta d} e^{\frac{-E_a}{k_BT}} \quad (7)$$

Liu et al. [15] have clearly shown the exponential $\exp(-\beta d)$ fall off in field-effect transistor (FET) mobility $\mu$ as $d$ increases with alkanedithiols for medium-size PbSe QDs as in Equation (8), which is due to a reduced rate of tunneling as wavefunction overlap decreases.

$$\mu = \mu_0 e^{-0.865\beta d} e^{\frac{-\Delta E}{k_BT}} \quad (8)$$

We assume that the dependence also holds true for smaller PbS QDs. After lengthening the ligand and thus increasing the distance $d$, we anticipate that the temperature dependent term must compensate for the increased $d$ and the reduced tunneling term to restore the value of $k_{CS}$ and become competitive with $k_{RR}$ to produce quenching. This can be
qualitatively seen in the data sets, in which the temperature at which quenching occurs increases with \( d \). If we assume that the activation barrier \( E_a \) is unchanged through the dithiol series, we are able to link \( E_a \) for different values of \( d \) and observe a trend in the prefactor \( \alpha \) that matches what is expected from the term \( \exp(-\beta d) \). Figure 10 is the result of the fitting \( \alpha \) for 1.12 eV PbS QDs, linking \( E_a \) and but not \( \alpha \). The plot of \( \alpha \) vs. distance fits well to a single exponential decay. The exponent \( \beta \) (equal to \( 1/\tau \) in the plots) is between 0.7 and 2.4 for PbS QDs, 1.2 and 2.5 for PbSe QDs. They trend to lower values with larger size, which may be an indication that the value of \( \beta \) (measured to be 1.1 for only one size in Liu et al. \textsuperscript{15}) depends not just on the ligand but also on the QD size.

Figure 10.1. Curve Fit \( \alpha-d \) (\( E_a \) Linked) for 1.12 eV Bandgap PbS Treated Films.
Figure 10.2. Global Fit for PbS $\alpha$-$d$ ($E_a$ Linked) Exponential Relationship.

Figure 11.1. $E_a$-$\Delta E$ ($E_a$ Linked) for PbS and PbSe Treated Films.
Figure 11.2. \(E_a\) -1st Exciton Energy (\(E_a\) Linked) for PbS and PbSe Treated Films.

Liu et al.\(^{[15]}\) considered the site energy dispersion \(\Delta E\), defined as the energetic width of the QD size distribution (often measured by the half-width of the lowest exciton absorption band), as the only source of the activation energy. However, we did not see a clear trend with size dispersion as shown in Figure 11.1. For example, for the two largest PbS QD samples vary by more than 250 meV in 1st exciton energy, but \(\Delta E\) is nearly identical. \(E_a\) varies by a factor of 2.5 for these samples, suggesting that the trend of \(E_a\) vs. band gap is more meaningful than the trend of \(E_a\) vs. \(\Delta E\). Figure 11.2 displays the trend of \(E_a\) with 1st exciton energy. Since the site energy dispersion is not necessarily the only contribution of \(E_a\), we can think about other ways that it changes versus distance.

In the band tail model, \(E_a\) is approximately the energy from the quasi-Fermi level within the band tail to the transport level \(E_T\), which we assume occurs somewhere below the band gap \(E_g\), which we will define as \(<1S_e - 1S_h>\). This energy is proportional to the band tail slope measured previously, which we know is affected by the disorder of the sample and decreased QD density induced by ligand exchanges. If the available thermal energy creates an electron distribution in which some electrons achieve energy equal to \(E_T\), which is the
energy at which the density of states is high enough that carriers begin percolation and PL is highly quenched, then we can use Fermi’s Golden rule to describe the rate of charge separation.

\[ k_{CS} \propto |V|^2 \rho(E) \]  

(9)

\(|V|\) is the coupling energy, which has a material-dependent pre-factor but whose dependence on distance is like \(\exp(-\beta d)\), as discussed previously. \(\rho(E)\) is the density of final states at the energy \(E_T\) that should depend on energy like an exponential, if we assume that we have an Urbach tail below the band gap.

If \(V\) decreases with increasing \(d\), then the carriers must be excited to a higher energy to reach \(E_T\) (that is, \(E_T\) has moved upwards toward the band gap), and a higher \(E_a\) should be observed. In other words, the reduction in the magnitude of \(\rho(E)\) upon the increase in \(d\) due to the lower QD density means that \(E_T\) rises as well. We predict a linear relationship between \(E_a\) and \(d\) since they both appear in exponential terms in Equation 9.

### 3.5. \(E_a-d\) Relationship for All Treated Films

We observe a linear relationship between \(E_a\) and \(d\) below in Figure 12.1 for PbS QDs and Figure 12.2 for PbSe QDs in dashed line, at small \(d\) and it holds for all samples. The data get more difficult to fit above a separation of 10 Angstroms, so we cannot be sure if the dependence exhibits saturation. In principle, the curvature of these plots should reveal whether the DOS actually changes shape when \(d\) increases (change in band tail parameters due to increased disorder), or there is simply a requirement for an electron to achieve a higher energy within the unchanged DOS in order to achieve transport. This requires further analysis of these curves, which is saved for future work.
3.6. **Atomic Layer Deposition (ALD) Effect for PbS Treated Films**

We are also using this analysis to see what effects an ALD coating of Al$_2$O$_3$ and other surface treatments have on $E_a$ and other fit parameters. We compare the PLQY of dip-coated
films on sapphire substrates with and without ALD. Table 2 shows that ALD has a lower PLQY value at 20K indicating that ALD may be hastening charge transport but that the QD surface may still have deep traps and carriers are finding them more quickly.

<table>
<thead>
<tr>
<th>PbS 1st Exciton Energy/eV</th>
<th>Treatment</th>
<th>PLQY No ALD</th>
<th>PLQY ALD</th>
</tr>
</thead>
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<tr>
<td>1.12</td>
<td>None</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>1.12</td>
<td>EDT</td>
<td>0.021</td>
<td>0.016</td>
</tr>
<tr>
<td>1.12</td>
<td>PrDT</td>
<td>0.022</td>
<td>0.0031</td>
</tr>
<tr>
<td>1.12</td>
<td>HDT</td>
<td>0.074</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Table 2. PLQY for 1.12 eV Bandgap PbS Film No ALD/ALD Coating.

The PL quenching curves in Figure 13 show that PL is still fully quenched as temperature increased, so we assume that we are still in the regime where the density of deep traps is high enough such that all separated carriers eventually find a non-radiative recombination center. If a surface treatment were to significantly reduce the deep trap density then the PL quenching curve will exhibit incomplete quenching at higher temperatures even when inter-QD coupling is strong. We believe we have not yet reached the regime where passivation is sufficient to where faster transport means better charge collection. However, it is interesting that neither $\alpha$ (Figure 10.2) nor $E_a$ (Figure 12.1) have a clear trend with ligand length, instead remaining mostly constant. This suggests that the activation barrier for PL quenching in ALD-infilled films is no longer related to the nature of the ligand but rather the matrix or surface properties of the QD. It is interesting to note that $\alpha$ and $E_a$ for ALD films take on average values similar to those for the PrDT or HDT films without ALD.
3.7. Photoconductivity ($\sigma$) – PL Correlation

One important question is: how do $T$-dependent PL and $T$-dependent FET mobility relate to each other? If the gate bias in an FET fills trap states that are important for transport, then there is probably no relationship. \cite{18, 19}
It may be that the better comparison for temperature-dependent PL is with temperature-dependent photoconductivity ($\sigma$). We would expect that the two are inversely related since they both involve the same process, thermally-activated charge separation. One difference is that PL quenching in principle only requires one event – the initial charge separation. We have justified the use of a simple Arrhenius equation for describing this. For photoconductivity ($\sigma$), a larger number of events occur, and these are described theoretically following the formalism of near-neighbor hopping (NNH) or variable-range hopping (VRH). The correlation of conductivity versus temperature ($\sigma$ vs $T$) has an Arrhenius term as shown in Equation 10, but it has an exponent that varies from one, depending on the hopping mechanism.$^{[17]$

$$\sigma = \sigma_0 e^{-\frac{T^*}{T}}$$  \hspace{1cm} (10)

where $\sigma_0$ is the pre-exponential factor, $T^*$ is a fitting parameter with units of Kelvin, and $Z$ is a parameter to describes the power of temperature dependence.

**Figure 14.1.** $\sigma$ and Integrated PL vs $T$ of 1.36 eV Bandgap PbS HDT Film.

**Figure 14.2.** $\log(\sigma)$ vs $T^{-1}$ of 1.36 eV Bandgap PbS HDT Film.
Figure 14.3. $\log \sigma$ vs $T^1$ and $T^{0.5}$ of 1.36 eV Bandgap PbS HDT Film.

Figure 14.1 shows that higher photoconductivity of 915 nm (1.36 eV) PbS QD treated with 1mM hexanedithiol (HDT) with increasing temperature leads to lower PL intensity with increasing temperature, as radiative recombination pathways cannot compete with charge separation. This suggests that the PL is an indicator of transport, at least in these films.\(^{[20]}\) Figure 14.2 shows that the plot of $\log (\sigma)$ vs $T$ for 1.36eV PbS QD treated with HDT, the temperature dependence is deviated from a simple linear relationship over the given temperature range implying that the charge transport cannot be simply described by one model of NNH or VRH alone. Figure 14.3 shows that a quite clear transition was observed from the plot where the $Z$ value is close to 0.5 at lower temperature corresponding to VRH model and close to 1 at higher temperature consistent with NNH model.

As mentioned in the 3.7 ALD section above, we also postulate that some chemical treatments could shift PL quenching to higher temperatures because of improved surface passivation (i.e., fewer deep traps for fast recombination) and/or barriers to charge separation (i.e., carriers remain localized). Correlation of PL quenching with either photoconductance or FET mobility provides the key to determining which of the two mechanisms results in altered PL quenching, since simply localizing the carriers is not advantageous.
4. OUTLOOK

We can imagine several directions that would be fruitful to pursue for this project. The primary goal is simply to add more detail to the simple models that were put forth here, including: distinguishing tunneling and hopping, considering specific phonon effects, and the possibility of band-like transport. \cite{21}

In addition, we would like to study the chemical nature of trap states emission more thoroughly, including various surface treatments and measurements of photocurrent, PL lifetime and trap state density. \cite{22} Finally, efforts are underway to correlate these PL related results to PV performance, which provides the final link to applications.

In conclusion, we have shown that temperature-dependent PL is a sensitive probe of charge transport, through our understanding of the occupation of near-gap band tail states. We have found an all-optical measure of the tunneling decay parameter, which has been previously measured only by dark electrical measurements. Our measurement includes a larger range of sizes, showing a size dependent tunneling parameter, or a size-dependent activation barrier that results from movement of the transport edge with respect to quasi-Fermi level of the band tail. We have shown that thermally-activated PL quenching then characterizes carrier motion and the ultimate fate of carriers in a QD array.
REFERENCES


APPENDIX

Table 1. Information for the Dithiol Solutions.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Formula</th>
<th>Molecular Density g/mL</th>
<th>Length/Angstroms</th>
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<tr>
<td>1,2-Ethanedithiol</td>
<td>C₂H₆S₂</td>
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<td>178.36</td>
<td>11.75</td>
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Table 2. α Value (Eₐ Linked) Value for All PbS Treated Films

<table>
<thead>
<tr>
<th>PbS Ligand Length/Angstroms</th>
<th>α -1.78 eV No ALD</th>
<th>α -1.39 eV No ALD</th>
<th>α -1.12 eV No ALD</th>
<th>α -1.12 eV ALD</th>
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<td>Linked Eₐ /meV</td>
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<td>295</td>
<td>294</td>
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Table 3.1. Eₐ & ΔE Value (α Linked) for All PbS Treated Films

<table>
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<tr>
<th>PbS1st Exciton/eV</th>
<th>PbS 1st Exciton/nm</th>
<th>Eₐ/meV</th>
<th>ΔE /meV</th>
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Table 3.2. Eₐ & ΔE Value (α Linked) for All PbSe Treated Films

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### Table 4.1. $E_a$ Value ($\alpha$ Linked) for All PbS Treated Films

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<th>$E_a$/meV-1.78 eV No ALD</th>
<th>$E_a$/meV-1.39 eV No ALD</th>
<th>$E_a$/meV-1.12 eV No ALD</th>
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<td>5.50</td>
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<td>258</td>
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<td>Linked $\alpha$</td>
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### Table 4.2. $E_a$ Value ($\alpha$ Linked) for All PbSe Treated Films

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<th>PbSe Ligand Length/Ang</th>
<th>$E_a$/meV-1.59 eV</th>
<th>$E_a$/meV-1.36 eV</th>
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<tr>
<td>9.50</td>
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<td>725</td>
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Figure 1. PL of 1.78 eV PbS Treated with EDT, PeDT, BDT, PeDT, HDT and ODT.
Figure 2. PL of 1.39 eV PbS Treated with EDT, PeDT, BDT, PeDT, HDT, and ODT.
Figure 3. Global Fit $E_a$ ($\alpha$ Linked) for 1.78 eV PbS Treated Films.

Figure 4.1. Global Fit $\alpha$ ($E_a$ Linked) for 1.39 eV PbS Treated Films.
Figure 4.2. Global Fit $E_a$ ($\alpha$ Linked) for 1.39 eV PbS Treated Films.

Figure 5.1. Curving Fit $\alpha$ ($E_a$ Linked) for 1.39 eV PbS Treated Films.
Figure 5.2. Curving Fit $\alpha (E_a \text{ Linked})$ for 1.78 eV PbS Treated Films.