

# Plasmonically Enhanced Photoluminescence of Nanoscale Semiconductors

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## ABSTRACT

Recent work has shown that plasmonic structures enhance the emitted light of nanoscale semiconductor materials, such as the photoluminescence of colloidal quantum dots (QDs) and MoS<sub>2</sub> 2D materials. This project will compare the photoluminescence of CdSe colloidal quantum dots and MoS<sub>2</sub>. A variety of studies will be performed such as photobleaching effects, how photoluminescence relates to lifetime of sample, and polarization studies. In addition, this project will further the understanding of plasmonically enhanced photoluminescence between these semiconductor nanostructures and metal nanostructures. Initial studies will drop cast colloidal metal nanospheres onto quantum dots and MoS<sub>2</sub>, while future work will fabricate gold structures with electron beam lithography.

**Keywords:** MoS<sub>2</sub>, enhancement, photoluminescence, nanostructures, 2D materials, plasmon

## 1. INTRODUCTION

Monolayer MoS<sub>2</sub> and quantum dots (QDs) are both nanoscale semiconductors capable of photoluminescence (PL). PL occurs when an incoming light excites an electron initially in the ground state to an excited state. The electron spontaneously relaxes back to the ground state and emits a photon with energy equal to the energy difference of the band gap. QDs and monolayer MoS<sub>2</sub> are both crystalline semiconductor materials that are efficient at PL because they are direct band gap structures<sup>1,2</sup>. QDs have 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. On the other hand, MoS<sub>2</sub> in bulk is an indirect band gap and does not produce PL, but when brought down to a few to single layer, the electrons are also confined in the quantum regime by the thin, crystalline sheets<sup>1</sup>. When QDs produce PL, there is a single peak wavelength, but when MoS<sub>2</sub> monolayers produce PL, there are two peak wavelengths at 671 nm and 627 nm. Figures 1a and 1c show an image of the sample and Figures 1b and 1d show the PL of the spectrum of each of these.

Recently, both materials have both received significant attention<sup>3</sup> and have shown potential in applications such as optoelectronics<sup>4,5</sup>, photovoltaic cells<sup>1,5</sup>, and sensor applications<sup>4,6-8</sup>. 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 strength, age, polarization of the produced light, and effects of photobleaching.

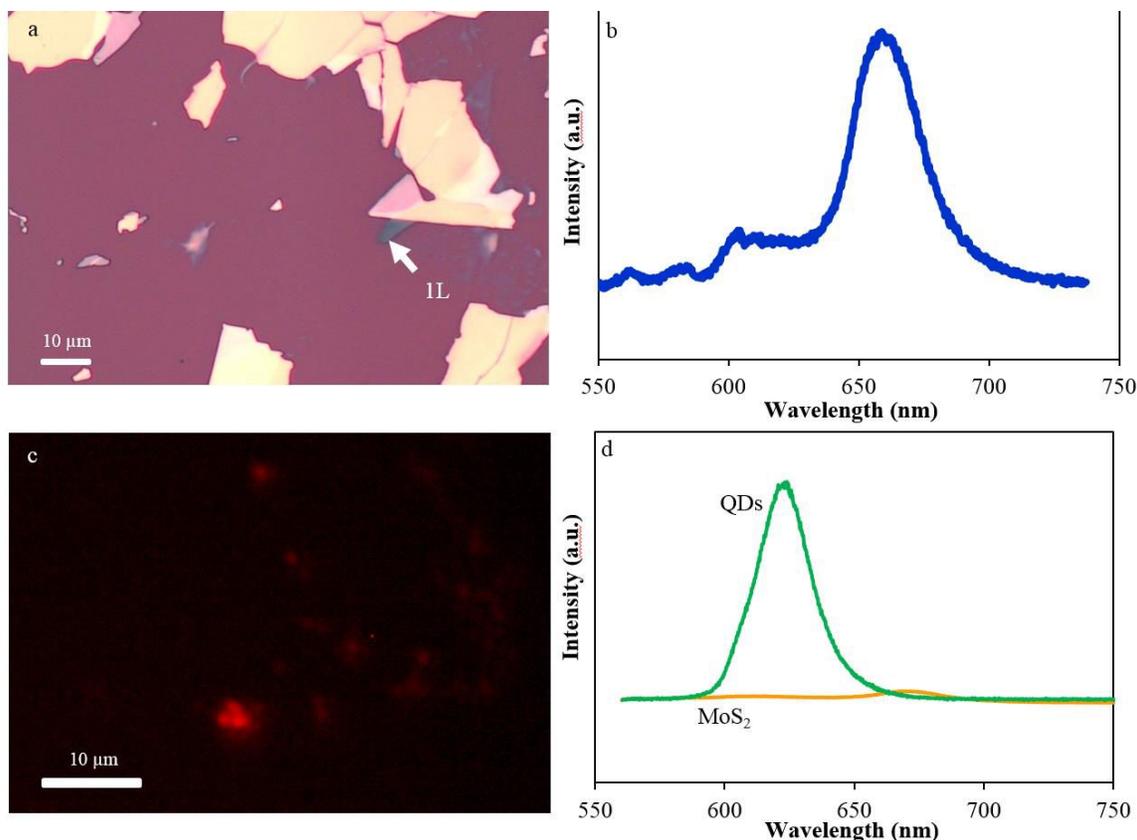


Figure 1: a. Image of MoS<sub>2</sub> flake taken with a 50x objective. The area labeled “1L” is an example of a monolayer, while the other colored flakes are multilayered. b. PL spectrum of a monolayer area of MoS<sub>2</sub>. c. Image of QDs illuminated by a laser which is filtered out of image. d. Comparison of intensity of MoS<sub>2</sub> PL and QD PL under the same incoming laser power and exposure time.

## 2. METHODS

CdSe core QDs were produced in the methods described in Abraham et. al<sup>9</sup>. These methods generate 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. 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<sub>2</sub> was mechanically exfoliated onto oxidized silicon wafers using the scotch tape method<sup>10</sup>. Samples of MoS<sub>2</sub> were taken from bulk MoS<sub>2</sub> using scotch tape and pressed onto the substrates to deposit mono- and few-layer MoS<sub>2</sub>. Monolayers were found and images were then taken using a 20x (NA 0.45) microscope and a brightfield set up illuminated by a white LED light.

All wafers with samples were placed on an xyz-stage that was positioned normal to a 50x microscope objective at the focal plane of the objective. For photoluminescent studies, a 532 nm, continuous wave diode laser passed through a linear polarizer to ensure that the incoming light was completely polarized, a step attenuator with optical density (OD) that ranged from 0.0 to 4.0 to vary the incoming light power to 3.08 kW/cm<sup>2</sup> to 0.01 kW/cm<sup>2</sup>, and a lens which allowed the light to focus onto the sample. The incoming light then passed through the 50x microscope objective (NA=0.55) and shined onto the sample. The PL light and reflected light then passed back through the microscope objective and long pass color filters (570 nm) which blocked most of the laser light, but allowed the PL light to pass through. The PL light

then passed through a lens and was shined onto a CMOS camera or a spectrometer with a CCD readout. The spectrometer had a Czerny-Turner<sup>11</sup> configuration and blazed grating at 750 nm and 300 grooves/mm. PL experimental set up can be found in Abraham et. al<sup>9</sup>.

### 3. RESULTS

Figure 1d includes a comparison of MoS<sub>2</sub> PL and QD PL. The spectrum of each was taken when illuminated by the same 532 nm laser attenuated to just under 1 mW and taken with an exposure time of 10 seconds. Figure 1d shows that under the same conditions, QDs produce a more intense PL.

To study the effects of photobleaching, samples were found as quickly as possible under the lowest possible excitation light. For MoS<sub>2</sub> flakes, this was a brightfield set up and for QDs this was an 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. A 532 nm laser was attenuated to just under 1 mW and data began almost immediately. Spectra were taken with an exposure time of 10 seconds and every six spectra were averaged, resulting in a data point about every minute. Figure 2 shows the intensity of the peak wavelength of these data points. This data shows that QDs lose about half their initial intensity after about 15 minutes but that MoS<sub>2</sub> is not subject to the same photobleaching effects that QDs are.

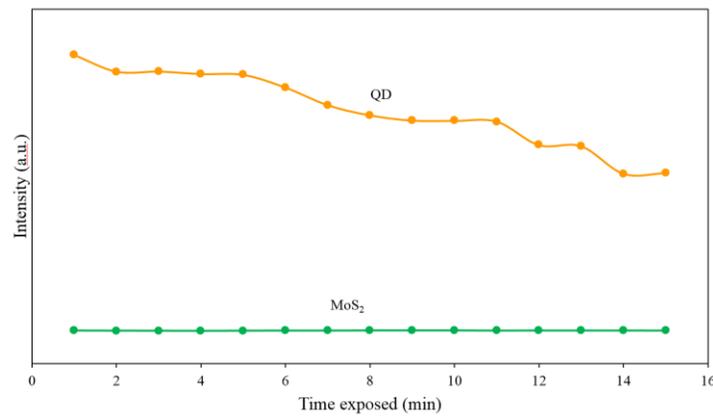


Figure 2: Shows change of intensity of the peak wavelength as a result of time exposed to laser. As time increases, QD PL decreases (a) but MoS<sub>2</sub> PL does not change (b).

For polarization studies, a half-wave plate was placed in the incoming light path after the linear polarizer and a linear polarizer was placed between the sample and the spectrometer to act as an analyzer. A single QD or monolayer flake was examined for each incoming polarization. The linear polarizer began with vertical transmission axis at 0° and spectra were taken every 10° with the same exposure times. Figure 3 shows a comparison of the peak wavelength's intensity for each of these spectra. Figure 3 also compares different incoming polarizations with red at a vertical incoming polarization and blue at a horizontal (HWP rotated 45°) incoming polarization.

Figure 3 shows that neither the MoS<sub>2</sub> flakes nor the QDs produce significantly polarized light by comparing the intensity of the peak wavelength from each rotation of the analyzer. The QD polarized light seems to have an inconsistency at 0°; however, Figure 2 shows that QDs are prone to photobleaching so the more time the QD spends under incoming light, the weaker the PL becomes. The weaker intensity of QD's 360° (as compared to its initial 0°) is most likely caused by this. MoS<sub>2</sub> dependencies not effected by photobleaching so 0° and 360° is about the same.

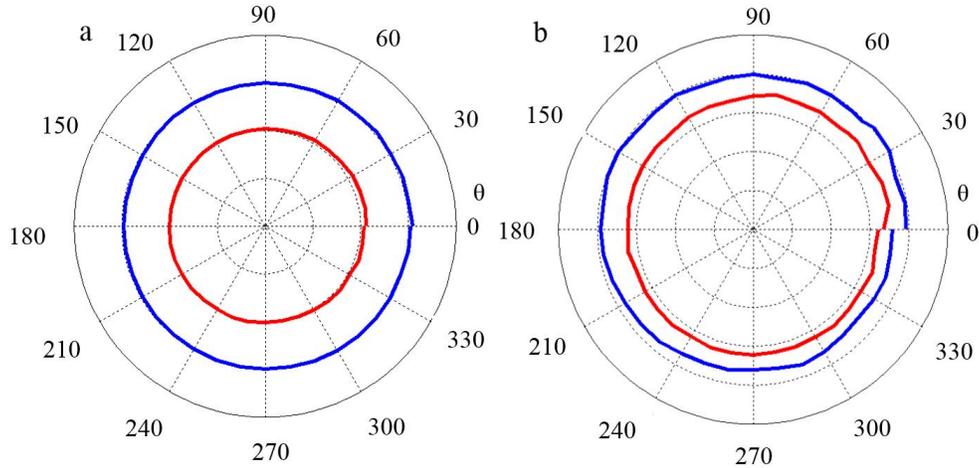


Figure 3: Polar plot comparing the intensities of the peak wavelength as a polarizer analyzing the PL light rotates. Results show that the light produced by MoS<sub>2</sub> monolayers (a) and spherical QDs (b) is unpolarized. The out coming polarization of single QDs and MoS<sub>2</sub> were tested with different incoming polarizations (incoming vertical-red and incoming horizontal-blue).

Finally, the effects of age were studied. For both MoS<sub>2</sub> 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 on the order of days for the remainder of the study. Figure 4 shows the change of intensity of the peak wavelength for QDs and MoS<sub>2</sub>. For MoS<sub>2</sub>, 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.

The data shows that QDs produce less PL as they spend more time on a wafer. Previous work has also shown that QDs continue this trend for at least 2 months<sup>9</sup>. MoS<sub>2</sub> on the other hand has a slight increase after three days and then continues to decrease despite a consistent incoming laser power and exposure time. It is likely this could have been caused by different positioning of the MoS<sub>2</sub> within the setup after each day, giving variation in the measured intensity value.

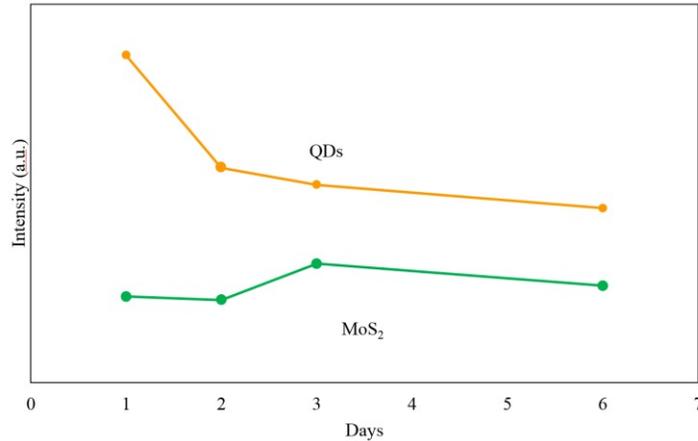


Figure 4: Shows change in intensity of peak wavelength for QD (a) and MoS<sub>2</sub> (b) as a function of time spent on the wafer.

#### 4. CONCLUSION AND FUTURE WORK

The results show that MoS<sub>2</sub> and QDs each have their own benefits and negatives. QDs produce a stronger signal while MoS<sub>2</sub> produces more consistent light when exposed to an excitation light. Both MoS<sub>2</sub> and QDs produce unpolarized excitation light that does not depend on the polarization of the incoming light source. Although the results of the age study were non-conclusive, they did show that the intensity of MoS<sub>2</sub> and QDs tends to decrease with the amount of time they spend on a wafer.

Futures studies include continuing the age study to observe more long term effects of remaining on a wafer for QDs and MoS<sub>2</sub> and repeating the age studies to include different areas within the slit to account for the error that occurred on day 3. In addition, QDs and MoS<sub>2</sub> samples will be combined with silver nanoparticles that exhibit plasmonic behaviors and resonate with both the 532 nm of the laser and the peak wavelength of PL. Previous research has shown that coupling the effects of plasmons and PL enhances the produced light<sup>12,13</sup>, but to our knowledge, dependency on the order of the enhancement has yet to be investigated. Future studies will compare the intensity of the produced light of plasmonically enhanced PL and the intensity of the produced light of PL that occurs from plasmonic enhancement. Finally, this study will couple MoS<sub>2</sub> flakes and QDs with nanostructures with sub-10 nm gaps. Previous research has shown that the enhancement that occurs within these gaps are exponentially stronger than the enhancement that occurs from a regular geometric shape<sup>14</sup>. We believe that pairing these will also produce exponentially stronger enhancement of PL than the regular geometric shapes that was mentioned above.

#### ACKNOWLEDGEMENTS

This work resulted from research performed through the National Science Foundation (NSF) Research Experience for Undergraduates (REU) grant awarded to the Physics Department of the University of Arkansas. Travel Support to present as SPIE Photonics West is provided by Student Undergraduate Research Fellowship (SURF) sponsored by the Arkansas Department of Higher Education. A special thanks to David French for guidance and training throughout this experiment. Thank you very much for your support.

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