Emissions of Quantum Dots Due to Surface Plasmon Enhancement

Brady Frank Hood

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Quantum dots are small particles in the nanometer range where the effects of quantum mechanics is evident. Quantum dots are fabricated with characteristics that cause them to emit specific wavelengths of light when excited by incident light of various wavelengths. In this experiment the characteristics of quantum dots are explored when they are combined with a substrate of metallic nanoparticles. Metallic nanoparticles are similar in size to quantum dots, but composed of metal, where quantum dots are composed of semiconducting materials. In this project a sample is irradiated with controlled wavelength light from a high power pulsed laser source, and the spectrum of emitted light examined with a spectrometer.
Emissions of Quantum Dots Due to Surface Plasmon Enhancement

Brady Hood

April 27, 2012

Abstract

Quantum dots are small particles in the nanometer range where the effects of quantum mechanics is evident. Quantum dots are fabricated with characteristics that cause them to emit specific wavelengths of light when excited by incident light of various wavelengths. In this experiment the characteristics of quantum dots are explored when they are combined with a substrate of metallic nanoparticles. Metallic nanoparticles are similar in size to quantum dots, but composed of metal, where quantum dots are composed of semiconducting materials. In this project a sample is irradiated with controlled wavelength light from a high power pulsed laser source, and the spectrum of emitted light examined with a spectrometer.
**Introduction**

**Objective**

The purpose of this experiment is to study the emission spectrum of quantum dots under various conditions.

**Apparatus**

The apparatus consists of a DCR-11 Pulsed Nd:YAG laser, dichroic mirrors, optical filters, standard mirrors, a microscope objective, a biconvex lens, a microscope objective, various quantum dot samples, various stands and holders, a BTC112E TE Cooled Array Spectrometer, BWSpec 3.26 spectrometer software, and a computer.

**Background**

**Quantum Dots**

Quantum dots are small clusters of 100-10,000 atoms made normally of a semiconducting material. Quantum dots are a subclass of similar sized structures known collectively as nanoparticles. The other most common types of nanoparticles are made of metal. Nanoparticles are range from 1-10nm in diameter, which is very small compared to visible matter, and hence cannot be seen directly. Because the energy levels of atoms and molecules are inversely proportional their masses, the wavelengths of light that they absorb and emit varies with different sizes. This is illustrated in Figure 1 below.

![Figure 1](image-url)

*Figure 1*

*The effect of size on the emission spectrum of quantum dots (1).*
Quantum dot fabrication methods provide for fine control over their size allowing them to be tuned to absorb or emit light in specific wavelength ranges. This makes quantum dots very effective for uses in multiple areas of research such as biological tagging, diode lasers, transistors, photo detectors, and solar cells.

The Nd:YAG Laser

The laser used in this experiment was a DCR-11 Pulsed Nd:YAG laser. Nd:YAG stands for Neodymium-Doped Yttrium Aluminum Garnet which is the lasing medium in the laser cavity. The primary wavelength that the Nd:YAG laser produces is 1064μm in the near infrared region of the electromagnetic spectrum. However, by frequency doubling and mixing using the primary wavelength, other wavelengths can be produced as well. The laser is shown below in Figure 2.

![Image of Nd:YAG laser](image)

**Figure 2**

*The Nd:YAG laser showing the harmonic generator attached to the exit of the beam cavity on the left.*

Frequency doubling and frequency mixing produces the wavelengths 532nm (green), 355nm, and 266nm (both near ultraviolet), and is performed by the harmonic generator after the beam leaves the lasing cavity. Frequency doubling is achieved by placing nonlinear crystals in the beam path which can convert two photons into one with twice the energy and half the wavelength of the originals. This second harmonic (532nm) of 1064nm can be frequency doubled again to produce a third harmonic (266nm), or the second harmonic can be summed with 1064nm to produce 355nm.

All of the wavelengths produced are pulsed beams ranging from 4-9 ns per pulse. The length of time per pulse is referred to as the pulse width and is used with the
frequency and pulse energy to determine the average and peak pulse powers for each wavelength. The nanosecond time scale is achieved by q-switching the laser cavity. Q-switching involves keeping the light in the laser cavity from resonating while pumping the laser medium to attain a large population of excited atoms in the gain medium. When the light is allowed to resonate, a high power pulse of light is generated from the laser. The Nd:YAG’s 532nm beam has a peak power of around 20MW. Some pulse characteristics for each wavelength are shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>1064 nm</th>
<th>532nm</th>
<th>355nm</th>
<th>266nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Width (msec)</td>
<td>8-9</td>
<td>6-7</td>
<td>5-6</td>
<td>4-5</td>
</tr>
<tr>
<td>Pulse Energy (mJ)</td>
<td>275</td>
<td>135</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Pulse Energy Stability</td>
<td>±4%</td>
<td>±7%</td>
<td>±10%</td>
<td>±15%</td>
</tr>
</tbody>
</table>

Table 1

Pulse characteristics of the Nd:YAG (2).

Optics of the Microscope Objective

The microscope objective in this experiment is used to focus the laser beam onto the planar sample. The microscope objective (or simply objective) is a system of lenses enclosed in a small metal housing that has a high magnification power for observing light emission that is normally too weak to be seen by the eye or seen efficiently enough to make a quantitative measurement.

Although all of the components of the objective can be difficult to describe optically, to the end user it can be essentially treated as one equivalent lens with a diameter and focal length equal to the aperture size and focal length respectively of the lens system that comprises the objective.

The intensity of light that the objective focuses onto the quantum dot sample depends on the sample’s proximity to the focal point. This can be seen in Figure 3 below. At the focal point all of the light will be focused into a small area with a high intensity, whereas away from the focal point a larger area will be illuminated with lower intensity. Having the sample precisely at the focal point is not always desired because at high powers the focused laser can burn the quantum dots.
Spectroscopy

Spectroscopy deals with the interaction of light with matter. The main qualities of quantum dots are their optical properties, so the two main areas of interest in this experiment are emission and absorption. Both emission and absorption are due to electrons in a material being excited to higher energy levels and then relaxing back down to their ground state.

As stated earlier, a quantum dot’s absorption is inversely proportional to its size since a particle’s energy levels relates to its mass. Quantum dots emit light over a fairly narrow wavelength range owing to their specific colors, but they can absorb light over a much larger range of wavelengths. A particular quantum dot is largely defined by its peak emission wavelength since that will be the color that it appears to be to the naked eye. An example of the emission and adsorption spectrum of a quantum dot is shown in Figure 4.
Figure 4
Absorption and emission data for a particular type of quantum dot obtained from the manufacturer.

To study the emission of quantum dots in this experiment a digital BTC112E TE Cooled Array Spectrometer was used. The spectrometer works by accepting light focused into a fiber optic cable, dispersing this light into its component wavelengths with a diffraction grating, and then reflecting this light onto a photodetector array. This is shown conceptually in Figure 5. All of this is done in the small sealed spectrometer housing. The spectrum data is then interpreted using the BWSpec software on the computer connected to the spectrometer.

Figure 5
Schematic of how a spectrometer works by diffracting light and reflecting it onto a detector (4).
Two Photon Excitation

Two photon excitation is a nonlinear effect that occurs when the number density of photons incident on a material is high. Normally a single photon with the correct energy can be absorbed by an atom and promote it to an excited state. In some cases however two photons whose energies add up to the transition energy can be absorbed simultaneously by the atom. When the atom relaxes to the ground state, it will emit only a single photon with an energy equal to the transition energy. This is depicted in Figure 6 below.

![Figure 6](image)

*Figure 6*

*Single and two photon excitation both producing an emitted photon of the same energy (5).*

The probability of two photon adsorption is very low compared to normal single photon adsorption. Because of this a sample must be exactly at the focal point of a focused beam of light to receive a large enough photon intensity to produce the effect.

Surface Plasmons

Surface plasmons can collectively be thought of as a wave occurring over a solid’s surface. This occurs from the oscillating electric field of incident radiation inducing the electrons of a solid to accumulate at the surface as opposed to being evenly distributed throughout the material. Since a metal has many free electrons, in the case of metallic nanoparticles this state of dislocated electrons together with the holes they leave behind induces an electric dipole with a field opposing the incident radiation. This is shown in Figure 7 below.
Incident light causing a polarization of a nanoparticles resulting in an opposing electric dipole (6).

Depending on the characteristics of the metal, there will be a resonant frequency of plasmonic oscillation; and the strength of the plasmonic effect will depend on how close the incident radiation is to this resonant frequency.

When an electron recombines with a hole or relaxes to a lower state it will reemit the energy it initially absorbed. Since the excited electrons want to oscillate at the resonant plasmonic frequency, the reemitted energy may be slightly shifted from the incident excitation wavelength. Because of this, the effect on the emission spectra of quantum dots together with metallic nanoparticles is an area of interest to researchers and is explored in this experiment.

At high intensities metallic nanoparticles can also exhibit band filling effects in their emission spectra. This is a result of the spacing of the valence and conduction bands in the metal and occurs at energies above those required for plasmonic excitation. An example of an emission spectrum with and without band filling is shown in Figure 8 below.

Two emission spectra of intensity vs. wavelength from the same source. The left graph shows band filling as an extra hump on the left side of the emission curve.
Optical Filters

- **Dichroic Filters**
  
  Dichroic filters are optical filters that are used to selectively transmit or reflect certain wavelengths of light. They are available over a wide range of filtering abilities and may reflect all or only some percentage of a range of wavelengths. Two transmission vs. wavelength graphs (also known as transfer functions) are shown in Figure 9 below.

![Figure 9](image)

Two transmission vs. wavelength graphs describing two different dichroic filters.

The transfer function of a dichroic filter can shift depending on its angle of incidence with incoming light. When angled at 45 degrees certain dichroic filters can act as mirrors since they will almost completely reflect selected wavelengths. Having this property the filter is often referred to as a dichroic mirror.

Of particular use in this experiment were those types of dichroic filters that selectively blocked 1064nm or 532nm light which are the first and second harmonics produced by the Nd:YAG laser. Such filters allow the two different wavelengths produced by the laser to be separated from each other; and they allow the intense laser light to be filtered out of the emitted quantum dot light so that it does not damage the spectrometer.

- **Neutral Density Filters**
  
  Neutral density filters act as attenuators allowing the intensity of light to be controlled. Based on their optical density they absorb different amounts of light of most wavelengths. In this experiment a rotating attenuator was used which allowed for the percentage of attenuation to be varied quickly in successive measurements. The rotating attenuator is shown in Figure 10 below.
Figure 10
The rotating attenuator used in this experiment showing reflection of light increasing in the counterclockwise direction.
Procedure

Experimental Design

Figure 11
The optical setup used in this experiment.

The optical setup of the experiment used is shown above in Figure 11. It was designed prior to using it in this experiment, and was partially in place when I started using the Nd:YAG. The modifications made were to add the microscope objective and sample holding stand, the spectrometer base and collecting lens, several light barriers, and to realign all of the original optics.

The main purpose of the setup is to split the 1064nm and 532nm light into two separate beams, route them separately to the sample, and then collect the emitted light with the spectrometer while filtering out all of the reflected laser light. The general path of the two beams is shown in Figure 12.
Figure 12
The initial path of the two beams. The incoming laser beam with both wavelengths superimposed is shown in blue. The separated beams are shown in green for 532nm and red for 1064nm.

1. Initially the laser beam enters the setup and is split by a dichroic mirror at 45 degrees. The mirror reflects the 532nm and transmits the 1064nm.

   a. After the dichroic mirror the 532 passes through a dichroic filter which further filters any remaining 1064 light from the beam and directs it onto an absorbing surface. Next the 532 is reflected at 45 degrees from a normal aluminum reflecting mirror, and then reflected again at 45 degrees by another aluminum mirror in the direction of the sample.

   b. After the dichroic mirror the 1064 is reflected at 45 degrees by another dichroic mirror which also serves to filter any remaining 532 from the beam by transmission through the mirror onto an absorbing surface. This is done twice more, each time reflecting the beam 45 degrees by a dichroic mirror and eventually pointing the beam in the direction of the sample.
2. Both beams follow nearly the same path to the sample and spectrometer. Their paths are described below and in reference to Figure 13 above.

a. The 532 passes through two dichroic mirrors that would reflect any 1064 light in the beam at points 1 and 2. It then is focused by the microscope objective at 3 onto the sample at 4.

b. The 1064 is reflected 45 degrees by the dichroic mirror at 2 which would transmit any 532 light in the beam. It then is focused by the microscope objective at 3 onto the sample at 4.

3. In both cases of using 532 or 1064, the emitted light from the sample radiates out like a point source part of which goes back into the objective at 3. It then passes through the dichroic mirror at 2 which would filter out any 1064 light. Next it is reflected 45 degrees by the dichroic mirror at 1 (filtering 532) and focused by the collecting lens at 5.

4. Finally the collecting lens focuses the light into a fiber optic cable that goes to the spectrometer which registers the data on the computer. The fiber optic cable and spectrometer are shown in a different optical setup in Figure 14 below.
Figure 14  
*The fiber optic cable on the far right and the spectrometer in a different experimental setup.*

**Measurements**

The measurements taken in this experiment were to look for two photon excitation using 1064nm laser light, and band filling effects in quantum dots on a substrate of gold metallic nanoparticles using 532nm laser light.

**Samples**

Samples are made by depositing quantum dots onto a glass microscope slide. The quantum dots used were purchased from a manufacturer and are suspended in a solution of the solvent toluene. The quantum dots used in this experiment were made of a cadmium and selenium compound.

For making a high concentration sample, an arbitrary amount of the solution is dropped onto a glass slide with a pipette. The toluene quickly evaporates, and a dried spot of quantum dots are left as shown in Figure 15.
To make a quantum dot sample with metallic nanoparticles, first, a thin layer of metallic nanoparticles is deposited onto the slide by physical vapor deposition. Then, a thin layer of low concentration quantum dots is spin coated over the metal. This type of sample preparation was performed by another student. A sample prepared in this way is shown in Figure 16.

Figure 15
A quantum dot sample without metallic nanoparticles.

Figure 16
A sample with a thin layer of quantum dots spin coated over metallic nanoparticles in the center.
Data and Analysis

Two photon excitation was found using the primary 1064nm beam Q-switched on a sample with a high concentration of quantum dots (QD). The spectrum obtained is shown in Figure 17, and has a low intensity compared to what would be found using 523nm light. Because of this, it is not surprising that two photon excitation could not be detected on lower concentration QD samples with metallic nanoparticles despite plasmonic enhancement.

![Figure 17](image)

*Figure 17*

*Two photon excitation on a high concentration 633nm emission quantum dot sample using 1064nm laser light taken for 60s.*

All of the graphs below are relative intensity vs. wavelength emission spectra from different QD samples using the 532nm beam in Q-switch mode at an average power of 1.35W, pulse width of 6.5ns, and power per pulse of 135mJ.

![Graph](image)

*Figure 18*

*Band filling on a high concentration 633nm emission quantum dot sample taken for 1s.*
Figure 18 above shows a strong band filling effect from a sample of high concentration QDs. It serves as a good example of the characteristic band filling “hump” on the left side of the spectrum that can be harder to see in some of the following graphs.

Not all combinations of QD and metallic nanoparticles show large enhancement, and the enhancement effect can decay based on how old the sample is. Figure 19 shows the most effective sample that was used at the time of this report which was not a fresh sample, but showed some signs of plasmonic enhancement. The sample was of 616nm adsorption QDs spin coated on a thin layer of gold nanoparticles.

Several careful measurements were taken using this sample on areas with metal and on areas with only the spin coating. In each case the 532nm light was attenuated with the rotating attenuator in increments of 5.55% corresponding to 20 degree rotations. Below, Figure 20 shows three levels of attenuation of the spectrum taken on the metal and Figure 21 shows the same three levels taken on an area of the same sample with only spin coating. Each measurement was taken over 10s. The band filling effect can be seen to decay away with attenuation resulting in the normal Gaussian shaped spectrum of a QD like that shown in Figure 17.
Three measurements taken of 616 nm absorption quantum dots with metal taken for 10s where the laser power was 62% Green, 80% Blue, and 95% Red.

Figure 20

Three measurements taken of 616 nm absorption quantum dots away from the metal taken for 10s where the laser power was 62% Green, 80% Blue, and 95% Red.

Figure 21

Corresponding data, taken on the metal and away from the metal, for each amount of attenuation was normalized and subtracted from one another using Excel. This was done to look for signs of enhancement on band filling due to plasmons that might not occur on the areas of the sample with only spin coating. If there was such an enhancement, there should be a significant difference in the areas of the normalized curves.

The results showed a very small difference that could not be considered larger that the error due to signal noise. Since the sample used was not new, and therefore had weakened enhancement, the results cannot be used to say anything conclusive about the effect of plasmons on band filling.
Errors

Several possible sources of error could be from uncalibrated components of the experimental setup. The optical components were all carefully aligned, but this can never be achieved exactly. Also, optical equipment is known to move slowly over time due to building vibrations.

The Nd:YAG laser needs to be tested for calibration of power stability and line width. Some measurements not reported showed 266nm laser data which the laser is set not to produce. It is believed that this is coming from some nonlinear effect of the optical elements in the setup since very high lasing powers are being used. It could also be due to the harmonic generator not being correctly calibrated. This is suspected since the residual laser light detected in spectrum data is shifted slightly away from the expected wavelength value.

Conclusion

Two photon excitation was able to be detected using the primary 1064nm beam in long pulse mode on a sample with a high concentration of quantum dots. Two photon excitation is a second order nonlinear optical effect much weaker than normal single photon excitation; and since the high concentration sample had very low intensity, it is not surprising that two photon excitation could not be detected on the lower concentration quantum dot samples even if there was a plasmonic enhancement.

The 616nm absorption sample with metallic nanoparticles showed some plasmonic enhancement of emission intensity despite the sample being several months old. Band filling was shown to gradually decay away leaving the normal spectral emission shape in this sample when the laser light was attenuated by about 50%. When this attenuation was measured on the metal and away from the metal and then compared, the results did not show a difference large enough that could be considered outside of the error due to background noise.

The results from the sample used to look for band filling enhancement cannot be used to make any definite conclusions about the possibility of this effect in general. At the time of this report the equipment needed to deposit metal and make new samples is under repair. Once it is working, new samples can be made, and the measurements described will be repeated with samples that show a large plasmonic emission enhancement.
References


