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Optical Enhancement of Photoluminescence with Colloidal Quantum Dots

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ABSTRACT

This work investigates colloidal, semiconductor Cadmium Selenide (CdSe) QDs with optical spectroscopy measurements. A custom-built microscope has been used for photoluminescence spectroscopy and has collected images, videos, and spectra of samples to study the effects of substrates, sample density, uniformity, and QD aging with time. This set up will be used to detect single to a few molecules, shown by fluorescent intermittency, or QD blinking. Differences in the spectrum will be noted as related to the age of samples, the density of the quantum dots, and the concentration of samples. Further experiments include the potential plasmonic enhancement of QD photoluminescence by gold nanoparticles or nanostructures.

Keywords: Photoluminescence, Quantum Blinking, single quantum dots

1. INTRODUCTION

Quantum dots (QDs) are structures that exhibit properties between atomic and bulk materials Semiconductor QDs are made from crystalline semiconductor materials, and therefore are sometimes called nanocrystals. They can be grown epitaxially with a self-assembled technique[1] and they can be synthesized chemically[2].

QDs exhibit a property called photoluminescence because they are direct band-gap structures. During photoluminescence, incident light excites an electron. As the electron spontaneously relaxes back to its original state, a photon with energy equal to the energy difference of the band gap is emitted. The spectrum of a QD is known to vary depending on the size, material, and structure of the quantum dots; thus, they can be constructed to produce a variety of wavelengths[3]. This is because QDs are structures with all three dimensions in the quantum confinement regime, where their size is below the exciton Bohr radius. In QDs electrons are confined in all three directions and the electron energy levels are quantized. The strong control over the emission spectrum has yielded a variety of applications including medical imaging[4,5], detecting metallic impurities[6] and solar technology[7]. When observing a singular quantum dot, they appear to blink randomly. This is called fluorescent intermittency and is a result of charging of the QDs[8]. QDs also have interesting applications including imaging live cells[9] and studying the efficiency of photon absorption, optical coupling, and single photon emission[10].

2. METHODS

CdSe core samples were synthesized by modification of a literature method[11]. In short, 0.04 M cadmium (Cd) precursor was prepared by degassing a mixture of CdO, oleic acid (OA) and 1-octadecene (ODE) under vacuum for 30 minutes and then heating to 200°C under argon flow until the solution became clear. The temperature was then reduced to 50°C and at that point octadecylamine (ODA) and tri-octylphosphine oxide (TOPO) ligands were added, the reaction mixture was again degassed and heated to 300°C under argon flow. At this temperature, 0.04 M Se precursor solution (made from Se, tributylphosphine and 1-octadecene) was abruptly injected and, within a few seconds, the heating mantle was removed and the reaction was quenched by adding them to cold hexane to avoid further growth of particles.

The shelling of CdSe core was accomplished by applying successive ion layer absorption and reaction (SILAR)[12] and thermal cycling (TC)[13] methods. Generally, the 0.08 M Cd or Zn precursors were prepared the same way as for the Cd precursor and the 0.08 M S precursor was prepared in the same way as that of Se (described above). The CdSe core solution was prepared by mixing together 3 mL of CdSe in hexane, 1.5 g ODA and 3 mL of ODE in a 3-necked reaction

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flask. Then, calculated amounts of S and Zn or Cd for one monolayer (ML) at a time were injected alternatively, at a lower temperature of 180°C and allowed to equilibrate for 5 minutes each followed by growth of particles by raising temperature to 210°C for CdS and 230°C for ZnS shells for 20 more minutes. The S precursor was always injected first. Approximately 1 mL aliquots were taken out after the growth of each ML and dissolved in hexane. The first 5 ML injections were for the CdS shell while the last 3 ML injections were for the ZnS shell. To confirm the actual growth of monolayers, the diameters of particles were measured using Transmission electron microscopy (TEM).

This produced QDs composed of a layer of CdSe surrounded by CdS then ZnS with a diameter of 13 nm and a peak emission wavelength measured to be 621 nm with a Fluorometer. To take photoluminescent measurements, samples were prepared by diluting a stock solution of CdSe QDs in hexane to a variety of concentrations. The QD solution was drop cast onto silica wafers meaning that a single drop of the dilute solution was dropped onto a cleaned silica wafer and allowed to dry. This allowed for a random spreading of QDs onto the silica wafers. The wafer with the QDs on the surface was then mounted on the xyz-stage of the optical setup shown in Figure 1.

A 532 nm, continuous wave diode laser was used as the excitation light source in this experiment. The laser 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 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[14] configuration spectrometer with blazed grating at 750 nm and 300 grooves/mm with a CCD readout. Figure 1 shows the complete experimental set up.

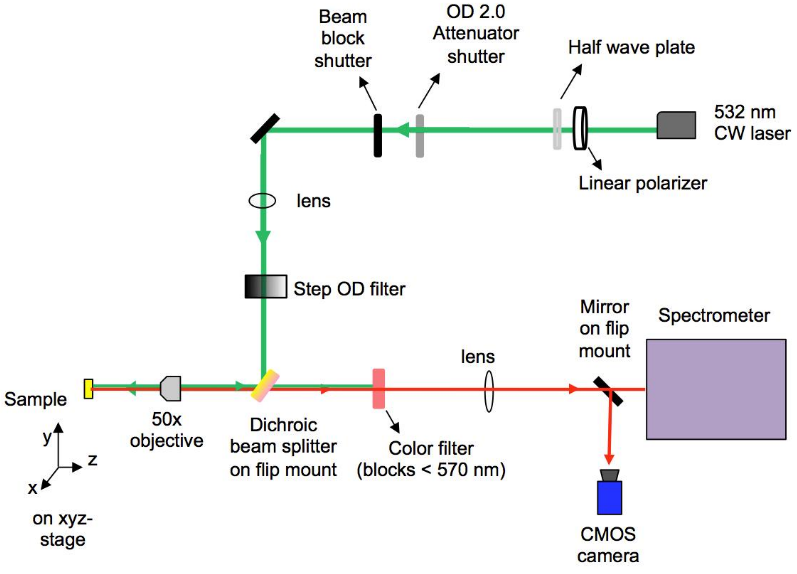

Figure 1: Experimental set up. Green arrows, starting at the laser, represent the excitation light and red arrows, coming off the sample, represent the luminescence from the QD samples.

The CMOS was used for finding samples 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 and to show QD blinking of a single quantum dot.

The first step 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. 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.

3. RESULTS

The microphotoluminscence 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. The most likely explanation is that more concentrated samples can aggregate which is known to lead to red-shifting. 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^2 and a 1000 ms exposure time. The small peak at 532 nm is the high intensity excitation laser leaking through the color filters.

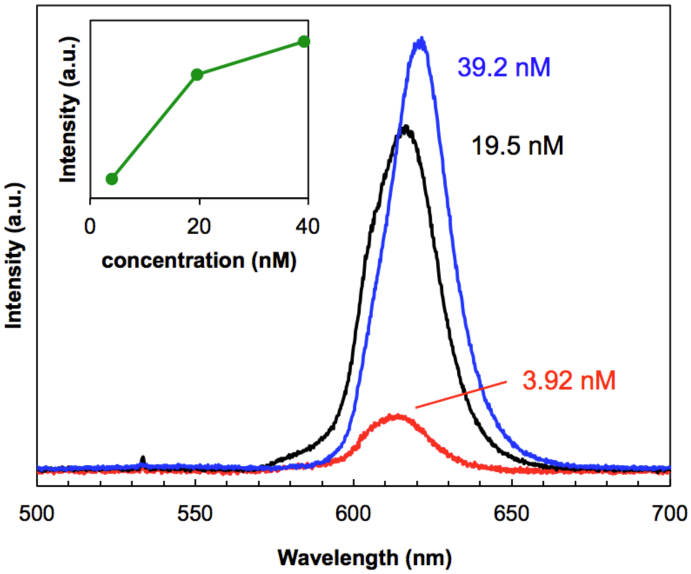

Figure 2: Spectra of QD ensembles of different concentrations showing peak wavelength. Note: small peak at 532 nm due to excitation laser.

Figure 3 shows how the spectrum changes as the 39.2 nM sample ages. Day 0 is defined as the day the samples were deposited on a silica wafer. The wafer was consistently stored in a dark, closed environment when not in use. Each data point was taken with an excitation light of 1.25 kW/cm^2 and a 1000 ms exposure time; however, so far, a systematic way of creating uniformity in the quantum dots has yet to be established. Because of this, each data point is comprised of ensembles of QDs of varying densities which produce different intensities on the same day. The large margin of error can be attributed to the varying density, but this data does show an obvious decrease in intensity as the QDs age. Future work will measure the same region of interest every time and show how the intensity of the same area changes with age. To minimize error in this study various locations were measured each day. These are the different points shown in the inset. The inset plots the max intensity at the peak as a function of days.

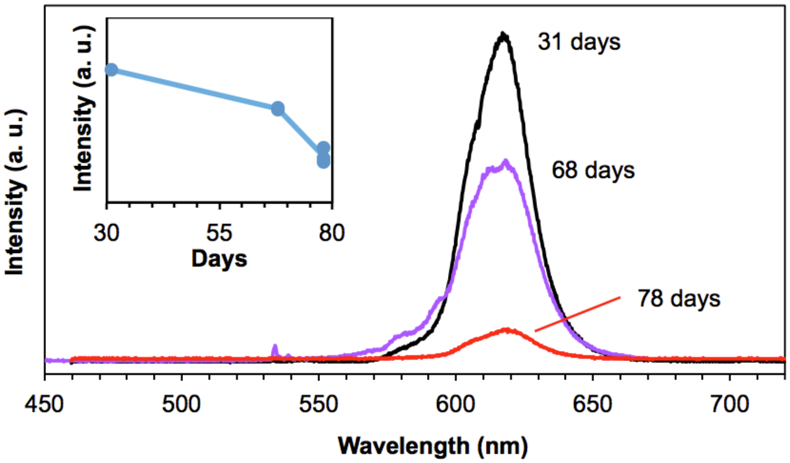

Figure 3: Changes in QD spectrum as the samples aged.

Next, fluorescent intermittency (or QD blinking) was observed with the CMOS camera as shown in Figure 4. 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 4 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.

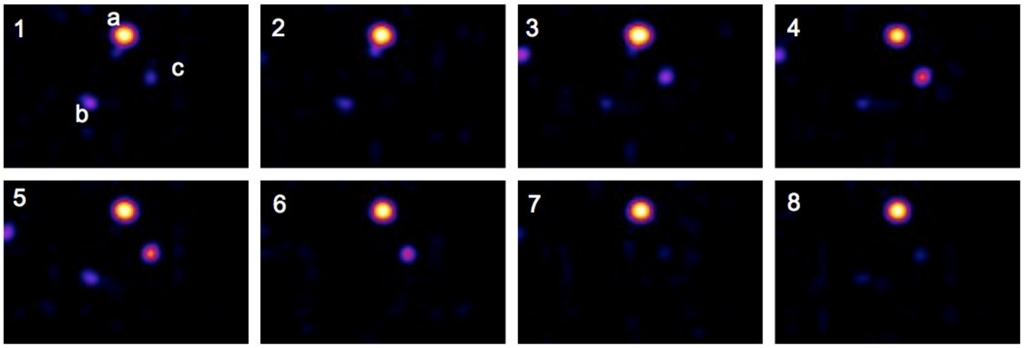

Figure 4: Consecutive frames (labeled 1-8) of a video of QDs. Quantum blinking shown by dots *b* and *c* and a cluster of QDs not exhibiting quantum blinking shown by *a*. Each frame is 0.2 seconds long.

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. These results are plotted in Figure 5. 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 5 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.

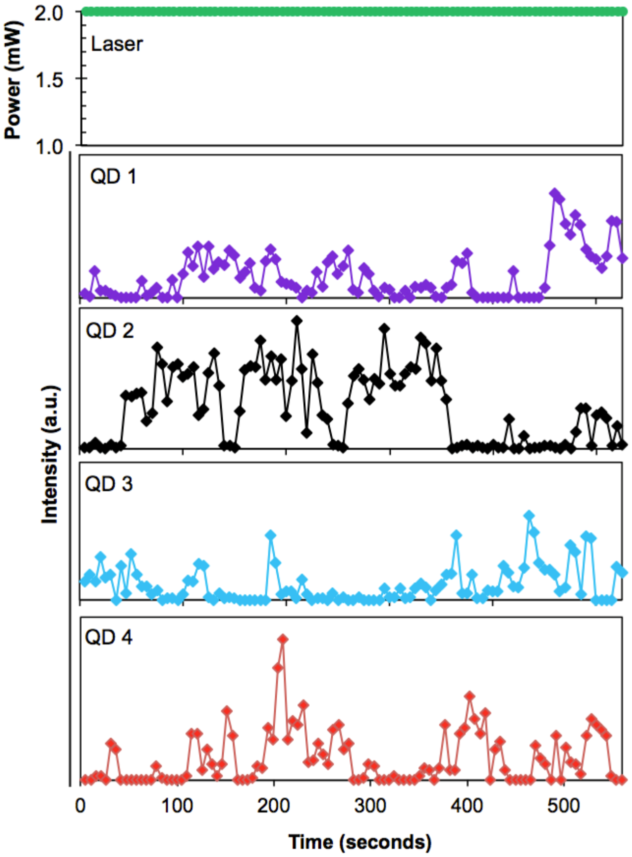

Figure 5: Changes in intensity due to quantum blinking compared to the intensity of the excitation light.

4. CONCLUSION AND FUTURE WORK

This work has done some preliminary investigations on core-shell ZnSe CdSe quantum dots. It has begun to observe quantum blinking and has made some preliminary measurements on age and concentration effects.

Future work is needed to thoroughly study the effects of sample age, uniformity, density, and substrate effects in a more controlled manner to reduce other variables in the measurements. Additionally, further work hopes to enhance QD luminescence with unique plasmonic nanoparticles. Plasmons are waves of charge that occur on the surface of metals when light is shown on them. The electric field from an excitation light causes the electrons within the metal to oscillate and scatter light. A future goal of this experiment is to couple QDs with gold nanoparticles that exhibit plasmonic effects. The spectrum will be analyzed to show how changes in distance between the gold and quantum dot, concentration of the coupling, etc. affect the scattered light.

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