Optical characterization of the photoluminescence
of nanoscale semiconductor materials

An Undergraduate Honors thesis in the Department of Physics,
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May 2016
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ABSTRACT

Photoluminescent qualities of nanoscale semiconductors have caused these materials to gain recent popularity and shown a variety of applications. Because of this, it is important to understand how different material’s photoluminescence changes and how different photoluminescent materials differ. This work aims to characterize two types of semiconductors capable of photoluminescence, CdSe core-shell quantum dots and two-dimensional MoS$_2$ in terms of the overall intensity of the produced light, effects of age on the sample, polarization of the produced light, and effects of photobleaching. In addition, quantum dots have been characterized by the effects of concentration and single quantum dots were isolated, which allowed for quantum blinking to be observed.
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ACKNOWLEDGEMENTS

I would like to thank Dr. Joseph B. Herzog for his amazing mentorship throughout this study and my undergraduate career as a whole and for the countless times he has supported me and given me advice. I would also like to thank David French for teaching me to use the set up in this experiment and helping me when problems arose.

In addition, I would like to thank Dr. Hugh Churchill, Dr. Joseph B. Herzog, Dr. Daniel Luecking, and Dr. Chaim Goodman-Strauss for serving on my honors thesis committee.

Note: much of this work has been submitted and accepted for publications: See G. Abraham et al. [6–7].
CHAPTER 1:
INTRODUCTION

In this work, the photoluminescence (PL) of two nanocrystal semiconductors, quantum dots (QDs) and MoS$_2$, will be compared and contrasted. Recently, both materials have both received significant attention$^2$ and have shown potential in applications such as optoelectronics$^{3,4}$, photovoltaic cells$^{4,5}$, and sensor applications$^6$. Because of these similar uses, it is important to know the pros and cons for each material. This study aims to compare the two sources of PL in terms of age, polarization of the produced light, and effects of photobleaching$^1$. In addition, this work will seek to further characterize QD PL in terms of the effects of concentration and the isolation of single QDs to observe quantum blinking$^7$.

Photoluminescence

Photoluminescence is a process in which a material absorbs light and emits subsequent light$^8$. PL occurs when an electron that is initially in the ground state is raised to an excited state by an incoming light that is equal to or greater than the energy band gap between the ground and excited state. The electron spontaneously relaxes back to the ground state and emits a photon with energy near the energy difference of the band gap, known as the peak wavelength$^1$.

Core-Shell Quantum Dots

Core-shell QDs are a type of QD that have a core of one material and a shell of another while still maintaining a nanoscale diameter. This gives the QDs three dimensions in the quantum confinement regime caused by the changes in band gaps of the materials, confining the electrons and quantizing the energy levels. This allows for a strong control over the PL peak wavelength that depends on their size, material, and structure of the QD$^1$. 

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MoS$_2$

MoS$_2$, or Molybdenum disulfide, is a metal dichalcogenide which in bulk is an indirect band gap and does not produce PL. When brought down to a few layers or to a single layer, the band gap shifts from indirect to direct$^9$ and electrons within MoS$_2$ are confined in the quantum regime by the thin, crystalline sheets$^{1,5}$. This allows MoS$_2$ to produce PL, but as opposed to QDs, the peak PL wavelength is consistent at 670 nm with a lower peak wavelength at 611 nm.
CHAPTER 2:
MATERIALS

CdSe core QDs were produced in the methods described in Abraham et. al (2015)\textsuperscript{7}. These methods generated colloidal QDs which are composed of a core of CdSe surrounded by a layer of CdS and an outer shell of ZnS, a total diameter of 13 nm, and a peak emission wavelength of 621 nm which was confirmed using a fluorometer. The QDs were then stored in hexane and diluted to 19.5 nM for experimental use. To take photoluminescent measurements, the dilute solution of QDs was drop cast onto silica wafers and the hexane was allowed to evaporate so the QDs were distributed randomly onto the wafer.

MoS\textsubscript{2} was mechanically exfoliated onto silica wafers using the scotch tape method\textsuperscript{9}. Samples of MoS\textsubscript{2} were taken from bulk MoS\textsubscript{2} using scotch tape and pressed onto silica wafers to deposit mono- and few-layer MoS\textsubscript{2}. Monolayers were found and images were then taken using a 20x (NA 0.45) microscope and a bright field set up illuminated by a white LED light.

Once made, samples were stored in ambient conditions to allow for age of sample studies to occur. The storage methods for both were as similar as possible to reduce any effects storage may have on photoluminescence.
CHAPTER 3:

METHODS

The following description of this experimental set up can be found published in Abraham et. al (2015). A 532 nm, continuous wave diode laser was used as the excitation light source in this experiment. This laser was selected because its energy is larger than the energy band gap of both the QDs and MoS$_2$ while being at a low enough energy so the MoS$_2$ samples would not be damaged. The laser was first transmitted through a linear polarizer to ensure that the excitation light was completely polarized, and then a half wave plate was used to rotate the excitation light’s polarization. In addition, the excitation light could have been attenuated by a step optical density filter with possible attenuation of optical density (OD) ranging from 0.0 – 4.0 which varied the light intensity at the sample from 3.08 kW/cm$^2$ to 0.01 W/cm$^2$ respectively to prevent photo-bleaching.

The attenuated light was then focused by a lens with a focal length of 500 mm, through a dichroic beam splitter, and onto the back of the microscope objective. The dichroic glass was used so that there is a maximum reflection for the incident laser wavelength and maximum transmission of the emitted wavelengths from the QD sample. The light was focused onto the back aperture of a 50x microscope objective (NA = 0.55) so that the laser light was dispersed over a large area to illuminate as much of the sample possible.

During spectroscopy and imaging, the sample was placed at the focal plane of the microscope. This focused and collected the emitted photoluminescent (PL) light from the QDs. Both this emitted light and the reflected laser light were collected back through the microscope objective. The longer wavelength light passed more efficiently back through the dichroic beam splitter while the shorter wavelength light (the laser) was attenuated as it transmitted through the
dichroic glass, but the dichroic beam splitter did not block all of the laser light; therefore, the laser light was then filtered out with a glass color filter that filters wavelengths below 570 nm. The light was then focused with a lens of focal length 200 mm onto either a CMOS camera or a Czerny-Turner\textsuperscript{10} configuration spectrometer with blazed grating at 750 nm and 300 grooves/mm with a CCD readout. Figure 1 shows the complete experimental setup\textsuperscript{7}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{setup.png}
\caption{Experimental set up. Green arrows, starting at the laser, represent the excitation light and red arrows, coming off the sample, represent the luminescence from the QD and MoS\textsubscript{2} samples. Image from Abraham et al., (2015).\textsuperscript{7}}
\end{figure}

The CMOS camera was used for finding samples of both QDs and MoS\textsubscript{2} and taking videos of overall changes in the intensity of the QD blinking. The spectrometer was used for evaluating changes in the spectrum as a variety of variables were changed for both samples and to show QD blinking of a single quantum dot.

The first step of the experiment measured the spectrum of the QDs using the spectrometer. This allowed for confirmation that the sample preparation did not damage the quantum dots, and that the light being viewed in the CMOS was indeed the emitted light from
the QD sample. The central PL emission wavelength was found to be 621 nm, which matched with the fluorometer results. Next the study examined the effects of concentration to find the optimal concentration of the QDs. Then the study isolated a one or a few QDs to observe QD blinking. This was done on the CMOS camera because it has a higher resolution than the CCD camera. Changes in the intensity and visibility of QD blinking were noted. Finally, MoS$_2$ samples were included and a variety of characterizations of MoS$_2$ and QDs were compared including the effects of the age of sample, the effects of photobleaching, and the polarization of the produced light.
CHAPTER 4:
RESULTS

The following sections are separated by those results that cannot be taken for MoS\textsubscript{2} and results that can be taken for both MoS\textsubscript{2} and QDs.

4.1 Results for only QDs

As was shown in Abraham et. al (2015)\textsuperscript{7}, the microphotoluminescence QD ensemble spectrum was measured and are plotted in Figure 2. The three spectra were taken from samples of varying diluted concentrations of the same stock. The comparison shows that the peak wavelength shifts from 615 nm to 621 nm as the concentration of the QDs increased. This is most likely due to aggregation, a process in which QDs which are in close proximity to each other cause the peak wavelength to shift toward higher wavelengths. These spectra were taken of clusters of quantum dots, rather than single QDs because clusters were brighter and prevented QD blinking from affecting the produced light during data acquisition. Figure 2 shows the spectra of different QD clusters produced by the same stock solution diluted to 3.915 nM, 19.50 nM, and 39.15 nM and drop cast onto wafers. The spectra were taken with the excitation light being attenuated to 1.25 kW/cm\textsuperscript{2} and a 1000 ms exposure time. The small peak at 532 nm is the high intensity excitation laser leaking through the color filters\textsuperscript{7}.
Figure 2: Spectra of QD ensembles of different concentrations showing peak wavelength. Note: small peak at 532 nm due to excitation laser. Image from Abraham et al., (2015)^7.

Next, fluorescent intermittency (or QD blinking) was observed with the CMOS camera as shown in Figure 3. QD blinking is only visible at low sample densities when a few or single QDs have been isolated. If the light produced from a cluster of QDs is seen, the spectrum remains quite consistent because the time it takes for a cycle of photoluminescence varies for each quantum dot, and the changes in intensity are unnoticeable; however, if a single QD or a relatively small number can be isolated, QD blinking, or fluorescence intermittence, can be noticed. The individual to a few QDs appear as a blinking diffraction limited spot. This is visible in Figure 3 which shows individual, consecutive frames of a blinking sample. The top dot, labeled $a$, is consistently illuminated while other dots, $b$ and $c$, flash on and off. This indicates that $a$ may be a cluster of QDs while $b$ and $c$ are single or very few quantum dots. Figure 4 was taken of a sample produced from the stock solution diluted to 39.2 nM. The video was taken with
the excitation light being attenuated to 1.25 kW/cm$^2$ and 5.23 frames per second, making each frame 0.2 seconds$^7$.

![Figure 3: Consecutive frames (labeled 1-8) of a video of QDs. Quantum blinking shown by dots b and c and a cluster of QDs not exhibiting quantum blinking shown by a. Each frame is 0.2 seconds long. Image from Abraham et al., (2015)$^7$.](image)

To confirm that the intensity fluctuations were caused by QD blinking and not changes in the power of the laser, the changes in intensity of the blinking were compared to the changes in intensity of the laser over the same time period as was demonstrated in Abraham et al. (2015)$^7$. These results are plotted in Figure 4. The dramatic florescent intermittency of the QDs with a steady excitation light indicate that QD blinking is occurring, rather than fluctuations in the laser intensity. This comparison is exhibited in Figure 4 which shows blinking of several QDs and compares those changes to changes in the laser fluctuation over the same length of time. This also indicates that any changes in the spectrum of the QDs over time are due to the QDs themselves and not changes in the excitation light$^7$. 

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7 Abraham et al., (2015)
4.2 Results that compare MoS$_2$ and QDs

The first comparison made between MoS$_2$ and QD PL in Abraham et. al (2016) was the sample type and overall PL intensity. Figure 5a and 5c show images of the different types of samples and compares their size; however, Figure 5c only shows QDs as diffraction limited spots because they are actually too small to view with the current experimental set up. Figure 5b shows the two peaks of MoS$_2$ PL, and Figure 5d shows the PL spectra of both QDs and MoS$_2$ under the same experimental conditions. Both are illuminated by a laser attenuated to just below 1 mW with an exposure time of 10000 ms. Figure 5d shows that generally QDs produce a stronger light
than MoS$_2$. Because of this, and to reduce the effects of photobleaching (see Figure 6) QDs were mostly given an exposure time of only 500 ms for the rest of this experiment.

To study the effects of photobleaching, samples were found as quickly as possible under the lowest possible excitation light. For MoS$_2$ flakes, this was a brightfield set up and for QDs this was a highly attenuated laser shining onto a CMOS camera. Once the sample was found, the excitation light was quickly blocked and the set up was switched to shine into the spectrometer. The same 532 nm laser was attenuated to just under 1 mW and data began almost immediately. Spectra were taken every 10 seconds with an exposure time of 10 seconds. Figure 6 shows the average intensity of the peak wavelength every minute. This data shows that QDs lose about half

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**Figure 5:** A comparison of the different types of samples of MoS$_2$ (Figure 5a) and QDs (Figure 5c) and their respective PL spectra. MoS$_2$ PL spectrum is shown in Figure 5b while the overall intensity of MoS$_2$ PL and QD PL given the same experimental conditions is compared in Figure 5d. Images from Abraham et. al (2016)$^1$. 

![Image of MoS$_2$ and QDs samples with PL spectra](image-url)
their initial intensity after about 15 minutes but that MoS$_2$ is not subject to the same photobleaching effects that QDs are, as was demonstrated in Abraham et. al (2016)$^1$.

![Figure 6: Shows change of intensity of the peak wavelength as a result of time exposed to laser. As time increases, QD PL decreases (a) but MoS$_2$ PL does not (b). Image from Abraham et. al (2016)$^1$.](image)

To further understand the effects of photobleaching, different intensities of incoming light were shined onto the samples by adjusting the attenuator shown in Figure 1. Again, the same careful steps were taken to ensure that the sample received the least possible light before data collection began. Spectra was taken every 10 seconds and each data point is the average of six spectra.

Previous work, such as Castellanos-Gomez et. al has stated that for MoS$_2$, damage to the sample does not occur below 1 mW of incoming light$^{11}$. Above 1 mW, laser heating occurs and is capable of evaporating the sample off of the wafer$^{11}$. The data shows that below 1 mW and at 1 mW, no photobleaching of MoS$_2$ flakes occurs, but above 1 mW there is a drastic decrease in the PL, the longer the laser shines on the sample. Figure 8 shows each individual sample normalized to its maximum intensity.
Figure 7: A comparison of MoS$_2$’s PL with different incoming light intensities. Shows that MoS$_2$ does not photobleach under 1 mW.

A similar study was performed for QD photobleaching. The results show that QDs undergo a short period immediately after exposure called photobrightening$^{12,13}$. At this time, the intensity of the PL increases before photobleaching begins and causes the intensity to decrease. The results in Figure 9 were taken with a couple of days between the first set of data (0.5 mW and 1.0 mW) and the rest of the data. With this in mind, Figure 9 shows that as the more intense the incoming laser light, the greater the effects of photobleaching and photobrightening. It is possible that there is a limit to this in which the laser light is so intense that photobrightening doesn’t have a chance to take effect and photobleaching takes place almost immediately; however, this must be looked into further before a conclusion can be drawn.
Figure 8: QD exposure to laser data showing both a period of photobrightening and a period of photobleaching.

For polarization studies, a half-wave plate was placed in the incoming light path and a linear polarizer was placed between the sample and the spectrometer. A single QD or monolayer flake was examined for each incoming polarization. The linear polarizer began at 0° was rotated to increase by 10° and spectra were taken with the same exposure times. Figure 7 shows a comparison of the peak wavelength’s intensity for each of these spectra. Figure 7 also compares different incoming polarizations with red at a vertical incoming polarization and blue at a horizontal (HWP rotated 45°) incoming polarization\(^1\).

Figure 7, from Abraham et al. (2016)\(^1\), shows that neither the MoS\(_2\) flakes nor the QDs produce polarized light. The QD polarized light seems to have an inconsistency at 0°; however, Figure 6 shows that QDs are prone to photobleaching so the more time the QD spends under incoming light, the weaker the PL becomes. MoS\(_2\) does not show this dependence so 0° and 360° are about the same\(^1\).
Figure 9: Polar plot showing that the light produced by spherical QDs (a) and MoS$_2$ monolayers is unpolarized. The outgoing polarization of single QDs and MoS$_2$ were tested with different incoming polarizations (vertical-red-and horizontal-blue). Image from Abraham et. al., (2016)$^1$.

Finally, the effects of age were studied. For both MoS$_2$ and QDs, samples were prepared and spectrum were taken within the hour. Spectrum with the same incoming laser power and exposure time were then taken frequently as possible (at the most daily) for the remainder of the study. Figure 8 shows the change of intensity of the peak wavelength for QDs and MoS$_2$ as time progressed. For MoS$_2$, the same monolayer flake was examined each day, but due to the randomness of the QD wafer, a QD was selected at random for each day. When data was not being taken, both wafers were stored under the same conditions$^1$. 
Figure 10: Shows change in intensity of peak wavelength for QD (a) and MoS$_2$ (b) as a function of time spent on the wafer. Image from Abraham et. al (2016)$^1$.

In addition, because QDs were studied for longer than MoS$_2$, a more extensive study of the effects of age was performed with QDs. Figure 9 shows that even after two months, QD PL loses intensity.

Figure 11: Shows changes in intensity of peak wavelength for QDs for a longer period of time. Image from Abraham et. al (2015)$^7$. 

![Graph showing change in intensity of peak wavelength for QDs and MoS$_2$](image-url)
CHAPTER 5:
CONCLUSION

This work has done some investigations on core-shell ZnSe CdSe quantum dots and MoS$_2$. It has shown that both produce unpolarized light that does not depend on the polarization of the incoming light. In addition, it has shown that the intensity of the peak wavelength decreases as the sample spends time on a wafer for both QD and MoS$_2$ samples. Despite these similarities, QDs and MoS$_2$ have a variety of differences in the way they produce light. These results have shown that MoS$_2$ is not prone to the same photobleaching effects that QDs are, but overall produce a generally weaker signal than QDs while under the same experimental conditions. In addition, this work has been able to observe quantum blinking in QDs and found an optimal concentration at which QD samples should be prepared to allow for isolation of a single QD, yet still have enough QDs on a wafer for experimental use. We hope these results help to clarify the more efficient PL material as MoS$_2$ and QDs are used in more and more applications.


